

Reactions of acylferrate anion $[\text{CH}_3\text{COFe}(\text{CO})_4]^-$ with methyl iodide and acetylenes. Synthesis of mono- and dinuclear alkenyl ketone iron complexes. X-ray structure of $[\text{NEt}_4][\text{IFe}(\text{CO})_3(\text{COCPh})_2]$

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Abstract

Collman's reagent $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ (**1**) reacts with a half equivalent of methyl iodide and diphenylacetylene in acetone at 25 °C for 10 min to give $[\text{NEt}_4][\text{Fe}_2(\text{CO})_6(\mu_2\text{-CPh=CPhCOCH}_3)]$ (**2**). When the reaction of $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ (**1**) was carried out with an excess of methyl iodide a mixture of $[\text{NEt}_4][\text{IFe}(\text{CO})_3(\text{C(O)CPh})_2]$ (**3**) and $[\text{Fe}_2(\text{CO})_6\{\mu\text{-CPhCPhCCH}_3(\text{OCH}_3)\}]$ (**4**) complexes were obtained. Complex **3** was characterized by X-ray analyses. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Alkyne; Carbonyl; Dinuclear

1. Introduction

Alkenyl–transition-metal complexes have frequently been assumed to be key intermediates in various catalytic or non-catalytic organic syntheses by acetylenic compounds using transition-metal complexes [1]. The chemistry of iron and alkynes involves, amongst other species, the formation of complexes with alkenyl, acryloyl and ferracyclopentadiene ligands. All these ligands are related. Recently, it has been reported that the reaction of undecacarbonyltriferrate with α - β -unsaturated acyl-halides gives unstable acryloyl complexes that decompose to unexpected vinyl complexes via decarbonylation [2]. More recently, it has been reported that Collman's reagent $\text{Na}[\text{RCOFe}(\text{CO})_4]$ reacts with alkynes followed by $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ oxidation to give the corresponding cyclobutenediones and α - β -unsaturated carboxylic acids. It appears that in these reactions the

intermediate iron species (not characterized) contained acryloyl and ferracyclopentendienone ligands.

In the course of our studies on the chemistry of dinuclear vinyl carbonyl ferrates [3], we prepared these species from mononuclear iron complexes in a one-pot-synthesis fashion. This paper deals with the reaction of Collman's reagent $[\text{CH}_3\text{COFe}(\text{CO})_4]^-$ with alkynes and methyl iodide in aprotic solvents, which involves the elimination of acetone and the formation of mono and dinuclear iron anionic or neutral species.

2. Results and discussion

First, we checked the reactivity of diphenylacetylene towards $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ (**1**) [4]. No reaction occurred at room temperature. Reactivity of **1** toward diphenylacetylene was then studied further in the presence of unsaturated 16 e iron species that could 'activate' alkynes and react with **1**. Acetyleneiron tetracarbonyls $\text{Fe}(\text{CO})_4(\text{RC}\equiv\text{CR})$ are generally thought

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to be intermediates in reactions of acetylenes with $\text{Fe}(\text{CO})_5$ and $\text{Fe}_2(\text{CO})_9$, and there is only one well documented stable example: $\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2(\text{SiMe}_3)_2)$, a compound stabilized by a bulky bistrimethylsilylacetylene. In the absence of stabilizing bulky groups on the acetylene, these simple π -complexes $\text{Fe}(\text{CO})_4(\text{RC}\equiv\text{CR})$ are thought to be exceedingly reactive to further acetylene additions, resulting in the generation of a multitude of coordinated organic ligands via acetylene coupling [5]. In a previous study we obtained dinuclear vinyl iron complexes from hydride iron complexes and ironcarbonyl π -complexes $\text{Fe}(\text{CO})_4(\text{RC}\equiv\text{CR})$ generated from the reaction of $\text{Fe}_2(\text{CO})_9$ with acetylenes in tetrahydrofuran. In the present report we generated these species by reacting Collman's reagent with alkyl iodides. It has been suggested that acetone and 'Fe(CO)₄-solvent' species [6] are generated in the former reaction.

