

# Coordination of an amino-phosphino macrocycle with ( $\eta^5$ -cyclopentadienyl)- and ( $\eta^5$ -pentamethylcyclopentadienyl)-iron complexes

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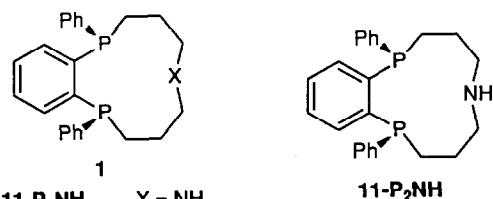
## Abstract

The coordination chemistry of a phospho-macrocycle *meso-cis*-2,10-diphenyl-6-aza-2,10-diphenylphabicyclo[9.4.0]pentadeca-11(1),12,14-triene (11-P<sub>2</sub>NH) with ( $\eta^5$ -cyclopentadienyl)dicarbonyliron and ( $\eta^5$ -pentamethylcyclopentadienyl)dicarbonyliron was investigated. Thus 11-P<sub>2</sub>NH reacts with CpFe(CO)<sub>2</sub>I in benzene under photochemical conditions to yield a mixture of [*P,P'*,*N*-(11-P<sub>2</sub>NH)FeCp]I (2) and [*P,P'*-(11-P<sub>2</sub>NH)Fe(CO)Cp]I (3). Conversion of 3 into 2 was achieved by photochemical treatment of 3 in acetonitrile. The amine donor of the macrocycle in 2 was slowly transformed into a coordinating imine moiety. Similar behaviour was observed for the pentamethylcyclopentadienyl analogue. The crystal structure of [*P,P'*,*N*-(11-P<sub>2</sub>NH)FeCp\*]I is determined.

**Key words:** Iron; Macrocycle; Phosphine; Imine

## 1. Introduction

Due to the difficult synthesis of macrocyclic phosphines, the coordination chemistry involving such ligands has been less well investigated compared with other systems [1]. Incorporation of an *o*-phenylene-bisphosphino moiety into the large rings, developed by Kyba and coworkers [2,3] in a series of 11-member macrocycles (11-P<sub>2</sub>X), allows the corresponding metal complexes to exhibit unusual properties [4]. However, studies concerning such macrocyclic ring systems are limited. Here, we report the coordination behaviour of 11-P<sub>2</sub>NH with CpFe(CO)<sub>2</sub>I and Cp\*Fe(CO)<sub>2</sub>I.



11-P <sub>2</sub> NH	X = NH
11-P <sub>2</sub> S	X = S
11-P <sub>2</sub> O	X = O
11-P <sub>2</sub> As	X = AsPh
11-P <sub>3</sub>	X = PPh
11-P <sub>2</sub> NMe	X = NMe
11-P <sub>2</sub> NPh	X = NPh

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## 2. Results and discussion

### 2.1. Complexation

Photochemical ligand substitution of CpFe(CO)<sub>2</sub>I by macrocyclic 11-P<sub>2</sub>NH in benzene solution produced a precipitate, which was a mixture of [*P,P'*,*N*-(11-P<sub>2</sub>NH)FeCp]I (2) and [*P,P'*-(11-P<sub>2</sub>NH)FeCp(CO)]I (3) in a ratio of *ca.* 1:1 (Section 3). Recrystallization of this mixture from a chloroform and pentane solution allowed complex 2 to be separated from 3. Both complexes were characterized by spectroscopic analysis. A singlet absorption pattern in the <sup>31</sup>P nuclear magnetic resonance (NMR) spectra of 2 and 3 indicates that both phosphorus donors of 11-P<sub>2</sub>NH coordinate to the metal centre. The absence of IR absorption in the carbonyl region and the 1:1 electrolyte property of 2 are consistent with the assigned structure in which the nitrogen donor is coordinated to the metal centre. This formula is further confirmed by analogy with [*P,P'*,*N*-(11-P<sub>2</sub>NH)FeCp\*]I (5), which is illustrated by its crystal structure (Fig. 1). The IR absorption at 1954 cm<sup>-1</sup> and <sup>13</sup>C NMR resonance at 215.5 ppm (t, *J*<sub>P-C</sub> = 26 Hz) clearly show the existence of an Fe-CO moiety in complex 3.

