Journal of Organometallic Chemistry, 458 (1993) 199–204

JOM 23630

Synthesis, some reactions, and molecular structure of the $Pd(BF_4)_2$ complex of 1,1′-bis(diphenylphosphino)ferrocene

Masaru Sato, Hiroaki Shigeta and Masato Sekino
Chemical Analysis Centre, Saitama University, Urawa, Saitama 338 (Japan)

Sadatoshi Akabori
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274 (Japan)

(Received December 11, 1992; in revised form February 27, 1993)

Abstract

1,1′-Bis(diphenylphosphino)ferrocene (dppf) reacted with $[Pd(CH_3CN)_4](BF_4)_2$ in the presence of one equivalent of phosphines to give a stable 1/1 complex in which there is a bonding interaction between Fe and Pd atoms. An X-ray structure determination of $[(dppf)Pd(PPh_3)](BF_4)_2$ confirms the presence of a dative bond (2.877(2) Å). In the case of ligands other than phosphines, no complex with a metal–metal bond was obtained.

1. Introduction

Ferrocene derivatives with electron-donating heteroatoms at the 1,1′-positions are a useful organometallic ligand for preparing heterobimetallic complexes. 1,1′-Bis(diphenylphosphino)ferrocene (dppf) (**1**) is representative and its complexes with various transition metals have been prepared [1–18]. However, only a few complexes involving a strong metal–metal interaction have been reported. Seyferth [19] and Akabori [20,21] showed the presence of dative Fe–Pd and Fe–Pt bonds in (triphenylphosphine)(1,1′-ferrocenedithiolato-S,S′,Fe)palladium(II) (**2a**) and -platinum(II) (**2b**), respectively. The $Pd(BF_4)_2$ complexes (**3**) of trithia [n](1,1′)ferrocenophanes ($n = 7$ or 9) were also reported to contain a similar Fe–Pd bond [22,23]. It was reported that 1,1′-bis(alkylthio)ferrocene reacted with $Pd(BF_4)_2$ in the presence of triphenylphosphine to give the complex (**4**) with a structure similar to that in **2a** [24,25]. We here report the details of the complex of **1** with $Pd(BF_4)_2$ [26*].

2. Results and discussion

Compound **1** was treated with the strongly acidic compound $[Pd(CH_3CN)_4](BF_4)_2$ [27] (prepared from $Pd(CH_3CN)_2Cl_2$ and two equivalents of $AgBF_4$ in acetone) in the presence of one equivalent of triphenylphosphine to give a 1/1 complex, $[(dppf)Pd(PPh_3)](BF_4)_2$ (**5a**) as dark green needles in moderate yield. In a similar manner, the complexes with methyldiphenylphosphine (**5b**) and tributylphosphine (**5c**) were obtained in 22 and 51% yields, respectively. However, no complex with dimethylphenylphosphine was isolated following the same procedure.

The ^1H NMR spectrum of **5a** showed the α and β protons of the ferrocenyl ring as broad singlets at δ 4.57 and 5.95, respectively (*vide infra*). These signals remained broad singlets between -80 and $+60$°C, although the α-protons shifted from δ 4.83 at -80°C to 4.51 at $+62$°C. This indicates that **5a** has a rigid structure. The IR spectrum of **5a** showed the out-of-plane bending vibration, which is a good diagnostic probe for the oxidation state of the ferrocene moiety [28], at 842 cm^{-1}. The value is similar to that in the sulphide complexes **4** (848 cm^{-1} in the case of R = Me) [25] and the thiolate complex **2a** (830 and 838 cm^{-1}), although the intensity is rather weak compared with

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Correspondence to: Dr. M. Sato.

* Reference number with an asterisk indicates a note in the list of references.

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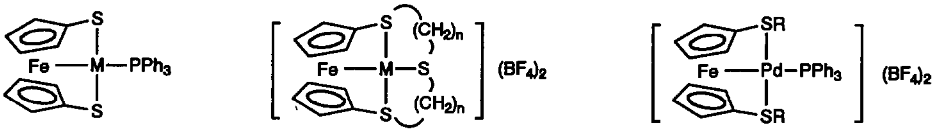


2a: M = Pd
2b: M = Pt

3: M=Pd or Pt, n=7 or 9

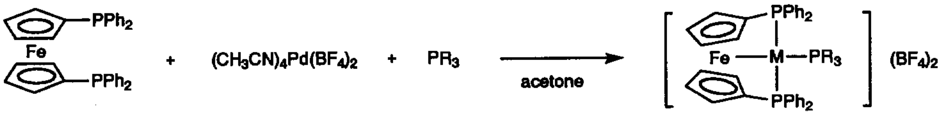
4: R = Ph or Alk

Scheme 1.

those of the others. The visible spectrum of **5a** showed three absorption bands at 380 (ϵ 14500), 477 (7300), and 624sh nm (1000). The pattern of the spectrum is closely similar to that in the sulphide complexes **4** [380 (ϵ 5730), 450 (16500), and 580sh nm (484) in the case of R = Me] [25].