2.1. Reaction of $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ with a half equivalent of methyl iodide and diphenylacetylene

When the mononuclear anion complex $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ (**1**) was treated with half an equivalent of methyl iodide and diphenylacetylene in acetone at 25 °C for 10 min, **1** reacted completely. Infrared analysis in the $\nu(\text{CO})$ stretching region of the reaction mixture after crystallization confirms the existence of the anionic complex $[\text{NEt}_4][\text{Fe}_2(\text{CO})_6(\mu_2\text{-CPh=CPhCO-CH}_3)]$ (**2**) as the sole product formed during the reac-

tion. Complex **2** was isolated in 81% yield by recrystallization in dichloromethane–diethyl ether mixtures. This product showed three infrared-active bands in the $\nu(\text{CO})$ stretching region. The ^1H - and ^{13}C -NMR data gave evidence of the insertion of the alkyne by the appearance of a multiplet centered at 6.9 ppm, characteristic of the phenyl groups. In addition, a ^1H -NMR resonance at 1.96 ppm and a ^{13}C -NMR resonance at 167.21 were specifically attributed to the coordinated ketonic carbonyl group [7].

The data lead us to suggest for **2** the structure shown in Fig. 1. In this structure the CPhCPh entity is π -bonded to Fe(1), while $\text{C}(\text{CH}_3)\text{O}$ is bonded through oxygen to Fe(2). The structure of **2** reveals a coupling between two iron–carbonyl fragments and the formation of an alkenyl ketone diiron complex.

A possible reaction pathway for the formation of this product is shown in Scheme 1. There is a first reaction of **1** with methyl iodide that generates the unstable species 'Fe(CO)₄' and acetone. This species reacts with acetylene to form the short-lived species $\text{Fe}(\text{CO})_4(\text{RC}\equiv\text{CR})$. This type of complex has been isolated by Carty et al. [8] and recently by Takats and co-workers [9,10]. The alkyne intermediate $\text{Fe}(\text{CO})_4(\text{RCCR})$ reacts then with a second molecule of **1** to give the dinuclear complex **2**.

2.2. Reaction of $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ with an excess of methyl iodide and diphenylacetylene

Treatment of a solution of $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ (**1**) with an excess of methyl iodide in acetone for 10 min and then with diphenylacetylene at 25 °C overnight resulted in a black solution of the complex $[\text{NEt}_4][\text{IFe}(\text{CO})_3(\text{C}(\text{O})\text{CPh})_2]$ (**3**). Complex **3** was isolated in 70% yield by recrystallization in dichloromethane–methanol mixtures. Extraction of the residue yielded an air-stable orange material which was identified as $[\text{Fe}_2(\text{CO})_6\{\mu\text{-CPhCPhCCH}_3(\text{OCH}_3)\}]$ (**4**) through comparison of its characteristic IR, ^1H - and ^{13}C -NMR spectra with the spectra reported in the literature [11]. The IR spectrum of **3** exhibited three characteristic absorptions due to terminal $\nu(\text{CO})$ vibrations and one broad band at 1627 cm^{-1} characteristic of a ketonic carbonyl. The low number of resonances in the ^{13}C -NMR spectrum is consistent with a symmetrical disposition of the acetylenic fragment and ketonic carbonyls on the molecule. The peak at 169.39 ppm is assigned to the sp^2 carbons bearing the phenyl groups. The lowest-field signal at 257.5 ppm is then attributed to the ketonic carbons. The resulting complex can be described as an anionic ferracyclopentendione complex. Few examples of this type of structure have been reported in the literature [12].

