

Molecular structure and electrochemical properties of the Pt^{II} complex of 1,1'-bis(methylthio)ferrocene and the Pd^{II} complexes of 1,4,7-trithia[7]- and 1,5,9-trithia[9] (1,1')ferrocenophanes

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Abstract

Molecular structures of (triphenylphosphine) [1,1'-bis(methylthio)ferrocene-*S,S'*,*Fe*]Pt(BF₄)₂ (1), (1,5,9-trithia[9]ferrocenophane-*S,S',S'',Fe*)Pd(BF₄)₂ (2), and (acetonitrile)(1,4,7-trithia[7]ferrocenophane-*S,S',S'',Fe*)Pd(BF₄)₂ (3) were determined by X-ray analyses. The Pt in 1 and the Pd atom in 2 have a somewhat distorted square-planar geometry including the Fe atom of the ferrocene moiety, while the Pd atom in 3 is coordinated by one equivalent of acetonitrile and takes a distorted tetragonal-pyramidal geometry. The distances of the Fe–M bond (M = Pd, Pt) in 1–3 are 2.851(2), 2.827(2), and 3.0962(8) Å, respectively. Cyclic voltammetry of 1–3 gave no reversible wave, but afforded some information supporting the presence of a dative bond.

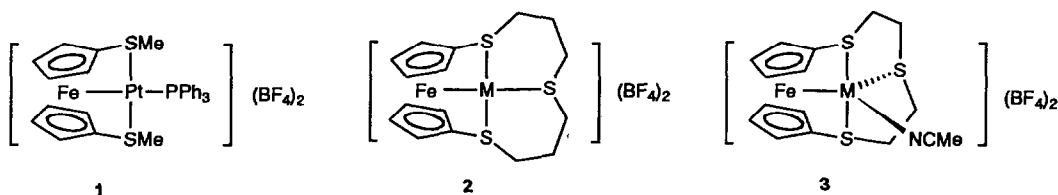
Key words: Platinum; Palladium; Electrochemistry; Ferrocene; X-ray diffraction

1. Introduction

The Fe atom of ferrocene is a basic site [1] and has a potential ability for coordination to Lewis-acidic metals [2,3]. However, only a few complexes which have a metal–metal bonding interaction between the Fe atom of ferrocene and transition metals have been reported. Nesmeyanov and co-workers first reported the Fe–Au bonding interaction in a cationic complex [Fc(AuPPh₃)₂]⁺BF₄[−] [4]. A similar bonding interaction was found in the Cu and Ag complexes of N,N-dimethyl-

aminomethylferrocene [5,6]. Seyferth isolated the complex involving a Fe–Pd dative bond from the reaction between 1,2,3-trithia[3] (1,1')ferrocenophane and Pd(PPh₃)₄ [7]. A similar Pt complex was also prepared [8]. We also reported the synthesis of Pd and Pt complexes of trithia[*n*](1,1')ferrocenophanes [9], 1,1'-bis(alkylthio)ferrocenes [10], and 1,1'-bis(diphenylphosphino)ferrocene (dppf) [11]. Recently, Ru and Os cluster complexes involving a bonding interaction between Ru or Os atom and the Fe atom of dppf were reported [12,13]. We now report the molecular structure and the electrochemical property of the cationic Pt^{II} complex (1) of 1,1'-bis(methylthio)ferrocene and the Pd^{II} com-

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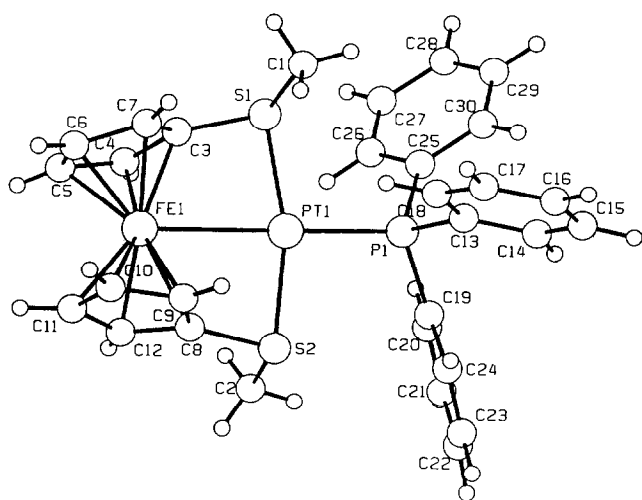


Fig. 1. Structural view of complex 1.

plexes (**2** and **3**) of 1,5,9-trithia[9](1,1')ferrocenophane and 1,4,7-trithia[7](1,1')ferrocenophane, respectively.

