

Note

Reactions of $[\text{Fe}_3\text{Cp}_2(\text{CO})_3(\mu\text{-CO})(\mu_3\text{-CO})(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3)]$ with diphosphines: X-ray structure of a complex in which two tri-iron clusters are linked only by $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$

François Y. Pétilion ^{a,*}, Françoise Robin-Le Guen ^{a,1}, René Rumin ^a,
Philippe Schollhammer ^a, Jean Talarmin ^a, Kenneth W. Muir ^{b,*}

^a UMR CNRS 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique, UFR Sciences et Techniques Université de Bretagne Occidentale, 6 Avenue Le Gorgeu, CS 93837, 29238 Brest-Cedex 3, France

^b Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland, United Kingdom

Received 21 December 2005; received in revised form 27 January 2006; accepted 12 February 2006

Available online 6 March 2006

Abstract

Reactions of the trinuclear iron cluster $[\text{Fe}_3\text{Cp}_2(\text{CO})_3(\mu\text{-CO})(\mu_3\text{-CO})(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3)]$ (**1**) with the bis(phosphino) ligands dppe and dppe give different results: dppe yields mainly the hexanuclear compound (**2**) in which two tri-iron cluster units are linked by the diphosphine, although a trinuclear derivative (**3**) with a chelating dppe ligand is also obtained as a minor product, whereas dpmm displaces carbonyl to give complexes containing exclusively a single tri-iron unit, though the phosphine may be either dangling (**4**) or chelating (**5**). The complexes **2–5** have been characterised by elemental analyses and from their IR and NMR spectra, supplemented in the case of **2** by a single crystal X-ray diffraction analysis.

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Keywords: Iron; Diphosphine ligand; Trinuclear and hexanuclear clusters; Molecular structure

1. Introduction

Our attempts to model the di-iron subsite of all-iron hydrogenase [1] have led us to take an interest in the syntheses and solid-state structures of model compounds containing pairs of di- or tri-iron moieties linked only by a single diphosphine ligand. Examples of such iron derivatives, characterised by spectroscopy, have been reported [2] but only rarely have the solid-state structures of these compounds also been determined [3]. Analogous complexes, in which, for example, Ru, Os or Co clusters are linked only by a diphosphine, have also been previously

characterised by X-ray methods [4] or by spectroscopy [5]. Usually the bridging ligand is an $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ diphosphinoethane and there appear to be only two structurally characterised examples in which an $\text{R}_2\text{PCH}_2\text{PR}_2$ diphosphinomethane plays the bridging role [6]. We now describe attempts to prepare new compounds of this type by reacting the trinuclear iron compound $[\text{Fe}_3\text{Cp}_2(\text{CO})_3(\mu\text{-CO})(\mu_3\text{-CO})(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3)]$ (**1**) [7] with bis(diphenylphosphino)ethane (dppe) and -methane (dpmm).

2. Results and discussion

The reaction of **1** with 0.5 equiv. of dppe in refluxing tetrahydrofuran, followed by chromatographic separation, gave two new compounds: $[\{\text{Fe}_3\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu_3\text{-CO})(\mu_3\text{-}\eta^1, \eta^1, \eta^2\text{-CF}_3\text{C}_2\text{CF}_3)\}_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$ (**2**) and $[\text{Fe}_3\text{Cp}_2(\text{CO})\{\eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\mu\text{-CO})(\mu_3\text{-CO})(\mu\text{-}\eta^1, \eta^2, \eta^2\text{-CF}_3\text{C}_2\text{CF}_3)]$ (**3**) in 63.5% and 23.5% yields, respectively

* Corresponding authors.

E-mail addresses: francois.petillon@univ-brest.fr (F.Y. Pétilion), ken@chem.gla.ac.uk (K.W. Muir).

¹ UMR CNRS 6503, Organométallique et Catalyse, Institut de Chimie de Rennes, IUT Lannion, rue E. Branly, 22300 Lannion, France.

