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Syntheses, characterization and structures of $CpFe(CO)(\mu\text{-}I)(\mu\text{-dppm})M(CO)_4$ (M = Cr, Mo, W)

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Abstract

Reaction of $CpFe(CO)I(\eta^1\text{-dppm})$ with $M(CO)_4(L)_2$ (L = acetonitrile or norbornadiene) affords the heterobimetallic complexes $CpFe(CO)(\mu\text{-}I)(\mu\text{-dppm})M(CO)_4$ (**1**, **2** and **3** for M = Cr, Mo and W, respectively). These new complexes have been characterized by elemental analyses and IR, mass, ^1H and ^{31}P NMR spectroscopies. The crystal structures of **1** and **3** reveal that the two heterometal atoms are not bonded but are bridged by a dppm and an iodide ligands. Compound **1** crystallizes in a space group $P2_1/c$ with $a = 10.664(3)$ Å, $b = 15.495(4)$ Å, $c = 20.494(3)$ Å, $\beta = 92.37(2)°$, $V = 3383(1)$ Å^3, $Z = 4$ and $R/R_F = 0.058/0.050$. Compound **3** crystallizes in a space group $P2_1/c$ with $a = 10.668(2)$ Å, $b = 15.567(2)$ Å, $c = 20.512(2)$ Å, $\beta = 92.65(1)°$, $V = 3402.7(8)$Å^3, $Z = 4$ and $R/R_F = 0.048/0.066$. © 1998 Elsevier Science S.A.

Keywords: Heterobimetallic complexes; Acetonitrile; Norbornadiene

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1. Introduction

Heterobimetallic complexes have attracted continuing interests since the different reactivities of the metals may be exploited in chemical transformations. Generally, these complexes involve one or two bridging ligands to support the M–M′ backbone. The bidentate diphosphine ligands, particularly $Ph_2PCH_2PPh_2$ (dppm), are most frequently used [1]. One way to prepare dppm-bridged heterobimetallic complexes is to start with a dppm-chelated complex, which may undergo dppm ring opening and coordinate another metal fragment. Complexes such as $M(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ (M = Cr, Mo, or W) [2–5], $RuH_2(dppm)_2$ [6], $[M(CO)(\eta^2\text{-dppm})_2]Cl$ (M = Rh or Ir) [7], $FeX_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ (X = Br, I) [8], $PdCl_2(dppm)$ and $[Pd(\eta^2\text{-dppm})_2]Cl_2$ [9] have been treated with mononuclear Pt or Pd complexes to form a heterobimetallic system. Alternatively, the complexes containing a pendent η^1-dppm ligand, such as $CpNi(SR)(\eta^1\text{-dppm})$, $CpNi(CN)(\eta^1\text{-dppm})$ [10], $[Pt(CCR)_2(\eta^1\text{-dppm})_2]$ [11], $Fe(CO)_4(\eta^1\text{-dppm})$ [12–15], $\{[CpFe(CO)_2(\eta^1\text{-dppm})]^+\}$ [16] and $CpFe(CO)(COMe)(\eta^1\text{-dppm})$ [17], are also capable of binding another metal moiety. We have been interested in the systematic chemistry of diphosphine ligands with homonuclear and heteronuclear metal clusters [18–23]. Presented in this paper are results concerning preparation of the iron-d^6 metal complexes $CpFe(CO)(\mu\text{-}I)(\mu\text{-dppm})M(CO)_4$, in which the two metal units are linked by an iodide and a dppm ligands.

2. Results and discussion

Reactions of $CpFe(CO)I(\eta^1\text{-dppm})$ with $Mo(CO)_4(NCMe)_2$ and $W(CO)_4(NCMe)_2$ afford $CpFe(CO)(\mu\text{-}I)(\mu\text{-dppm})Mo(CO)_4$ (**2**) (61%) and $CpFe(CO)(\mu\text{-}I)(\mu\text{-dppm})W(CO)_4$ (**3**) (65%), respectively. Since the chromium analog $Cr(CO)_4(NCMe)_2$ cannot be prepared in situ by treating $Cr(CO)_6$ with Me_3NO in acetoniltrile solution. $Cr(CO)_4$(norbornadiene) is prepared instead to react with

