

Tri- and tetra-metallic complexes containing phospho-alkyne ligands. First examples of $\mu_3(\eta^2-\perp)$ bonded phospho-alkynes; crystal and molecular structure of $[\text{Fe}_2\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{CO})_6(\text{Me}_3\text{CCP})]^*$

Saud I. Al-Resayes **, Peter B. Hitchcock, Mohamed F. Meidine and John F. Nixon *

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex (Great Britain)

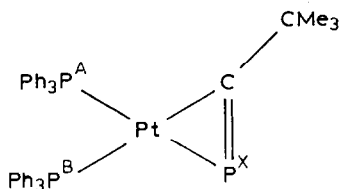
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Abstract

A new $\mu_3(\eta^2-\perp)$ coordination mode for a phospho-alkyne has been established in the complexes $[\text{Fe}_2\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{CO})_6(\text{Me}_3\text{CCP})]$ and $[\text{Fe}_3\text{Pt}\{(\text{Ph}_2\text{PCH}_2)_3\text{CMe}\}(\text{CO})_{10}(\text{Me}_3\text{CCP})]$.

Introduction

Several years ago [1], we reported the first example of a coordinated phospho-alkyne ligand, $\text{RC}\equiv\text{P}$, ($\text{R} = \text{CMe}_3$) bonded in an η^2 -fashion in the zerovalent platinum complex **1**. Complex **1** has to further available ligating modes to other suitable



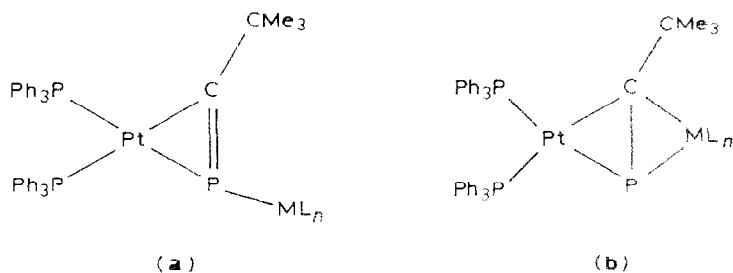
(1)

$[\text{ML}_n]$ fragments, namely (a) in an η^1 -fashion via the phosphorus lone pair electrons

* Dedicated to my colleague Prof. Colin Eaborn, F.R.S., on the occasion of his 65th birthday, in recognition of his important contributions to organometallic chemistry (J.F.N.).

** Present address: Department of Chemistry, College of Science, King Saud University, Riyadh, S. Arabia.

and/or (b) in a further η^2 -mode utilising the π -bond of the coordinated $\text{RC}\equiv\text{P}$ moiety, viz.:

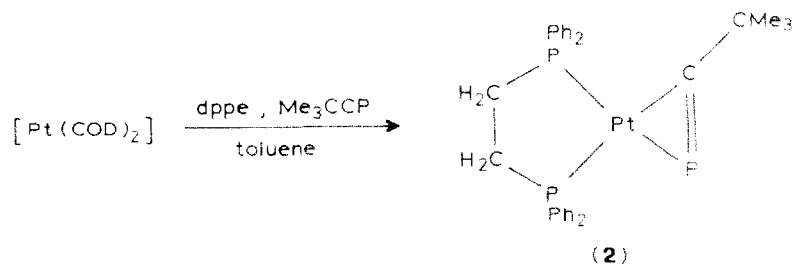


Both types of interaction do occur [2a,b] but in this paper we report a third unexpected type of behaviour of a coordinated phospho-alkyne ligand leading to a novel μ_3 -(η^2 - \perp) ligating mode, known previously only for a few alkyne metal complexes. A preliminary account of part of this work has been published elsewhere [2c].

Results and discussion

In order to minimize unwanted ligand exchange between phosphines and carbon monoxide, phospho-alkyne derivatives of **1** in which the two PPh_3 ligands were replaced by $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (dppe) or $(\text{MeC}(\text{CH}_2\text{PPh}_2)_3)$ (triphos) were first synthesized.

Complex **2**, $[\text{Pt}(\text{dppe})(\text{Me}_3\text{CCP})]$, is readily made by treatment of $[\text{Pt}(\text{COD})_2]$ (COD = 1,5-cyclooctadiene) in toluene solution with dppe, followed by Me_3CCP or (in higher yield and purity) by first isolating the $[\text{Pt}(\text{dppe})_2]$ complex and treating it at room temperature with Me_3CCP in a mixture of toluene and hexane (1/3).



Likewise, complex $[\text{Pt}(\text{triphos})(\text{Me}_3\text{CCP})]$ (**3**) was obtained in high yield from the reaction of equimolar amounts of Me_3CCP and $[\text{Pt}(\text{triphos})(\text{PPh}_3)]$ at room temperature in toluene. Addition of Me_3CCP gave an immediate colour change from yellow to very pale yellow, and the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The product was readily purified from free PPh_3 to give a high yield of $[\text{Pt}(\text{triphos})(\text{Me}_3\text{CCP})]$ (**3**), whose formulation was confirmed by elemental analysis, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (vide infra).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2**, shown in Fig. 1, exhibits the characteristic pattern of lines expected for an [ABX] spin system (A, B, and X = phosphorus), each showing characteristic ^{195}Pt satellites. Three distinct resonances occur for the

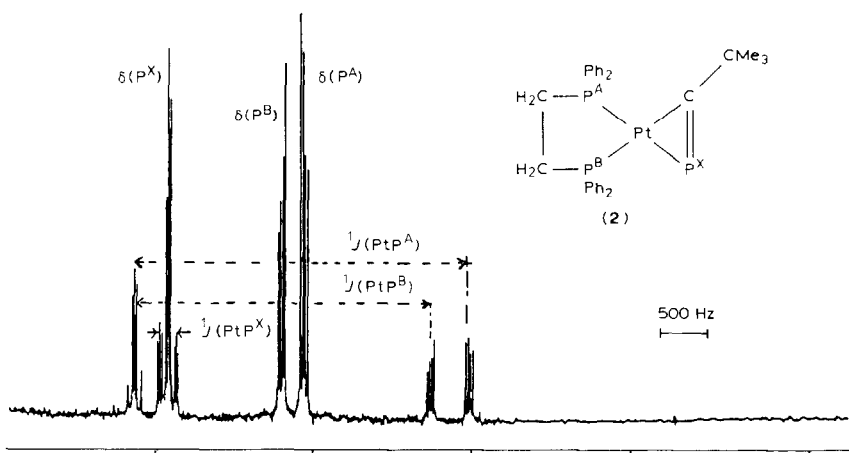


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pt}(\text{dppe})(\text{Me}_3\text{CCP})]$ (**2**) in toluene.

non-equivalent phosphorus nuclei, P^{A} , P^{B} , and P^{X} , each exhibiting a doublet of doublets pattern. Chemical shift data are listed in Table 1, and of particular interest is the very small value of the $^1J(\text{PtP})$ coupling constant for the coordinated Me_3CCP (166 Hz) (cf. 62 Hz for $[\text{Pt}(\text{PPh}_3)_2(\text{Me}_3\text{CCP})]$ discussed elsewhere [1]), which reflects the low s -character of the P–Pt bond in the η^2 -coordinated phospho-alkyne.