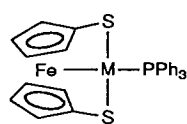
2. Results and discussion

Recrystallization of (triphenylphosphine) [1,1'-bis(methylthio)ferrocene-*S,S'*,*Fe*]Pt(BF₄)₂ (**1**) from acetone/diethyl ether by a diffusion method gave crystals suitable for X-ray analysis. The crystals contain one equivalent of acetone in the crystal lattice. The molecular structure of the cationic part in **1** is depicted in Fig. 1 and the selected bond distances and bond angles are summarized in Table 1. The coordination sphere around the Pt atom in **1** has a slightly distorted square-planar configuration. The Fe–Pt–P and S–Pt–S angles are 177.12(7)° and 164.8(1)°, respectively. The Pt atom is by 0.015 Å above the plane made by the Fe, S, S, and P atoms. This geometry is very similar to those in (triphenylphosphine)(1,1'-ferrocenedithiolato-*S,S'*,*Fe*)palladium(II) (**4a**) [7], -platinum(II) (**4b**) [8] and (triphenylphosphine) [1,1'-bis(diphenylphosphino)ferrocene-*P,P'*,*Fe*]palladium(II) (**5**) [11]. The S–Pt–S angle in **1**, for example, is very close to that in **4b** (165.3°). The Fe–Pt distance in **1** is 2.851(2) Å, being rather shorter than that in **4b** (2.935(2) Å). The value is

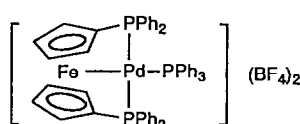
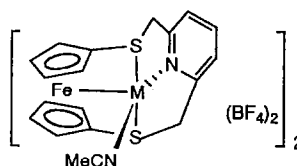
TABLE 1. Selected bond distances (Å) and bond angles (°) for **1**

Bond distances			
Fe–Pt	2.851(2)	Pt–P	2.249(3)
Pt–S(1)	2.271(3)	Pt–S(2)	2.083(3)
Fe–C(3)	2.09(1)	Fe–C(4)	2.07(1)
Fe–C(5)	2.06(1)	Fe–C(6)	2.04(1)
Fe–C(7)	2.08(1)	Fe–C(8)	2.10(1)
Fe–C(9)	2.10(1)	Fe–C(10)	2.08(2)
Fe–C(11)	2.04(2)	Fe–C(12)	2.06(1)
S(1)–C(1)	1.80(1)	S(1)–C(3)	1.74(1)
S(2)–C(2)	1.82(1)	S(2)–C(8)	1.74(1)
P–C(13)	1.82(1)	P–C(19)	1.81(1)
P–C(25)	1.82(1)		
Bond angles			
Fe–Pt–S(1)	82.35(9)	Fe–Pt–S(2)	83.00(9)
Fe–Pt–P	177.12(7)	S(1)–Pt–S(2)	164.8(1)
S(1)–Pt–P	97.5(1)	S(2)–Pt–P	97.4(1)
C(3)–Fe–C(8)	131.4(4)	C(4)–Fe–C(12)	112.9(5)
C(5)–Fe–C(11)	95.1(6)	C(6)–Fe–C(10)	95.7(7)
C(7)–Fe–C(9)	113.9(5)	Pt–S(1)–C(1)	110.0(5)
Pt–S(1)–C(3)	86.3(4)	C(1)–S(1)–C(3)	103.3(6)
Pt–S(2)–C(2)	107.3(5)	Pt–S(2)–C(8)	84.9(4)
C(2)–S(2)–C(8)	102.2(6)	Pt–P–C(13)	112.6(4)
Pt–P–C(19)	112.3(4)	Pt–P–C(25)	111.2(3)
Fe–C(3)–S(1)	125.0(5)	Fe–C(8)–S(2)	126.0(7)

