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Iron–rhodium complexes with a single bridging diphosphine ligand: the crystal structure of $[CpFe(\mu\text{-}CO)_2(\mu\text{-dppm})RhI_2]$

Ian Mansfield [a], Nagwa Nawar [b,*], Anthony K. Smith [a], Nicola C. Tong [a]

[a] *Department of Chemistry, University of Liverpool, Donnan Laboratories, Grove Street, PO Box 147, Liverpool L69 3BX, UK*
[b] *Department of Chemistry, Faculty of Science, Mansoura University, Mansoura 35516, Egypt*

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Abstract

The mononuclear complexes $[FeCpI(CO)_2]$ **1**, $[FeCp(CO)_2(\eta^1\text{-dppm})]I$ **2**, $[FeCp(CO)(\eta^2\text{-dppm})]I$ **3**, $[FeCp(CO)_2(\eta^1\text{-dppen})]I$ **5** and $[FeCp(CO)(\eta^2\text{-dppen})]I$ **6** [dppen = $Ph_2PC(=CH_2)PPh_2$] have been synthesised and reacted with $[Rh_2Cl_2(CO)_4]$ to produce heterobimetallic complexes of the type $[CpFe(\mu\text{-}CO)_2(\mu\text{-}PP)RhX_2]$ (X = Cl or I). The structure of $[CpFe(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PCH_2PPh_2\}RhI_2]$ **4** has been determined by X-ray crystallography.

Keywords: Iron; Rhodium; Heterobimetallics; Diphosphine; Cyclopentadienyl; Iodine

1. Introduction

The ability to synthesise organometallic compounds containing two or more different metal atoms is becoming increasingly more valuable to inorganic chemists. The interest in such heterobimetallic complexes extends towards catalytic applications and to new metal-assisted organic chemistry.

As our contribution to this area, we have been studying the ring-opening reactions of $[RuClCp(\eta^2\text{-dppen})]$ [dppen = $(PPh_2)_2C{=}CH_2$] and $[RuClCp(\eta^2\text{-dppa})]$ [dppa = $(PPh_2)_2NH$] with $[Rh_2Cl_2(CO)_4]$, which lead to the formation of the heterobimetallic complexes $[CpRu(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PC(=CH_2)PPh_2\}RhCl_2]$ [1] and $[CpRu(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PNHPPh_2\}RhCl_2]$ [2]. We have previously reported the ring-opening reaction of $[Fe(CO)_3(\eta^2\text{-dppen})]$ or the reaction of $[Fe(CO)_4(\eta^1\text{-dppen})]$ with $[Rh_2Cl_2(CO)_4]$ to give $[(CO)_4Fe(\mu\text{-dppen})RhCl(CO)]$ [3]. As an extension of our work on the Fe–Rh and Ru–Rh systems [4], we have synthesised the complexes $[FeCp(CO)_2(\eta^1\text{-dppm})]I$ **2** and $[FeCp(CO)(\eta^2\text{-dppm})]I$ **3** [5–8], and now report that treatment of **2** or **3** with $[Rh_2Cl_2(CO)_4]$ leads to the formation of the heterobimetallic complex $[CpFe(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PCH_2PPh_2\}RhI_2]$ **4**. Similarly, reactions of the iron–dppen complexes $[FeCp(CO)_2(\eta^1\text{-dppen})]I$ **5** and $[CpFe(CO)(\eta^2\text{-dppen})]I$ **6** with $[Rh_2Cl_2(CO)_4]$ to give $[CpFe(\mu\text{-}CO)_2(\mu\text{-dppen})RhI_2]$ **7** are described.