Similarly, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** (Fig. 2) also shows three distinct resonances for the non-equivalent coordinated phosphine atoms, each exhibiting a doublet of doublets pattern, but in this case overlapping of lines leads to triplet patterns. In addition, an extra line is observed (without platinum satellites) which is readily assigned to the “dangling” phosphorus P^{C} of the triphos ligand. Chemical shifts and coupling constant data for **3** are listed in Table 1 and, as in the case of **2**, $^1J(\text{PtP}^{\text{X}})$ is very small, at 144 Hz.

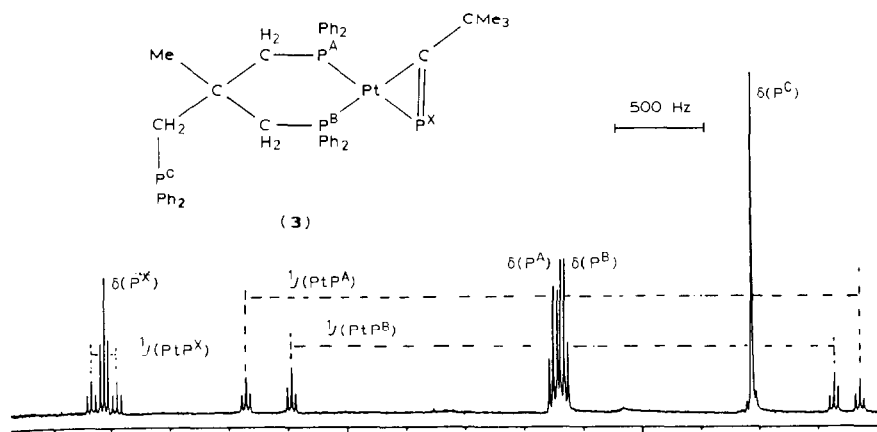
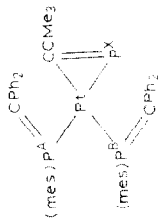


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pt}(\text{triphos})(\text{Me}_3\text{CCP})]$ (**3**), in toluene.

Table 1
 $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data for some mononuclear $\text{Me}_3\text{CC}(\text{PPt})^0$ platinum(0) complexes

Compound	$\delta(\text{P}^{\text{A}})^{\text{a}}$	$\delta(\text{P}^{\text{B}})^{\text{a}}$	$\delta(\text{P}^{\text{X}})^{\text{a}}$	$^1J(\text{PtP}^{\text{A}})^{\text{b}}$	$^1J(\text{PtB}^{\text{B}})^{\text{b}}$	$^1J(\text{PtP}^{\text{X}})^{\text{b}}$	$^2J(\text{P}^{\text{A}}\text{P}^{\text{B}})^{\text{b}}$	$^2J(\text{P}^{\text{A}}\text{P}^{\text{X}})^{\text{b}}$	$^2J(\text{P}^{\text{B}}\text{P}^{\text{X}})^{\text{b}}$	Ref.
1	+28.8	+26.3	+84.1	3587	3206	62	20	24	15	1
3	+6.2	+4.4	+82.7	3381	2986	144	22	22	22	This work
2	+47.4	+53.1	+87.7	3308	2930	166	44	27	21	This work



^a In ppm relative to 85% H_3PO_4 (measured relative to $\text{P}(\text{OMe})_3$ and converted by addition of -141) (high field shifts are negative). ^b In Hz.

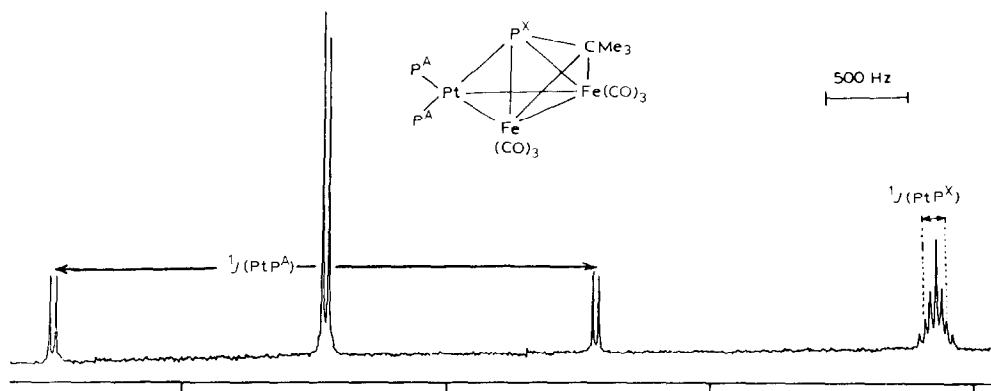
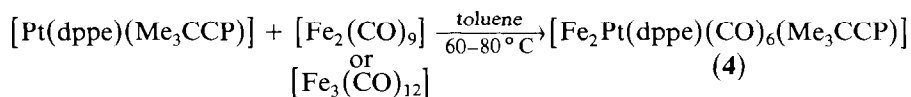


Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{Me}_3\text{CCP})]$ (**4**), in toluene.

A feature of all the spectra of the η^2 -mononuclear Me_3CCP^0 complexes is the large down-field movement of the ^{31}P chemical shift of the coordinated Me_3CCP (ca. 150 ppm) relative to the free ligand value [3]. The most important features of the spectra of all the mononuclear complexes are: (a) the very low magnitude of $^1J(\text{PtP})$ for the coordinated Me_3CCP ligand, and (b) the small *trans*-coupling constant $^2J(\text{PP})$. The small magnitudes provide strong support for the dependence of such coupling constants on the *s*-character of the phosphorus donor orbital. For typical square-planar R_3P platinum complexes, the *trans*-coupling $^2J(\text{PP})$ values lie usually in the 500 Hz range; likewise $^1J(\text{PtP})$ values are normally 3000–4000 Hz [19].

*Reaction of $[\text{Pt}(\text{dppe})(\text{Me}_3\text{CCP})]$ (**2**) with $[\text{Fe}_2(\text{CO})_9]$ or $[\text{Fe}_3(\text{CO})_{12}]$*

Treatment of a mixture of **2** in toluene with a two-fold excess of $[\text{Fe}_2(\text{CO})_9]$, or a slight excess of an equimolar amount of $[\text{Fe}_3(\text{CO})_{12}]$, gave quantitatively the deep cherry-red crystalline trimetallic complex $[\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{Me}_3\text{CCP})]$ (**4**).



The IR spectrum of **4** shows only four $\nu(\text{CO})$ bands, at 2012m, 1967s, 1925vs, and 1898w cm^{-1} . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4**, shown in Fig. 3, exhibits a low field doublet pattern with ^{195}Pt satellites, indicating that there are two magnetically equivalent phosphorus nuclei of the dppe ligand ($\delta(\text{P}^A) + 64.1$ ppm, $^1J(\text{PtP}^A)$ 3329 Hz). In addition, a triplet with platinum satellites ($\delta(\text{P}^X) - 51.8$ ppm, $^1J(\text{PtP}^X)$ 128 Hz) is assigned to the phosphorus of the coordinated Me_3CCP (see Table 2).