somewhat longer than the sum (2.54 Å) of the covalent radii of Fe and Pt atoms [14]. However, the Fe–Pt bond in **1** is necessary for acquiring a stable electron-configuration (16-electron configuration) around the Pt^{II} atom. Therefore, the bond from the Fe atom to the Pt^{II} atom will have the nature of a weak dative bond. The rather long Fe–Pt distance is not unreasonable because there have been reported Pt–Pt distances up to 2.77 [15] and Fe–Fe distances up to 2.89 Å [16]. The Pt–S distances (2.271(3) and 2.283(3) Å) in **1** are within the normal range observed in some Pt^{II} sulfides (2.25–2.30 Å) [17,18] and are a little shorter than that in **4b** (2.299(4) and 2.294(4) Å). Furthermore, the Pt^{II}–P distance (2.249(3) Å) is somewhat longer than that in **4b** (2.201(3) Å) but within the range of those observed in typical Pt^{II}–PPh₃ complexes (2.218–2.359 Å) [19–25]. The decrease of the Fe–Pt distance in **1** compared with that in **4b** may reflect on the increase of the Pt–P bond, while the coordination mode observed in **1** seems to be typical for a square-planar Pt^{II} complex.



4a M = Pd
4b M = Pt

**5****6**

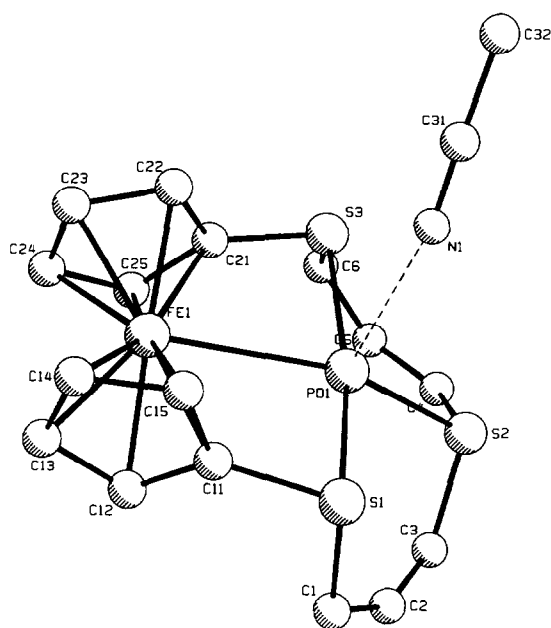


Fig. 2. Structural view of complex 2.

(1,5,9-Trithia[9]ferrocenophane-*S,S',S''*,*Fe*)Pd(BF₄)₂ (**2**) was recrystallized from acetonitrile/diethyl ether by a diffusion method to give crystals adequate for X-ray analysis. The crystals contain one equivalent of acetonitrile. The structural view of complex **2** is shown in Fig. 2 and selected bond distances and angles are summarized in Table 2. The coordination sphere around the Pd^{II} atom in **2** seems to retain a square-

TABLE 2. Selected bond distances (Å) and bond angles (°) for **2**

Bond distances			
Fe–Pd	2.827(2)	Pd–S(1)	2.274(3)
Pd–S(2)	2.315(3)	Pd–S(3)	2.268(3)
Fe–C(11)	2.08(1)	Fe–C(12)	2.079(9)
Fe–C(13)	2.04(1)	Fe–C(14)	2.04(1)
Fe–C(15)	2.05(1)	Fe–C(21)	2.117(9)
Fe–C(22)	2.06(1)	Fe–C(23)	2.03(1)
Fe–C(24)	2.03(1)	Fe–C(25)	2.066(9)
S(1)–C(1)	1.86(1)	S(1)–C(11)	1.76(1)
S(2)–C(3)	1.78(1)	S(2)–C(4)	1.79(1)
S(3)–C(6)	1.80(1)	S(3)–C(21)	1.718(9)
Bond angles			
FePd–S(1)	84.02(9)	Fe–Pd–S(2)	156.79(9)
Fe–Pd–S(3)	84.16(8)	S(1)–Pd–S(3)	166.5(1)
S(1)–Pd–S(2)	95.7(1)	S(2)–Pd–S(3)	97.7(1)
C(11)–Fe–C(21)	129.3(4)	C(12)–Fe–C(25)	111.2(4)
C(13)–Fe–C(24)	92.4(4)	C(14)–Fe–C(23)	93.6(5)
C(15)–Fe–C(22)	113.1(5)	Pd–S(1)–C(1)	105.5(5)
Pd–S(1)–C(11)	83.6(3)	C(1)–S(1)–C(11)	105.4(5)
Pd–S(3)–C(6)	108.5(5)	Pd–S(3)–C(21)	83.8(3)
C(6)–S(3)–C(21)	105.4(5)	Pd–S(2)–C(3)	103.8(5)
Pd–S(2)–C(4)	104.1(5)	C(3)–S(2)–C(4)	100.8(9)
Fe–C(21)–S(3)	127.2(5)	Fe–C(11)–S(1)	127.1(5)