In the ^{13}C NMR spectrum of **5a**, the ferrocenyl ring carbons appeared as triplets at 57.90 ($J = 21.3$ Hz), 72.21 ($J = 5.2$ Hz), and 87.67 ppm ($J = 3.8$ Hz). The signal at 57.90 remained as a triplet in the gated decoupling measurement and was then assigned as the *ipso* carbon atom. The signals at 72.21 and 87.67 were assigned to α- and β-carbons, respectively, since J_{ccp} is generally larger than J_{cccp}. On the basis of this assignment and the result of the selective decoupling, the proton signals at δ 4.57 and 5.95 are assigned to the α- and β-protons of the ferrocenyl ring, respectively. The complexation of **1** with $Pd(BF_4)_2$ causes the downfield shift of Δ 0.59 and 1.71 ppm in the α- and β-protons from those of the free ligand, respectively, and the corresponding shifts are considerably larger than those observed in complex (dppf)$PdCl_2$ (**6**) (Δ ~0.15 ppm for both protons) [2]. The large downfield shift of the β-proton signal is noteworthy. The large separation ($\Delta\delta$ 1.38) between the chemical shifts of the α- and β-protons was also observed in the sulphide complexes **4** ($\Delta\delta$ ~2.5) and was explained by the magnetic anisotropy of the Fe–Pd dative bond [24]. The ^{1}H NMR data seem to suggest that **5a** has a structure containing a Fe–Pd dative bond similar to that proposed in the sulphide complexes **4**. In the ^{13}C NMR spectrum of **5a**, it is worthy of note that the β-carbon signal shifted downfield (Δ 15.17 ppm) and the *ipso* carbon signal shifted upfield (Δ 18.80 ppm) compared with those in **1**, although the α-carbon signal remained unchanged. This may suggest that the large separation between the α- and β-proton signals of the ferrocenyl ring is not due only to the magnetic anisotropy of the Fe–Pd dative bond.

In complex **5a**, the upfield shift of the *ipso* carbon signal in the phenyl group of triphenylphosphine (Δ 16.78 ppm) is similar to that of the *ipso* carbon signal in the ferrocenyl ring (Δ 18.79 ppm). The very small upfield shifts (Δ 7.34 and 4.13 ppm) were also observed for the *ipso* carbon signal in the phenyl ring of triphenylphosphine and that in the ferrocenyl ring in the $PdCl_2$ complex **6**, respectively. These results suggest that the electron density flows out much more from the corresponding carbon atoms to the phosphorus atoms coordinated to the Pd^{II} atom in **5a** than in **6**. The ^{31}P NMR spectrum was very informative for elucidating the structure of complexes **5**. Complex **5a** showed one doublet ($J = 15.7$ Hz) at −14.68 ppm and one triplet ($J = 15.5$ Hz) at +38.02 ppm (d_6-acetone). The signal of the P atom of triphenylphosphine in complex **2a** is observed as a singlet at +39.50 ppm. The magnitude of the coupling constant is representative for the square-planar complexes having *cis* configuration (J(PPdP) = 8.0 Hz in *cis*-$PdCl_2(Me_3P)_2$ [29] and J(PPtP) = 20.0 Hz in *cis*-$PtCl_2(Bu_3P)\{(PhO)_3P\}$ [30]). From the spectrum it is evident that the P atoms of dppf are in *trans* configuration to each other and *cis* to the P atom of triphenylphosphine in complex **5a**. It is noteworthy that the P signal of dppf in **5a** appears at −14.68 ppm, while that in **6** is observed as a singlet at +34.71 ppm (in d_6-DMSO). These results give strong support for the structure proposed for complexes **5** which involve a Fe–Pd dative bond.



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5 **a**: R_3 = Ph_3
b: R_3 = Ph_2Me
c: R_3 = Bu_3

Scheme 2.