Table 2

$^{31}\text{P}\{^1\text{H}\}$ NMR data for **4** and **5**

Compound	$\delta(\text{P}^A)^a$	$\delta(\text{P}^X)^a$	$\delta(\text{P}^C)^a$	$^1J(\text{PtP}^A)^b$	$^1J(\text{PtP}^X)^b$	$^2J(\text{P}^A\text{P}^X)^b$
4	+64.1	-51.8	-	3329	128	36
5	+12.7	-37.5	+56.6	3262	152	34

^a In ppm relative to 85% H_3PO_4 . ^b In Hz.

Table 3

P–C bond lengths of coordinated Me₃CCP

Compound	<i>r</i> (P–C) (Å)	Ref.
[Pd ₂ Pt ₃ (PPh ₃) ₅ (Me ₃ CCP) ₃]	1.62(2)	15
[Pt(PPh ₃) ₂ (Me ₃ CCP)]	1.672(17)	1
[Co ₂ (CO) ₆ (Me ₃ CCP)W(CO) ₅]	1.695(6)	12
[Fe ₂ Pt(dppe)(CO) ₆ (Me ₃ CCP)] (4)	1.706(3)	this work
[Mo ₂ (CO) ₄ (η ⁵ -C ₅ H ₅) ₂ (Me ₃ CCP)]	1.719(3)	13
[Mo ₂ (CO) ₄ (η ⁵ -C ₅ H ₅) ₂ (Me ₃ CCP)W(CO) ₅]	1.733(12)	14
[Mo ₂ (CO) ₄ (η ⁵ -C ₅ H ₅) ₂ (Me ₃ CCP)Os ₃ (CO) ₁₁]	1.86(1)	16

The ³¹P{¹H} NMR data reveal that complex **4** has a plane of symmetry. Likewise, the low value of ¹*J*(PtP^X) indicates that the phosphorus of Me₃CCP is not coordinated to the platinum metal via its lone pair. Another interesting feature of the ³¹P{¹H} NMR spectrum of **4** is that the chemical shift of the coordinated

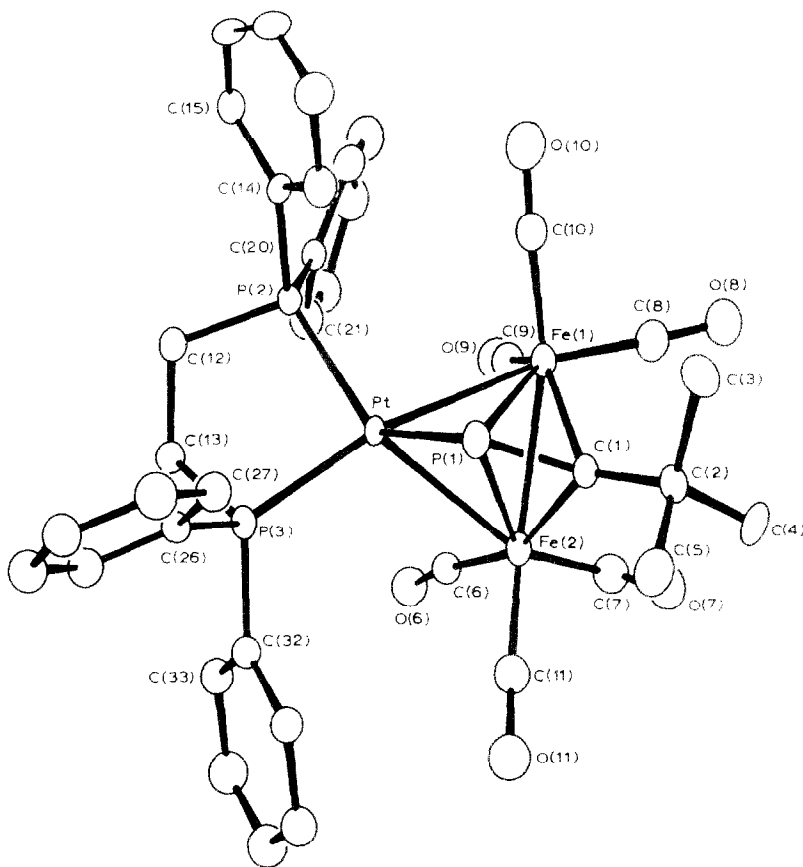


Fig. 4. X-ray structure of [Fe₂Pt(dppe)(CO)₆(Me₃CCP)] (**4**) showing the atomic numbering scheme.

