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Carbon–carbon bond formation at diiron centres

V *. Synthesis of anionic vinyl-bridged diiron complexes and their reactivity toward alkynes

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Abstract

The reaction of acetylenes with $[\text{PPh}_4][\text{HFe}(\text{CO})_4]$ in the presence of $\text{Fe}_2(\text{CO})_9$ in THF solution leads to the formation in high yields of the complexes $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}^1=\text{CR}^2\text{H})]$ where $\text{R}^1 = \text{Ph}$ and $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{R}^2 = \text{Ph}$; $\text{R}^1 = \text{tBu}$ and $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{SiMe}_3$ and $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{CO}_2\text{Me}$ and $\text{R}^2 = \text{H}$. The complex $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CH}=\text{CRH})]$ with $\text{R} = \text{H}$ or Ph reacts with the alkynes $\text{R}^3\text{C}\equiv\text{CR}^3$ ($\text{R}^3 = \text{Ph}$, $\text{C}(\text{O})\text{OMe}$, CF_3) in a different way from that previously observed for the alkyne with $\text{R}^3 = \text{Ph}$. The reaction involves insertion of the alkyne into the iron–carbon σ bond of the alkenyl bridge, to give $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CR}^3\text{CR}^3\text{CHCHR})]$ complexes ($\text{R} = \text{H}$). Depending on the R^3 group, two modes of bonding of the organic bridge have been observed, $\mu\text{-}\eta^2, \eta^2$ ($\text{R}^3 = \text{Ph}$) and $\mu\text{-}\eta^3, \eta^1$ ($\text{R}^3 = \text{CF}_3$). The complexes have been obtained from these reactions $[\text{PPh}_4]\text{-}[\text{Fe}_2(\text{CO})_6(\mu\text{-CR}^3\text{CR}^3\text{C}(\text{O})\text{CHCH}(\text{R}))]$ with $\text{R}^3 = \text{Ph}$; $\text{R} = \text{H}$; $\text{R}^3 = \text{CF}_3$ or $\text{C}(\text{O})\text{OMe}$; $\text{R} = \text{Ph}$.

Introduction

Knowledge of the synthesis and reactions of polynuclear complexes containing organic bridges is still rather incomplete and in many cases reinvestigation of earlier

* For part IV see ref. 2.

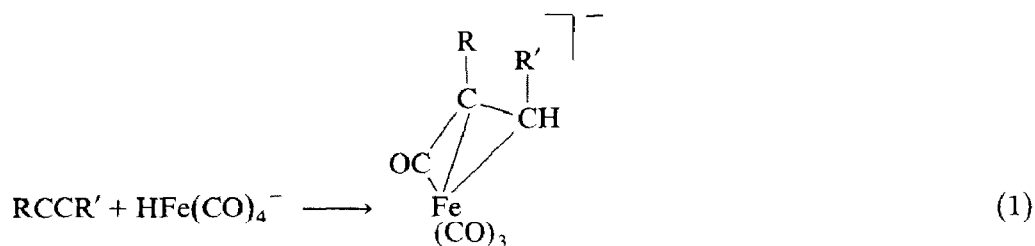
reports reveals new items of interest. This is the case for Seyferth's work on the dinuclear iron thiolate anionic complexes: $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-RS})]^-$, which provided an easy way of forming organic bridges from organic halides [1]. We recently initiated a study of the reactivity of related dinuclear anionic iron complexes, $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}^1=\text{CR}^2\text{H})]^-$, with electrophiles and acetylenes, observing C-C bond formation in most cases [2-4]. The dinuclear anionic complexes of departure were obtained from the anionic cluster $[\text{HFe}_3(\text{CO})_{11}]^-$ and acetylenes, and were separated from other products of the reaction by recrystallization [5]. In the reactions of $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}^1=\text{CHR}^2)]^-$ with acetylenes the products were found to depend upon the alkyne. In the case of the anionic complexes with $\text{R}^1 = \text{R}^2 = \text{Ph}$ [3], there were two types of reaction for the alkynes $\text{R}^3\text{C}\equiv\text{CR}^3$; (i) insertion of both the alkyne and carbon monoxide ($\text{R}^3 = \text{CF}_3, \text{CO}_2\text{Me}$) into the Fe-C bond of the ethenyl ligand (complex I), and (ii) insertion of the alkyne ($\text{R}^3 = \text{CF}_3$) into the carbon-hydrogen bond of the ethenyl ligand (complex II).