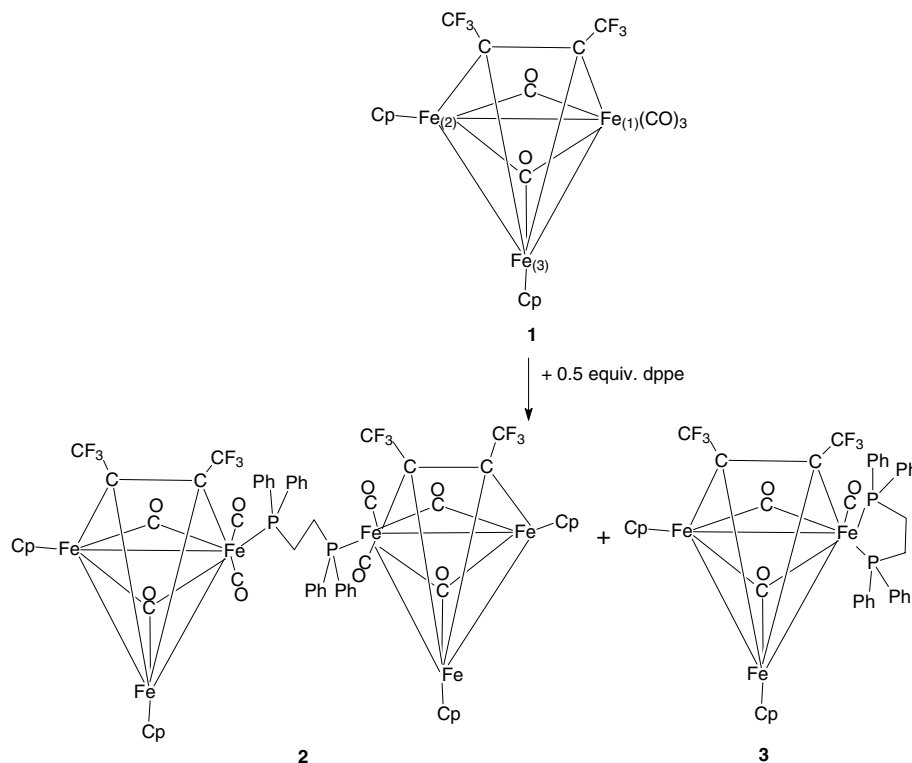
(Scheme 1). These compounds have been characterised by elemental analysis, IR and ^1H , ^{19}F , ^{31}P - $\{^1\text{H}\}$ and ^{13}C - $\{^1\text{H}\}$ NMR data, together with a single crystal X-ray diffraction study for **2**.

The molecular structure of **2** (Fig. 1a) is derived by replacing the same terminal carbonyl group in each of two molecules of **1** by the donor phosphorus atoms of a dppe ligand which then acts as the sole link between the two iron triangles. These triangles, labelled a and b in Fig. 1a, though crystallographically independent, display essentially identical structures which closely resemble that of their parent **1** [8]. In each tri-iron framework the alkyne is related to the Fe_3 triangle in μ_3 - η^2 -parallel fashion which is the most common form of attachment of an alkyne to a M_3 triangle [9]. The Fe1-Fe2 bonds in **2** [2.650(1) and 2.654(1) Å] are a little longer than the other Fe-Fe bonds [2.514(1)–2.528(1) Å], a feature also found in **1**. Unsurprisingly, the main differences between **1** and **2** occur in the coordination of Fe1 and seem to reflect the replacement of CO by phosphine, a stronger σ -donor and weaker π -acid: thus the semi-bridging Fe1-C8 distances [2.352(7) and 2.357(7) Å] are appreciably longer than the corresponding value in **1** [2.23(1) Å]. In contrast the μ_3 - Fe-C distances [means 2.10, 2.06 and 1.93 Å for Fe1 , Fe2 and Fe3] are somewhat more regular than comparable values in **1** [2.17(1), 2.02(1) and 1.86(1) Å].

The shape of a molecule of **2** is largely determined by the torsion angles in the $\text{Fe2a-Fe1a-P1-C1-C2-P2-Fe1b-Fe2b}$ chain [$-88.5(2)^\circ$, $-52.6(4)^\circ$, $-162.1(3)^\circ$, $173.6(3)^\circ$ and $110.5(2)^\circ$] which imply near eclipse across C1-C2

and C2-P2 but a gauche arrangement across P1-C1 . The difference in sign of the torsion angles across Fe1a-P1 and P2-Fe1b arises because the two cluster units are near mirror images of each other. Finally, given current interest in crystals capable of occluding large volumes of solvent, it is worth noting that 19.6% of the cell volume of **2** is void space containing disordered dichloromethane.