Table 4

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

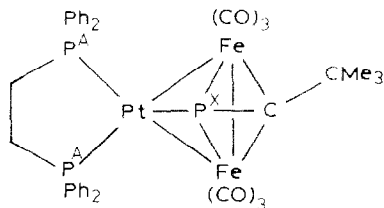
<i>(a) Distances</i>			
Pt–Fe(1)	2.671(1)	Pt–Fe(2)	2.669(1)
Pt–P(1)	2.343(2)	Pt–P(2)	2.263(2)
Pt–P(3)	2.270(2)	Fe(1)–Fe(2)	2.518(1)
Fe(1)–P(1)	2.343(2)	Fe(1)–C(1)	2.080(6)
Fe(1)–C(8)	1.728(8)	Fe(1)–C(9)	1.761(7)
Fe(1)–C(10)	1.758(7)	Fe(2)–P(1)	2.446(2)
Fe(2)–C(1)	1.974(6)	Fe(2)–C(6)	1.759(6)
Fe(2)–C(7)	1.738(7)	Fe(2)–C(11)	1.752(7)
P(1)–C(1)	1.703(6)	P(2)–C(12)	1.849(6)
P(2)–C(14)	1.816(6)	P(2)–C(20)	1.812(6)
P(3)–C(13)	1.833(6)	P(3)–C(26)	1.835(6)
P(3)–C(32)	1.814(6)	C(1)–C(2)	1.526(8)
C(2)–C(3)	1.540(9)	C(2)–C(4)	1.546(9)
C(2)–C(5)	1.562(10)	C(6)–O(6)	1.177(7)
C(7)–O(7)	1.165(8)	C(8)–O(8)	1.178(8)
C(9)–O(9)	1.158(7)	C(10)–O(10)	1.163(8)
C(11)–O(11)	1.160(7)	C(12)–C(13)	1.530(8)
C(14)–C(15)	1.396(8)	C(14)–C(19)	1.380(9)
C(15)–C(16)	1.396(9)	C(16)–C(17)	1.394(10)
C(17)–C(18)	1.371(11)	C(18)–C(19)	1.422(10)
C(20)–C(21)	1.394(9)	C(20)–C(25)	1.393(9)
C(21)–C(22)	1.406(11)	C(22)–C(23)	1.403(12)
C(23)–C(24)	1.323(12)	C(24)–C(25)	1.468(11)
C(26)–C(27)	1.383(9)	C(26)–C(31)	1.390(9)
C(27)–C(28)	1.412(10)	C(28)–C(29)	1.384(11)
C(29)–C(30)	1.389(10)	C(30)–C(31)	1.424(10)
C(32)–C(33)	1.379(9)	C(32)–C(37)	1.387(8)
C(33)–C(34)	1.422(10)	C(34)–C(35)	1.370(11)
C(35)–C(36)	1.391(10)	C(36)–C(37)	1.423(9)
Pt...C(6)	2.569(6)	Pt...C(9)	2.811(7)
<i>(b) Angles</i>			
Fe(1)–Pt–Fe(2)	56.26(2)	Fe(1)–Pt–P(1)	55.25(4)
Fe(1)–Pt–P(2)	106.09(4)	Fe(1)–Pt–P(3)	168.11(4)
Fe(2)–Pt–P(1)	57.98(4)	Fe(2)–Pt–P(2)	155.64(4)
Fe(2)–Pt–P(3)	111.86(4)	P(1)–Pt–P(2)	129.17(6)
P(1)–Pt–P(3)	120.61(5)	P(2)–Pt–P(3)	85.10(6)
Pt–Fe(1)–Fe(2)	61.83(3)	Pt–Fe(1)–P(1)	55.24(4)
Pt–Fe(1)–C(1)	90.6(2)	Pt–Fe(1)–C(8)	162.9(2)
Pt–Fe(1)–C(9)	75.7(2)	Pt–Fe(1)–C(10)	102.2(2)
Fe(2)–Fe(1)–P(1)	60.29(5)	Fe(2)–Fe(1)–C(1)	49.7(2)
Fe(2)–Fe(1)–C(8)	107.0(2)	Fe(2)–Fe(1)–C(9)	89.0(2)
Fe(2)–Fe(1)–C(10)	156.2(2)	P(1)–Fe(1)–C(1)	44.8(2)
P(1)–Fe(1)–C(8)	132.8(2)	P(1)–Fe(1)–C(9)	129.7(2)
P(1)–Fe(1)–C(10)	96.4(2)	C(1)–Fe(1)–C(8)	90.7(3)
C(1)–Fe(1)–C(9)	137.2(3)	C(1)–Fe(1)–C(10)	118.0(3)
C(8)–Fe(1)–C(9)	91.9(3)	C(8)–Fe(1)–C(10)	92.3(3)
C(9)–Fe(1)–C(10)	104.6(3)	Pt–Fe(2)–Fe(1)	61.90(3)
Pt–Fe(2)–P(1)	54.30(4)	Pt–Fe(2)–C(1)	93.0(2)
Pt–Fe(2)–C(6)	67.3(2)	Pt–Fe(2)–C(7)	141.7(2)
Pt–Fe(2)–C(11)	118.1(2)	Fe(1)–Fe(2)–P(1)	56.30(4)
Fe(1)–Fe(2)–C(1)	53.5(2)	Fe(1)–Fe(2)–C(6)	104.0(2)
Fe(1)–Fe(2)–C(7)	94.4(2)	Fe(1)–Fe(2)–C(11)	153.9(2)

Table 4 (continued)

P(1)–Fe(2)–C(1)	43.7(2)	P(1)–Fe(2)–C(6)	121.1(2)
P(1)–Fe(2)–C(7)	138.1(2)	P(1)–Fe(2)–C(11)	101.1(2)
C(1)–Fe(2)–C(6)	156.5(3)	C(1)–Fe(2)–C(7)	95.6(3)
C(1)–Fe(2)–C(11)	101.7(3)	C(6)–Fe(2)–C(7)	92.8(3)
C(6)–Fe(2)–C(11)	99.1(3)	C(7)–Fe(2)–C(11)	96.5(3)
Pt–P(1)–Fe(1)	69.51(5)	Pt–P(1)–Fe(2)	67.72(4)
Pt–P(1)–C(1)	113.6(2)	Fe(1)–P(1)–Fe(2)	63.40(5)
Fe(1)–P(1)–C(1)	59.4(2)	Fe(2)–P(1)–C(1)	53.2(2)
Pt–P(2)–C(12)	109.0(2)	Pt–P(2)–C(14)	116.6(2)
Pt–P(2)–C(20)	116.8(2)	C(12)–P(2)–C(14)	103.0(3)
C(12)–P(2)–C(20)	103.5(3)	C(14)–P(2)–C(20)	106.2(3)
Pt–P(3)–C(13)	107.2(2)	Pt–P(3)–C(26)	115.5(2)
Pt–P(3)–C(32)	119.4(2)	C(13)–P(3)–C(26)	103.2(3)
C(13)–P(3)–C(32)	105.8(3)	C(26)–P(3)–C(32)	104.2(3)
Fe(1)–C(1)–Fe(2)	76.8(2)	Fe(1)–C(1)–P(1)	75.8(2)
Fe(1)–C(1)–C(2)	133.0(4)	Fe(2)–C(1)–P(1)	83.0(3)
Fe(2)–C(1)–C(2)	137.4(5)	P(1)–C(1)–C(2)	128.1(5)
C(1)–C(2)–C(3)	109.8(6)	C(1)–C(2)–C(4)	111.7(6)
C(1)–C(2)–C(5)	107.5(5)	C(3)–C(2)–C(4)	110.8(6)
C(3)–C(2)–C(5)	109.5(6)	C(4)–C(2)–C(5)	107.5(6)
Fe(2)–C(6)–O(6)	170.4(6)	Fe(2)–C(7)–O(7)	175.1(7)
Fe(1)–C(8)–O(8)	174.6(7)	Fe(1)–C(9)–O(9)	172.1(6)
Fe(1)–C(10)–O(10)	178.2(7)	Fe(2)–C(11)–O(11)	178.2(7)
P(2)–C(12)–C(13)	110.3(4)	P(t)–C(13)–C(12)	107.7(4)
P(2)–C(14)–C(15)	119.8(5)	P(2)–C(14)–C(19)	119.8(5)
C(15)–C(14)–C(19)	120.4(6)	C(14)–C(15)–C(16)	119.8(6)
C(15)–C(16)–C(17)	120.4(7)	C(16)–C(17)–C(18)	119.4(7)
C(17)–C(18)–C(19)	121.0(8)	C(14)–C(19)–C(18)	118.9(7)
P(2)–C(20)–C(21)	117.8(5)	P(2)–C(20)–C(25)	121.4(5)
C(21)–C(20)–C(25)	120.5(6)	C(20)–C(21)–C(22)	121.4(7)
C(21)–C(22)–C(23)	117.3(8)	C(22)–C(23)–C(24)	122.9(9)
C(23)–C(24)–C(25)	120.7(9)	C(20)–C(25)–C(24)	116.9(7)
P(2)–C(26)–C(27)	120.0(5)	P(3)–C(26)–C(31)	117.6(5)
C(27)–C(26)–C(31)	122.4(6)	C(26)–C(27)–C(28)	118.8(7)
C(27)–C(28)–C(29)	120.5(8)	C(28)–C(29)–C(30)	119.8(7)
C(29)–C(30)–C(31)	121.0(7)	C(26)–C(31)–C(30)	117.5(6)
P(3)–C(32)–C(33)	122.0(5)	P(3)–C(32)–C(37)	117.1(5)
C(33)–C(32)–C(37)	120.7(6)	C(32)–C(33)–C(34)	120.0(7)
C(33)–C(34)–C(35)	119.2(8)	C(34)–C(35)–C(36)	121.7(7)
C(35)–C(36)–C(37)	118.9(7)	C(32)–C(37)–C(36)	119.6(6)

Me₃CCP has moved upfield by about 140 ppm from its position in the ³¹P{¹H} NMR spectrum of **2**.