We describe below a new easy way of obtaining ethenyl-bridged dinuclear anionic iron complexes and an extension of the scope of their reactions with acetylenes to include the complexes with $\text{R}^1 = \text{H}; \text{R}^2 = \text{Ph}$ and $\text{R}^1 = \text{R}^2 = \text{H}$. The study was, however, limited to the electrophilic alkynes $\text{CF}_3\text{C}\equiv\text{CCF}_3$, $\text{MeOC(O)C}\equiv\text{CC(O)OMe}$ and $\text{PhC}\equiv\text{CPh}$, as the other alkynes did not react or gave intractable mixtures.

Results and discussion

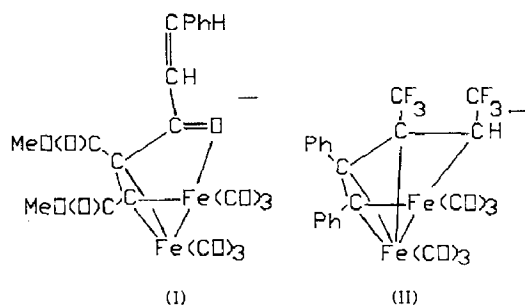
Synthesis of $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}^1=\text{CR}^2\text{H})]^-$ with $\text{R}^1 = \text{R}^2 = \text{H}$, Ph and $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$

With the aim of finding a better route to the dinuclear complexes $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}^1=\text{CR}^2\text{H})]^-$ we investigated the reactions of the anionic hydride $[\text{HFe}(\text{CO})_4]^-$ with acetylenes. Mitsudo et al. showed that $[\text{HFe}(\text{CO})_4]^-$ reacts only with activated acetylenes the reaction giving rise to formation of an η^3 -acryloyl ligand (see eq. 1) [6]. We used this type of complex as a source of alkenyl-bridged iron-cobalt complexes by decarbonylating the acryloyl ligand [7].



($\text{R} = \text{R}' = \text{CO(O)Me}$; $\text{R} = \text{CO(O)Me}$, $\text{R}' = \text{H}$)

The acetylenes $\text{R}^1\text{C}\equiv\text{CR}^2$ with $\text{R}^1 = \text{R}^2 = \text{H}$ and Ph ; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{tBu}$, $\text{R}^2 = \text{H}$; and $\text{R}^1 = \text{SiMe}_3$, $\text{R}^2 = \text{H}$, did not react with $[\text{HFe}(\text{CO})_4]^-$ in THF solution, but when $\text{Fe}_2(\text{CO})_9$ was added and the mixture heated at 70°C a rapid reaction occurred. The $\text{Fe}_2(\text{CO})_9$ dissolved and the solution turned red. Within 1 h the reaction was complete and the anionic complexes $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}^1=\text{CR}^2\text{H})]^-$ were present as only products, and in high yield. An identical product was obtained when the reaction was performed with methylpropiolate, the reaction of which with $[\text{HFe}(\text{CO})_4]^-$ has been described by Mitsudo et al. [6]. Thus



a mixture of $[\text{HFe}(\text{CO})_4]^-$, the alkyne, and $\text{Fe}_2(\text{CO})_9$ in THF gives a similar anionic vinyl-bridged diiron complex. All the new products were characterized by elemental analyses and by spectroscopy. The ^1H NMR spectra of products show the characteristic signals of the vinylic protons. For the complexes obtained from terminal alkynes two signals integrating two protons were assigned to geminal hydrogens, indicating a geometry for the vinyl ligand different from that in the vinylic complexes made by Mathieu et al. [5]. On the basis of these results we conclude that the stereochemistry of the reaction of alkynes with $[\text{HFe}(\text{CO})_4]^-$ is different from that observed with $[\text{HFe}_3(\text{CO})_{11}]^-$. The role of $\text{Fe}_2(\text{CO})_9$ in THF must be to activate the acetylenes by complexation before the insertion into the H-Fe bond.

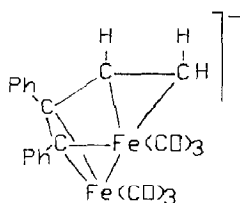
Reaction of $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CH}=\text{CH}_2)]$ with $\text{PhC}\equiv\text{CPh}$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$
 $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CH}=\text{CH}_2)]$ was found to react with diphenylacetylene in boiling acetone to give two new products, **7** and **8**, which were separated by crystallization.