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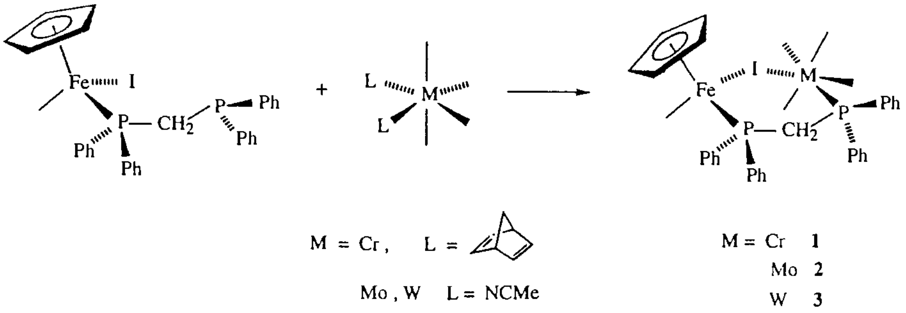
CpFe(CO)I(η^1-dppm), leading to CpFe(CO)(μ-I)(μ-dppm)Cr(CO)$_4$ (**1**) in 54% yield (Eq. (1)). The dppm-bridged bimetallic complexes containing Fe atom and Rh, Pd, or Pt atom are common, but the mixed d^8–d^6 metal complexes are relatively few. Compounds **1**–**3** can thus be added into this category.



(1)

Compounds **1**, **2**, and **3** form air-stable, brown crystalline solids, which give satisfactory C and H analyses. Their IR spectra in the carbonyl stretching region are similar, suggesting great resemblance of their structures. The ^{1}H NMR spectra of these compounds display a multiplet between 7.1 and 7.7 ppm for the phenyl protons and a sharp singlet at ca. 4.3 ppm for the Cp proton resonances. The two diastereotopic methylene protons of dppm ligand appear as two sets of doublet of doublet of doublets due to coupling to each other and to the two phosphorus atoms. The ^{31}P{^{1}H} NMR spectra of them display two separate doublet signals for the two inequivalent phosphine moieties. The resonances of the Fe-bonded phosphorus atoms are essentially identical (59.3, 59.6 and 60.1 ppm for **1**, **2** and **3**, respectively). The other phosphorus resonances are shifted upfield from 42.3 ppm for **1** to 21.6 and 6.1 ppm for **2** and **3**. It has been noted that, for the metal phosphine complexes

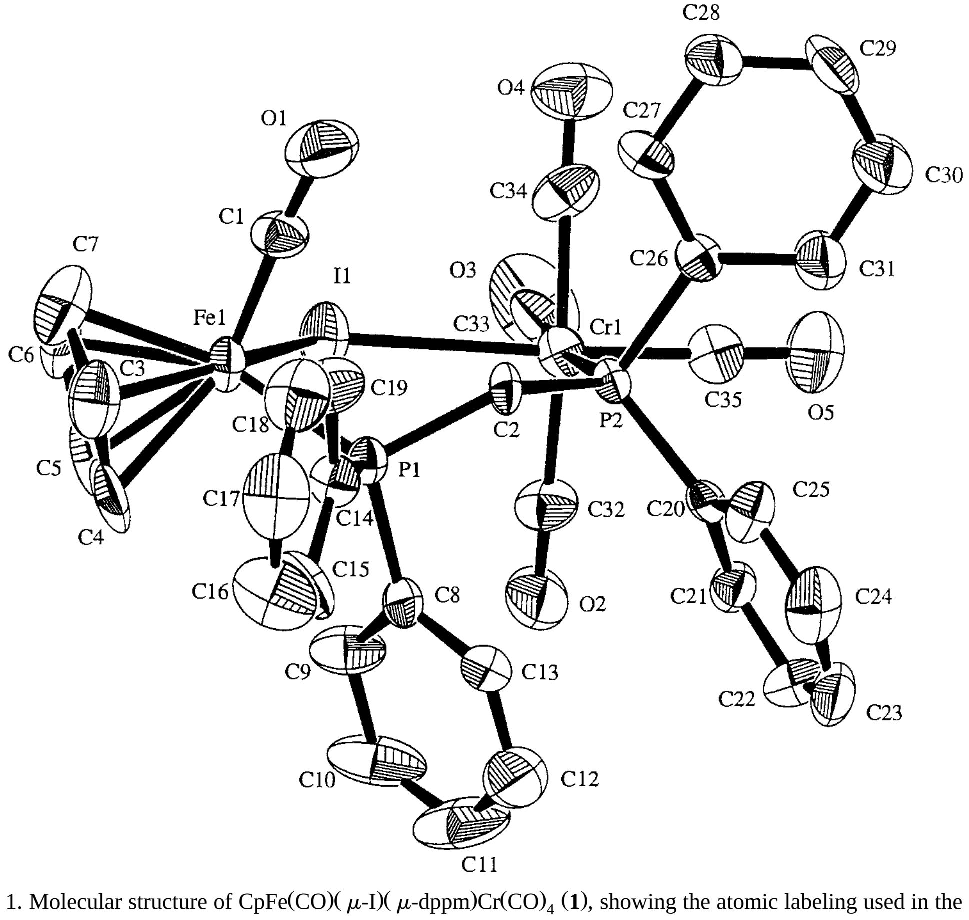


Fig. 1. Molecular structure of CpFe(CO)(μ-I)(μ-dppm)Cr(CO)$_4$ (**1**), showing the atomic labeling used in the text.

of same structure, one generally observes a high-field shift of the ^{31}P resonance as one descends in a given group [24].