A single crystal X-ray diffraction study of **4** reveals the molecular structure shown in Fig. 4. Bond lengths and bond angles are listed in Table 4.



(4)

Description of the structure of $[\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{Me}_3\text{CCP})]$ (4)

The X-ray diffraction study reveals that the metal atoms are located at the corners of an isosceles triangle. The $\text{C}\equiv\text{P}$ fragment is stereochemically disposed above the plane of the three metal atoms ($\text{Fe}(1), \text{Fe}(2), \text{Pt}$) such that phosphorus $\text{P}(1)$ is coordinated to all three metal atoms and the carbon $\text{C}(1)$ is bonded to the two iron atoms ($\text{Fe}(1)$ and $\text{Fe}(2)$). This $\mu_3-(\eta^2-\perp)$ type of bonding is the first of its kind to be established for a phospho-alkyne ligand. The bonding is, however, similar to that in the relatively rare examples known for alkynes and carbynes in the complexes $[\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)]$ [4], $[\text{Ni}_4(\text{CNCMe}_3)_4(\text{C}_2\text{Ph}_2)_3]$ [5], $[\text{Ni}_4(\text{CO})_4\{\text{C}_2(\text{CF}_3)_2\}_3]$ [6], $[\text{Ni}(\text{PMe}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ $[\text{Fe}_2\text{Ni}(\mu_3\text{-C}_2\text{Ph}_2)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ [7], and $[\text{W}_2\text{Fe}(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)_2\{\text{C}_2(\text{C}_6\text{H}_4\text{Me})_2\}]$ [8,9].

The dimensions and bond angles of the Me_3CCP phospho-alkyne moiety coordinated to the three metal atoms are shown in Fig. 5. The phospho-alkyne- $\text{P}(1)$ bonding distances to the three atoms ($\text{Fe}(1), \text{Fe}(2), \text{Pt}$) are 2.343(2), 2.446(2), and 2.343(2) Å, respectively, indicating that the phosphorus $\text{P}(1)$ is positioned nearly in the middle of the isosceles triangle of the three metal atoms. The phospho-alkyne- $\text{C}(1)$ bonding distances to the two iron atoms are 1.974(6) and 2.080(6) Å (average 2.027 Å), and this is comparable with values found in analogous alkyne complexes (average 2.056 Å) [10]. The $\text{Fe}-\text{C}$ bond lengths of terminal carbonyls range from 1.728 to 1.761 Å (average 1.745 Å), and two of the three carbonyls on $\text{Fe}(1)$ and one of the three on $\text{Fe}(2)$ lie in plane of the three metal atoms, within experimental error.

A number of further structural features of interest are apparent in complex 4. The $\text{Fe}-\text{Fe}$ distance is 2.518(1) Å, which may be compared with those found in related complexes having $\text{RC}\equiv\text{CR}$ or $\text{RC}\equiv\text{M}$ fragments perpendicular to the $\text{Fe}-\text{Fe}$ axis [4]. The $\text{Pt}-\text{P}(1)$ bond length 2.343(2) Å is only slightly longer than the $\text{Pt}-\text{P}(2)$ or $\text{Pt}-\text{P}(3)$ bonds of the dppe ligand, even though the phosphorus lone pair on Me_3CCP appears not to share significantly in platinum-phospho-alkyne bonding. Interestingly, there is a preference for $\text{P}(1)$ rather than $\text{C}(1)$ of the Me_3CCP ligand

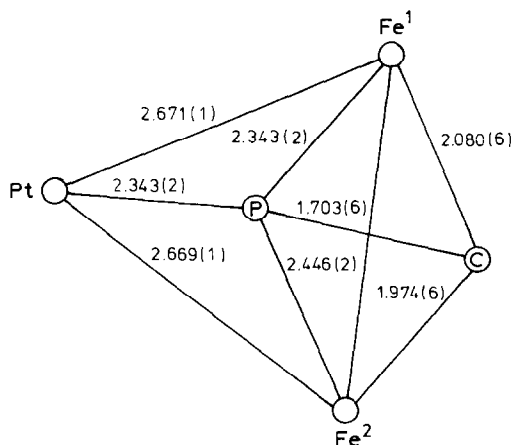


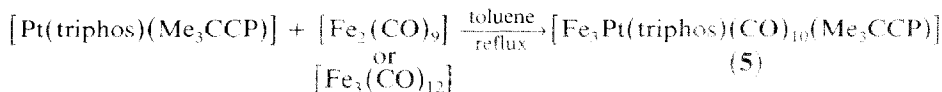
Fig. 5. Important bond lengths (Å) in the inner coordination sphere of $[\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{Me}_3\text{CCP})]$, (4).

involved in the μ_3 -bonding moiety, but whether this is a general phenomenon or not must await further synthetic studies.

An important feature of the structure is the considerable lengthening of the P–C bond of the coordinated phospho-alkyne from 1.54 Å in the free ligand [11] to 1.703(6) Å in **4**. This P–C bond length is more typical of a phospho-alkene C=P double bond which is typically 1.67 Å [3] (see Table 3). This lengthening has been noted in a number of other Me_3CCP metal complexes: e.g. 1.672(17) Å in $[\text{Pt}(\text{PPh}_3)_2(\text{Me}_3\text{CCP})]$ [1], 1.695(6) Å in $[\text{Co}_2(\text{CO})_6(\text{Me}_3\text{CCP})\text{W}(\text{CO})_5]$ [12], 1.719(3) Å in $[\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me}_3\text{CCP})]$ [13], 1.733(12) Å in $[\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me}_3\text{CCP})\text{W}(\text{CO})_5]$ [14], and 1.62(2) Å in $[\text{Pd}_2\text{Pt}_3(\text{PPh}_3)_3(\text{Me}_3\text{CCP})_3]$ [15]. In the complex $[\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me}_3\text{CCP})\text{Os}_3(\text{CO})_{11}]$, the P–C bond length is particularly long (1.86(1) Å), which is more typical for a P–C single bond [16].

*Reaction of $[\text{Pt}(\text{triphos})(\text{Me}_3\text{CCP})]$ (**3**) with $[\text{Fe}_2(\text{CO})_9]$ or $[\text{Fe}_3(\text{CO})_{12}]$*

In an analogous way to that described above, a mixture of **3** in toluene treated with a three-fold excess of $[\text{Fe}_2(\text{CO})_9]$ or with a two-fold excess of $[\text{Fe}_3(\text{CO})_{12}]$ gave yields of the deep-red micro-crystalline tetrametallic complex $[\text{Fe}_3\text{Pt}(\text{triphos})(\text{CO})_{10}(\text{Me}_3\text{CCP})]$ (**5**), which was characterized by elemental analysis, IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.