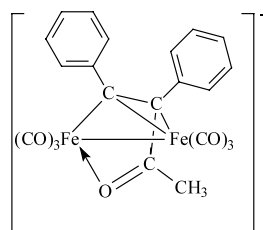
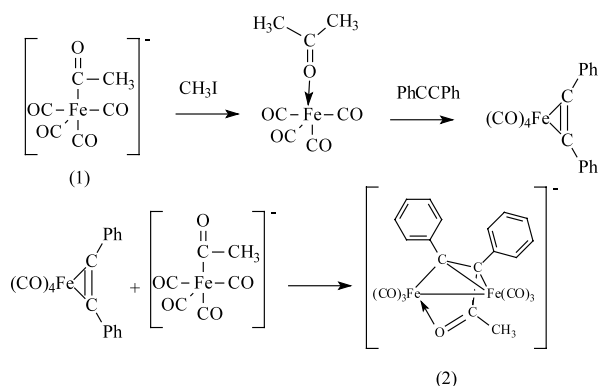


Fig. 1. Structure of complex **2**.



Scheme 1.

Table 1
Crystallographic data and refinement parameters for **3**

Empirical formula	C ₁₉ H ₁₀ Fe ₂ IO ₆ ·C ₈ H ₂₀ N
Formula weight	717.13
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	10.877(2)
<i>b</i> (Å)	11.325(2)
<i>c</i> (Å)	13.445(2)
α (°)	73.47(2)
β (°)	83.07(2)
γ (°)	64.49(2)
<i>V</i> (Å ³)	1432.9(4)
<i>Z</i>	2
<i>D</i> _{calc} (mg m ^{−3})	1.662
Absorption coefficient (mm ^{−1})	2.116
<i>F</i> (000)	718
Crystal size (mm)	0.1 × 0.2 × 0.2
Theta range for data collection (°)	1.6–30
Index ranges	−15 ≤ <i>h</i> ≤ 15, −15 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 5
Reflections collected	3448
Independent reflections	3448
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/parameters	3398/344
Goodness-of-fit on <i>F</i> ²	1.075
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0355, <i>wR</i> ₂ = 0.0768
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1933, <i>wR</i> ₂ = 0.1464
Extinction coefficient	0.0000(6)
Largest difference peak and hole (e Å ^{−3})	0.274 and −0.242

3. X-ray structure determination of [Net₄][Fe(CO)₃(COCPh)₂]

Suitable single crystals of the titled complex were obtained by slow evaporation of a dichloromethane–methanol solution at room temperature. Crystallographic data, selected distances and angles are listed in Tables 1 and 2.

A perspective view of [Fe(CO)₃(COCPh)₂][−] with the labeling scheme is shown in Fig. 2. The anion consists of one iron atom coordinated to a iodine atom, three terminal CO groups and two CO groups inserted between the metal and the alkyne molecule, forming a five-member heterocyclic ring. The Fe–I bond is approximately perpendicular to the herocyclic ring. The distance Fe–I (2.622 Å) is within the normal range of other Fe–I mononuclear complexes [13–15]. The iron is in a slightly distorted octahedral environment. As the two Fe–CO bond lengths *trans* to the heterocyclic ring are slightly asymmetrical (1.76(2), 1.835(23) Å), the apical Fe–C(19) distance *trans* to the iodine is shorter than the others (1.54(2) Å). The Fe–CO (ketonic) bond lengths, 1.993 and 1.960 Å, are within the range of

values found in the Fe–C(sp²) bonds, though slightly shorter than the mean values. This could indicate some π -interaction between these carbons and the metal, and thus explain the low field resonance in the ¹³C spectra. Comparable Fe–C distances were observed in [Fe(CO)₄{(CO)₂C₄Me₂}] and [Fe(CO)₄{(CO)₂C₄Et₂}] [16,17].