The bridging iodide and dppm ligands are normally considered as four-electron donors, resulting in a total of 36 valence electrons for these bimetallic complexes. This electron count requires no metal–metal bond to provide an 18-electron configuration on each metal atom. To support this prediction, single-crystal diffraction study was performed. Shown in Figs. 1 and 2 are the ORTEP drawings of compounds **1** and **3**, respectively. Selected bond distances and bond angles are collected in Table 1. The two molecular structures are very similar, where the coordination about the iron atom retains a piano-stool configuration and the coordination about the Cr (and W) atom is a distorted octahedron. The two heterometal atoms are linked by a dppm ligand and an iodine atom. The slight differences of bond distances and angles between **1** and **3** can be rationalized in terms of the relative size of chromium and tungsten atoms. The Fe–Cr distance (4.72 Å) and Fe–W distance (4.77 Å) are too long for metal–metal interaction, in consistent with the expectation.

All the carbonyl ligands are terminal, with the M–C–O angles in the range 173(1)–177(1)° for **1** and 174(1)–179(1)° for **3**. The iodide ligand apparently imposes substantial *trans* influence on the opposite carbonyl ligand, such that the Cr(1)–C(35) (1.80(1) Å) and W(1)–C(35) (1.95(1) Å) distances are ca. 0.05 Å shorter than the other M–CO bond lengths. We note that the cyclopentadienyl group is bonded to the iron atom asymmetrically, with the Fe–C distances ranging from 2.07(1) Å through 2.12(1) Å for **1** and **3**. Again, the shortest Fe(1)–C(3) bond length is likely due to *trans* influence from the iodide ligand (∠I(1)–Fe(1)–C(3) = 157°).

The Fe–I–M angles in **1** (121.98(6)°) and **3** (120.86(4)°) are quite large. Usually, the M–I–M′ angles fall in the range 60–110°, and those angles larger than 110° are observed in a few cases when the metals are late transition or in high oxidation states [25]. If the M–X–M′ angle is smaller than 70°, a metal–metal bond should subsist. For example, it is 57.1° in [(OC)$_3$Fe(μ-dppm)(μ-I)PtI] [26,27], 68.3(1)° in Fe(CO)$_3$(μ-Br)(μ-dppm)Re(CO)$_3$ [28] and 69.3(1)–72.2(2)° in [Ru$_2$X$_3$(tacn)$_2$](PF$_6$)$_2$ [29], which all contain metal–metal bonding. The P(1)–C(2)–P(2) angles measured for **1** (122.5(7)°) and **3** (121.0(5)°) are comparable with the parent complex CpFe(CO)I(η^1-dppm(O)) (121.0(6)°) [30], while a more acute P–C–P angle is observed if the metal–metal bond is present, such as 113.8(4)° in [(OC)$_3$Fe(μ-dppm)(μ-I)PtI] [27], 112.7(3)°

