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Improved synthesis of di- and trinuclear iron carbonyl complexes containing bridging diphenylethenyl ligand. X-ray structure of $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PhC{=}CHPh)]$

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Abstract

The cluster anion $[PPh_4][HFe_3(CO)_{11}]$ (**1**) reacts with one equivalent of methyl iodide and diphenylacetylene in acetone at room temperature to give the dinuclear complex $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PhC{=}CHPh)]$ (**2**) in high yield. The same reaction performed in boiling acetone yields only the trinuclear cluster $[PPh_4][HFe_3(CO)_9(\mu\text{-}PhC{=}CPh)]$ (**3**). When the reaction of $[PPh_4][HFe_3(CO)_{11}]$ (**1**) is carried out with an excess of methyl iodide at room temperature, the dinuclear neutral complex $[Fe_2(CO)_6\{\mu\text{-}CPhCPhCH(OCH_3)\}]$ (**4**) is obtained as a sole product of the reaction. Complex **2** was characterized by X-ray analyses.

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Keywords: Iron; Alkyne; Carbonyl; Dinuclear; Trinuclear

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1. Introduction

The insertion of acetylenes into the anionic cluster $[HFe_3(CO)_{11}]^-$ provides a general route to di- and trinuclear μ-ethenyl complexes [1,2]. These reactions are complex and depend on the nature of the alkynes and that of the reaction conditions. There is no general way of selectively obtaining only dinuclear complexes. We have shown recently that the reaction of Collman's reagent with diphenylacetylene and CH_3I could be modulated to obtain mono- or dinuclear complexes of iron with alkene ligands [3]. To pursue this study with the aim of comparing the reactivity of Collman's reagent with the well-known reactivity of the trinuclear iron cluster $[PPh_4][HFe_3(CO)_{11}]$ (**1**) with acetylenes, we have extended our work to the study of the reactivity of $[PPh_4][HFe_3(CO)_{11}]$–diphenylacetylene–CH_3I mixtures in several conditions in a single-pot operation.

2. Results and discussion

In a previous work, Mathieu and coworker [1] showed that $[PPh_4][HFe_3(CO)_{11}]$ (**1**) reacts with diphenylacetylene in acetone at room temperature to give the anionic trinuclear complex $[PPh_4][Fe_3(CO)_{10}(\mu\text{-}CPh{=}CHPh)]$ and in boiling acetone also affords a mixture of $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CPh{=}CHPh)]$ (**2**) and $[PPh_4]$-$[HFe_3(CO)_9(\mu\text{-}CPh{=}CPh)]$ (**3**) in an equal ratio that needs to be separated by recrystallization. First, we checked the same reaction at room temperature by adding one equivalent of methyl iodide (Scheme 1).

2.1. Reaction of $[PPh_4][HFe_3(CO)_{11}]$ with one equivalent of methyl iodide and diphenylacetylene at room temperature

When the anionic cluster $[PPh_4][HFe_3(CO)_{11}]$ (**1**) was treated with one equivalent of methyl iodide and diphenylacetylene in acetone at 25 °C for 1 day, the reaction was completed. Infrared analysis of the solution in the $\nu(CO)$ stretching region confirmed the existence of the anionic complex $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CPh{=}CHPh)]$ (**2**) as the sole product formed during the

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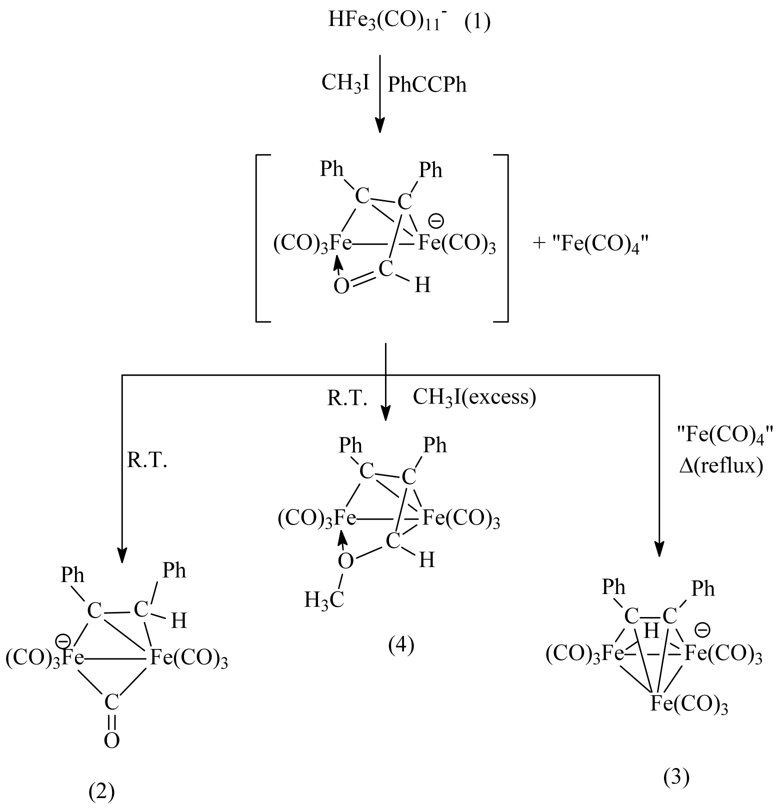