If the reaction was carried out in acetonitrile solution, only complex 2 was obtained. Conversion of com-

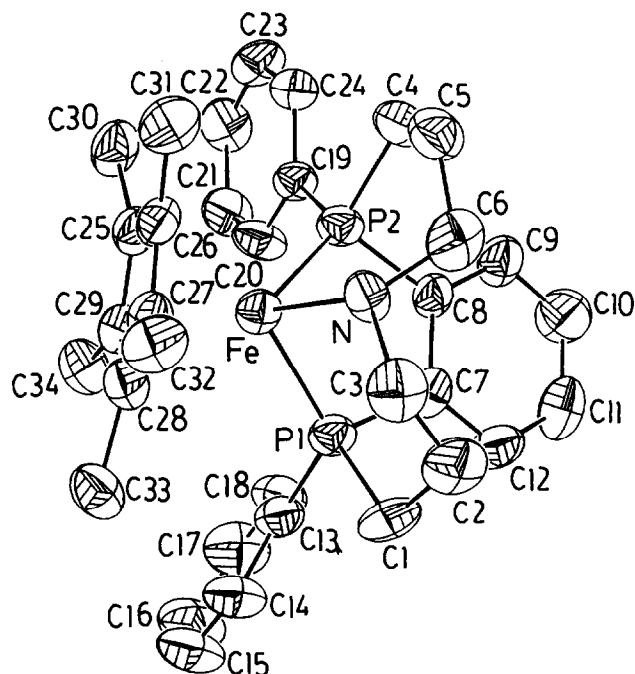


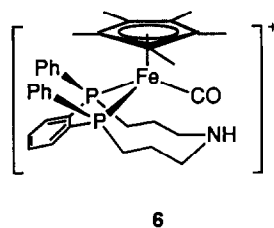
Fig. 1. ORTEP plot of  $[P,P',N-(11-P_2NH)FeCp^*]^+$ .

plex 3 into 2 was achieved photochemically in acetonitrile and the reaction was monitored by a  $^{31}P$  NMR spectrometer. An acetonitrile- $d_3$  solution of 3 in an NMR tube was irradiated with light and a new species with a  $^{31}P$  shift at 100 ppm appeared, which was believed to be  $[P,P'-(11-P_2NH)FeCp(CH_3CN)]I$ . Such species disappeared immediately accompanied by the formation of 2.

It has been demonstrated that the ligand substitution of  $CpFe(CO)_2I$  by phosphines occurs via the replacement of one of the carbonyl ligands, followed by iodide, to form  $[CpFeL_2(CO)]^+$  species, where L = phosphine [5]. Scheme 1 shows a possible pathway for the formation of 2 and 3. Dissociation of the carbonyl ligand of  $CpFe(CO)_2I$ , followed by the coordination of either phosphorus moiety of the macrocycle 11- $P_2NH$ , produces A and B; intermediate B readily undergoes substitution of the second carbonyl ligand by another phosphorus donor to form an intermediate 4, whose iodide ligand is replaced by the amine donor to yield 2. However, in intermediate A, the subsequent substitution of the iodide ligand by another phosphorus of the *o*-phenylene moiety results in the formation of 3, which is hardly soluble in benzene. In a polar solvent, such as acetonitrile, complex 3 becomes soluble and the carbonyl ligand is readily substituted by the amine donor under photochemical conditions to give 2.