Table 2
Selected bond lengths (Å) and angles (°) for **3**

<i>Bond lengths</i>	
Fe–I	2.622(3)
Fe–C(19)	1.54(2)
Fe–C(17)	1.76(2)
Fe–C(18)	1.835(13)
Fe–C(4)	1.960(10)
Fe–C(1)	1.993(10)
O(1)–C(1)	1.182(11)
O(2)–C(4)	1.204(10)
O(3)–C(17)	1.155(14)
O(4)–C(18)	1.082(11)
O(5)–C(19)	1.25(2)
<i>Bond angles</i>	
C(19)–Fe–C(17)	96.8(8)
C(19)–Fe–C(18)	94.8(7)
C(17)–Fe–C(18)	96.2(5)
C(19)–Fe–C(4)	88.2(7)
C(17)–Fe–C(4)	90.0(5)
C(18)–Fe–C(4)	172.8(4)
C(1)–Fe–I	88.2(4)
O(1)–C(1)–C(2)	120.8(9)
O(1)–C(1)–Fe	126.6(8)
C(2)–C(1)–Fe	112.2(8)
C(3)–C(2)–C(5)	126.5(10)
C(3)–C(2)–C(1)	113.2(8)
C(5)–C(2)–C(1)	120.2(10)
C(2)–C(3)–C(4)	116.5(9)
C(2)–C(3)–C(11)	125.2(8)
C(4)–C(3)–C(11)	117.8(9)
O(2)–C(4)–C(3)	118.7(9)
O(2)–C(4)–Fe	127.9(7)
C(3)–C(4)–Fe	113.3(7)

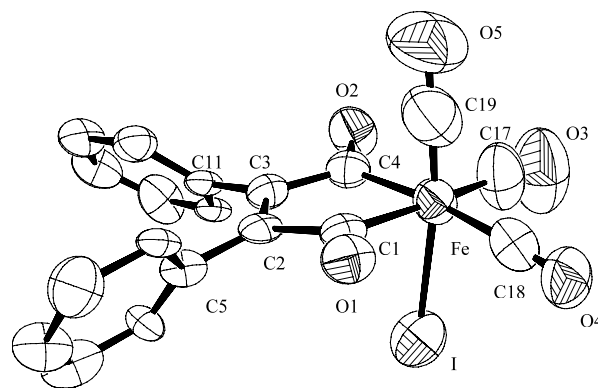
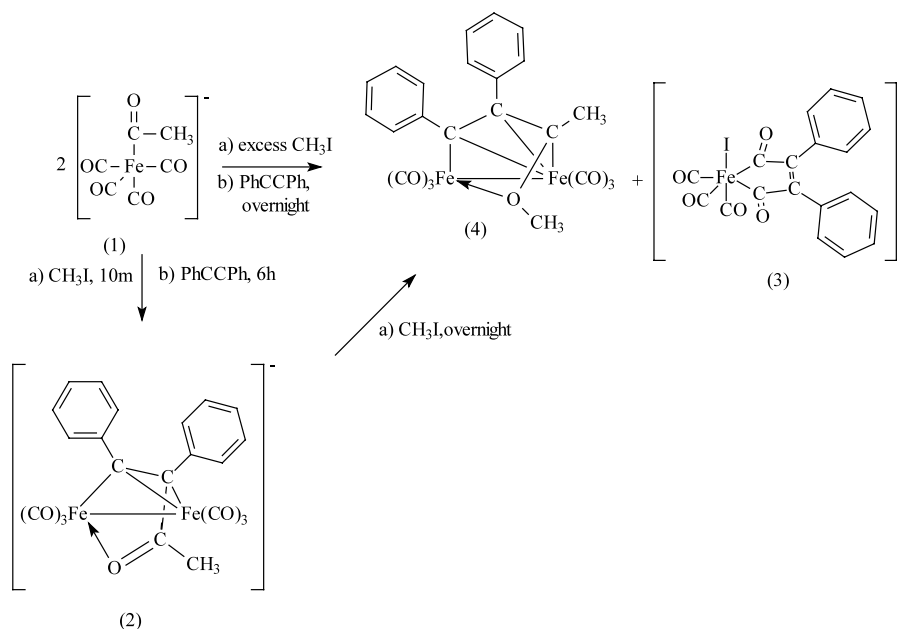


Fig. 2. View of the molecular structure of **3** together with the atomic numeric scheme.



Scheme 2.

4. Conclusion

In summary, we showed that the one-pot reaction of diphenylacetylene and CH₃I in an equimolar or in excess amount with the Collman's reagent could be modulated to obtain mono or dinuclear complexes of iron with alkene ligands (Scheme 2). Recently, a similar reaction with [HFe(CO)₄][−] and CH₃I, which after workup with CuCl₂·H₂O led to the corresponding cyclobutenediones, has been reported [18]. Complex 3 could be the intermediate of the above reactions and supports the significance of η²-alkynyl ligands as intermediates in the conversion of alkynes to organic cyclic compounds.