NMR analyses of **2** reveal the existence of two products in solution (see Section 4) that are assumed to be two isomers **2a** and **2b**. The ^{31}P - $\{^1\text{H}\}$ spectrum of each of them exhibits a singlet at 51.6 (**2a**) and 51.4 (**2b**) ppm, which is due to equivalent phosphorus atoms, showing that the solution structure is consistent with that observed in the solid state. On standing in solution at room temperature the ratio of **2b** to **2a**, initially equimolar, increases to 1:0.7 after 2 h. The transformation process that is responsible for the **2a** \rightarrow **2b** conversion is therefore slow. No fluxional phenomena could be detected on the NMR (^{19}F , ^{31}P) time scale, over the temperature range 298–358 K in toluene d_8 . On the basis of these data, an isomerism involving a rotation around either a Fe-P or a C-C single bond, affording a pair of rotamers should be ruled out. Indeed, the rotation energy needed for such a process is not as high to give stable rotamers in the NMR time scale at room temperature. A possible isomerization process involving an alkyne rotation and migration of the semibridging CO ligand in one of the two isomers from one edge of the Fe_3 triangle to another to give the second isomer, has been examined to account for the existence of **2a** and **2b** in solution. Such a process implies that the hexafluorobut-2-yne



Scheme 1.

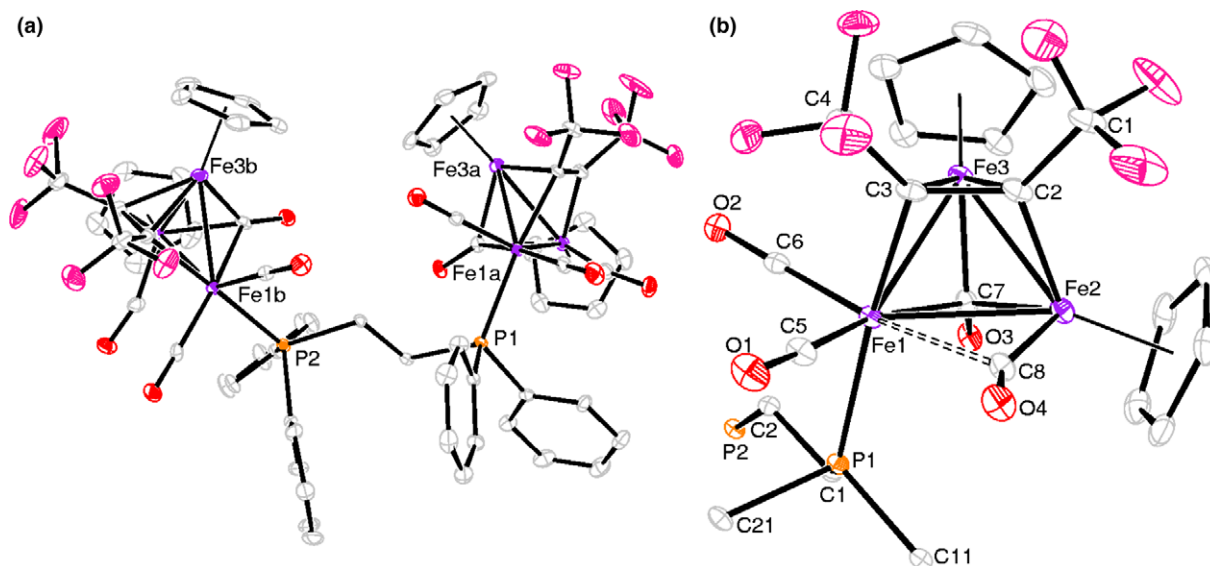


Fig. 1. (a) An overall view of a molecule of **2**. A consistent atom numbering system has been used for the two independent cluster moieties; corresponding atoms are distinguished where necessary by the letters a and b. (b) A view of the metal coordination in cluster moiety a of **2** with hydrogen atoms and some phenyl carbon atoms omitted. Selected distances (Å) in moieties a and b: Fe–Fe 2.514(1)–2.528(1) except Fe1–Fe2 2.650(1) and 2.654(1), Fe–P 2.305(2) and 2.310(2), Fe1–CCF₃ 2.012(6) and 2.013(6), Fe2–CCF₃ 1.956(7) and 1.960(7), Fe3–CCF₃ 1.942(7) and 1.964(7), Fe1–CO 1.762(8)–1.795(8), μ_3 -Fe1–CO 2.108(6) and 2.098(7), μ_3 -Fe2–CO 2.070(6) and 2.059(7), μ_3 -Fe3–CO 1.924(7) and 1.940(8), Fe1–C8 2.352(7) and 2.357(7), Fe2–C8 1.801(8) and 1.814(7) and C2–C3 1.418(9) and 1.419(9). 10% Probability ellipsoids are shown.