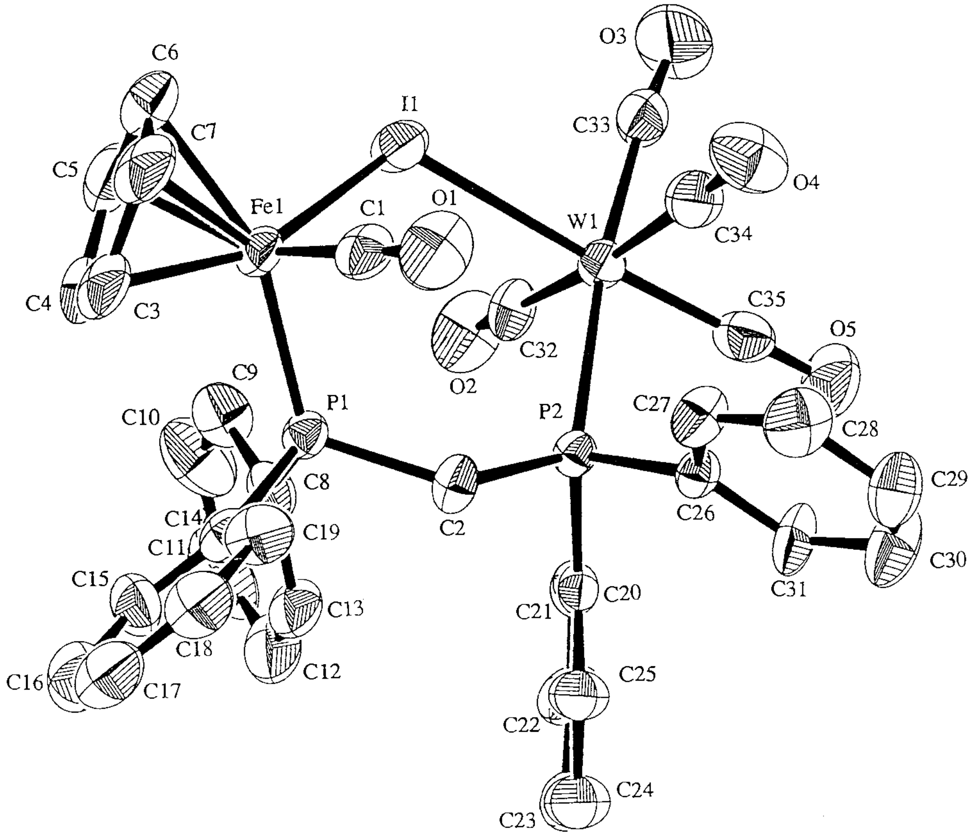


Fig. 2. Molecular structure of CpFe(CO)(μ-I)(μ-dppm)W(CO)$_4$ (**3**), showing the other view of the complex.

Table 1
Selected bond distances and angles for **1** and **3**

	1 (M = Cr)	**3** (M = W)
Bond distances (Å)		
I(1)–Fe(1)	2.605(2)	2.605(2)
I(1)–M(1)	2.786(2)	2.8774(8)
Fe(1)–P(1)	2.214(4)	2.219(3)
Fe(1)–C(1)	1.71(1)	1.72(1)
Fe(2)–C(3)	2.07(1)	2.07(1)
Fe(1)–C(4)	2.12(1)	2.11(1)
Fe(1)–C(5)	2.09(1)	2.10(1)
Fe(1)–C(6)	2.08(1)	2.10(1)
Fe(1)–C(7)	2.09(1)	2.07(1)
M(1)–P(2)	2.399(4)	2.515(3)
M(1)–C(32)	1.87(1)	2.04(1)
M(1)–C(33)	1.90(2)	2.00(1)
M(1)–C(34)	1.84(1)	2.01(1)
M(1)–C(35)	1.80(1)	1.95(1)
P(1)–C(2)	1.83(1)	1.85(1)
P(1)–C(8)	1.81(1)	1.82(1)
P(1)–C(14)	1.85(1)	1.85(1)
P(2)–C(2)	1.88(1)	1.87(1)
P(2)–C(20)	1.84(1)	1.84(1)
P(2)–C(26)	1.84(1)	1.838(9)
O(1)–C(1)	1.17(1)	1.18(1)
O(2)–C(32)	1.17(1)	1.13(1)
O(3)–C(33)	1.13(2)	1.12(1)
O(4)–C(34)	1.17(1)	1.14(1)
O(5)–C(35)	1.17(1)	1.17(1)
C(3)–C(4)	1.42(2)	1.42(2)
C(4)–C(5)	1.39(2)	1.39(2)
C(5)–C(6)	1.43(2)	1.40(2)
C(6)–C(7)	1.36(2)	1.38(2)
C(3)–C(7)	1.40(2)	1.42(2)
Bond angles (°)		
I(1)–M(1)–P(2)	98.3(1)	96.93(6)
I(1)–M(1)–C(32)	89.6(4)	89.8(3)
I(1)–M(1)–C(33)	88.5(4)	88.6(3)
I(1)–M(1)–C(34)	87.2(4)	89.3(3)
I(1)–M(1)–C(35)	175.8(4)	177.2(3)
P(2)–M(1)–C(32)	96.4(4)	97.3(3)
P(2)–M(1)–C(33)	172.6(4)	173.6(3)
P(2)–M(1)–C(34)	91.9(5)	90.0(3)
P(2)–M(1)–C(35)	85.3(4)	85.1(3)
C(32)–M(1)–C(33)	86.6(6)	86.0(5)
C(32)–M(1)–C(34)	171.5(6)	172.7(4)
C(32)–M(1)–C(35)	92.3(6)	91.8(5)
C(33)–M(1)–C(34)	85.4(6)	86.7(5)
C(33)–M(1)–C(35)	87.8(6)	89.3(5)
C(34)–M(1)–C(35)	90.4(6)	88.7(5)
M(1)–I(1)–Fe(1)	121.97(6)	120.86(4)
I(1)–Fe(1)–P(1)	96.2(1)	97.61(8)
I(1)–Fe(1)–C(1)	91.3(5)	90.8(4)
I(1)–Fe(1)–C(3)	157.5(5)	157.3(4)
I(1)–Fe(1)–C(4)	125.6(5)	125.3(4)
I(1)–Fe(1)–C(5)	93.6(4)	93.1(4)
I(1)–Fe(1)–C(6)	93.9(4)	92.6(4)
I(1)–Fe(1)–C(7)	126.3(5)	125.4(4)
P(1)–Fe(1)–C(1)	92.3(5)	90.7(4)
P(1)–Fe(1)–C(3)	100.1(5)	98.8(4)
P(1)–Fe(1)–C(4)	89.9(4)	89.7(4)
P(1)–Fe(1)–C(5)	117.0(5)	117.0(4)
P(1)–Fe(1)–C(6)	155.7(5)	154.8(4)
P(1)–Fe(1)–C(7)	137.5(5)	137.0(4)

Table 1 (continued).