5. Experimental

5.1. General data

All reactions were performed under nitrogen by using standard Schlenk tube techniques. All the solvents were distilled and dried before use. Infrared spectra were recorded on a Perkin–Elmer FT 1710 spectrophotometer on KBr disks or with CH₂Cl₂ solutions. Mass spectra were obtained on a Hewlett Packard H.P. 2985 GC/MS. NMR spectra were recorded on a Bruker AC-250 (¹H, 250 MHz; ¹³C, 62 MHz) spectrometer in CDCl₃ or (CD₃)₂CO solutions. Elemental analyses were obtained by the staff of the Chemical Analysis Service of the University Autònoma de Barcelona. Iron pentacarbonyl was purchased commercially.

6. X-ray crystal structure determination of 3

6.1. Data collection and processing

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections (8 < θ < 12°) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo–K_α radiation, using ω–2θ scan-technique. Three thousand four hundred and forty-eight reflections were measured in the range 1.6 < θ < 30.0°. One thousand one hundred and ninety-three reflections were assumed as observed applying the condition *I* > 2 σ(*I*). Three reflections were measured every 2 h as orientation and intensity control, significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made.

The structure was solved by Patterson synthesis, using SHELXS computer program [19] and refined by full-matrix least-squares method with SHELX93 computer program [20], using 3398 reflections, (very negative intensities were not assumed). The function minimized was $\sum w [|F_o|^2 - |F_c|^2]^2$, where $w = \sigma^2(I) + [(0.0529 P)^2 + 0.1390 P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$, *f*, *f'* and *f''* were taken from International Tables of X-Ray Crystallography (International Tables of X-Ray Crystallography, (1974), Ed. Kynoch press, Vol. IV, pp. 99–100 and 149). The extinction coefficient was 0.0610, *wR*(on |*F*|²) = 0.076 and goodness of fit = 1.075 for all observed reflections. Number of refined parameters was 344. Maximum shift/Estimated S.D. = 2.5, Mean shift/Estimated S.D. = 0.10. Maximum and

minimum peaks in final difference synthesis was 0.274 and $-0.242 \text{ e}\text{\AA}^{-3}$, respectively. Tables of atomic coordinates, thermal parameters, bond lengths and angles are deposited as supplementary material.

7. Reaction of $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ with CH_3I and diphenylacetylene

To a solution of $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ (1 g, 2.93 mmol) in 30 ml of acetone was added CH_3I (0.09 ml, 1.47 mmol). The contents were stirred for 10 min at 25 °C. Subsequently, diphenylacetylene (0.26 g, 1.47 mmol) was added, and the mixture was stirred for a further 6 h at 25 °C. The black solution was filtered off and the solvent was evaporated. The residue was crystallized in dichloromethane–diethyl ether mixtures and the resulting black solid was isolated in 81% yield.

Anal. Calc. for $\text{C}_{30}\text{H}_{33}\text{Fe}_2\text{NO}_7$: C, 57.08; H, 5.27; N, 2.22. Found: C, 57.12; H, 5.15; N, 2.22%. IR: $\nu(\text{CO})$ (CH_2Cl_2) 2025(s), 1957(vs), 1884(w), (cm^{-1}) ^1H -NMR ($(\text{CD}_3)_2\text{CO}$): δ 1.4 (t, $J = 7.3 \text{ Hz}$, 12H, $\text{N}^-(\text{CH}_2\text{CH}_3)$), 1.96 (s, 3H, $\text{CH}_3\text{C}(\text{O} \rightarrow \text{Fe})$), 3.45 (q, $J = 7.3 \text{ Hz}$, 8H, $\text{N}^+(\text{CH}_2\text{CH}_3)$), 6.8–7.7 (m, 10H, C_6H_5) ppm. ^{13}C -NMR ($(\text{CD}_3)_2\text{CO}$): δ 7.48 ($\text{N}^+(\text{CH}_2\text{CH}_3)$), 23.16 ($\text{CH}_3\text{C}(\text{O} \rightarrow \text{Fe})$), 52.80 ($\text{N}^+(\text{CH}_2\text{CH}_3)$), 86.31 ($\text{CPh}=\text{CPh}-\text{C}(\text{CH}_3)\text{C}(\text{O} \rightarrow \text{Fe})$), 122.31–152.59 (C_6H_5), 162.62 ($\text{CPh}=\text{CPh}-\text{C}(\text{CH}_3)\text{O} \rightarrow \text{Fe}$), 167.21 ($\text{CPh}=\text{CPh}-\text{C}(\text{CH}_3)\text{O} \rightarrow \text{Fe}$), 221 (CO) ppm.