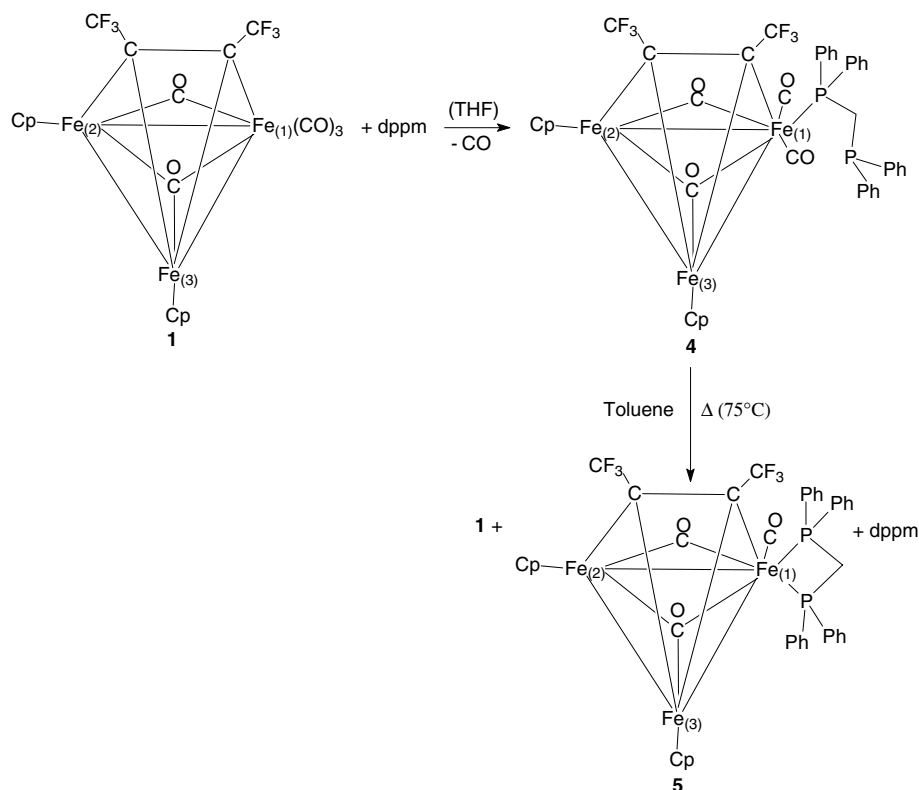
ligand has either an asymmetrical or symmetrical position [10] in the related isomers. This is not observed in the ¹⁹F NMR spectra of **2a** and **2b**, which both show two inequivalent CF₃ groups. This observation excludes for **2a** and **2b** an isomerism due to alternate position of the alkyne and the semibridging CO ligands in cluster **2**. Finally, NMR data could agree with an isomerism involving basal-apical exchanges of the phosphine ligand at Fe(1) in the cluster compound **2**. The heating at 80 °C of a toluene *d*₈ solution of **2** in the NMR tube was monitored by following changes in the ¹⁹F NMR spectra with time. Transformation of **2** into **3** and **1** was observed. For example, after 15 min of heating, the solution contained 60%, 18.5% and 21.5% of **2**, **3** and **1**, respectively. After 180 min of heating, the related yields of **2**, **3** and **1** were 16%, 39.5% and 44.5%, respectively. These thermal data show that no fluxional process involving isomers **2** can be detected in toluene *d*₈ at temperature higher than 80 °C by NMR technics.

Spectroscopic data for solutions of **3** are in agreement with the formulation proposed in Scheme 1. In particular, compound **3** exhibits the IR bands expected for terminal, semi-bridging and triply-bridging carbonyl groups: the presence of such ligands in the molecule is confirmed by the ¹³C NMR downfield chemical shifts at 213.5, 249.6 and 292.0 ppm, respectively. The ³¹P–{¹H} NMR spectrum of **3** shows a pair of doublets at 82.5 and 69.3 ppm (³J_{P–P} = 13.5 Hz), these shifts are typical for those observed when dppe acts as a chelating ligand, replacing two terminal CO groups at Fe1 [3b].