Scheme 1.

reaction. Complex **2** was isolated in 90% yield by recrystallization in a dichloromethane–methanol mixture. All analytical and spectroscopic data of this complex are in concordance with data previously reported in the literature.

2.2. *Reaction of [PPh$_4$][HFe$_3$(CO)$_{11}$] with one equivalent of methyl iodide and diphenylacetylene in boiling acetone*

Reaction of [PPh$_4$][HFe$_3$(CO)$_{11}$] (**1**) with one equivalent of methyl iodide and diphenylacetylene in boiling acetone is complete in 12 h and affords after work up of the trinuclear complex [PPh$_4$][HFe$_3$(CO)$_9$(μ-CPh=CPh)] (**3**). Complex **3** was isolated by recrystallization in dichloromethane–methanol mixtures in 90% yield as black crystals. All spectroscopic data of this complex are in agreement with data previously reported in the literature.

2.3. *Reaction of [PPh$_4$][HFe$_3$(CO)$_{11}$] with an excess of methyl iodide and diphenylacetylene*

Treatment of a solution of [PPh$_4$][HFe$_3$(CO)$_{11}$] (**1**) in acetone with an excess of methyl iodide and diphenylacetylene for 24 h at room temperature gave a red solution of the air-stable complex **4**. The characterization of **4** was facilitated by the similarity of its ^{1}H- and ^{13}C-NMR spectra to those previously synthesized and, in one case, structurally elucidated by X-ray diffraction, metal-propen-1-ylidene complexes [3]. The IR spectrum of **4** exhibited five characteristic absorptions due to the terminal ν(CO) vibrations. The parent ion in the mass spectrum was detected at m/z 502, with fragment ions corresponding to the successive loss of six COs. The ^{1}H-NMR spectrum of **4** showed the expected signals of phenyl groups of diphenylacetylene together with the signals of one olefinic hydrogen at δ 5.31 ppm and one OMe group at 2.97 ppm. No coupling of the olefinic hydrogen with the methyl group was observed. The ^{13}C-NMR spectrum showed, in addition to signals of phenyl groups and carbonyls, three resonances characteristic of a ferrafurane ring at δ 173.5 C$^{\alpha}$, 96.48 C$^{\beta}$ and 124.97 C$^{\gamma}$. The analysis and spectral data are in accordance with the [Fe$_2$(CO)$_6${μ-CPhCPhCH(OCH$_3$)}] formulation (see Fig. 1).

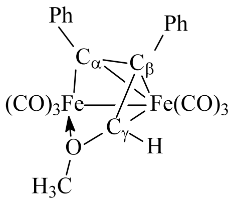

Fig. 1.

These experimental results prompted us to postulate the existence of the anionic intermediate in the formation of complexes **2**, **3** and **4** presented in Scheme 1. This key compound would explain the formation of the neutral complex $[Fe_2(CO)_6\{\mu\text{-CPhCPhCH}(OCH_3)\}]$ (**4**), and its formation is also congruent with the formation of the diphenylethenyl dinuclear anionic complex $[PPh_4][Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-CPh=CHPh})]$ (**2**) through a decarbonylation process. The formation of the hydride–alkyne complex $[PPh_4][HFe_3(CO)_9(\mu\text{-CPh=CPh})]$ (**3**) from this intermediate at reflux in acetone can be explained by a rearrangement of "$Fe(CO)_x$" fragments in the presence of both the alkyne and hydride ligands. It can be pointed out that this anionic cluster was usually obtained under reflux conditions, thus proving that it is a very stable compound. The role of CH_3I in this set of reactions is possibly the activation of a coordinated CO ligand through the formation of an unstable acetyl group. In a first step, the formal coupling of this activated CO with the alkyne and the hydride led to the formation of an oxopropenyl group. The room temperature and reflux restructuring of iron carbonyl and ligand fragments should give products **2** and **3**.