2. Results and discussion

Irradiation of equimolar amounts of $[FeCpI(CO)_2]$ **1** and dppm in THF produces $[FeCp(CO)_2(\eta^1\text{-dppm})]I$ **2** and $[FeCp(CO)(\eta^2\text{-dppm})]I$ **3** depending on the time of irradiation (Scheme 1). The infrared spectrum of complex **2** shows $\nu(CO)$ bands at 2028 and 1990 cm^{-1} and the ^{31}P NMR spectrum of **2** shows a resonance at δ 62.8 (d, $J_{PP} = 51$ Hz) due to the phosphorus atom coordinated to Fe and a resonance centred at δ −25.4 (d, $J_{PP} = 51$ Hz) due to the uncoordinated phosphorus atom. Analysis by FAB mass spectroscopy showed a peak at $m/z = 561$, which corresponds to M^+–I. The spectrum also shows peaks at $m/z = 533$ and 505, corresponding to the loss of the two carbonyl groups. A peak at $m/z = 320$, corresponding to the loss of 185 amu, suggests the loss of PPh_2. Also, a peak at $m/z = 121$, due to CpFe, is observed. The infrared spectrum of complex **3** shows a $\nu(CO)$ band at 1950 cm^{-1} and the ^{31}P NMR spectrum of **3** shows the expected singlet at δ 26.5.

The green solid of complexes **2** or **3** has been reacted with $[Rh_2Cl_2(CO)_4]$ to give, after TLC, the heterobimetallic complex $[CpFe(\mu\text{-}CO)_2(\mu\text{-dppm})RhI_2]$ **4**. It is likely that other complexes, namely $[CpFe(\mu\text{-}CO)_2(\mu\text{-dppm})RhClI]$ and $[CpFe(\mu\text{-}CO)_2(\mu\text{-}$

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[*] Corresponding author.

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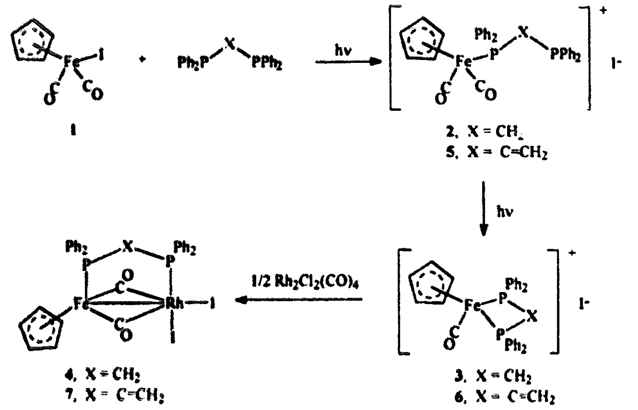

Scheme 1.

dppm)RhCl$_2$] [9], are also formed in this reaction, but no other product was extracted from the TLC plate. The formation of mixed halide derivatives of this type has previously been observed in analogous Ru–Rh complexes [10]. Complex **4** has been characterised by spectroscopic methods (Table 1) and by a single crystal X-ray structure determination. The IR spectrum of **4** shows a strong band at 1810 cm^{-1} due to the μ-CO ligands. A doublet (δ 76.3, J_{PP} = 69 Hz) and doublet of doublets (δ 46.2, J_{PP} = 69, J_{PRh} = 124 Hz) in the ^{31}P NMR spectrum of **4** verifies a bridging dppm ligand between Fe and Rh. The P–P and P–Rh couplings are similar to those previously reported for [CpRu(μ-CO)$_2$(μ-dppm)RhCl$_2$] [1] and [CpFe(μ-CO)$_2$(μ-dppm)RhCl$_2$] [9]. The structure of **4** is shown in Fig. 1, bond lengths and angles are given in Table 2, and atom parameters in Table 3. Interesting points to note include the non-symmetrical carbonyl groups [e.g. Fe(1)–C(1) = 1.85 Å, Rh(1)–C(1) = 2.06 Å] and dppm ligand [Fe(1)–P(1) = 2.208 Å, Rh(1)–P(2) = 2.285 Å]. The structure is very similar to that determined previously for the mixed crystal [CpFe(μ-CO)$_2$(μ-dppm)RhMe$_{0.4}$Cl$_{1.6}$], although it is noteworthy that the Fe–Rh bond length in **4** [2.616(3) Å] is significantly shorter than that in the mixed crystal [2.633(4) Å], despite the presence of the larger iodide ligands in **4**.