With the aim of linking two tri-iron cluster units through a diphosphine with a shorter P–CH₂–P chain, we

have heated under reflux a tetrahydrofuran solution containing **1** and bis(diphenylphosphino)methane (dppm). Whatever the mole ratio of the reactants (cluster:dppm = 1:1 or 2:1), only product **4** containing a single tri-iron cluster unit was formed. Prolonged heating of **4** in toluene at higher temperature did not produce the desired double tri-iron cluster compound linked by dppm; instead, complex **5** containing again a single tri-iron cluster unit was obtained (Scheme 2). The failure to form a dppm complex analogous to **2**, and indeed the general reluctance of dppm to act as a single bridge between cluster units, is probably attributable to steric hindrance.

Compounds **4** and **5** have been fully characterised by elemental analyses, IR and NMR data. The ³¹P–{¹H} NMR spectrum of **4** contains two doublets at δ –25.9 and 46.7 (²J_{P–P} = 49.0 Hz) indicating inequivalent ³¹P nuclei. These chemical shifts are consistent with a monodentate dppm ligand [3b,11]; in particular, the high field signal is close to that of the free ligand, confirming the presence of a dangling group. All the other analytical and spectroscopic data for **4** (see Section 4) support the structure proposed in Scheme 2. The conversion of **4** into **5** involves the loss of one terminal carbonyl ligand and the retention of the two carbonyls in semi- and triply-bridging positions, as clearly shown by IR and ¹³C NMR experiments. Thus, it appears that the dppm acts in **5** as a chelating ligand after replacement of a further CO group at Fe(1). The ³¹P–{¹H} NMR spectrum of **5** contains doublets at δ 34.95 and 12.75; the absence of a highfield signal similar to that at δ –25.9 in the corresponding spectrum of **4**, combined with the dramatic lowering of the ²J_{P–P}



coupling constant to 6.3 Hz, compared with 49.0 Hz in **4**, confirms the chelating coordination mode of the dppm ligand in **5**.

3. Conclusion

Reactions of the trinuclear iron compound $[\text{Fe}_3\text{Cp}_2(\text{CO})_3(\mu\text{-CO})((\mu_3\text{-CO})(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3))]$ (**1**), with bis(diphenylphosphino)methane (dppm) yield complexes **4** and, on prolonged heating, **5** in which terminal carbonyl ligands have been replaced by, respectively one (**4**) or two (**5**) phosphorus atoms of the dppm ligand. If the distance between the donor phosphorus atoms of the diphosphine is increased by interposing an additional CH_2 group as in dppe the reaction gives mainly **2**, containing two tri-iron cluster units linked by the diphosphine.

4. Experimental

4.1. General procedures

Reactions were performed under dinitrogen using standard Schlenk techniques, the solvents being deoxygenated and dried by standard methods. The literature methods were used for the preparation of **1** [7]. All other reagents were commercial grade and were used as obtained. IR spectra were obtained with a Perkin–Elmer 1430 spectrophotometer in the $\nu(\text{CO})$ region. NMR spectra were recorded at room temperature on either Bruker AC 300 or JEOL

FX 100 spectrometers, relative to tetramethylsilane as an internal reference (^1H , ^{13}C) or to external H_3PO_4 (^{31}P) and CFCl_3 (^{19}F). Chemical analyses were performed by the “Centre de Microanalyses du CNRS” of Vernaison (France).

4.2. Preparation of **2** and **3**

The complex **1** (200 mg, 0.333 mmol) and 0.5 equiv. of dppe (66 mg) were heated in deoxygenated tetrahydrofuran (15 ml) at reflux for 2.5 h. The mixture was evaporated to dryness under vacuum and then extracted with CH_2Cl_2 . Chromatography of the dichloromethane solution on a silica gel column eluting with a mixture of hexane, CH_2Cl_2 and diethyl ether (69.5/30/0.5) afforded a dark-green band, from which **3** (74 mg, 23.5% yield) was obtained. Further elution with the same mixture of solvents gave a violet fraction, from which **2** (168 mg, 63.5% yield) was isolated as an equimolar mixture of two inseparable isomers **2a** and **2b** by chromatography. Dark-violet crystals of **2b** grew from a 1:1 hexane/ CH_2Cl_2 solution of a mixture of **2a** and **2b** at -20°C , after two weeks. **2**: Anal. Calc. for $\text{C}_{62}\text{H}_{44}\text{F}_{12}\text{-Fe}_6\text{O}_8\text{P}_2$: C, 48.3; H, 2.9; Fe, 21.7. Found: C, 48.5; H, 3.0; Fe, 21.6%. IR (CH_2Cl_2 , cm^{-1}), $\nu(\text{CO})$: 2010 (s), 1952 (s), 1852 (m), 1665 (s). ^1H - $\{^{31}\text{P}\}$ NMR (CDCl_3), **2a**: δ 6.75–7.00 (m, 20H, C_6H_5), 5.11 (s, 5H, C_5H_5), 4.16 (s, 5H, C_5H_5), 2.45 ($[\text{AB}]_2$, 4H, $\text{CH}_2\text{-CH}_2$); **2b**: δ 7.50–7.00 (m, 20H, C_6H_5), 5.08 (s, 5H, C_5H_5), 4.07 (s, 5H, C_5H_5), 2.73 (m, 2H, CH_2), 2.05 (m, 2H, CH_2). ^{19}F NMR (CDCl_3),