8. Reaction of $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ with an excess of CH_3I and diphenylacetylene

To a solution of $[\text{NEt}_4][\text{CH}_3\text{COFe}(\text{CO})_4]$ (1 g, 2.93 mmol) in 30 ml of acetone was added CH_3I (0.27 ml, 4.4 mmol). The contents were stirred for 10 min at 25 °C. Subsequently, diphenylacetylene (0.26 g, 1.47 mmol) was added, and the mixture was stirred overnight at 25 °C. The black solution was filtered off and the solvent was evaporated. The residue was crystallized in dichloromethane–methanol mixtures and the resulting black solid $[\text{NEt}_4][\text{Fe}(\text{CO})_3(\text{COCPh})_2]$ was isolated in 70% yield. The mother solution was evaporated to dryness and extracted with pentane ($2 \times 10 \text{ ml}$). Concentration of this solution and cooling to $-20 \text{ }^\circ\text{C}$ gave 53 mg of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-CPhCPh-CCH}_3(\text{OCH}_3)\}]$.

Anal. Calc. for $\text{C}_{27}\text{H}_{32}\text{FeINO}_5$: C, 51.21; H, 5.09; N, 2.21. Found: C, 51.42; H, 4.99; N, 2.10%. IR: $\nu(\text{CO})$ (cm^{-1}) ^1H -NMR ($(\text{CD}_3)_2\text{CO}$): δ 1.39 (t, $J = 7.3 \text{ Hz}$, 12H, $\text{N}^+(\text{CH}_2\text{CH}_3)$), 3.43 (q, $J = 7.3 \text{ Hz}$, 8H, $\text{N}^+(\text{CH}_2\text{CH}_3)$), 6.8–7.7 (m, 10H, C_6H_5) ppm. ^{13}C -NMR ($(\text{CD}_3)_2\text{CO}$): δ 7.46 ($\text{N}^+(\text{CH}_2\text{CH}_3)$), 52.78 ($\text{N}^+(\text{CH}_2\text{CH}_3)$), 124.05–136.40 (C_6H_5), 169.39 (CPh), 205.88, 216.7 ($\text{C}=\text{O}$), 257.5 ($\text{Fe}-\text{C}=\text{O}$), ppm.

Anal. Calc. for $\text{C}_{23}\text{H}_{16}\text{Fe}_2\text{O}_7$: C, 53.53; H, 3.10. Found: C, 53.55; H, 3.14%. IR: $\nu(\text{CO})$ (cm^{-1}) ^1H -NMR (CDCl_3): δ 1.9 (s, 3H, CCH_3), 2.81 (s, 3H, $\text{CH}_3\text{O} \rightarrow \text{Fe}$), 7–7.8 (m, 10H, C_6H_5) ppm. ^{13}C -NMR (CDCl_3): δ 19.26 (CCH_3), 70.47 ($\text{CH}_3\text{O} \rightarrow \text{Fe}$), 89.7 ($\text{CPh}=\text{CPh}$), 109.70 (CCH_3), 123.14–148.60 (C_6H_5), 175.45 ($\text{CPh}=\text{CPh}$), 221.57 (CO) ppm. Mass Spectrum m/z 515.95 (M^+), 178 (B).

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