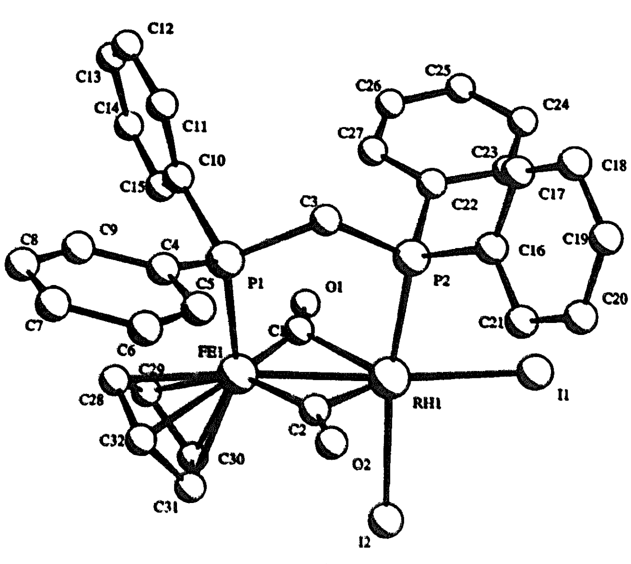

Fig. 1. The molecular structure of [CpFe(μ-CO)$_2$(μ-dppm)RhI$_2$] **4**.

We have also prepared the analogous dppen complexes [FeCp(CO)$_2$(η^1-dppen)]I **5** and [FeCp(CO)(η^2-dppen)]I **6**. Complex **1** reacts with dppen on irradiation for 90 min to give complex **5** and for 150 min to give complex **6**. The complexes **5** and **6** were identified from their IR spectra, which show ν(CO) bands at 1980 and 1950 cm^{-1} respectively (Table 1). The ^{31}P NMR spectrum of **5** shows a doublet at δ 73.2 (J_{PP} = 56 Hz) due to the phosphorus atom coordinated to Fe and a doublet centred at δ −13.8 (J_{PP} = 56 Hz) due to the uncoordinated phosphorus atom. This shows that complex **5** is analogous to complex **2** and similar to that previously reported for [Fe(CO)$_4$(η^1-dppen)] [11]. Complex **6** shows a singlet at δ 42.8 due to the two equivalent phosphorus atoms. Analysis by FAB mass spectroscopy did not give a molecular ion peak at the desired position of m/z = 672. A peak at m/z = 545 however was observed, corresponding to M$^+$–I. The spectrum also shows a peak at m/z = 517, corresponding to the further loss of the carbonyl group. Elemental analysis shows good agreement between theoretical and obtained values for both **5** and **6**.

Table 1
Spectroscopic data

Complex	IR in CH$_2$Cl$_2$ (cm^{-1})	^{31}P{^{1}H} NMR in C$_6$D$_6$ (δ)
1 [FeCpI(CO)$_2$]	2035	
2 [FeCp(CO)$_2$(η^1-dppm)]I	2028, 1990	62.8 (d, J_{PP} 51 Hz) −25.4 (d, J_{PP} 51 Hz)
3 [FeCp(CO)(η^2-dppm)]I	1950	26.5 (s)
4 [CpFe(μ-CO)$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)RhI$_2$]	1810	76.3 (d, J_{PP} 69 Hz) 46.2 (dd, J_{PP} 69, J_{PRh} 124 Hz)
5 [FeCp(CO)$_2$(η^1-dppen)]I	1980	73.2 (d, J_{PP} 56 Hz) −13.8 (d, J_{PP} 56 Hz)
6 [FeCp(CO)(η^2-dppen)]I	1950	42.8 (s)
7 [CpFe(μ-CO)$_2$(μ-dppen)RhI$_2$]	1817	83.1 (d, J_{PP} 74 Hz) 47.8 (dd, J_{PP} 74, J_{PRh} 133 Hz)