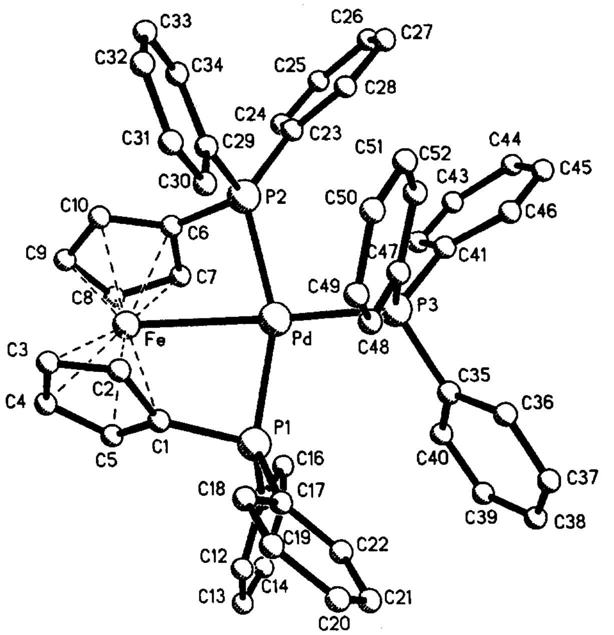
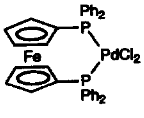


Fig. 1. Molecular structure of **5a**.



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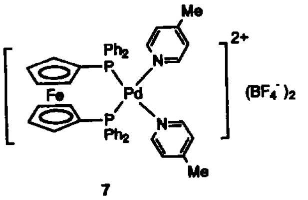

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The molecular structure of **5a** was determined by a single X-ray diffraction. The ball-and-stick expression of the molecule **5a**, along with the numbering, is shown in Fig. 1. The selected bond distances and bond angles are summarized in Tables 1 and 2 respectively. The Pd atom has a slightly distorted square-planar coordination geometry including the Fe atom of the ferrocenyl moiety, in which the two P atoms of dppf are in the *trans* position to each other and the Fe atom of ferrocene and the P atom of triphenylphosphine are also in *trans* positions; Fe-Pd-P3 176.9(1)° and P1-Pd-P2 155.9(1)°. The Pd-P3 distance (2.270(3) Å) is somewhat longer than the corresponding Pd-P distance (2.241(2) Å) in complex **2a** [19,31] and is within the range of typical Pd-PPh_3 complexes [2.230(4)-2.349(2) Å]. The Pd-P1 (2.292(4) Å) and Pd-P2 distances (2.318(3) Å) are similar to that in the $PdCl_2$ complex **6** (2.283(1) and 2.301(1) Å) [2]. The Fe-Pd distance (2.877(2) Å) in complex **5a** is quite similar to that in complex **2a** (2.878(1) Å), indicating that there is a weak dative bond between the Fe and Pd atoms in **5a** although it is significantly longer than those observed in clusters containing Fe-Pd single bonds (2.599(1)-2.698(1) Å) [32]. The angle P1-Pd-P2 is quite different from that in the $PdCl_2$ complex **6** (99.07(5)°) and similar to that in complex **2a** (168.6°). The tilting angle of the Cp ring in the ferrocene moiety in **5a** is 19.6°, being different from that in complex **6** (6.2°) and very close to that in **2a** (19.6°). These structural parameters have been proved to be useful for distinguishing between both types of complex. No remarkable difference is observed in the Fe-C distances in the ferrocene moiety, which are 2.07(2) Å on average. The C-C bond distances in the Cp rings are 1.40(2) Å on average and show no clear bond alternation.

TABLE 1. Selected bond lengths (Å)

Pd-Fe	2.877(2)	Pd-P(1)	2.292(4)
Pd-P(2)	2.318(3)	Pd-P(3)	2.270(3)
Fe-C(1)	2.09(1)	Fe-C(2)	2.06(1)
Fe-C(3)	2.06(1)	Fe-C(4)	2.07(2)
Fe-C(5)	2.06(1)	Fe-C(6)	2.09(1)
Fe-C(7)	2.08(2)	Fe-C(8)	2.08(2)
Fe-C(9)	2.06(2)	Fe-C(10)	2.08(2)
P(1)-C(1)	1.79(1)	P(1)-C(11)	1.78(1)
P(1)-C(17)	1.79(1)	P(2)-C(6)	1.79(1)
P(2)-C(23)	1.81(1)	P(2)-C(29)	1.81(1)
P(3)-C(35)	1.78(1)	P(3)-C(41)	1.84(1)
P(3)-C(47)	1.81(1)	C(1)-C(2)	1.45(2)
C(1)-C(5)	1.39(2)	C(2)-C(3)	1.37(2)
C(3)-C(4)	1.42(2)	C(4)-C(5)	1.37(2)
C(6)-C(7)	1.42(2)	C(6)-C(10)	1.37(2)
C(7)-C(8)	1.42(2)	C(8)-C(9)	1.42(2)
C(9)-C(10)	1.37(2)		