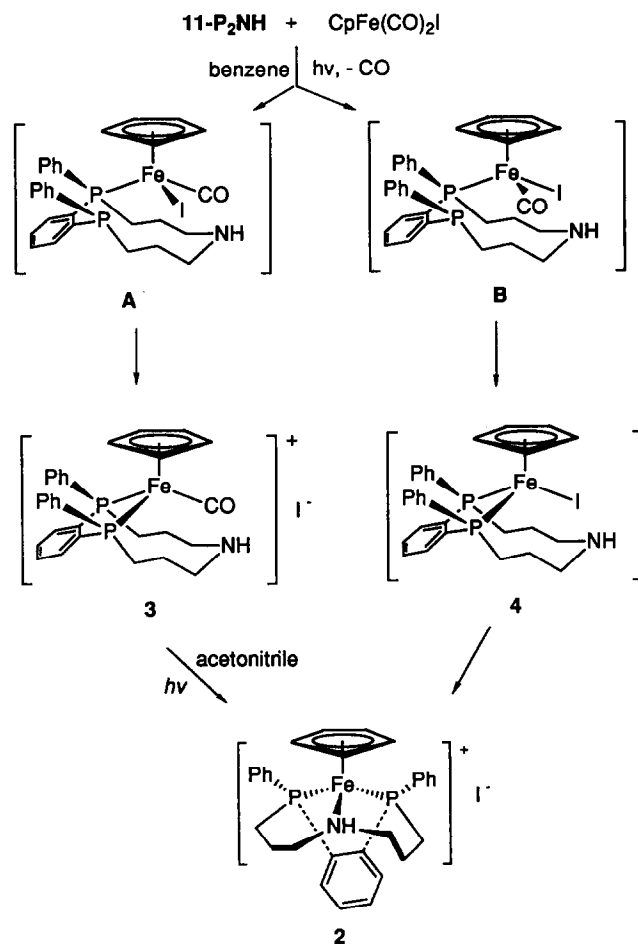
The complexation of the pentamethylcyclopentadienyl-iron analogue is similar to that of  $CpFe(CO)_2I$ . The reaction of  $Cp^*Fe(CO)_2I$  with 11- $P_2NH$  gave

$[P,P',N-(11-P_2NH)FeCp^*]I$  (5) and  $[P,P'-(11-P_2NH)FeCp^*(CO)]I$  (6) in a ratio of *ca.* 1:1. The similar spectroscopic data of 5 and 6 and 2 and 3 allows us to identify these complexes easily. Moreover, the crystal structure of 5 (Fig. 1) was determined to confirm the formulation.



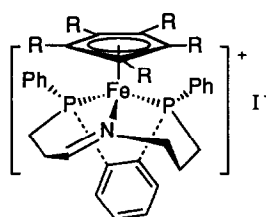
## 2.2. Imine formation

The coordinating amine moiety in complexes 2 and 5 slowly converted into imine in the presence of air to yield 7 and 8 respectively. This conversion is accelerated by the addition of a small amount of  $I_2$  in the solution. The  $^{31}P$  NMR spectra of these imine com-



Scheme 1.

plexes exhibit a pair of doublets:  $\delta$  105.5 (d,  $J = 45.8$  Hz) and 92.7 (d,  $J = 45.8$  Hz) for **7**; 94.6 (d,  $J = 30.5$  Hz) and 83.0 (d,  $J = 30.5$  Hz) for **8**. The characteristic resonances of N=C-H in  $^1\text{H}$  NMR spectra appear at  $\delta$  8.4 (multiplet) for **7** and  $\delta$  8.55 (multiplet) for **8**, while N=C in  $^{13}\text{C}$  NMR appears at  $\delta$  180.5 (d,  $J = 8.4$  Hz) for **7** and  $\delta$  179.8 (d,  $J = 10.2$  Hz) for **8**. These spectral data conclusively suggest that the imine moiety is present in the complexes.