The IR spectrum of **5** consists of six bands in the carbonyl stretching region, at 2048s, 2019m, 1968s.br, 1945vs, 1930w, and 1895w cm^{-1} . The additional carbonyl stretching bands observed for **5** compared with **4** suggested that the extra $[\text{Fe}(\text{CO})_4]$ unit might be coordinated via the “dangling” phosphorus of the triphos ligand, as shown in Fig. 7.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** supports the structural formulation. Chemical shift and coupling constant data are summarised in Table 2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** is similar to the spectrum of **4** except for an additional singlet ($\delta(\text{P}^{\text{C}})$ 57 ppm), due to the “dangling” phosphorus P^{C} of triphos coordinated to the $[\text{Fe}(\text{CO})_4]$ unit. The chemical shift of P^{C} has moved from -27.7 ppm in the original complex, **3** by over 80 ppm. The remaining lines in the spectrum consist of a simple $[\text{A}_2\text{X}]$ pattern (A and X = ^{31}P), with ^{195}Pt satellites, where the A_2 nuclei represent the two equivalent phosphorus atoms of the triphos ligand coordinated to platinum ($\delta(\text{P}^{\text{A}})$ +13 ppm). Likewise, X represents the Me_3CCP phosphorus ($\delta(\text{P}^{\text{X}})$ –38 ppm). One of the ^{195}Pt satellites of P^{A} has overlapped with the P^{X}

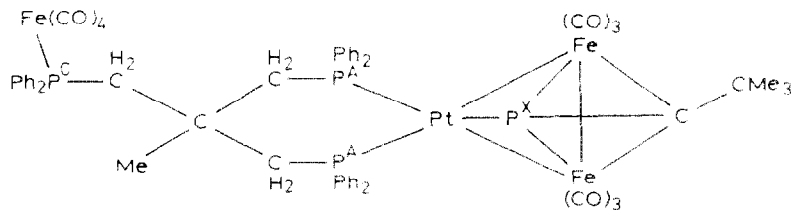


Fig. 7. Proposed molecular structure of **5**.

resonance and its ^{195}Pt satellites, but analysis of the spectrum affords $^1J(\text{PtP}^{\text{A}})$ 3262, $^1J(\text{PtP}^{\text{X}})$ 152, and $^2J(\text{P}^{\text{A}}\text{P}^{\text{X}})$ 34 Hz. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** was also measured at 360 MHz, and the spectrum simplified; identical coupling constants were more readily obtained.

These results illustrate the usefulness of the isolobal relationship [17,18] between the fragments $\text{RC} \longleftrightarrow \text{P} \longleftrightarrow \text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5) \longleftrightarrow \text{Co}(\text{CO})_3$ [19–22], which has been developed widely by Stone and co-workers in recent years. This can be seen in the similarity between the coordination abilities of alkynes ($\text{RC}\equiv\text{CR}$) and carbynes ($\text{RC}\equiv\text{ML}_n$) towards low-valent metal species (including metal carbonyls), which afford heteronuclear metal clusters [10,18,23–25].

The present work indicates that phospho-alkynes may also prove to be important building blocks for organometallic synthesis. However, it is important to note that sometimes the reaction pathway may differ. For example, $[\text{W}_2\text{Fe}(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)_2\{\text{C}_2(\text{C}_6\text{H}_4\text{Me})_2\}]$ [8,9] results from coupling of two RC fragments in the reaction of the carbyne compound $[\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\{\text{C}_2(\text{C}_6\text{H}_4\text{Me})_2\}]$ with $[\text{Fe}_2(\text{CO})_9]$. Likewise, Stone and coworkers [26] found that the analogous reaction of the carbyne complex $[\text{PtW}(\mu\text{-CR})(\text{CO})_2(\text{PMe}_2\text{Ph})_2(\eta^5\text{-C}_5\text{H}_5)]$ in tetrahydrofuran with $[\text{Fe}_2(\text{CO})_9]$ (in which the carbyne complex $[\text{W}(\mu\text{-CR})(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ is isolobal with Me_3CCP) gave products containing only one iron, rather than two as in the phospho-alkyne case.

In view of the known ligating properties of the coordinated Me_3CCP in clusters of the type $[\text{Co}_2(\text{CO})_6(\text{Me}_3\text{CCP})]$ and $[\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me}_3\text{CCP})]$ [13] with other metal fragments, e.g. $[\text{W}(\text{CO})_5]$ [12], $[\text{Os}_3(\text{CO})_{11}]$ [16] and $[\text{Ru}_3(\text{CO})_{11}]$ [16], it was of interest to study the donor properties of complex **4**. However, an attempt to coordinate the lone pair of the phosphorus of Me_3CCP in complex **4** to platinum by interaction with $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ in toluene, under mild conditions, was unsuccessful and no reaction was detected by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Similarly, a mixture of **4** with $[\text{W}(\text{CO})_5(\text{THF})]$ in THF solution at room temperature showed no evidence of reaction.

These results, however, do provide strong further support for the formulation of $[\text{Fe}_3\text{Pt}(\text{triphos})(\text{CO})_{10}(\text{Me}_3\text{CCP})]$ (**5**) as involving bonding of the $[\text{Fe}(\text{CO})_4]$ fragment to the “dangling” phosphorus of the triphos ligand, rather than via the phosphorus or Me_3CCP .

The basic character of the phosphorus lone-pair of Me_3CCP in **4** was further investigated. MeI was added to a toluene solution of **4** at room temperature and, after stirring the mixture for 1 h, the course of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a simple singlet with ^{195}Pt satellites, corresponding to *cis*- $[\text{PtI}_2(\text{dppe})]$ ($\delta(\text{P})$ +46.4 ppm; lit. [26] $\delta(\text{P})$ 45.9 ppm; $^1J(\text{PtP})$ 3374 Hz; lit. [27] $^1J(\text{PtP})$ 3388 Hz).

In view of the removal of the $[\text{Pt}(\text{dppe})]$ fragment by MeI , an attempt was made to remove the $[\text{Fe}_2(\text{CO})_6]$ fragment from **4** by treatment with CO, but no reaction occurred. Likewise, unlike the analogous alkyne complex $[\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)]$ [4], complex **4** does not react further with Me_3CCP .

Experimental

All manipulations were carried out under an atmosphere of dry dinitrogen or argon, when stated. All reactions were handled by standard vacuum and Schlenk-

ware techniques. Solvents were dried by standard methods and freshly distilled under dinitrogen before use unless otherwise stated. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained using either Bruker WP80 (32.4 MHz) or Bruker WM360 (145.8 MHz) spectrometers, both operating in the FT mode. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer ($4000\text{--}250\text{ cm}^{-1}$) or Perkin-Elmer 1430 spectrometer ($4000\text{--}200\text{ cm}^{-1}$). Elemental analyses were carried out by Mrs. A.G. Olney of this School. Me_3CCP was prepared according to literature procedures [28] and $[\text{Pt}(\text{PPh}_3)(\text{triphos})]$ was made as described elsewhere [29].