2.4. *X-ray structure determination of $[PPh_4][Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-PhC=CHPh})]$*

The structure of complex **2** was confirmed by a single-crystal X-ray diffraction study. The molecular geometry and atom numbering scheme are shown in Fig. 2. Bond lengths and angles are in Table 1. Two $Fe(CO)_3$ units are linked by a single metal–metal bond (2.537(1) Å). The 1,2-diphenylethenyl bridge is η^1-bonded to Fe1 with Fe1–C2 distance of 2.017(3) Å and asymmetrically η^2-bonded to Fe1 and Fe2 (C2–Fe2: 2.042(3) Å and C3–Fe2: 2.173(3) Å). C3–Fe2 bond is shorter than those normally observed in dinuclear iron complexes with 1,2-diphenylethenyl ligand and ethoxymethylidyne, phosphido, thiolate or chloride bridges [4]. The phenyl groups are in a *cis* configuration forming a torsion angle of 19.62°. The orientation of 1,2-diphenyl ligand and bridging carbonyl in this molecular structure forms a *cisoid* configuration with a dihedral angle between the planes formed by Fe1Fe2C2 and Fe1Fe2C1 of 118.22°. The coordination around Fe1 and Fe2 were both highly distorted octahedron as has been reported in other ethenyldiiron complexes. The μ-CO bridging ligand is asymmetrically linked to the two iron atoms, with the lengths of the bonds for Fe1–C1 and Fe2–C1 being 1.892(3) and 2.069(3) Å, respectively. The Fe–CO bond lengths average 1.785(6) Å with the seemingly shorter distances that for Fe1–C102 (1.752(4) Å), i.e. to the CO ligand *trans* to the Fe–Fe bond.

3. Conclusion

The μ-ethenyl complexes are excellent precursors for the study of formation of carbon–carbon bond formation in dinuclear centers, ligand substitution and synthesis of heterobimetallic complexes [5]. The reaction reported here has provided a simple and quite general route to the synthesis of di- and trinuclear complexes with diphenylethenyl ligand. We are currently examining the broader scope of this synthetic route to other acetylenes and complexes.

4. Experimental

4.1. *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 CH_2Cl_2 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; ^{13}C, 62 MHz) spectrometer in $CDCl_3$ or $(CD_3)_2CO$ solutions. Elemental analyses were obtained by the staff of the Chemical Analysis Service of the Universitat Autonoma de Barcelona.

4.2. *X-ray crystal structure determination of* **2**

X-ray diffraction study of **2**: $C_{45}H_{31}Fe_2O_7P$, $F_w = 826.37$, monoclinic, $a = 12.009(3)$ Å, $b = 11.546(3)$ Å, $c = 28.932(6)$ Å, $\alpha = 90.00°$, $\beta = 90.87(2)°$, $\gamma = 90.00°$, $V = 4011.1(17)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections), space group $P2_1/c$, $Z = 4$, $D_{calc} = 1.368$ g cm^{-3}, $\mu(\text{Mo–K}_\alpha) = 8.69$ cm^{-1}. Data collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation ($\gamma = 0.71069$) and an $\omega-2\theta$ scan, ω scan width $= 0.80 + 0.35 \tan\theta$, ω scan speed = 1.3–5.5°. Reflection ranges for the data collection: $1° < \theta < 25°$, $0 \leq h \leq 12$, $0 \leq k \leq 13$, $-34 \leq l \leq 34$. Lp and empirical absorption corrections were applied, $T_{min} = 0.813$, $T_{max} = 1.000$. 6716 unique reflections, 4831 with $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-86) [6] and refined by full-matrix least-squares procedures on F^2 for all reflections [7]. All non-hydrogen atoms of **2** were refined anisotropically and hydrogen atoms bonded to carbon atoms were placed in calculated positions. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 3.4756P]$, where $P = (F_o^2 + 2F_c^2)/3$. Final $R(F)$ and $R_w(F^2)$ values were 0.0370 and 0.0744, respectively, for reflections with $I > 2\sigma(I)$.