2a: δ -50.2 (q, $^5J_{F-F} = 13.0$ Hz, CF_3), -48.0 (q, br, $^5J_{F-F} = 13.0$ Hz, CF_3); **2b**: -50.1 (q, $^5J_{F-F} = 13.0$ Hz, CF_3), -47.8 (q, br, $^5J_{F-F} = 13.0$ Hz, CF_3). $^{31}P\{-^1H\}$ NMR ($CDCl_3$), **2a**: δ 51.6 (s, br, PPh_2); **2b**: δ 51.4 (s, br, PPh_2). $^{13}C\{-^1H\}$ NMR (CD_2Cl_2), **2a**: δ 292.05 (dd, $J_{C-P} = J'_{C-P} = 4.0$ Hz, μ_3-CO), 228.2 (s, $\mu-CO$), 216.1 (dd, $J_{C-P} = J'_{C-P} = 7.0$ Hz, CO), 212.6 (dd, $J_{C-P} = J'_{C-P} = 11.0$ Hz, CO), 165.5 (m, $C(CF_3)$), 153.7 (m, $C(CF_3)$), 135.4–127.0 (m, C_6H_5 and CF_3), 92.2 (s, C_5H_5), 87.75 (s, C_5H_5), 20.3 (dd, $J_{C-P} = J'_{C-P} = 7.5$ Hz, CH_2); **2b**: δ 289.9 (dd, $J_{C-P} = J'_{C-P} = 4.0$ Hz, μ_3-CO), 228.0 (s, $\mu-CO$), 216.5 (dd, $J_{C-P} = J'_{C-P} = 7.5$ Hz, CO), 213.1 (dd, $J_{C-P} = J'_{C-P} = 11.0$ Hz, CO), 165.5 (m, $C(CF_3)$), 153.7 (m, $C(CF_3)$), 135.4–127.0 (m, C_6H_5 and CF_3), 92.1 (s, C_5H_5), 87.7 (s, C_5H_5), 20.9 (dd, $J_{C-P} = J'_{C-P} = 8.0$ Hz, CH_2). **3**: Anal. Calc. for $C_{62}H_{34}F_6Fe_3O_3P_2$: C, 54.8; H, 3.6; Fe, 17.8. Found: C, 54.7; H, 3.8; Fe, 17.9%. IR (CH_2Cl_2 , cm^{-1}), $\nu(CO)$: 1950(s), 1792(s), 1644(s). $^1H\{-^{31}P\}$ NMR (CD_2Cl_2): δ 8.25–6.75 (m, 20H, Ph), 4.95 (s, 5H, Cp), 4.04 (s, 5H, Cp), 3.10–2.35 (AA'BB', 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ -44.25 (dq, $^5J_{F-F} = 13.5$ Hz, $^4J_{P-F} = 2.5$ Hz), -47.8 (q, $^5J_{F-F} = 13.5$ Hz). ^{31}P NMR ($CDCl_3$): δ 82.5 (d, $^3J_{P-P} = 13.5$ Hz, PPh_2), 69.3 (dq, $^3J_{P-P} = 13.5$ Hz, $^4J_{P-F} = 2.5$ Hz, PPh_2). $^{13}C\{-^1H\}$ NMR (CD_2Cl_2): δ 292.0 (dd, $J_{C-P} = J'_{C-P} = 8.0$ Hz, μ_3-CO), 249.6 (dd, $J_{C-P} = 9.0$ Hz, $J'_{C-P} = 10.0$ Hz, $\mu-CO$), 213.5 (dd, $J_{C-P} = 19.0$ Hz, $J'_{C-P} = 12.5$ Hz, CO), 164.7 (q, br, $^2J_{C-F} = 37.0$ Hz, $C-CF_3$), 152.1 (q, br, $^2J_{C-F} = 36.0$ Hz, $C-CF_3$), 139.5–127.0 (m, C_6H_5), 130.8 (q, $J_{C-F} = 277.0$ Hz, CF_3), 130.0 (q, $J_{C-F} = 277.0$ Hz, CF_3), 93.1 (s, C_5H_5), 87.8 (s, C_5H_5), 34.0 (dd, $J_{C-P} = 25.5$ Hz, $J'_{C-P} = 15.0$ Hz, $P-CH_2$), 32.3 (dd, $J_{C-P} = 26.0$ Hz, $J'_{C-P} = 12.0$ Hz, $P-CH_2$).