Preparation of $[\text{Pt}(\text{dppe})(\text{Me}_3\text{CCP})]$ (2)

This complex is best prepared by displacement of dppe from $[\text{Pt}(\text{dppe})_2]$, made from $[\text{Pt}(\text{COD})_2]$ by the procedure described below.

(a) *Preparation of bis[1,2-bis(diphenylphosphino)ethane]platinum(0)*. A solution of 1,2-bis(diphenylphosphino)ethane (0.8 g, 2 mmol) in toluene (5 cm^3) was added dropwise to a solution of $[\text{Pt}(\text{COD})_2]$ (0.4 g, 1 mmol) in toluene (5 cm^3). The solution turned bright yellow and the mixture was stirred for a further 1 h at room temperature. The solution was filtered, and the volatiles removed in vacuo. The residue was washed with hexane ($2 \times 5\text{ cm}^3$) and dried in vacuo to yield $[\text{Pt}(\text{dppe})_2]$ as a yellow powder (0.8 g, 81%). Found: C, 63.25; H, 5.18. $\text{C}_{52}\text{H}_{48}\text{P}_4\text{Pt}$ calcd.: C, 63.6; H, 4.89%. $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene): $\delta(\text{P}) -110$ ppm (relative to $\text{P}(\text{OMe})_3$); $^1J(\text{PtP})$ 3733 Hz.

(b) *Reaction of $[\text{Pt}(\text{dppe})_2]$ with Me_3CCP* . To a suspension of $[\text{Pt}(\text{dppe})_2]$ (3.0 g, 3.024 mmol) in dry toluene (10 cm^3) and petroleum ether (20 cm^3 ; $60\text{--}80^\circ\text{C}$) was added Me_3CCP (0.350 g, 3.496 mmol) in petroleum ether (10 cm^3). The mixture was stirred at room temperature for two days to complete the reaction. The mixture gave an off-white solid precipitate, which was filtered and washed with petroleum ether ($60\text{--}80^\circ\text{C}$) and dried in vacuo to afford the white microcrystalline complex **2**, m.p. $> 250^\circ\text{C}$, $\{[1,2\text{-bis(diphenylphosphino)ethane-}P,P\}\{2,2\text{-dimethylpropylidynephosphine-}P,C\}\}$ platinum(0) (1.5 g, 71.5%). A second crop of crystals (0.39 g, 14.3%) was isolated by pumping the mother liquor to dryness under reduced pressure, and recrystallizing the solid from a mixture of dichloromethane and petroleum ether ($60\text{--}80^\circ\text{C}$) (1/1) at -20°C . (Found: C, 52.58; H, 4.72; $\text{C}_{31}\text{H}_{33}\text{P}_3\text{Pt}$ calcd.: C, 53.68; H, 4.79%). IR spectrum (KBr): 3060w, 2950w,br, 2875sh, 2318w, 1737vs, 1720vs, 1700vs, 1680sh, 1670m, 1650sh, 1625s,br, 1595sh, 1580w, 1562w, 1550sh, 1522w, 1510w, 1500sh, 1489s, 1480sh, 1460w, 1440vs, 1420m, 1398w, 1362m, 1330s,br, 1278sh, 1220w, 1200w, 1160w, 1150w, 1110s,br, 1090w, 1035w, 1007m, 908s, 889m,br, 830s, 790sh, 757vs, 710vs,br, 635sh, 620m, 590sh, 580sh, 530vs,br, 490s,br, 450sh,sh, 410w,br cm^{-1} .

Preparation of $[\text{Pt}\{\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3\}(\text{Me}_3\text{CCP})]$ (3)

To a solution of $[\text{Pt}(\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3)\text{PPh}_3]$ (0.541 g, 0.50 mmol) in dry toluene (15 cm^3) under dinitrogen was added Me_3CCP (0.050 g, 0.50 mmol) in toluene (10 cm^3). The mixture turned pale yellow immediately, and was then left stirring at room temperature for 2 h. The solvent was removed under reduced pressure and the product washed several times with petroleum ether ($60\text{--}80^\circ\text{C}$) to remove triphenylphosphine. The resulting solid was dried under vacuum to give the off-white microcrystalline complex $\{[1,1,1\text{-tris(diphenylphosphinomethyl)ethane-}P^1,P^2\}\{2,2\text{-dimethylpropylidynephosphine-}P,C\}\}$ platinum(0) (0.45 g, 98%).

(Found: C, 59.49; H, 5.22. $C_{46}H_{48}P_4Pt$ calcd.: C, 60.06; H, 5.26%). IR spectrum (KBr): 3050m,br, 2900m,br, 1580m, 1570sh, 1552sh, 1480s, 1470s, 1452s, 1430vs, 1410w, 1375w, 1343w, 1327sh, 1302m, 1270w, 1230w, 1184m, 1155w, 1143m, 1102sh, 1090sh, 1087vs, 1067m, 1050sh, 1022s, 999m, 960sh, 825s, 740vs, 720m, 700vs,br, 618sh, 540w, 500vs, 490sh, 443w cm^{-1} .

Preparation of $[Fe_2Pt(dppe)(CO)_6(Me_3CCP)]$ (4)

(a) *Reaction of $[Pt(dppe)(Me_3CCP)]$ with $[Fe_2(CO)_9]$.* $[Pt(dppe)(Me_3CCP)]$ (0.30 g, 0.433 mmol) was dissolved in toluene (30 cm^3) and a two-fold excess of $[Fe_2(CO)_9]$ (0.315 g, 0.866 mmol) was added. The mixture was heated under reflux under dinitrogen for ca. 1.5 h, in which time the colour of the solution changed to deep red. The mixture was allowed to cool to room temperature, and the volatile materials were removed under reduced pressure. The solid product was recrystallized from dichloromethane and petroleum ether (60–80 °C) to give the deep red crystalline complex (4) $[(\mu-1,2-bis(diphenylphosphino)ethane-P,P)\{(\mu-2,2-dimethylpropylidene-P,C-bis(tricarbonyliron)(Fe,Fe,P))\}platinum(0)(Fe-Fe)2(Fe-Pr)]$ (0.420 g, 100%), m.p. 220 °C. (Found: C, 45.20; H, 3.42, $C_{37}H_{33}Fe_2O_6P_3Pt$ calcd.: C, 45.65; H, 3.42%). IR spectrum (Nujol) $\nu(CO)$: 2021m, 1967s, 1925vs, and 1898w cm^{-1} . The formulation of the complex was confirmed by a single crystal X-ray structure determination.