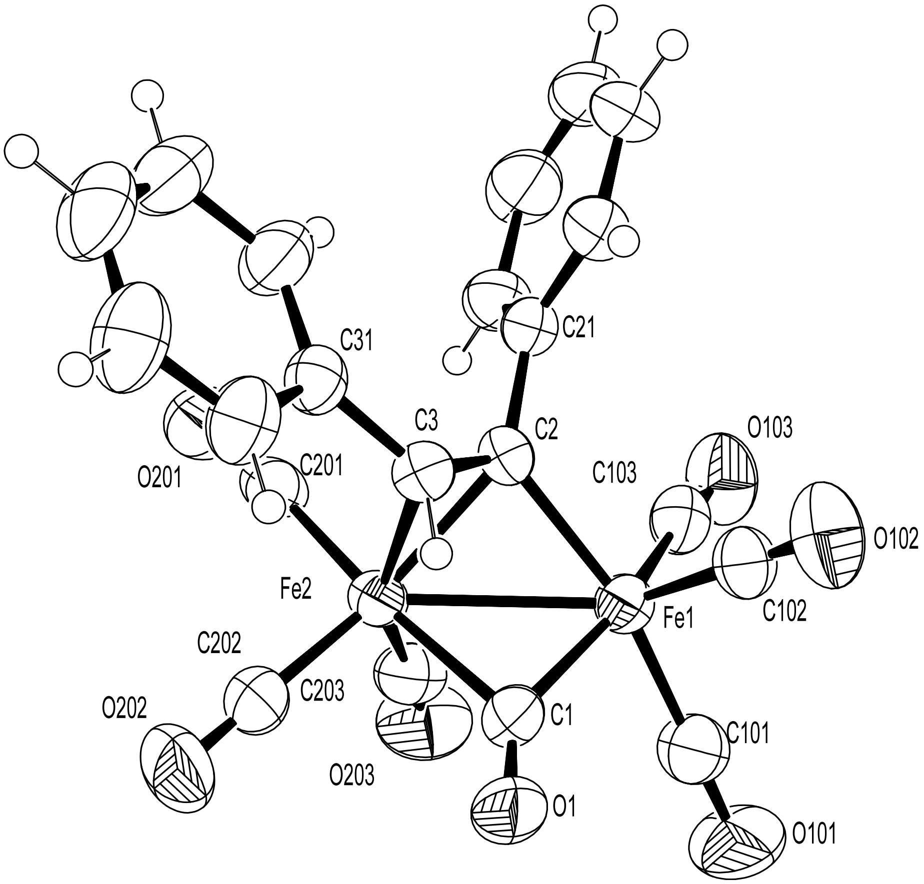

Fig. 2. View of the molecular structure of anion **2** together with the atomic numbering scheme.

4.3. Reaction of [PPh$_4$][HFe$_3$(CO)$_{11}$] with CH$_3$I and diphenylacetylene at room temperature

To a solution of [PPh$_4$][HFe$_3$(CO)$_{11}$] [8] (1 g, 1.23 mol) in 35 ml of acetone were added CH$_3$I (0.08 ml, 1.23 mmol) and diphenylacetylene (0.22 g, 1.23 mmol). The solution was stirred for 1 day at 25 °C then evaporated to dryness. The residue was crystallized in dichloromethane–methanol mixtures and the resulting black solid [PPh$_4$][Fe$_2$(CO)$_6$(μ-CO)(μ-CPh=CHPh)] was isolated in 90% yield.

Anal. Calc. for C$_{44}$H$_{31}$Fe$_2$O$_6$P: C, 66.19; H, 3.91. Found: C, 66.12; H, 3.89%. IR ν(CO) (cm^{-1}) (CH$_2$Cl$_2$): 2025 (m), 1976 (s), 1930 (s), 1742 w (broad). ^{1}H-NMR ((CD$_3$)$_2$CO): δ 3.48 (s, 1H, C*H*), 6.8–7.7 (m, 10H, C$_6$*H*$_5$) ppm. ^{13}C-NMR ((CD$_3$)$_2$CO): δ 76 (CPh=*C*HPh), 167 (*C*Ph=CHPh), 116–151 (*C*$_6$H$_5$), 220 (*C*O) ppm.

4.4. Reaction of [PPh$_4$][HFe$_3$(CO)$_{11}$] with CH$_3$I and diphenylacetylene in boiling acetone

To a solution of [PPh$_4$][HFe$_3$(CO)$_{11}$] (1 g, 1.23 mol) in 35 ml of acetone were added CH$_3$I (0.08 ml, 1.23 mmol) and diphenylacetylene (0.22 g, 1.23 mmol). The solution was refluxed for 12 h and then evaporated to dryness. The residue was crystallized in dichloromethane–methanol mixtures and the resulting black solid [PPh$_4$][HFe$_3$(CO)$_9$(μ-PhC=CPh)] was isolated in 90% yield.