	1 (M = Cr)	**3** (M = W)
C(1)–Fe(1)–C(3)	103.4(7)	104.5(6)
C(1)–Fe(1)–C(4)	142.5(7)	143.6(6)
C(1)–Fe(1)–C(5)	149.5(7)	151.2(5)
C(1)–Fe(1)–C(6)	109.6(7)	112.3(5)
C(1)–Fe(1)–C(7)	87.7(7)	89.6(5)
Fe(1)–P(1)–C(2)	117.0(4)	117.1(3)
Fe(1)–P(1)–C(8)	120.7(5)	120.1(4)
Fe(1)–P(1)–C(14)	108.8(4)	108.7(3)
C(2)–P(1)–C(8)	104.6(5)	105.6(5)
C(2)–P(1)–C(14)	99.1(6)	98.9(5)
C(8)–P(1)–C(14)	103.8(6)	103.6(5)
M(1)–P(2)–C(2)	124.7(4)	125.2(3)
M(1)–P(2)–C(20)	118.3(4)	117.7(3)
M(1)–P(2)–C(26)	109.6(4)	108.9(3)
C(2)–P(2)–C(20)	100.2(5)	101.1(4)
C(2)–P(2)–C(26)	98.4(5)	98.2(4)
C(20)–P(2)–C(26)	101.8(5)	102.0(4)
Fe(1)–C(1)–O(1)	176 (1)	179 (1)
P(1)–C(2)–P(2)	122.5(7)	121.0(5)

in $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtPPh_3]$ [9e], 106.0(7)° in $\{[(\eta^2\text{-dppm})Pt(\mu\text{-dppm})W(CO)_2Cp]^+\}$ [31] and 105.8(3)° in $Mo_2Br_4(dppm)_2$ [32].

It is apparent that CpFe(CO)I(η^1-dppm) is a useful block to prepare heterobimetallic complexes. We have thought to remove a carbonyl ligand from **3** in order to introduce an Fe–W bond. However, photolysis or thermolysis of **3** only led to $W(CO)_4(\eta^2\text{-dppm})$. Attempts to replace the iodide ligand by treating **3** with PhC≡CLi gave no reaction. Alternative methods of activating these compounds under reducing conditions to make higher nuclear mixed-metal clusters are under way.

3. Experimental section

3.1. General methods

All experimental manipulations were carried out under an argon atmosphere using standard Schlenk techniques. $Cr(CO)_4(nbd)$ [33] (nbd = norbornadiene) and

Table 2
Crystal data and refinement details for **1** and **3**

	1	**3**
Formula	$C_{35}H_{27}CrFeIO_5P_2$	$C_{35}H_{27}FeIO_5P_2W$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.664(3)	10.668(2)
b (Å)	15.495(4)	15.567(2)
c (Å)	20.494(3)	20.512(2)
β (°)	92.37(2)	92.65(1)
V (Å^3)	3383(1)	3402.7(8)
Z	4	4
D_{calc} (g cm^{-3})	1.618	1.866
$F(000)$	1640.00	1840.00
Radiation λ (Å)	0.71069	0.71069
T (K)	296	297
μ (cm^{-1})	17.97	48.50
Scan width	$1.78 + 0.34 \tan\theta$	$0.63 + 0.30 \tan\theta$
$2\theta_{max}$ (°)	47.1	50.0
No. of unique data	5243	6245
No. of data with $I > 3\sigma(I)$	3311	4249
R[a]	0.059	0.048
R_w[b]	0.051	0.066
Goodness of fit	4.32	1.85

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

CpFe(CO)I(η^1-dppm) [34] were prepared by literature methods. Cr(CO)$_6$, Mo(CO)$_6$, and W(CO)$_6$ purchased from Strem were used without further purification. Dichloromethane and *n*-hexane were distilled over CaH$_2$, and acetonitrile was distilled over P$_2$O$_5$ before use. Anhydrous Me$_3$NO was obtained from Me$_3$NO $\cdot$ 2H$_2$O (Aldrich) by sublimation under vacuum twice. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Kieselgel DGF$_{254}$). ^{1}H and ^{31}P NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 and 121.4 MHz, respectively. Infrared spectra were taken on a Hitachi I-2001 spectrometer. Fast atom bombardment (FAB) mass spectra were obtained on a VG Blotch-5022 mass spectrometer. Elemental analyses were performed at the National Chung-Hsing University, Taichung, Taiwan.