(b) *Reaction of $[Pt(dppe)(Me_3CCP)]$ with $[Fe_3(CO)_{12}]$.* To a solution of $[Pt(dppe)(Me_3CCP)]$ (0.162 g, 0.234 mmol) in dry toluene (20 cm^3) under dinitrogen was added solid $[Fe_3(CO)_{12}]$ (0.118 g, 0.234 mmol). The mixture was heated under reflux for 1.5 h, and the colour of the solution changed to deep red. The solution was allowed to cool to room temperature, and the final product $[Fe_2Pt(dppe)(CO)_6-(Me_3CCP)]$ isolated by the same procedure described in (a) above. The yield has quantitative (0.227 g, 100%), and elemental analysis, m.p., IR and $^{31}P\{^1H\}$ NMR spectra were in full agreement with that observed in (a).

Preparation of $[Fe_3Pt(triphos)(CO)_{10}(Me_3CCP)]$, (5)

(a) *Reaction of $[Pt(triphos)(Me_3CCP)]$ with $[Fe_2(CO)_9]$.* $[Pt(triphos)(Me_3CCP)]$ (0.45 g, 0.489 mmol) was dissolved in toluene (25 cm^3) and a three-fold excess of $[Fe_2(CO)_9]$ (0.543 g, 1.469 mmol) was added. The mixture was heated under reflux under dinitrogen for ca. 3 h, during which time the colour of the solution changed to deep red. The mixture was allowed to cool to room temperature, and the volatile materials were removed under reduced pressure. The solid product was washed with petroleum ether (60–80 °C) and dried in vacuo to give the deep red microcrystalline complex $[(\mu-2,2-dimethylpropylidene-phosphine-P,C)bis(tricarbonyliron)\{tetracarbonyl(1,1,1-tris(diphenylphosphinomethyl)ethane-P^1)iron\}-P^2,P^3]platinum(0)-2(Fe-P)(P-Pr)(Fe-Fe)2(Fe-Pr)]$ (0.54 g, 84%). Found: C, 49.20; H, 3.57. $C_{56}H_{48}Fe_3O_{10}P_4Pt$ calcd.: C, 49.19; H, 3.54%). IR spectrum (Nujol) $\nu(CO)$: 2048s, 2019m, 1968s,br, 1945vs, 1930w, and 1895w cm^{-1} .

(b) *Reaction of $[Pt(triphos)(Me_3CCP)]$ with $[Fe_3(CO)_{12}]$.* Similarly, using an identical procedure to that described above, a two-fold excess of $[Fe_3(CO)_{12}]$ (0.328 g, 0.652 mmol) was treated with $[Pt(triphos)(Me_3CCP)]$ (0.30 g, 0.326 mmol) to afford the deep red microcrystalline complex $[Fe_3Pt(triphos)(CO)_{10}(Me_3CCP)]$ (0.353 g, 79%). (Found: C, 49.22; H, 3.58; $C_{56}H_{48}Fe_3O_{10}P_4Pt$ calcd.: C, 49.19; H, 3.54%), which was identical with the sample made by route (a).

Table 5

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
Pt	2855.0(2)	1914.8(3)	1518.4(1)
Fe(1)	1713.0(9)	60.2(11)	1695.2(5)
Fe(2)	3322.3(9)	-325.2(11)	1331.3(5)
P(1)	1846(2)	779(2)	854(1)
P(2)	2381(2)	3428(2)	1999(1)
P(3)	4042(2)	3201(2)	1316(1)
C(1)	1902(6)	-702(8)	981(3)
C(2)	1345(7)	-1700(8)	643(4)
C(3)	175(8)	-1544(11)	587(5)
C(4)	1686(9)	-2930(8)	875(5)
C(5)	1647(9)	-1619(11)	83(4)
C(6)	4295(6)	385(8)	1784(3)
C(7)	3564(8)	-1687(9)	1645(4)
C(8)	1324(8)	-1283(10)	1913(4)
C(9)	2484(7)	360(9)	2318(4)
C(10)	524(7)	726(9)	1724(4)
C(11)	4007(7)	-600(9)	821(4)
C(12)	3197(6)	4730(8)	1935(3)
C(13)	4251(6)	4332(8)	1838(3)
C(14)	1087(6)	3998(8)	1787(3)
C(15)	734(7)	4915(9)	2072(4)
C(15)	-263(7)	5350(9)	1911(4)
C(17)	-908(8)	4874(10)	1469(4)
C(18)	-543(9)	4002(11)	1181(5)
C(19)	469(8)	3545(10)	1339(4)
C(20)	2547(6)	3212(8)	2710(3)
C(21)	3542(8)	3029(10)	2990(4)
C(22)	3739(10)	2855(12)	3543(5)
C(23)	2889(10)	2832(12)	3798(5)
C(24)	1930(10)	2926(12)	3539(5)
C(25)	1707(8)	3101(9)	2962(4)
C(26)	3636(6)	4069(8)	708(3)
C(27)	2740(8)	3778(10)	361(4)
C(28)	2447(9)	4459(11)	-104(5)
C(29)	3036(8)	5415(10)	-205(4)
C(30)	3932(8)	5693(10)	148(4)
C(31)	4253(7)	5014(9)	618(4)
C(32)	5309(6)	2660(8)	1263(3)
C(33)	6162(8)	2884(9)	1649(4)
C(34)	7120(9)	2347(12)	1616(5)
C(35)	7183(8)	1623(11)	1194(4)
C(36)	6335(8)	1399(10)	798(4)
C(37)	5378(7)	1939(8)	833(4)
O(6)	4996(5)	699(6)	2107(3)
O(7)	3754(6)	-2556(8)	1889(3)
O(8)	1065(6)	-2158(7)	2101(3)
O(9)	2948(5)	435(7)	2747(3)
O(10)	-266(6)	1145(8)	1752(3)
O(11)	4448(6)	-811(7)	481(3)

Crystal data: $C_{37}H_{33}Fe_2O_6P_3Pt$, $M = 917.4$, monoclinic, a 13.238(1), b 11.295(2), c 25.642(2) Å, β 100.72(1)°, U 3767.2 Å³, $Z = 4$, D_c 1.72 g cm⁻³, $F(000) = 1912$. Monochromated Mo- K_α radiation, λ 0.71069 Å, μ 48.5 cm⁻¹. Space group $P2_1/c$ from systematic absences.

Data were measured on an Enraf–Nonius CAD4 diffractometer using a crystal of size ca. 0.40 × 0.22 × 0.30 mm. Intensities for $hk \pm l$ reflections with $2 < \theta < 22^\circ$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (0.8 + 0.35\tan\theta)^\circ$. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lp effects and for absorption (empirically) and after averaging any equivalent reflections, 3954 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02I)^2]^{1/2}/Lp$.

The structure was solved by routine heavy atom methods. Refinement of non-hydrogen atoms, with Pt, Fe, P, and the C atoms of the Me₃CCP group anisotropic, was by full matrix least squares. Refinement converged at $R = 0.040$, $R' = 0.052$, when the maximum shift/error was 0.01 and the weighting scheme was $w = 1/\sigma^2(F)$. No attempt was made to include H atoms.

The structure solution and refinement was done on a PDP11/34 computer using the Enraf–Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 31. Final atom coordinates are listed in Table 5, and lists of temperature factors and final structure factors are available from the authors.

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