TABLE 2. Bond angles (°) for **5a**

Fe-Pd-P(1)	79.6(1)	Fe-Pd-P(2)	77.3(1)
Fe-Pd-P(3)	176.9(1)	P(1)-Pd-P(2)	155.9(1)
P(1)-Pd-P(3)	102.3(1)	P(2)-Pd-P(3)	100.5(1)
C(1)-Fe-C(2)	41.0(5)	C(1)-Fe-C(5)	39.1(5)
C(2)-Fe-C(3)	38.9(5)	C(3)-Fe-C(4)	40.1(6)
C(4)-Fe-C(5)	38.6(6)	C(6)-Fe-C(7)	39.9(5)
C(6)-Fe-C(10)	38.4(6)	C(7)-Fe-C(8)	40.0(6)
C(8)-Fe-C(9)	40.2(6)	C(9)-Fe-C(10)	38.5(6)
C(1)-Fe-C(6)	136.1(5)	C(2)-Fe-C(10)	118.1(6)
C(3)-Fe-C(9)	101.1(6)	C(4)-Fe-C(8)	101.0(6)
C(5)-Fe-C(7)	120.9(6)	Pd-P(1)-C(1)	86.8(4)
Pd-P(1)-C(11)	120.4(4)	Pd-P(1)-C(17)	123.2(4)
C(1)-P(1)-C(17)	110.7(6)	C(11)-P(1)-C(17)	107.7(6)
Pd-P(2)-C(6)	88.2(5)	Pd-P(2)-C(23)	127.7(4)
Pd-P(2)-C(29)	115.5(4)	C(6)-P(2)-C(23)	108.5(6)
C(6)-P(2)-C(29)	108.1(6)	C(23)-P(2)-C(29)	105.8(6)
Pd-P(3)-C(35)	116.2(4)	Pd-P(3)-C(41)	113.6(4)
Pd-P(3)-C(47)	105.4(4)	C(35)-P(3)-C(41)	101.6(6)
C(35)-P(3)-C(47)	109.9(6)	C(41)-P(3)-C(47)	110.3(6)
Fe-C(1)-P(1)	118.8(7)	Fe-C(6)-P(2)	114.7(7)

The electronic spectrum of complex **5a** showed three absorptions with relatively large coefficients as described above. The displacement by other phosphines of the phosphine ligand *trans* to the Fe atom in the complexes **5** produced an appreciable change in the

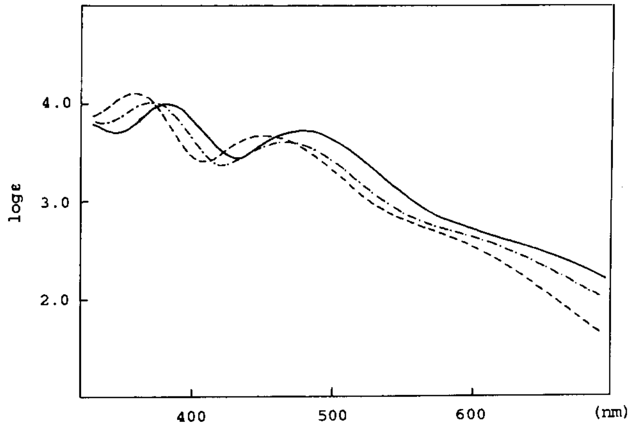

Fig. 2. Electronic spectra of **5a** (———), **5b** (·–·–·), and **5c** (------) in acetone.