3.2. *Synthesis of CpFe(CO)(μ-I)(μ-dppm)Cr(CO)$_4$* (**1**)

An 100 ml Schlenk flask was equipped with a magnetic stir bar and a reflux condenser connected to an oil bubbler. CpFe(CO)I(η^1-dppm) (150 mg, 0.23 mmol), Cr(CO)$_4$(nbd) (150 mg, 0.56 mmol), and dichloromethane (20 ml) were introduced into the flask against an argon flow. The mixture was heated to reflux for 16 h under Ar. The volatile materials were removed

Table 3
Selected atomic coordinates of **1**

Atom	*x*	*y*	*z*	B_{eq}
I(1)	0.12711(9)	0.25877(6)	0.72395(4)	3.64(2)
Fe(1)	0.1134(2)	0.1395(1)	0.63433(9)	2.78(5)
Cr(1)	0.2691(2)	0.2372(1)	0.83999(9)	2.65(5)
P(1)	0.2894(3)	0.0725(2)	0.6653(2)	2.30(8)
P(2)	0.3392(3)	0.0923(2)	0.8222(2)	2.04(8)
O(1)	−0.0293(9)	0.0310(7)	0.7178(5)	5.6(3)
O(2)	0.4842(9)	0.3336(7)	0.7813(5)	5.1(3)
O(3)	0.191(1)	0.4157(7)	0.8835(6)	7.5(4)
O(4)	0.0330(9)	0.1795(7)	0.9031(5)	5.6(3)
O(5)	0.4049(9)	0.2218(6)	0.9692(5)	5.5(3)
C(1)	0.025(1)	0.075(1)	0.6826(7)	3.1(4)
C(2)	0.297(1)	0.0262(8)	0.7476(5)	2.4(3)
C(3)	0.083(2)	0.087(1)	0.5421(7)	4.9(5)
C(4)	0.179(1)	0.151(1)	0.5384(6)	4.8(5)
C(5)	0.123(2)	0.228(1)	0.5577(6)	4.6(5)
C(6)	−0.005(1)	0.211(1)	0.5720(7)	4.5(5)
C(7)	−0.028(1)	0.126(1)	0.5615(8)	5.1(5)
C(8)	0.440(1)	0.1242(9)	0.6570(6)	2.9(4)
C(9)	0.446(1)	0.2100(9)	0.6358(7)	4.1(4)
C(10)	0.562(2)	0.248(1)	0.6302(8)	5.8(5)
C(11)	0.672(2)	0.204(1)	0.6468(9)	7.1(6)
C(12)	0.665(2)	0.120(1)	0.6669(8)	5.8(6)
C(13)	0.551(1)	0.0817(9)	0.6721(6)	3.4(4)
C(14)	0.302(1)	−0.0279(8)	0.6173(6)	2.7(3)
C(15)	0.388(1)	−0.0380(9)	0.5700(6)	4.0(4)
C(16)	0.388(2)	−0.113(1)	0.5320(8)	5.6(5)
C(17)	0.302(2)	−0.1774(10)	0.5445(8)	5.3(5)
C(18)	0.214(1)	−0.166(1)	0.5873(8)	4.9(5)
C(19)	0.214(1)	−0.0926(10)	0.6260(7)	4.0(4)
C(20)	0.508(1)	0.0694(8)	0.8314(5)	2.2(3)
C(21)	0.598(1)	0.1330(8)	0.8373(6)	2.8(3)
C(22)	0.724(1)	0.114(1)	0.8386(7)	4.3(4)
C(23)	0.763(1)	0.031(1)	0.8350(7)	4.8(5)
C(24)	0.676(2)	−0.0335(10)	0.8331(7)	4.4(5)
C(25)	0.550(1)	−0.0151(9)	0.8307(6)	3.4(4)
C(26)	0.275(1)	0.0203(7)	0.8839(6)	2.4(3)
C(27)	0.152(1)	−0.0093(8)	0.8774(6)	3.1(4)
C(28)	0.101(1)	−0.0551(9)	0.9280(7)	3.7(4)
C(29)	0.171(1)	−0.0736(10)	0.9843(6)	4.3(4)
C(30)	0.290(1)	−0.045(1)	0.9905(7)	5.4(5)
C(31)	0.343(1)	0.0010(9)	0.9424(7)	4.0(4)
C(32)	0.404(1)	0.2918(9)	0.8022(7)	3.5(4)
C(33)	0.271(1)	0.3491(10)	0.8659(7)	4.2(4)
C(34)	0.124(1)	0.1990(9)	0.8767(7)	3.9(4)
C(35)	0.353(1)	0.2283(8)	0.9179(6)	3.2(4)