4.3. Preparation of 4

The complex **1** (120 mg, 0.20 mmol) and 1 equiv of dppm (77 mg) were heated in deoxygenated tetrahydrofuran (15 ml) at reflux for 1.5 h. The solvent was then removed under vacuum and the residue was dissolved in CH_2Cl_2 (3 ml) and chromatographed on silica gel. Elution with a mixture hexane/ CH_2Cl_2 (2.3:1) removed a violet band. Evaporation of the volatiles afforded **4** as a dark-violet powder (182 mg, 95% yield). Anal. Calc. for $C_{43}H_{32}F_6Fe_3O_4P_2$: C, 54.0; H, 3.4; Fe 17.5. Found: C, 53.9; H, 3.5; Fe, 17.7%. IR (CH_2Cl_2 , cm^{-1}), $\nu(CO)$: 2005 (s), 1944 (s), 1844 (s), 1660 (s). $^1H\{-^{31}P\}$ NMR ($CDCl_3$): δ 7.75–6.75 (m, 20H, C_6H_5), 4.97 (s, 5H, C_5H_5), 4.14 (s, C_5H_5), 3.65 and 3.19 (AB, $J_{H-H} = 15.0$ Hz, 2H, CH_2). ^{19}F NMR ($CDCl_3$): δ -47.9 (dq, $^5J_{F-F} = 13.0$ Hz, $^4J_{F-P} = 2.5$ Hz, CF_3), -50.2 (q, $^5J_{F-F} = 13.0$ Hz, CF_3). $^{31}P\{-^1H\}$ NMR ($CDCl_3$): δ 46.7 (d, br, $^2J_{P-P} = 49.0$ Hz, $FePPh_2$), -25.9 (d, $^2J_{P-P} = 49.0$ Hz, CH_2PPh_2). $^{13}C\{-^1H\}$ NMR (CD_2Cl_2): δ 292.3 (d, $^2J_{C-P} = 7.0$ Hz, μ_3-CO), 228.7 $^{(1)}$ (s, br, $\mu-CO$), 216.15 (d, $^2J_{C-P} = 15.0$ Hz, CO), 212.7 (d, $^2J_{C-P} = 22.0$ Hz, CO), 165.1 $^{(1)}$ (q, br, $^2J_{C-F} = 35.0$ Hz, CCF_3), 153.65 $^{(1)}$ (qq, $^2J_{C-F} = 35.0$ Hz, $^3J_{C-F} = 3.0$ Hz, CCF_3),

140.0–128.0 (m, C_6H_5 and CF_3), 92.2 (s, C_5H_5), 87.45 (s, C_5H_5), 24.75 (dd, $J_{C-P} = 34.0$ Hz, $J'_{C-P} = 21.5$ Hz, CH_2); $^{(1)}^{13}C\{-^1H\}$, $\{-^{31}P\}$.

4.4. Preparation of 5

A solution of complex **4** (150 mg, 0.157 mmol) in toluene (20 ml) was stirred for 2.5 h at 75 °C. After that time the colour of the solution turned from violet to greenish. The solvent was then removed in vacuo, the residue was extracted with dichloromethane (3 ml), and the extracts were chromatographed on silica gel. Elution with hexane/ CH_2Cl_2 (5:1) gave a red-brown fraction of **1** (22.2 mg, 23.6%). Further elution with a mixture hexane/ CH_2Cl_2 (2.3:1) removed a violet band, which gave, after evaporation of the volatiles, the starting compound **4** (43.5 mg, 29%). Finally, elution with hexane/ CH_2Cl_2 /ether (2.3:1:0.02) afforded a green fraction. Evaporation of solvents yielded a compound **5** as a green powder (68.7 mg, 47.2%).