spectral behaviour (Fig. 2). All three absorption maxima observed in the visible spectra of **5** shifted to a long wavelength in the following order when the phosphine ligand is displaced: PBu_3 (**5c**) < PPh_2Me (**5b**) < PPh_3 (**5a**). The shift to a long wavelength seems to parallel the decrease of the σ-donor ability of the phosphines. A similar but smaller shift to longer wavelength of the absorption maxima is also observed on the displacement of the sulphur atom (electro-negativity, 2.5) by the selenium atom (2.4) in the complexes **4**. In the ^1H NMR spectra of the complexes **5**, the difference of the chemical shift between the α- and β-protons of the ferrocenyl ring decreased as follows: **5a** ($\Delta\delta$ 1.38) > **5b** (1.23) > **5c** (1.10). This trend results mainly from the upfield shift of the β-proton signal since the chemical shift of the α-proton signal remains unchanged in the series (δ ~ 4.6 ppm). Such decrease of the separation of the α- and β-protons seems to be explained by the decreased anisotropy due to the weakening of the Fe–Pd dative bond. The decrease of the σ-donor ability of the phosphine ligands may therefore be responsible for the weakening of the Fe–Pd bonding interaction.

The reaction of **1** with $[Pd(CH_3CN)_4](BF_4)_2$ was examined in the presence of a ligand other than phosphines, for example, trimethylphosphite, triphenylphosphite, 4-methylpyridine, *p*-tolunitrile, tolane, phenylacetylene, and tetrahydrofuran. However, no definite product was isolated, except in the case of 4-methylpyridine, when the complex **7** that was isolated contained two equivalents of 4-methylpyridine. The ^1H NMR spectrum of **7** showed two signals of the ferrocenyl ring at δ 4.77 and 4.81 ppm, whose resonance pattern is similar to that in the $PdCl_2$ complex **6** [2]. The electronic spectrum of **7** showed two absorption maxima at 326 (log ϵ 3.59) and 506 (2.93). The shape of the absorption spectrum also resembles that of complex **6** [330 (log ϵ 3.42 and 462.5 nm (2.70)]. These results suggest that the structure of complex **7** is $[(dppf)Pd(4\text{-methylpyridine})_2](BF_4)_2$ and there is no interaction between the Fe and Pd atoms in the complex.

No change in the electronic spectrum of **5a** was observed on the addition of one equivalent of triphenylphosphine in acetone. However, the electronic spectrum of **5a** in acetonitrile is substantially different from that in acetone and rather similar to that of complex **6**. The ^1H NMR spectrum of **5a** in CD_3CN showed the ferrocenyl ring protons as very broad singlets at δ 4.94, 4.81, 4.59, and 3.73, indicating a certain dynamic process. In the ^{31}P NMR spectrum of **5a** in CD_3CN three broad singlets (2 : 1 : 1) were observed at 42.00, 29.20, and 29.55 ppm. The signal at +42 ppm is assigned to the P atom of dppf and the signals at 29.20 and 29.55 ppm to the P atom of triphenylphosphine coordinated to the central Pd atom. These results suggest that one acetonitrile coordinates to the Pd atom in the presence of excess acetonitrile and a dative Fe–Pd bond is destroyed. These results suggest that a dative Fe–Pd bond in complexes **5** is more easily broken by a coordinating ligand than that in the sulphide complexes **4**, because the ^1H NMR spectra of **4** can be measured without change in CD_3CN. This is probably because the electron density on the Pd atom in complexes **5** increased, by coordination of the phosphorus atoms on dppf, to a greater extent than that in complexes **4**, the sulphur ligand being a weak donor.

3. Experimental section

3.1. General

The IR spectra were taken on a Hitachi 270-50 infrared spectrometer. The electronic spectra were observed on a Shimadzu UV-2100 spectrophotometer. The ^1H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker AM 400 spectrometer. ^{31}P NMR were taken using H_3PO_4 as an external standard.

Materials: 1,1'-Bis(diphenylphosphino)ferrocene [33] and dichlorobis(acetonitrile)palladium(II) [34] were prepared according to the methods described in the literature.

3.2. (Triphenylphosphine)[1,1'-bis(diphenylphosphino)ferrocene-P,P,Fe)palladium(II) tetrafluoroborate (5a)