The main product, **7**, gives an infrared spectrum in the $\nu(\text{CO})$ stretching region very similar to that of complexes of type I, and the elemental analysis is consistent with the formulation $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{CHCH}_2)]$. ^1H and ^{13}C NMR data are also consistent with a structure of type I.

The ^1H NMR spectrum shows, except in addition to the phenyl resonances, signals typical of a non-coordinated vinyl group, with multiplets centered at δ 6.32, 5.41 and 4.94 ppm [8]. In the ^{13}C NMR spectrum, the vinyl group resonances appear at 138.6 (CH) and 111.9 ppm (CH_2), also consistent with a non-bonded olefin.

The other resonances observed were assigned by comparison with the spectra of the known $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-C}(\text{R})\text{C}(\text{R})\text{C}(\text{O})\text{CPhCPhH})]$ complexes (R = CF_3 , $\text{C}(\text{O})\text{OMe}$) [2]: 168.4 ppm (CO, O-bonded to Fe), 153.1 ppm (CPh group bridging the two Fe atoms) [9] and 92.7 ppm (CPh bonded to CO).

The second product, **8**, has a markedly different infrared spectrum, suggesting a different structure, and the elemental analysis is consistent with the formulation $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CPhCPhCHCH}_2)]$. The ^1H NMR spectrum confirms the view that it has a different structure, since (ignoring the phenyl resonances) the vinyl signals are consistent with a situation in which the methylene part is π -bonded [10] to a metal and the CH part is bonded to a carbon atom. This suggests a CPhCPhCHCH_2 chain structure for the bridging organic ligand. The ^{13}C NMR data are also consistent with this hypothesis [10]: the signal from the CH carbon appeared at 81.7 ppm, and that from the methylene carbon resonance at 42 ppm.

Fig. 1. Structure of complex **8**.

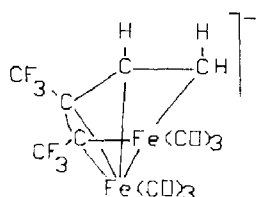
Again leaving aside the phenyl resonances, other signals can be attributed to a C(Ph) group bonded to two iron atoms (174.3 ppm) and a C(Ph) group π -bonded to one iron atom (90.7 ppm) [11].

The data lead us to suggest for **8** the structure shown in Fig. 1. In this structure the CPhCPh entity is π -bonded to Fe(1) while the CHCH₂ entity is bonded to Fe(2). The low value of $J(\text{HH})$ for the hydrogen atoms in *trans* disposition in the vinyl part of the bridge suggests that there is some deformation from planarity for this group, presumably owing to constraints in the organic bridging ligand.

The structure of complex **8** reveals that we have observed a new type of reaction of the dinuclear anionic iron complexes with ethenyl bridges, namely insertion of the alkyne into the iron-carbon of the ethenyl bridge with ejection of one molecule of carbon monoxide.

The reaction of CF₃C \equiv CCF₃ with [PPh₄][Fe₂(CO)₆(μ -CO)(μ -CH=CH₂)] occurs at room temperature and atmospheric pressure. In this case only one compound, **9**, is formed. Its infrared spectrum is very different from those of **7** and **8**, and closely resembles those of complexes of type II. Although the analytical data favour the formulation [PPh₄][Fe₂(CO)₆(μ -C(CF₃)C(CF₃)CHCH₂)], the NMR data indicate that the organic fragment is not the same as that in **8**. Specifically, the ¹H NMR spectrum contains a very unexpected number of resonances for the CHCH₂ group, three broad signals being observed, at 3.95, 0.73 and 0.70 ppm, all of the same intensity, showing that the CHCH₂ fragment cannot be a vinyl ligand. Moreover, the chemical shifts for two hydrogen atoms near 0.7 ppm suggest an alkyl character for the FeCH₂ bond. This is corroborated by the ¹³C NMR data for the CH₂ group, for which the resonance appears as a triplet centered at 16.70 ppm, with the CH resonance at 66.8 ppm.