Anal. Calc. for $C_{42}H_{32}F_6Fe_3O_3P_2$: C, 54.3; H, 3.5; Fe, 18.0. Found: C, 54.2; H, 3.6; Fe, 17.9%. IR (CH_2Cl_2 , cm^{-1}), $\nu(CO)$: 1940 (s), 1775 (s), 1627 (s). $^1H\{-^{31}P\}$ NMR (CD_2Cl_2): δ 8.20–6.75 (m, 20H, C_6H_5), 4.86 (s, 5H, C_5H_5), 4.47 and 4.18 (AB, $J_{A-B} = 15.0$ Hz, 2H, CH_2), 4.07 (s, 5H, C_5H_5). ^{19}F NMR (CD_2Cl_2): δ -43.9 (ddq, $^5J_{F-F} = 12.0$ Hz, $^4J_{P-F} = 6.3$ Hz, $^4J'_{P-F} = 4.5$ Hz, CF_3), -49.75 (q, $^5J_{F-F} = 12.0$ Hz, CF_3). $^{31}P\{-^1H\}$ NMR ($CDCl_3$): δ 34.95 (dq, $^2J_{P-P} = ^4J_{P-F} = 6.3$ Hz, PCH_2P), 12.75 (dq, $^2J_{P-P} = 6.3$ Hz, $^4J_{P-F} = 4.5$ Hz, PCH_2P). $^{13}C\{-^1H\}$ NMR (CD_2Cl_2): δ 295.65 (dd, $J_{C-P} = J'_{C-P} = 9.0$ Hz, μ_3-CO), 249.45 (dd, $J_{C-P} = J'_{C-P} = 8.5$ Hz, $\mu-CO$), 212.9 (dd, $J_{C-P} = 12.0$ Hz, $J'_{C-P} = 15.5$ Hz, CO), 162.6 $^{(1)}$ (qq, $^2J_{C-F} = 33.0$ Hz, $^3J_{C-F} = 4.0$ Hz, CCF_3), 150.6 $^{(1)}$ (qq, $^2J_{C-F} = 32.0$ Hz, $^3J_{C-F} = 4.0$ Hz, CCF_3), 140.0–127.8 (m, C_6H_5), 130.6 $^{(1)}$ (q, $J_{C-F} = 274.0$ Hz, CF_3), 130.2 $^{(1)}$ (q, $J_{C-F} = 274.0$ Hz, CF_3), 92.25 (s, C_5H_5), 87.05 (s, C_5H_5), 41.9 (dd, $J_{P-C} = J'_{P-C} = 21.0$ Hz, CH_2); $^{(1)}^{13}C\{-^1H\}\{-^{31}P\}$.

4.5. X-ray crystallography

Crystal data for **2**, $C_{62}H_{44}F_{12}Fe_6O_8P_2$, F. wt. 1542.01, 20 °C, $\lambda = 0.71073$ Å, monoclinic, space group $P2_1/n$, $a = 17.3075(11)$, $b = 22.549(2)$, $c = 18.0073(14)$ Å, $\beta = 103.779(9)^\circ$, $V = 6825.5(10)$ Å³, $Z = 4$, $D_{calc} = 1.501$ g cm^{-3} , $\mu = 1.370$ mm⁻¹, crystal size 0.25 × 0.10 × 0.10 mm, $\theta_{max} = 22.1^\circ$.

11 345 intensities were measured on a Nonius CAD4 diffractometer. After empirical absorption corrections (ψ -scans, transmission factors 0.895–0.705) and averaging [$R_{int} = 0.045$] the structure was solved by direct methods and refined by full-matrix least-squares on F^2 [12]. Adjustment of 727 parameters gave $R(F) = 0.053$, $wR(F^2) = 0.129$ for 5429 data with $I > 2\sigma(I)$ and $R(F) = 0.099$, $wR(F^2) = 0.142$ for all 8478 unique reflections. $|\Delta\rho| < 0.69$ e Å⁻³. In the final refinement Cp and Ph rings were refined as rigid

equilateral polygons. The unit cell contains two equivalent voids of 678 \AA^3 , centred on $(0, 1/2, 0)$ and $(1/2, 0, 1/2)$, which contain disordered dichloromethane. The most efficacious method of allowing for the scattering of the disordered solvent proved to be the non-parametric Fourier refinement technique of Spek [13] which assigned 42 electrons, i.e., about one CH_2Cl_2 molecule, to each void.

5. Supplementary materials

The crystallographic data for **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary Publication CCDC 292529. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

The authors thank the CNRS, the EPSRC and Glasgow and Brest Universities for financial support.

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