Table 2
Selected bond lengths (Å) and angles (°) for [CpFe(μ-CO)$_2$(μ-dppm)RhI$_2$] **4**

Fe(1)–Rh(1)	2.616(3)	Rh(1)–I(2)	2.699(4)
Fe(1)–P(1)	2.208(4)	P(1)–C(3)	1.85(1)
Fe(1)–C(1)	1.85(1)	P(2)–C(3)	1.82(1)
Fe(1)–C(2)	1.88(1)	Fe(1)–C(28)	2.08(1)
Rh(1)–P(2)	2.285(4)	Fe(1)–C(29)	2.12(1)
Rh(1)–C(1)	2.06(1)	Fe(1)–C(30)	2.13(1)
Rh(1)–C(2)	2.05(1)	Fe(1)–C(31)	2.10(1)
Rh(1)–I(1)	2.647(3)	Fe(1)–C(32)	2.09(1)
Rh(1)–Fe(1)–P(1)	98.6(1)	P(2)–Rh(1)–C(2)	90.1(3)
P(1)–Fe(1)–C(1)	92.7(3)	I(1)–Rh(1)–I(2)	87.3(1)
P(1)–Fe(1)–C(2)	89.5(3)	Fe(1)–C(1)–O(1)	151.3(9)
Fe(1)–Rh(1)–P(2)	94.6(1)	Fe(1)–C(2)–O(2)	149.6(9)
Fe(1)–Rh(1)–I(1)	170.14(9)	Rh(1)–C(1)–O(1)	123.9(9)
Fe(1)–Rh(1)–I(2)	92.8(1)	Rh(1)–C(2)–O(2)	126.7(8)
P(2)–Rh(1)–C(1)	88.6(3)	P(1)–C(3)–P(2)	117.3(5)

Table 3
Fractional atomic coordinates for [CpFe(μ-CO)$_2$(μ-dppm)RhI$_2$] **4**

Atom	x	y	z
I(1)	0.35500(6)	0.21340(4)	0.81908(5)
I(2)	0.30489(6)	0.26601(5)	1.03676(5)
Rh(1)	0.17441(6)	0.23889(5)	0.90286(5)
Fe(1)	−0.0031(1)	0.2350(1)	0.98990(8)
P(1)	−0.1255(2)	0.2354(2)	0.8878(2)
P(2)	0.0828(2)	0.2316(2)	0.7788(2)
O(1)	0.0923(6)	0.0670(4)	0.9415(4)
O(2)	0.0737(6)	0.4066(4)	0.9344(5)
C(1)	0.0728(9)	0.1416(7)	0.9456(6)
C(2)	0.0663(8)	0.3320(7)	0.9422(7)
C(3)	−0.0628(8)	0.2556(7)	0.7873(6)
C(4)	−0.2235(8)	0.3252(6)	0.8981(6)
C(5)	−0.1905(8)	0.4103(7)	0.8831(7)
C(6)	−0.259(1)	0.4795(7)	0.9009(7)
C(7)	−0.3636(9)	0.4642(7)	0.9328(7)
C(8)	−0.3948(8)	0.3795(7)	0.9482(7)
C(9)	−0.3264(8)	0.3110(7)	0.9304(6)
C(10)	−0.2137(8)	0.1404(6)	0.8688(6)
C(11)	−0.2975(8)	0.1437(7)	0.8102(7)
C(12)	−0.3647(9)	0.0732(8)	0.7967(7)
C(13)	−0.3480(9)	−0.0039(7)	0.8397(7)
C(14)	−0.263(1)	−0.0090(6)	0.8965(7)
C(15)	−0.1955(8)	0.0642(6)	0.9127(6)
C(16)	0.1150(7)	0.3138(6)	0.7017(6)
C(17)	0.0726(8)	0.3093(6)	0.6231(6)
C(18)	0.0838(9)	0.3784(7)	0.5698(6)
C(19)	0.139(1)	0.4539(7)	0.5958(7)
C(20)	0.184(1)	0.4579(7)	0.6728(8)
C(21)	0.1720(9)	0.3889(7)	0.7279(6)
C(22)	0.0884(8)	0.1282(6)	0.7267(6)
C(23)	0.1719(9)	0.1115(7)	0.6728(7)
C(24)	0.185(1)	0.0288(7)	0.6365(7)
C(25)	0.111(1)	−0.0372(7)	0.6588(7)
C(26)	0.033(1)	−0.0219(7)	0.7149(7)
C(27)	0.0203(8)	0.0593(7)	0.7505(7)
C(28)	−0.1312(8)	0.2247(7)	1.0716(6)
C(29)	−0.0531(9)	0.1604(7)	1.0927(6)
C(30)	0.045(1)	0.2051(8)	1.1134(6)
C(31)	0.0247(9)	0.2950(7)	1.1046(6)
C(32)	−0.0836(9)	0.3078(7)	1.0793(6)