A mixture of dichlorobis(acetonitrile)palladium(II) (26 mg, 0.1 mmol) and silver tetrafluoroborate (43 mg, 0.1 mmol) was stirred in dry acetone (3 ml) for 2 h at room temperature. The mixture was filtered and the precipitates were washed with dry acetone (1 ml). To the filtrate and the washing was added a solution of 1,1'-bis(diphenylphosphino)ferrocene (55 mg, 0.1 mmol) and triphenylphosphine (26 mg, 0.1 mmol) in dry benzene (4 ml) under stirring. After 10 min, dry ether (4 ml) was added to the resulting red-violet solution. The solution was kept overnight in a freezer to give the title complex as dark-green needles (54 mg, 49%), M.p. 120°C (dec). Found: C, 50.87; H, 3.76. $C_{40}H_{33}B_2F_8S_2PFePd$ calcd.: C, 50.85; H, 3.52%. Vis (acetone): 380 (log ϵ 4.00), 477 (3.72), and 650sh nm (2.48). ^1H NMR (acetone-d_6) δ 4.57 (s, 4H, H_α), 5.95 (s, 4H, H_β), and 7.2–7.7 (m, 35H, Ph). ^{13}C NMR (acetone-d_6) δ 57.90 (t, $J = 21.3$ Hz, Cp_{ipso}), 72.21 (t, $J = 5.2$ Hz, Cp_α), 87.67 (t, $J = 3.8$ Hz, Cp_β), 122.25 (td, $J = 29.3$ and 3.1 Hz, C_{ipso} in dppf), 130.11 (dt, $J = 52.4$ and 2.5 Hz, C_{ipso} in PPh_3), 130.63 (d, $J = 11.7$ Hz, C_m or C_o in PPh_3), 130.90 (t, $J = 6.0$ Hz, C_m or C_o in dppf), 133.66 (d, $J = 3.0$ Hz, C_p in PPh_3), 134.33 (s, C_p in dppf), 134.73 (d, $J = 11.7$ Hz, C_o or C_m in PPh_3), 135.33 (t, $J = 7.1$ H, C_o or C_m in dppf). ^{31}P NMR (acetone-d_6) δ −14.67 (d, $J = 15.7$ Hz, dppf) and 37.86 (t, $J = 15.5$ Hz, PPh_3).

3.3. (Methyldiphenylphosphine)[1,1'-bis(diphenylphosphino)ferrocene-P,P,Fe]palladium(II) tetrafluoroborate (5b)

Black fine needles (48 mg, 45%). M.p. 150°C (dec). Found: C, 54.61; H, 4.17. $C_{47}H_{41}B_2F_8P_3FePd$ calcd.: C, 54.56; H,3 .99%. Vis (acetone): 365 (log ϵ 4.00), 465 (3.60), and 610sh nm (2.57). ^1H NMR (acetone-d_6) δ 2.46 (d, $J = 12.2$ Hz, 3H, PMe), 4.63 (s, 4H, H_α), 5.86 (s, 4H, H_β), and 7.2–7.9 (m, 30H, Ph). ^{13}C NMR (acetone-d_6) δ 71.80 (t, $J = 5.6$ Hz, C_α), 86.30 (s, C_β), 130.45 (d, $J = 12.7$ Hz, Ph-*m* in $PMePh_2$), 130.98 (t, $J = 5.8$ Hz, Ph-*m* in dppf), 132.97 (d, $J = 11.4$ Hz, Ph-*o* in $PMePh_2$), 133.46 (d, $J = 2.5$ Hz, Ph-*p* in $PMePh_2$), 134.44 (s, Ph-*p* in dppf), 135.24 (t, $J = 7.0$ Hz, Ph-*o* in dppf). ^{31}P NMR (acetone-d_6) δ −10.63 (d, $J = 14.2$, dppf) and 25.91 (t, $J = 14.2$ Hz, PPh_2Me).

3.4. (Tributylphosphine)[1,1'-bis(diphenylphosphino)ferrocene-P,P,Fe)palladium(II) tetrafluoroborate (5c)

Dark red crystals (53 mg, 51%). M.p. 208°C (dec). Found: C, 54.73; H, 5.60. $C_{32}H_{55}B_2F_8P_3FePd \cdot 1/2C_6H_6$ calcd.: C, 54.70; H, 5.43%. Vis (acetone): 358 (log ϵ 4.11), 450 (3.67), and 560sh nm (2.62). ^1H NMR (acetone-d_6) δ 0.73 (t, $J = 7.4$ Hz, 9H), 1.10 (m, 6H), 1.30 (m, 12H), 1.82 (m, 6H), 4.46 (s, 4H, H_α), 5.36 (s, 4H, H_β), 7.5–8.0 (m, 20H, Ph). ^{13}C NMR (acetone-d_6) δ 13.81 (s, CH_3), 24.50 (d, $J = 15.9$ Hz, CH_2), 27.43 (d, $J = 3.8$ Hz, CH_2), 28.08 (td, $J = 28.6$ and 2.3 Hz, CH_2), 58.50 (t, $J = 21.7$ Hz, Cp_{ipso}), 71.56 (t, $J = 5.7$ Hz, Cp_α), 85.70 (t, $J = 3.9$ Hz, Cp_β), 123.71 (dt, $J = 28.6$ and 2.3 Hz, C_{ipso} in PPh_3), 129.14 (s, C_6H_6), 131.33 (t, $J = 6.0$ Hz, C_m or C_o in PPh_3), 134.85 (s, C_p in PPh_3), 135.44 (t, $J = 7.2$ Hz, C_o or C_m in PPh_3). ^{31}P NMR (acetone-d_6) δ −6.81 (d, $J = 13.8$ Hz, dppf) and 43.64 (t, $J = 13.7$ Hz, PPh_3).