under vacuum and the residue subjected to TLC, eluting with CH_2Cl_2/*n*-hexane (1:1, v/v). CpFe(CO)(μ-I)(μ-dppm)$Cr(CO)_4$ (**1**) (101 mg, 0.123 mmol, 54%) was obtained from the brown band. IR (CH_2Cl_2, ν_{CO}): 2010, 1960, 1910, 1900, 1850 cm^{-1}. ^1H NMR (CD_2Cl_2): 7.59–7.14 (m, 20 H), 4.37 (s, 5 H), 3.76–3.41 (m, 2 H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 59.29 (d, P–Fe), 42.30 (d, P–Cr) ppm. Mass spectroscopy (FAB) m/z: 824 (M^+), 796, 768, 740, 713. Anal. found C, 51.33; H, 3.67. $C_{35}H_{27}CrFeIO_5P_2$ calc. C, 51.00; H, 3.30.

Crystals of **1** found suitable for X-ray diffraction study were grown from CH_2Cl_2/*n*-hexane at −15°C.

3.3. Synthesis of CpFe(CO)(μ-I)(μ-dppm)$Mo(CO)_4$ (2)

$Mo(CO)_6$ (200 mg, 0.76 mmol) was placed in a Schlenk flask equipped with a magnetic stir bar and a rubber septum. The flask was evacuated and refilled with Ar twice, and acetonitrile (10 ml) was introduced. A solution of Me_3NO (125 mg, 1.67 mmol) in acetonitrile (10 ml) was added dropwisely into the flask by a syringe over a period of 10 min. The mixture was stirred at ambient temperature for 1 h, at which point the IR spectrum indicated $Mo(CO)_6$ was completely transformed to *cis*-$Mo(CO)_4(NCMe)_2$. The acetonitrile solvent was then removed under vacuum. A solution of

Table 4
Selected atomic coordinates of **3**

Atom	*x*	*y*	*z*	B_{eq}
W(1)	0.26765(4)	0.24239(3)	−0.15834(2)	2.58(1)
I(1)	0.12346(8)	0.26315(5)	−0.27936(4)	3.67(2)
Fe(1)	0.1116(1)	0.14063(10)	−0.36592(7)	2.75(3)
P(1)	0.2880(2)	0.0738(2)	−0.3346(1)	2.44(5)
P(2)	0.3396(2)	0.0912(2)	−0.1782(1)	2.20(5)
O(1)	−0.0294(8)	0.0349(7)	−0.2792(5)	5.9(3)
O(2)	0.4965(8)	0.3412(6)	−0.2172(5)	5.4(2)
O(3)	0.185(1)	0.4238(6)	−0.1130(5)	7.9(3)
O(4)	0.0248(9)	0.1751(6)	−0.0928(5)	5.7(3)
O(5)	0.4110(9)	0.2216(6)	−0.0236(4)	5.4(2)
C(1)	0.028(1)	0.0775(8)	−0.3148(6)	3.6(3)
C(2)	0.296(1)	0.0253(6)	−0.2520(5)	2.8(2)
C(3)	0.083(1)	0.0848(8)	−0.4570(6)	4.8(3)
C(4)	0.175(1)	0.150(1)	−0.4615(5)	4.5(3)
C(5)	0.120(1)	0.2267(9)	−0.4447(6)	4.8(3)
C(6)	−0.005(1)	0.2128(9)	−0.4303(6)	4.4(3)
C(7)	−0.029(1)	0.126(1)	−0.4382(6)	4.9(3)
C(8)	0.4386(9)	0.1264(7)	−0.3429(5)	3.0(2)
C(9)	0.443(1)	0.2097(7)	−0.3650(6)	3.8(3)
C(10)	0.560(2)	0.2502(9)	−0.3697(8)	5.8(4)
C(11)	0.669(1)	0.209(1)	−0.3528(8)	6.4(4)
C(12)	0.663(1)	0.124(1)	−0.3310(6)	5.2(4)
C(13)	0.552(1)	0.0832(8)	−0.3266(6)	4.0(3)
C(14)	0.301(1)	−0.0254(7)	−0.3834(5)	3.0(2)
C(15)	0.387(1)	−0.0365(8)	−0.4304(6)	4.2(3)
C(16)	0.388(1)	−0.1124(9)	−0.4669(6)	5.4(4)
C(17)	0.303(2)	−0.1748(9)	−0.4569(7)	5.3(4)
C(18)	0.217(1)	−0.1655(8)	−0.4115(7)	4.7(3)
C(19)	0.216(1)	−0.0913(8)	−0.3736(6)	4.1(3)
C(20)	0.5084(9)	0.0688(6)	−0.1686(4)	2.5(2)
C(21)	0.598(1)	0.1336(7)	−0.1620(5)	3.2(2)
C(22)	0.723(1)	0.1146(9)	−0.1591(6)	4.4(3)
C(23)	0.762(1)	0.031(1)	−0.1629(6)	4.9(3)
C(24)	0.676(1)	−0.0352(9)	−0.1658(7)	4.8(3)
C(25)	0.549(1)	−0.0160(8)	−0.1704(6)	4.0(3)
C(26)	0.2753(9)	0.0203(6)	−0.1163(4)	2.3(2)
C(27)	0.152(1)	−0.0104(7)	−0.1227(5)	3.4(2)
C(28)	0.100(1)	−0.0571(8)	−0.0738(7)	4.8(3)
C(29)	0.172(1)	−0.0749(9)	−0.0163(6)	5.0(3)
C(30)	0.292(1)	−0.047(1)	−0.0100(6)	5.6(4)
C(31)	0.344(1)	0.0009(8)	−0.0594(5)	4.2(3)
C(32)	0.415(1)	0.3037(7)	−0.1977(5)	3.1(2)
C(33)	0.211(1)	0.3590(8)	−0.1320(5)	4.2(3)
C(34)	0.114(1)	0.1969(8)	−0.1170(6)	3.7(3)
C(35)	0.358(1)	0.2310(7)	−0.0743(6)	3.8(3)