Reaction of complexes **5** or **6** with [Rh$_2$Cl$_2$(CO)$_4$] led to the formation of the heterobimetallic complex [CpFe(μ-CO)$_2${μ-dppen}RhI$_2$] **7**. Complex **7**, analogous to complex **4**, has been characterised by spectroscopic methods (Table 1). The IR spectrum of **7** shows a band in the ν(CO) region at 1815 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum of **7** shows a resonance at δ 83.14 (d, J_{PP} = 74 Hz) due to the phosphorus atom coordinated to Fe and a resonance centred at δ 47.8 (dd, J_{PP} = 74, J_{PRh} = 133 Hz) due to the phosphorus atom coordinated to Rh.

3. Experimental

All reactions were carried out under nitrogen unless otherwise stated, using dry degassed solvents and standard Schlenk-line techniques. IR spectra were recorded as dichloromethane solutions in 0.5 mm NaCl cells on a Perkin–Elmer 681 spectrophotometer; NMR spectra were recorded on Jeol FX-60 or Bruker WM250 instruments. Chemical shifts are relative to 85% H_3PO_4 for ^{31}P NMR spectra. Microanalyses were carried out in the Department of Chemistry, Liverpool University. FAB mass spectra were recorded on a VG 7070E spectrometer. The compounds dppm (PPh$_2$)$_2$CH$_2$, dppen (PPh$_2$)$_2$C=CH$_2$ [12], [FeCpI(CO)$_2$] [5–8] and [Rh$_2$Cl$_2$(CO)$_4$] [13] were prepared according to published procedures.

3.1. Preparation of [FeCp(CO)$_2$(η^1-dppm)]I 2

[FeCpI(CO)$_2$] (0.204 g, 6.7 × 10^{-4} mol) and dppm (0.284 g, 6.7 × 10^{-4} mol) were dissolved in THF (25 cm^3). The black solution was irradiated with UV (500 W) until IR monitoring showed the complete loss of the ν(CO) bands due to the starting material (30 min). The solvent was removed under vacuum to give [FeCp(CO)$_2$(η^1-dppm)]I as a dark green powder (0.41 g, 90% yield). Anal. Found: C, 56.1; H, 3.7. $C_{32}H_{27}FeIO_2P_2$ Calc.: C, 55.85; H, 3.95%.

3.2. Preparation of [FeCp(CO)(η^2-dppm)]I 3

The same procedure was carried out as described above, except that the black solution was irradiated with UV (500 W) until the IR spectrum showed the presence of only one ν(CO) band (150 min). The solvent was removed under vacuum to give [FeCp(CO)(η^2-dppm)]I as a dark green powder (0.35 g, 79% yield). Anal. Found: C, 56.3; H, 3.8. $C_{31}H_{27}FeIOP_2$ Calc.: C, 56.4; H, 4.1%.