3.5. Bis(4-methylpyridine)[1,1'-(diphenylphosphino)ferrocene-P,P]palladium(II) tetrafluoroborate (7)

A mixture of dichlorobis(acetonitrile)palladium(II) (26 mg, 0.1 mmol) and silver tetrafluoroborate (40 mg, 0.1 mmol) in dry acetone (2 ml) was stirred for 1 h. The resulting precipitates were filtered and washed with dry acetone (0.5 ml). To the filtrate and the washing was added a solution of dppf (55 mg, 0.1 mmol) in dry benzene (2.5 ml) and subsequently a solution of 4-methylpyridine (19 mg, 0.2 mmol) in benzene (1 ml). After stirring for several min, the solution was evaporated off. The residue was dissolved in acetone (3 ml). After dry ether (3 ml) had been added, the solution was kept in freezer overnight to give the title complex (55 mg, 53%) as red particles. M.p. 246°C (dec). Found: C, 54.29; H, 4.54; N, 2.74. $C_{46}H_{42}B_2F_8N_2P_2FePd \cdot 1/2C_3H_6O$ calcd.: C, 54.34; H, 4.32; N, 2.66%. ^1H NMR (acetone-d_6) δ 2.19 (s, 6H, CH_3), 4.77 (s, 4H, Fc), 4.81 (s, 4H, Fc), 6.98 (d, $J = 5.5$ Hz, 4H, Py), 7.64 (m, 8H), 7.74 (m, 4H), 7.94 (m, 8H), 8.49 (m, 4H, Py).

3.6. Structure determination

Crystal data of **5a**: $C_{52}H_{43}B_2F_8P_3FePd$, M = 1096.71, orthorhombic, Space group $P2_12_12_1$, $a = 12.528(3)$, $b = 19.305(3)$, $c = 19.729(6)$ Å, $V = 4772(2)$ Å^3, $Z = 4$, $D_x = 1.53$ g cm^{-3}, Absorption coefficient 0.84 mm^{-1}, $F(000) = 2216.0$. Crystal size 0.23 × 0.25 × 0.42 mm.

Data collection was performed at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å) by $\omega/2\theta$ scanning. Cell parameters were determined from a least-squares fitting of 24 reflections in the range $12 < \theta < 14°$. Crystal and instrument stability were monitored by remeasurement of two check reflections every 2 h. 7451 total reflections out to $\theta = 30°$; *hkl* ranges: $0 \leq h \leq 19$, $0 \leq k \leq 27$, $0 \leq l \leq 27$. Empirical ψ-scan absorption corrections were applied.

The structure was solved by the heavy atom method. A difference synthesis based on the Pd, Fe and three P atoms yielded all other non-hydrogen atoms. The H atoms were positioned according to the idealized geometry with d(C–H) = 1.00 Å and isotropic thermal parameters fixed at $U = 0.06$ Å^2. Fe, Pd, P, and C atoms were refined anisotropically and other non-H atoms isotropically using least-squares method. Convergence to conventional R values of $R = 0.046$ and $R_w = 0.039$ with a goodness-of-fit of 1.02 was obtained from 555 variable parameters and 2760 reflections with

$F \geq 4\sigma(F)$. The space group ($P2_12_12_1$) has no centric symmetry owing to the axial chirality of the dppf ligand. The absolute configuration was not determined.

References and notes

1 A.W. Rudie, D.W. Lichtenberg, M.L. Katcher and A. Davison, *Inorg. Chem., 17* (1978) 2859.

2 T. Hayashi, M. Konishi and M. Kumada, *Tetrahedron Lett.*, (1979), 1871; T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, *J. Am. Chem. Soc., 106* (1984) 158.