**7** R = H  
**8** R = CH<sub>3</sub>

### 2.3. X-Ray structural analysis

Complex **5** was obtained as single crystals and its structure was thus confirmed by X-ray analysis. The ORTEP plot of the cation of **5** is shown in Fig. 1, while some significant bond distances and angles are summarized in Table 1. The coordination of the iron metal is distorted octahedral, with one face occupied by the  $\eta^5$ -(C<sub>5</sub>Me<sub>5</sub>) group and the other face by two phosphorus atoms and the nitrogen donor from the macrocycle 11-P<sub>2</sub>NH. The metal-ligand bond distances (Fe-P = 2.193(4), 2.177(3) and Fe-N = 2.101(8) Å) and bond angles (P(1)-Fe-P(2) = 86.9(1)°, P(1)-Fe-N = 89.7(1)° and P(2)-Fe-N = 91.0(2)°) are all in the normal ranges. The ligand conformation of complex **5** consists of one five- and two six-membered chelate rings: the five-membered ring is attributed to *o*-phenylenebiphosphine-Fe, while the six-membered rings are defined by P(1)-Fe-N-C(3)-C(2)-C(1) and P(2)-Fe-N-C(6)-C(5)-C(4). The torsional angle along P(1)-Fe-N-C(3)-C(2)-C(1) gives the typical +, - alternation val-

TABLE 1. Some important bond distances (Å) and bond angles (°) for complex **5**

Fe-P(1)	2.193(4)	P(1)-Fe-P(2)	86.9(1)
Fe-P(2)	2.177(3)	P(1)-Fe-N	89.7(3)
Fe-N	2.101(8)	P(2)-Fe-N	91.0(2)
P(1)-C(1)	1.83(1)	Fe-P(1)-C(1)	115.8(4)
C(1)-C(2)	1.52(2)	Fe-P(1)-C(7)	109.2(4)
C(2)-C(3)	1.53(2)	Fe-P(1)-C(13)	123.8(4)
N-C(3)	1.49(1)	Fe-P(2)-C(4)	114.2(4)
P(2)-C(4)	1.81(1)	Fe-P(2)-C(8)	109.8(3)
C(4)-C(5)	1.53(2)	Fe-P(2)-C(19)	124.6(4)
C(5)-C(6)	1.52(2)	Fe-N-C(3)	116.8(6)
N-C(6)	1.44(1)	Fe-N-C(6)	121.4(6)

TABLE 2. Torsional angles for six-membered chelate rings for **5**

P(1)-Fe-N-C(3)-C(2)-C(1)	P(2)-Fe-N-C(6)-C(5)-C(4)
P(1)-Fe-N-C(3)	P(2)-Fe-N-C(6)
-47.9	0.2
Fe-N-C(3)-C(2)	Fe-N-C(6)-C(5)
71.6	56.6
N-C(3)-C(2)-C(1)	N-C(6)-C(5)-C(4)
-74.2	-77.2
C(3)-C(2)-C(1)-P(1)	C(6)-C(5)-C(4)-P(2)
59.3	25.8
C(2)-C(1)-P(1)-Fe	C(5)-C(4)-P(2)-Fe
-49.3	31.6
C(1)-P(1)-Fe-N	C(4)-P(2)-Fe-N
37.6	-39.5

ues for a chair form, while P(2)-Fe-N-C(6)-C(5)-C(4) gives a characteristic set of four positive and two negative values for a twisted boat form (Table 2). This observation is similar to those for the nickel(II) [3] and rhodium(I) [6] macrocyclic complexes, due to the "flagpole" interactions between hydrogens of C(2) and C(5) in chair conformations.

### 3. Experimental details

Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on either a Bruker AC-E 200 or a Bruker AM 300 spectrometer.  $^{31}\text{P}$  NMR spectra were determined on a Bruker AC-E 200 spectrometer at 81.01 MHz. The photochemical apparatus was a 450 W Conrad Hanovia medium-pressure mercury lamp (Ace Glass).

Phosphines were handled and prepared under a dry nitrogen atmosphere. Solvents and chemicals from commercial sources were used without further purification. 11-P<sub>2</sub>NH [3], CpFe(CO)<sub>2</sub>I and Cp\*Fe(CO)<sub>2</sub>I [7] were prepared according to literature methods.