CpFe(CO)I(η^1-dppm) (450 mg, 0.68 mmol) in dichloromethane (10 ml) was added into the flask by a syringe and the reaction mixture was stirred at ambient temperature for 4 h, leading to a solution color change from green to brown. The volatile materials were removed under vacuum and the residue subjected to TLC, eluting with CH_2Cl_2/n-hexane (1:1, v/v). CpFe(CO)(μ-I)(μ-dppm)Mo$(CO)_4$ (**2**) (401 mg, 61%) was isolated from the brown band. IR (CH_2Cl_2, ν_{CO}): 2010, 1960, 1915, 1888, 1855 cm^{-1}. ^1H NMR (CD_2Cl_2): 7.33–7.17 (m, 20 H), 4.34 (s, 5 H), 3.74–3.45 (m, 2 H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 59.65 (d, P–Fe), 21.68 (d, P–Mo) ppm. Mass spectroscopy (FAB) m/z: 869 (M^+), 842, 814, 784, 756, 728. Anal. found C, 47.53; H, 3.27. $C_{35}H_{27}FeIMoO_5P_2$ calc. C, 48.42; H, 3.13.

3.4. Synthesis of CpFe(CO)(μ-I)(μ-dppm)W$(CO)_4$ (3)

Sequential treatment of $W(CO)_6$ (400 mg, 1.14 mmol) with 2 equiv. of Me_3NO and CpFe(CO)I(η^1-dppm)(450 mg, 0.68 mmol) was carried out and worked up in a fashion identical to that above. The brown, air-stable complex CpFe(CO)(μ-I)(μ-dppm)W$(CO)_4$ (**3**) was obtained in 65% yield (424 mg). IR (CH_2Cl_2, ν_{CO}): 2010, 1965, 1905, 1885, 1855 cm^{-1}. ^1H NMR (CD_2Cl_2): 7.60–7.15(m, 20 H), 4.36(s, 5 H), 3.72–3.50(m, 2 H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 60.05 (d, P–Fe), 6.10 (d, P–W, with $J_{P-W} = 245$ Hz) ppm. Mass spectroscopy (FAB) m/z: 956 (M^+), 928, 900, 863, 844, 816. Anal. found C, 43.74; H, 2.98. $C_{35}H_{27}FeIO_5P_2W$ calc. C, 43.97; H, 2.85.

Crystals of **3** found suitable for X-ray diffraction study were grown from CH_2Cl_2/n-hexane at −15°C.

3.5. Structure determination for 1

A suitable crystal of **1** with approximate dimensions 0.33 × .041 × 0.51 mm was mounted on a glass fiber and aligned on the Rigaku AFC6S diffractometer. Diffraction data were collected with graphite monochromated Mo–Kα radiation using $\theta/2\theta$ scan mode. Cell parameters were determined from 20 carefully centered reflections with 2θ ranging from 8.70 to 14.69°. The systematic absences of $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) uniquely determines the space group to be $P2_1/c$ (#14). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques [35]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure [36]. The data collection and refinement parameters are collected in Table 2. Atomic positional parameters are given in Table 3.

3.6. Structure determination for 3

A suitable crystal of **3** with approximate dimensions 0.16 × 0.032 × 0.24 mm was mounted on a glass fiber and aligned to the diffractometer. Cell parameters were determined from 20 carefully centered reflections with 2θ ranging from 8.74 to 13.65°. The systematic absences of $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) uniquely determines the space group to be $P2_1/c$(#14). The structure was solved by direct methods and expanded using Fourier techniques [36]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The data collection and refinement parameters are collected in Table 2. Atomic positional parameters are given in Table 4.

Acknowledgements

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