3 W.R. Cullen, T.-J. Kim, F.W.B. Einstein and T. Jones, *Organometallics, 2* (1983) 714.

4 I.R. Butler, W.R. Cullen, T.-J. Kim, S.J. Rettig and J. Trotter, *Organometallics, 4* (1985) 972.

5 B. Longato, G. Pilloni, G.M. Bonola and B. Corain, *J. Chem. Soc., Chem. Commun.*, (1986) 1478.

6 S. Onaka, *Bull. Chem. Soc. Jpn., 59* (1986) 2359.

7 T.M. Miller, K.J. Ahmed and M.S. Wrighton, *Inorg. Chem., 28* (1989) 2347.

8 S. Onaka, A. Mizuno and S. Takagi, *Chem. Lett.*, (1989) 2037; S. Onaka, T. Moriya, S. Takagi, A. Mizuno and H. Furuta, *Bull. Chem. Soc. Jpn., 65* (1992) 1415.

9 D.T. Hill, G.R. Girard, F.L. McCabe, R.K. Johnson, P.D. Stupik, J.H. Zhang, W.M. Reiff and D.S. Eggleston, *Inorg. Chem., 28* (1989) 3529.

10 T.S.A. Hor and L.-T. Phang, *J. Organomet. Chem., 381* (1990) 121.

11 C.E. Housecroft, S.M. Owen, P.R. Raithby and B.A.M. Shaykn, *Organometallics, 9* (1990) 1617.

12 M. Saburi, K. Aoyagi, T. Kodama, T. Takahashi, Y. Uchida, K. Kozawa and T. Uchida, *Chem. Lett.*, (1990) 1909.

13 U. Casellato, B. Corain, R. Graziani, B. Longato and G. Pilloni, *Inorg. Chem., 29* (1990) 1193.

14 M.I. Bruce, P.A. Humphrey, O.B. Shawkataly, M.R. Snow, and E.R.T. Tiekink and W.R. Cullen, *Organometallics, 9* (1990) 2910.

15 B. Haggerty, C.E. Housecroft, A.L. Rheingold and B.A.M. Shaykh, *J. Chem. Soc., Dalton Trans.*, (1991) 2175.

16 W.R. Cullen, S.T. Rettig and T.-C. Zheng, *Organometallics, 11* (1992) 277.

17 W.R. Cullen, S.T. Rettig and T.-C. Zheng, *Organometallics, 11* (1992) 853.

18 Y.K. Yan, H.S.O. Chan, T.S.A. Hor, K.-L. Tan, L.-K. Liu and Y.-S. Wen, *J. Chem. Soc., Dalton Trans.*, (1992) 423.

19 D. Seyferth, B.W. Hames, T.G. Rucker, M. Cowie and R.S. Dickson, *Organometallics, 2* (1983) 472.

20 S. Akabori, T. Kumagai, T. Shirashige, S. Sato, K. Kawazoe, C. Tamura and M. Sato, *Organometallics, 6* (1987) 526.

21 S. Akabori, T. Kumagai, T. Shirashige, S. Sato, K. Kawazoe, C. Tamura and M. Sato, *Organometallics, 6* (1987) 2105.

22 M. Sato, K. Suzuki and S. Akabori, *Chem. Lett.*, (1987) 2239.

23 M. Sato, H. Asano, K. Suzuki, M. Katada and S. Akabori, *Bull. Chem. Soc. Jpn., 62* (1989) 3829.

24 M. Sato, M. Sekino and S. Akabori, *J. Organomet. Chem., 344* (1988) C31.

25 M. Sato, M. Sekino, M. Katada and S. Akabori, *J. Organomet. Chem., 377* (1989) 327.

26 A preliminary result is reported in reference 24.

27 L.S. Hegedus, T.A. Mulhern and H. Asada, *J. Am. Chem. Soc., 108* (1986) 6224.

28 J.A. Kramer and D.N. Hendrickson, *Inorg. Chem., 19* (1980) 3330.

29 R.J. Goodfellow, *J. Chem. Soc., Chem. Commun.*, (1968) 114.

30 J.F. Nixon and A. Pidcock, in E.F. Mooney (ed.), *Annual Review of NMR Spectroscopy*, Academic Press, London and New York, Vol. 2, 1968, 345.

31 M. Cowie and R.S. Dickson, *J. Organomet. Chem., 326* (1987) 269.

32 G. Longoni, M. Manassero and M. Sansoni, *J. Am. Chem. Soc., 102* (1980) 3242.