**3.1. (meso-cis-2,10-Diphenyl-6-aza-kN-2,10-diphenylphak<sup>2</sup>P-bicyclo[9.4.0]pentadeca-11(1),12,14-triene)( $\eta^5$ -cyclopentadienyl)iron(II) iodide (2) and carbonyl(meso-cis-2,10-diphenyl-6-aza-2,10-diphenylphak<sup>2</sup>P-bicyclo[9.4.0]pentadeca-11(1),12,14-triene)( $\eta^5$ -cyclopentadienyl)iron(II) iodide (3)**

A Pyrex flask was filled with a solution of 11-P<sub>2</sub>NH (154 mg, 0.394 mmol) and CpFe(CO)<sub>2</sub>I (119.7 mg, 0.394 mmol) in benzene (10 ml). The mixture was photolysed at room temperature for 4 h and brick red solids were precipitated. These were collected and recrystallized from chloroform and pentane. Both yellow and deep red solids were formed. These two solids were separated to give deep red crystalline complex **2** (125 mg, 50%) and yellow complex **3** (106.5 mg, 41%).

Complex **2**: m.p. 280–310°C (dec);  $^1\text{H}$  NMR  $\delta$  7.68–7.64 (m, 2H), 7.54–7.50 (m, 2H), 7.37–7.27 (m, 10H), 5.40–5.30 (br, 1H), 4.16 (s, 5H), 2.96–2.85 (m, 4H), 2.50–2.38 (m, 2H), 2.35–2.10 (m, 2H), 1.86–1.77 (m, 2H), 1.60–1.35 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  147.9 (t,  $J_{\text{P-C}} = 38.7$  Hz), 138.9 (t,  $J_{\text{P-C}} = 21$  Hz), 131.2–128.9 (m), 78.0, 53.7 (t,  $J_{\text{P-C}} = 5.3$  Hz), 25.6 (t,  $J_{\text{P-C}} = 9.9$  Hz),

21.4;  $^{31}\text{P}$  NMR  $\delta$  95.6; FAB mass  $M^+ = 511.94$ ; Anal. Calc. for  $\text{C}_{29}\text{H}_{32}\text{NP}_2\text{FeICHCl}_3$ : C, 47.50; H, 4.38; N, 1.85. Found: C, 47.20; H, 4.35; N, 1.90%.

Complex 3: m.p. 270–300°C (dec); IR (KBr)  $\nu(\text{CO}) = 1955\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.70–7.20 (m, 14H), 4.08 (s, 5H), 3.35–3.15 (m, 2H), 3.10–2.95 (m, 2H), 2.45–2.25 (m, 4H), 2.20–2.00 (m, 2H), 1.75–1.45 (m, 2H), –1.25 to –1.40 (br, 1H);  $^{13}\text{C}$  NMR  $\delta$  215.5 (t,  $J_{\text{P-C}} = 26\text{ Hz}$ ), 145.5–142.4 (m), 133.2–129.2 (m), 85.7, 47.6, 33.8 (t,  $J_{\text{P-C}} = 14\text{ Hz}$ ), 26.3;  $^{31}\text{P}$  NMR  $\delta$  89.0; FAB mass  $M^+ = 539.95$ ; Anal. Calc. for  $\text{C}_{30}\text{H}_{32}\text{NOP}_2\text{FeI}$ : C, 54.00; H, 4.83; N, 2.10. Found: C, 54.17; H, 4.82; N, 2.01%.

3.2. (*meso-cis-2,10-Diphenyl-6-aza-kN-2,10-diphenylphak<sup>2</sup>P-bicyclo[9.4.0]pentadeca-11(1),12,14-triene*)( $\eta^5$ -pentamethylcyclopentadienyl)iron(II) iodide (5) and *car4-bonyl(meso-cis-2,10-diphenyl-6-aza-2,10-diphenylphak<sup>2</sup>P-bicyclo[9.4.0]pentadeca-11(1),12,14-triene*)( $\eta^5$ -pentamethylcyclopentadienyl)iron(II) iodide (6)

The procedure for the preparation of 5 and 6 was similar to that for 2 and 3, except that  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}$  was used.