A similar situation was encountered for the complex [PPh₄][Fe₂(CO)₆(μ -CPhCPhCF₃C(CF₃)C(CF₃)H)], which has structure II: for that complex the C(CF₃) resonance appears at 60 ppm and the C(CF₃)H at 29.9 ppm. Thus we propose for **9** the similar structure shown in Fig. 2. This product results from the same type of reaction as that for **8**, but the mode of bonding of the bridging ligand

Fig. 2. Structure of complex **9**.

$C(CF_3)C(CF_3)CHCH_2$ is different. The $C(CF_3)C(CF_3)CH$ part is π -bonded to Fe(1) and the CH_2 group is σ -bonded to Fe(2). This difference in structure between **8** and **9** can be attributed to the presence of CF_3 groups in **9**.

Reaction of $[PPh_4][Fe_2(CO)_6(\mu-CO)(\mu-CH=CPhH)]$ with $MeOC(O)C\equiv CC(O)CMe$ and $CF_3C\equiv CCF_3$

With both of these alkynes, reaction occurs at room temperature and gives only one type of complex, with structure I: **10** ($R = MeO(CO)$) and **11** ($R = CF_3$). Complexes **10** and **11** have similar infrared spectra in the $\nu(CO)$ stretching region and their elemental analyses are consistent with the formulation $[PPh_4][Fe_2(CO)_6(\mu-CRCRC(O)CHCPhH)]$.

The proton NMR data for these two compounds are not very informative since the signals of the vinylic hydrogen atoms are obscured by the phenyl resonances, but this confirms that the ethenyl group is not π -bonded [8] to an Fe atom. The same problem arises with the ^{13}C NMR spectra, in which the phenyl resonances obscure the vinyl signals, but the other signals are consistent with the proposed structure. Specifically, resonances at 174.7 and 178.5 ppm for **10** and **11** are attributed to the coordinated ketonic carbonyl group [12], and in the case of **10**, two other resonances at 148.5 and 73.1 ppm are characteristic of $C(C(O)Me)$ groups bonded to two and one Fe atom respectively [9]. In the case of **11**, these two resonances were not observed, possibly because of broadening by coupling with the CF_3 groups.

This study of the reactions of alkynes with $[PPh_4][Fe_2(CO)_6(\mu-CO)(\mu-CR^1=CR^2H)]$ complexes ($R^1 = H, R^2 = H, Ph$) has revealed the occurrence of a third type of reaction, additional to the two observed for the complexes with $R^1 = R^2 = Ph$, namely insertion of the alkyne into the iron-carbon σ -bond of the ethenyl bridge. This difference is presumably related to a difference in the steric interaction between the two R groups.

Experimental

All the reactions were performed under dry nitrogen. 1H NMR spectra were recorded on a Bruker WH90 spectrometer with $(CD_3)_2CO$ solutions and ^{13}C NMR spectra on a Bruker WM 250 instrument with CD_2Cl_2 solutions. IR spectra were recorded on a Perkin Elmer 225 or a Perkin Elmer FT 1710 with CH_2Cl_2 solutions. Elemental analyses were performed in our laboratories.

The $[PPh_4][Fe_2(CO)_6(\mu-CO)(\mu-CH=CPhH)]$ [9] and $[PPh_4][Fe(CO)_3(C(O)C(COOMe)CH_2)]$ complexes were synthesized by published procedures [6].

Synthesis of $[PPh_4][Fe_2(CO)(\mu-CO)(\mu-CH=CH_2)]$ (I)

The complex $[PPh_4][HFe(CO)_4]$ (0.5 g, 0.98 mmol) and $Fe_2(CO)_9$ (0.5 g, 1.37 mmol) were added to 20 ml of THF at room temperature. The suspension was heated to $70^\circ C$ and acetylene gas was bubbled through for 10 min. The solution was then stirred for 30 min, cooled at room temperature, filtered through Celite, and evaporated to dryness. The solid residue was recrystallized from a $CH_2Cl_2/MeOH$ mixture 0.41 g (63%). IR $\nu(CO)$: 2028m, 1975vs, 1928vs and 1735m cm^{-1} . 1H NMR (ppm): 7.72 (m, PPh_4), 8.25 (dd, J_1 8 Hz, J_2 12 Hz, 1H), 2.67 (d, J_2 12 Hz, 1H), 2.15 (d, J_1 8 Hz, 1H). Anal. Found: C, 58.86; H, 3.42. $C_{33}H_{23}O_7PFe_2$ calcd.: C, 58.75; H, 3.41%.