Anal. Calc. for C$_{47}$H$_{31}$Fe$_3$O$_9$P: C, 60.16; H, 3.33. Found: C, 60.12; H, 3.34%. IR ν(CO) (cm^{-1}) (CH$_2$Cl$_2$): 2045 (m), 2005 (s), 1970 (s), 1965 (sh), 1945 (sh), 1905 (sh). ^{1}H-NMR ((CD$_3$)$_2$CO): δ −24.86 (s, 1H, Fe–*H*), 6.8–7.7 (m, 10H, C$_6$*H*$_5$) ppm. ^{13}C-NMR ((CD$_3$)$_2$CO): δ 175(*C*Ph=*C*Ph), 116–151 (*C*$_6$H$_5$), 221 (*C*O) ppm.

4.5. Reaction of [PPh$_4$][HFe$_3$(CO)$_{11}$] with an excess of CH$_3$I and diphenylacetylene

To a solution of [PPh$_4$][HFe$_3$(CO)$_{11}$] (1 g, 1.23 mol) in 35 ml of acetone were added CH$_3$I (0.3 ml, 4.6 mmol) and diphenylacetylene (0.22 g, 1.23 mmol). The contents were stirred for 1 day at 25 °C. The black solution was filtered-off and the solvent was evaporated. The residue was extracted with pentane (2 × 10 ml). Concentration of this solution and cooling to −20 °C gave [Fe$_2$(CO)$_6${μ-CPhCPhCH(OCH$_3$)}] (**4**) in 86% yield.

Anal. Calc. for C$_{22}$H$_{14}$Fe$_2$O$_7$: C, 52.66; H, 2.81. Found: C, 52.59; H, 2.82%. IR ν(CO) (cm^{-1}) (hexane): 2070 (m), 2021 (s), 2000 (m), 1984 (m), 1967 (m). ^{1}H-

Table 1
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths	
Fe1–C102	1.752(4)
Fe1–C101	1.782(4)
Fe1–C103	1.843(4)
Fe1–C1	1.892(3)
Fe1–C2	2.017(3)
Fe1–Fe2	2.5371(8)
Fe2–C203	1.762(4)
Fe2–C202	1.783(4)
Fe2–C201	1.790(4)
Fe2–C2	2.042(3)
Fe2–C1	2.069(3)
Fe2–C3	2.173(3)
C1–O1	1.176(3)
C2–C3	1.425(4)
C2–C21	1.491(4)
C101–O101	1.139(4)
C102–O102	1.149(4)
C103–O103	1.135(4)
C201–O201	1.144(4)
C202–O202	1.149(4)
C203–O203	1.156(4)
Bond angles	
C102–Fe1–C101	98.86(17)
C102–Fe1–C103	102.89(14)
C101–Fe1–C103	90.84(15)
C1–Fe1–C2	85.87(12)
C102–Fe1–Fe2	130.56(10)
C101–Fe1–Fe2	115.73(12)
C103–Fe1–Fe2	110.34(10)
C1–Fe1–Fe2	53.32(9)
C2–Fe1–Fe2	51.75(8)
C203–Fe2–C202	104.91(17)
C203–Fe2–C201	92.31(16)
C202–Fe2–C201	98.90(15)
C2–Fe2–C1	80.78(12)
C203–Fe2–Fe1	79.69(12)
C202–Fe2–Fe1	131.19(11)
C201–Fe2–Fe1	129.77(11)
C2–Fe2–Fe1	50.87(8)
C1–Fe2–Fe1	47.15(9)
C3–Fe2–Fe1	77.46(8)

NMR ($(CD_3)_2CO$): δ 2.97 (s, 3H, OCH_3), 5.31 (s, 1H, C*H*), 6.8–7.7 (m, 10H, C_6H_5) ppm. ^{13}C-NMR ($CDCl_3$): δ 72.83 ($CH_3O \rightarrow Fe$), 96.48 (CPh=*C*PhCH), 124.97 (CPh=CPh*C*H), 123.14–148.60 (C_6H_5), 173.50 (*C*Ph=CPhCH), 211 (*C*O) ppm. Mass spectrum: *m*/*z* 502.05 (M^+).

Acknowledgements

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