Complex 5: dark red crystalline solid (45%); m.p. 250–270°C (dec);  $^1\text{H}$  NMR  $\delta$  7.55–7.30 (m, 14H), 3.25–3.15 (br, 1H), 2.95–2.80 (m, 4H), 2.50–2.35 (m, 2H), 2.10–1.90 (m, 4H), 1.60–1.40 (m, 2H), 1.34 (s, 15H);  $^{13}\text{C}$  NMR  $\delta$  148.4 (t,  $J_{\text{P-C}} = 37.9\text{ Hz}$ ), 137.5 (t,  $J_{\text{P-C}} = 19.3\text{ Hz}$ ), 131.8–128.5 (m), 85.8, 52.2 (t,  $J_{\text{P-C}} = 4.7\text{ Hz}$ ), 22.7 (t,  $J_{\text{P-C}} = 10.2\text{ Hz}$ ), 20.9, 10.4;  $^{31}\text{P}$  NMR  $\delta$  85.53; FAB mass  $M^+ = 582.1$ ; Anal. Calc. for  $\text{C}_{34}\text{H}_{42}\text{NP}_2\text{FeICHCl}_3$ : C, 50.72; H, 5.23; N, 1.69. Found: C, 50.42; H, 5.05; N, 1.73%.

Complex 6: orange crystalline solid (43%); m.p. 270–285°C (dec); IR (KBr)  $\nu(\text{CO}) = 1927\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.90–7.25 (m, 12H), 6.80–6.60 (m, 2H), 3.38–3.20 (m, 2H), 2.60–2.46 (m, 2H), 2.44–2.24 (m, 2H), 2.22–2.00 (m, 2H), 1.70–1.50 (m, 2H), 1.16 (s, 15H), –1.40 to –1.60 (br, 1H);  $^{13}\text{C}$  NMR  $\delta$  219.3 (t,  $J_{\text{P-C}} = 26\text{ Hz}$ ), 146.9 (t,  $J_{\text{P-C}} = 40\text{ Hz}$ ), 137.0 (t,  $J_{\text{P-C}} = 17\text{ Hz}$ ), 133.2–128.8 (m), 94.9, 47.5, 32.7 (t,  $J_{\text{P-C}} = 14\text{ Hz}$ ), 26.5, 9.42;  $^{31}\text{P}$  NMR  $\delta$  85.0; FAB mass  $M^+ = 610.15$ ; Anal. Calc. for  $\text{C}_{35}\text{H}_{42}\text{NOP}_2\text{FeI}$ : C, 57.01; H, 5.74; N, 1.90. Found: C, 57.20; H, 5.53; N, 1.97%.

3.3. (*cis-2,10-Diphenyl-6-aza-kN-2,10-diphenylphak<sup>2</sup>P-bicyclo[9.4.0]pentadeca-5,11(1),12,14-tetraene*)( $\eta^5$ -cyclopentadienyl)iron(II) iodide (7)

A chloroform solution of complex 2 was exposed to air and followed by  $^{31}\text{P}$  NMR spectroscopy. After the conversion, the solution was filtered and concentrated to give the desired compound 7 quantitatively as an orange solid: m.p. 230–245°C (dec);  $^1\text{H}$  NMR  $\delta$  8.45–8.35 (m, 1H), 7.70–7.30 (m, 14H), 4.20–3.95 (m, 2H),

3.92 (s, 5H), 3.50–2.95 (m, 5H), 2.50–2.25 (m, 1H), 2.10–1.90 (m, 1H), 0.70–0.55 (m, 1H);  $^{31}\text{P}$  NMR  $\delta$  105.5 (d,  $J = 45.8\text{ Hz}$ ), 92.7 (d,  $J = 45.8\text{ Hz}$ ); FAB mass