3.3. Preparation of [CpFe(μ-CO)$_2${μ-Ph$_2$PCH$_2$PPh$_2$}RhI$_2$] 4

To a solution of complex **3** (0.30 g, 0.45 mmol) or complex **2** (0.31 g, 0.45 mmol) in THF (25 cm^3) was added a solution of $[Rh_2Cl_2(CO)_4]$ (0.087 g, 0.225 mmol) in THF (10 cm^3), and the mixture was stirred for 45 min. The solvent was removed in vacuo and the resulting red solid was purified by TLC (CH_2Cl_2:heptane, 5:1). Three bands were observed. The top band (red) gave complex **4** (0.12 g, 30%) as a red solid which was recrystallised from CH_2Cl_2–heptane. A middle (red) band was not isolated. The third band (green) band was unreacted **3**.

3.4. Preparation of [FeCp(CO)(η¹-dppen)I] 5

$[FeCpI(CO)_2]$ (0.094 g, 3.1×10^{-4} mol) and dppen (0.123 g, 3.1×10^{-4} mol) were dissolved in THF (40 cm^3). The black solution was irradiated with UV (500 W) until IR monitoring showed only one ν(CO) band (at 1980 cm^{-1}) (90 min). The solvent was removed in vacuo to give $[FeCp(CO)_2(\eta^1\text{-dppen})]I$ as a green powder (0.195 g, 90% yield). Anal. Found: C, 57.0; H, 4.1. $C_{33}H_{27}FeIO_2P_2$ Calc.: C, 56.6; H, 3.9%.

3.5. Preparation of [FeCp(CO)(η²-dppen)]I 6

The same procedure was carried out as for complex **5**, except that the black solution was irradiated with UV (500 W) until IR monitoring showed only one ν(CO) band present at 1950 cm^{-1} (250 min). The solvent was removed under vacuum to give a green solid which was characterised as **6** by ^{31}P NMR, IR and mass spectrometry (0.15 g, 71% yield). Anal. Found: C, 56.8; H, 4.3. $C_{32}H_{27}FeIOP_2$ Calc.: C, 57.2; H, 4.05%.

3.6. Preparation of [CpFe(μ-CO)₂(μ-dppen)RhI₂] 7

This complex was prepared in the same way as described for complex **4**, in 34% yield.

3.7. Crystal structure determination of [CpFe(μ-CO)₂(μ-dppm)RhI₂] 4

Crystals of complex **4** were grown from a CH_2Cl_2–heptane solution and a suitable red crystal of dimensions $0.20 \times 0.20 \times 0.30$ mm^3 was mounted on a glass fibre.

3.7.1. Crystal data

$C_{32}H_{27}FeI_2O_2P_2Rh$, $M = 918$, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.22(1)$, $b = 15.2(1)$, $c = 16.24(2)$ Å, b = 91.3(1)°, $U = 3025$ Å^3 (by least-squares refinement of angles from 10 reflections), Mo Kα radiation, $\lambda = 0.71069$ Å, $Z = 4$, $D_c = 2.01$ g cm^{-3}, $F(000) = 1768$, $\mu = 31.71$ cm^{-1}, $T = -120$ °C.

3.7.2. Data collection and processing

Rigaku AFC6S diffractometer, ω–2φ scan mode, 5842 reflections recorded, of which 5567 unique ($R_i = 9.2\%$) ($\varphi_{max} = 25.1°$). 3452 reflections with $I > 4\sigma(I)$ were used in refinement. An empirical absorption correction based on azimuthal scans was applied. Three standard reflections showed no significant intensity variation during data collection.

3.7.3. Structure analysis and refinement

The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and given isotropic thermal parameters 20% greater than the B_{eq} value of the atom to which they were bonded. Full-matrix least-squares refinement. The weighting scheme was $w = 4F_o^2/\sigma^2(F_o)^2$. Final R and R' values were 0.044 and 0.050. The TEXSAN structure analysis package was used [14].

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