Synthesis of [PPh₄][Fe₂(CO)₆(μ-CO)(μ-CR¹=CR²H)]: R¹ = Ph and R² = H (2); R¹ = R² = Ph (3); R¹ = ^tBu and R² = H (4); R¹ = H and R² = SiMe₃ (5); R¹ = CO₂Me and R² = H (6)

To a solution of 0.5 g (0.98 mmol) of [PPh₄][HFe(CO)₄] in 20 ml of THF were added 0.5 g (1.37 mmol) of Fe₂(CO)₉ and 1.00 mmol of the appropriate acetylene. The mixture was kept for 1 h at 70 °C, then cooled, filtered through Celite at room temperature, and evaporated to dryness. The residue was recrystallized from a CH₂Cl₂/MeOH mixture. The yields were 70–80%.

2. IR ν (CO): 2024m, 1976vs, 1930vs, 1735m cm⁻¹. ¹H NMR (ppm): 7.72 (m, PPh₄), 7.45 (m, Ph), 2.51 (s, 1H), 2.08 (s, 1H). Anal. Found: 62.48; 3.59. C₃₉H₂₇O₇PFe₂ calcd.: C, 62.40; H, 3.60%.

3. IR ν (CO): 2024m, 1976vs, 1930vs, 1742m cm⁻¹. ¹H NMR (ppm): 7.72 (m, PPh₄), 7.6–7.8 (m, Ph), 3.48 (s, 1H). Anal. Found: C, 65.40; H, 3.37. C₄₅H₃₁O₇PFe₂ calcd.: C, 65.38; H, 3.75%.

4. IR ν (CO): 2020m, 1966vs, 1920vs, 1726m cm⁻¹. ¹H NMR (ppm): 7.72 (m, PPh₄), 3.09 (s, 1H), 2.96 (s, 1H), 2.15 (s, 9H). Anal. Found C,61.2; H,4.51. C₃₇H₃₁O₇PFe₂ calcd.: C,60.85; H,4.25%.

5. IR ν (CO): 2020m, 1970vs, 1925vs, 1744m cm⁻¹. ¹H NMR (ppm): 7.72 (m, PPh₄), 2.66 (s, 1H), 2.25 (s, 1H), 0.22 (s, 9H). Anal. Found: C, 57.99; H, 4.18. C₃₆H₃₁O₇PSiFe₂ calcd.: C, 57.91; H, 4.16%.

6. IR ν (CO): 2035m, 1985vs, 1948sh, 1935vs, 1770m cm⁻¹. ¹H NMR (ppm): 7.72 (m, PPh₄), 3.65 (s, 3H), 2.79 (s, 1H), 1.81 (s, 1H). Anal. Found: 57.41; H, 3.39. C₃₅H₂₅O₉PFe₂ calcd.: C, 57.38; H, 3.42%.

Complex **6** was also made in the following way.

To a solution of 0.5 g (0.84 mmol) of [PPh₄][Fe(CO)₃(C(O)C(COOMe)CH₂)] in 20 ml of THF was added 0.5 g (1.3 mmol) of Fe₂(CO)₉. The suspension was stirred for 30 min at 70 °C and the red solution formed was then filtered through Celite and evaporated to dryness. The residue was recrystallized from a CH₂Cl₂/MeOH mixture. The yield was 0.43 g (70%).

Synthesis of 7 and 8

To a solution of [PPh₄][Fe₂(CO)₆(μ-CO)(μ-CHCH₂)] (1 g) in 20 ml of acetone was added PhC≡CPh (0.24 g). The solution was refluxed for 1 h then evaporated to dryness. The residue was taken up in methanol (10 ml) and the solution cooled to -20 °C to give **7** as brown crystals (0.8 g, 68% yield). IR ν (CO): 2025m, 1960s, 1930sh, 1885w cm⁻¹. ¹H NMR (ppm): 7.72 (m, PPh₄), 7.05 (m, Ph), 6.32 (dd, *J*₁ 17 Hz, *J*₂ 10 Hz; 1H), 5.41 (dd, *J*₁ 17 Hz, *J*₃ 3.3 Hz; 1H), 4.94 (dd, *J*₂ 10 Hz, *J*₃ 3.3 Hz; 1H). ¹³C NMR (phenyl resonances omitted) (ppm): 210.5, 168.4, 153.1, 138.6 (d, *J* 159 Hz), 111.9 (t, *J* 159 Hz), 92.7. Anal. Found: C, 65.54; H, 3.91. C₄₇H₃₃O₇PFe₂ calcd.: C, 66.59; H, 3.37%.