TABLE 3. Atomic parameters  $x$ ,  $y$ ,  $z$  and  $B_{\text{iso}}$

Atom	$x$	$y$	$z$	$B_{\text{iso}}$
I	0.77112(7)	0.92292(7)	0.14149(7)	4.86(5)
Fe	0.22803(13)	0.82771(13)	0.26119(12)	3.14(9)
P(1)	0.13357(24)	0.88528(25)	0.35214(23)	3.41(18)
P(2)	0.37018(24)	0.88464(24)	0.30526(22)	3.39(18)
N	0.2067(6)	0.9799(6)	0.1381(6)	3.7(5)
C(1)	0.0186(8)	0.9743(9)	0.2914(8)	4.5(8)
C(2)	0.0496(9)	1.0663(9)	0.1912(8)	5.1(8)
C(3)	0.0949(10)	1.0259(9)	0.1192(9)	5.3(8)
C(4)	0.4562(8)	0.9714(9)	0.2032(8)	4.4(7)
C(5)	0.3971(9)	1.0409(9)	0.1070(8)	4.9(7)
C(6)	0.2792(9)	1.0677(9)	0.1176(8)	4.8(7)
C(7)	0.2177(9)	0.9710(8)	0.3839(8)	3.5(7)
C(8)	0.3291(8)	0.9706(8)	0.3622(8)	3.4(6)
C(9)	0.3990(9)	1.0307(9)	0.3883(8)	4.3(8)
C(10)	0.3635(10)	1.0919(10)	0.4332(9)	5.7(9)
C(11)	0.2546(10)	1.0928(9)	0.4543(9)	5.5(9)
C(12)	0.1823(9)	1.0338(9)	0.4289(9)	4.7(8)
C(13)	0.0762(8)	0.7955(9)	0.4730(8)	3.8(7)
C(14)	–0.0250(9)	0.7546(9)	0.4841(8)	4.9(8)
C(15)	–0.0647(9)	0.6804(11)	0.5738(10)	6.6(10)
C(16)	–0.0038(10)	0.6467(11)	0.6541(9)	7.0(10)
C(17)	0.0971(10)	0.6882(10)	0.6488(8)	6.0(9)
C(18)	0.1361(9)	0.7615(9)	0.5583(8)	4.8(8)
C(19)	0.4665(8)	0.7965(8)	0.3985(7)	3.1(7)
C(20)	0.4306(8)	0.7300(9)	0.4929(8)	4.3(8)
C(21)	0.4978(9)	0.6621(9)	0.5661(8)	4.7(7)
C(22)	0.6053(9)	0.6562(9)	0.5456(9)	4.8(7)
C(23)	0.6446(8)	0.7193(9)	0.4530(8)	4.4(8)
C(24)	0.5757(8)	0.7906(9)	0.3790(8)	3.8(7)
C(25)	0.3090(8)	0.6857(8)	0.2744(8)	3.5(6)
C(26)	0.2759(9)	0.7503(8)	0.1759(8)	3.6(7)
C(27)	0.1612(9)	0.7552(8)	0.1772(8)	3.7(7)
C(28)	0.1246(9)	0.6993(8)	0.2752(8)	3.8(7)
C(29)	0.2171(8)	0.6581(8)	0.3370(7)	3.3(6)
C(30)	0.4219(9)	0.6412(9)	0.3027(8)	4.6(7)
C(31)	0.3465(9)	0.7850(9)	0.0875(8)	4.9(8)
C(32)	0.0908(9)	0.8005(9)	0.0866(8)	4.8(8)
C(33)	0.0079(9)	0.6720(9)	0.3063(8)	4.7(8)
C(34)	0.2123(9)	0.5810(9)	0.4441(8)	4.5(7)
C(35)	0.7325(11)	0.6432(11)	0.1613(10)	7.2(10)
Cl(1)	0.7219(4)	0.5595(4)	0.2890(3)	10.0(3)
Cl(2)	0.8471(3)	0.6076(4)	0.1150(3)	10.1(4)
Cl(3)	0.6211(4)	0.6330(5)	0.1013(4)	12.3(5)
C(36)	0.7018(12)	0.1791(11)	0.1821(10)	7.8(10)
Cl(4)	0.5781(4)	0.2478(4)	0.1553(4)	12.5(4)
Cl(5)	0.7182(4)	0.1083(4)	0.3069(3)	11.4(4)
Cl(6)	0.8044(4)	0.2742(4)	0.1279(3)	10.8(4)
C(37)	0.2879(24)	0.4391(23)	0.1058(21)	27.7(13)
Cl(7)	0.2621(6)	0.3093(6)	0.1936(5)	20.7(3)
Cl(8)	0.2336(6)	0.5176(6)	0.1727(6)	7.33(21)
Cl(9)	0.4048(11)	0.4700(11)	0.1174(10)	18.0(5)
Cl(10)	0.1809(13)	0.5156(13)	0.1169(12)	24.3(7)
Cl(11)	0.0986(12)	0.4163(12)	0.0922(11)	20.6(6)

$B_{\text{iso}}$  is the mean of the principal axes of the thermal ellipsoid.