Evaporation of the mother solution to dryness and recrystallization from ethanol gave **8** as red crystals (0.3 g, 25% yield). IR ν (CO): 2020s, 1955sh, 1935s, 1915m cm⁻¹. ¹H NMR (ppm): 7.72 (m, PPh₄), 6.9 (m, Ph), 4.72 (dd, *J*₁ 8 Hz, *J*₂ 6 Hz; 1H), 2.67 (d, *J*₂ 6 Hz; 1H), 1.07 (d, *J*₁ 8 Hz; 1H). ¹³C NMR (ppm) (phenyl resonances omitted): 225.3, 224.4, 220.7, 216.6, 174.7, 90.7, 81.7 (d, *J* 161.3 Hz), 42.0 (dd, *J*₁ 150 Hz, *J*₂ 161.3 Hz). Anal. Found: C, 66.37; H 4.49. C₄₆H₃₃O₆PFe₂ calcd.: C, 66.99; H, 4.49%.

Synthesis of complex 9

On a vacuum line, a stoichiometric amount of hexafluorobutyne was added to a solution of $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CHCH}_2)]$ (1 g) in 20 ml of dichloromethane. The solution was stirred at room temperature for 16 h then evaporated to dryness. Recrystallization from methanol at -20°C gave orange crystals of **9** (1 g, 85% yield). IR $\nu(\text{CO})$: 2037s, 1987vs, 1950s(broad) cm^{-1} . ^1H NMR (ppm): 7.72 (m, PPh_4), 7.5 (m, Ph), 4.0 (broad, 1H), 0.77 (d, J 3 Hz). ^{13}C NMR (phenyl resonances omitted) (ppm): 217.43, 131.7 (q, J 273), 125 (q, J 275), 66.8 (d, J 159), 16.69 (t, J 137). Anal. Found C, 53.41; H, 2.55. $\text{C}_{34}\text{H}_{23}\text{F}_6\text{O}_6\text{Fe}_2$ calcd.: C, 53.46; H, 2.85%.

Synthesis of complex 10

To a solution of $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CHCPhH})]$ (1 g) in 20 ml of dichloromethane was added $\text{MeOC(O)C}\equiv\text{CC(O)OMe}$ (0.2 ml). The solution was stirred for 1 h then evaporated to dryness. The residue was dissolved in methanol (10 ml) and the solution cooled to -20°C to give **10** as brown crystals (0.8 g, 68% yield). IR $\nu(\text{CO})$: 2035m, 1970s, 1945sh, 1898w cm^{-1} . ^1H NMR (ppm): 7.72 (m, PPh_4), 7.5–6.5 (m, Ph + 2H), 3.88 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (phenyl resonances omitted) (ppm): 220.13, 177.27, 174.65, 169.56, 148.53, 73.1, 51.38 (q, J 146 Hz). Anal. Found: C, 60.45; H, 3.70. $\text{C}_{45}\text{H}_{33}\text{O}_{11}\text{PF}_2$ calcd.: C, 60.58; H, 3.69%.

Synthesis of complex 11

On a vacuum line, a stoichiometric amount of hexafluorobutyne was added to a solution of $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CHCPhH})]$ (1 g) in 20 ml of dichloromethane. The solution was stirred at room temperature for two days then evaporated to dryness. The residue was recrystallized from methanol at -20°C to give brown crystals of **11** (0.4 g, 70% yield). IR $\nu(\text{CO})$: 2040m, 1975s, 1950sh, 1905w cm^{-1} . ^1H NMR (ppm): 7.72 (m, PPh_4), 7.5–6.5 (m, Ph + 2H). ^{13}C NMR (phenyl resonances omitted) (ppm): 219.8, 178.54, 123.47 (d, J 161 Hz). Anal. Found: C, 56.61; H, 2.99. $\text{C}_{43}\text{H}_{27}\text{F}_6\text{O}_7\text{PF}_2$ calcd.: C, 56.54; H, 3.07%.

Acknowledgement

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