$M^+ = 509.93$ . Anal. Calc. for  $C_{29}H_{30}NP_2FeI$ : C, 54.66; H, 4.75; N, 2.20. Found: C, 54.32; H, 4.65; N, 2.52%.

3.4. (*cis*-2,10-Diphenyl-6-aza-*kN*-2,10-diphenylphosphino-*k^2P*-bicyclo[9.4.0]pentadeca-5,11(1),12,14-tetraene)( $\eta^5$ -pentamethylcyclopentadienyl)iron(II) iodide (**8**)

This complex was prepared similarly to **7**. Complex **8**: m.p. 145–155°C (dec);  $^1H$  NMR  $\delta$  8.60–8.50 (m, 1H), 7.60–7.20 (m, 14H), 4.30–4.10 (m, 1H), 3.80–3.60 (m, 1H), 3.30–2.80 (m, 4H), 2.50–2.10 (m, 2H), 1.20–1.00 (m, 1H), 1.14 (s, 15H), 0.70–0.45 (m, 1H);  $^{31}P$  NMR  $\delta$  94.6 (d,  $J = 30.5$  Hz), 83.0 (d,  $J = 30.5$  Hz); FAB mass  $M^+ = 579.95$ . Anal. Calc. for  $C_{34}H_{40}NP_2FeI$ : C, 57.73; H, 5.70; N, 1.78. Found: C, 57.50; H, 5.37; N, 2.14%.

3.5. Crystal data

$C_{34}H_{42}NP_2FeI(CHCl_3)_3$ ,  $M = 1068.04$ ,  $a = 12.390(2)$ ,  $b = 13.814(2)$ ,  $c = 15.177(2)$  Å,  $\alpha = 63.04(1)^\circ$ ,  $\beta = 88.99(2)^\circ$ ,  $\gamma = 88.88(2)^\circ$ ,  $U = 2314.9(6)$  Å<sup>3</sup>, space group  $P-1$ ,  $Z = 2$ ,  $F(000) = 1072$ , crystal dimensions 0.5 mm  $\times$  0.2 mm  $\times$  0.2 mm,  $\mu(Mo K\alpha) = 1.43$  mm<sup>-1</sup>.

3.6. Data collection and processing

CAD4 diffractometer,  $\omega-2\theta$  mode with  $\omega$  scan width  $0.8 + 0.35 \tan \theta$ , scan speed 2.35–8.24 deg min<sup>-1</sup>, Mo  $K\alpha$  radiation source; 6035 reflections measured, giving 3808 with  $I > 2\sigma(I)$ . Crystal decay approximately 10% during data collection.

3.7. Structure analysis and refinement

The heavy atom method was used. The least-squares refinement was calculated with all non-hydrogen atoms anisotropic. The refinement details are as follows, where  $F_o$  and  $F_c$  are the observed and calculated structure factor amplitudes respectively; the function minimized was  $\sum w(F_o - F_c)^2$ , where  $w^{-1} = \sigma^2(F_o)$ ,  $\sigma(F_o)$  from counting statistics;  $R_f = \sum |F_o - F_c| / \sum(F_o)$ ;  $R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$ ;  $S = [\sum (w(F_o - F_c)^2) / (\text{no. of reflections} - \text{no. of params})]^{1/2}$ . For significant reflections,  $R_f = 0.064$ ,  $R_w = 0.048$ ,  $S = 2.96$ .

Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [8]. Computing program: NRCC SDP VAX Package [9]. The crystal contains three molecules of solvent  $CHCl_3$ , with one of them disordered.

The atomic coordinates and thermal parameters are given in Table 3. A full list of the bond distances and bond angles, anisotropic thermal parameters and structure factors is available from the authors (S.T.L.).

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