planar configuration, notwithstanding the Pd atom is incorporated into the thiamacrocycle. Thus, the angles S(1)–Pd–S(2), S(2)–Pd–S(3), Fe–Pd–S(1), and Fe–Pd–S(3) are 95.7(1), 97.7(1), 84.02(9), and 84.16(8), respectively. This is quite different from the coordination mode in (1,5,9,13-tetrathia[13]ferrocenophane-*S,S',S'',S'''*)Pd(BF₄)₂ in which the Pd(II) atom is surrounded in a square-planar mode by four S atoms of the thiamacrocycle and has no bonding interaction with the Fe atom [26]. However, complex **2** is considerably distorted as compared with those in **1**, **4a** [7], and **5** [11], which take a square-planar configuration with a little distortion. The S(1)–Pd–S(3) angle (166.5(1)°) in **2**, for example, is close to the corresponding angle in **4a** (168.60(7)°), but the Fe–Pd–S(2) angle (156.79(9)°) is considerably decreased compared with the corresponding angle (Fe–Pd–P, 172.97(5)°) in **4a**. These facts suggest that the distortion around the Pd^{II} atom in **2** is increased by the incorporation of the Pd^{II} atom into the thiamacrocycle which has no cavity large enough to incorporate the metal atom. However, since the Pd–N distance (2.84(1) Å) is far from the range of the normal Pd–N bond (2.0–2.2 Å) [27], **2** does not adopt a square-pyramid geometry in spite of its large distortion but the Pd^{II} atom has only a weak interaction with CH₃CN at an apical site. The Fe–Pd distance in **2** is 2.827(2) Å, being quite close to that in complex **4a** (2.878(1) Å) [7] and **5** (2.877(2) Å) [11], notwithstanding **2** contains a large distortion around the Pd atom. The presence of a dative bond between the Fe and Pd atoms may have an effect on the Pd–S(2) bond distance, because the Pd–S(2) distance (2.315(3) Å) is slightly longer than the Pd–S(1) (2.274(3) Å) and Pd–S(3) distances (2.268(3) Å). The Pd–S(1) and Pd–S(2) distances found in **2** are somewhat shorter than that for typical square-planar Pd^{II} sulfide complexes (2.31–2.37 Å) [17,28–30], suggesting a compression effect due to incorporation of the Pd^{II} atom into the thiamacrocycle.

Crystals suitable for X-ray analysis of (CH₃CN)-(1,4,7-trithia[7]ferrocenophane-*S,S',S''*,*Fe*)Pd(BF₄)₂ (**3**) were obtained by recrystallization from acetonitrile/diethyl ether. The crystals of **3** contain one equivalent of acetonitrile, which coordinates to the Pd^{II} atom. The structure of **3** is pictured in Fig. 3 and the selected bond distances and angles are summarized in Table 3. As seen in Fig. 3, the coordination mode around the Pd^{II} atom in **3** will be either a five-coordinate trigonal-bipyramid locating two S atoms at apical tops or a tetragonal-pyramid locating a Fe atom at an apical top, although it will be considerably distorted. A few Pd^{II} complexes having a trigonal bipyramidal [31] or a tetragonal-pyramidal configuration are reported [32] although the structures were not confirmed by X-ray

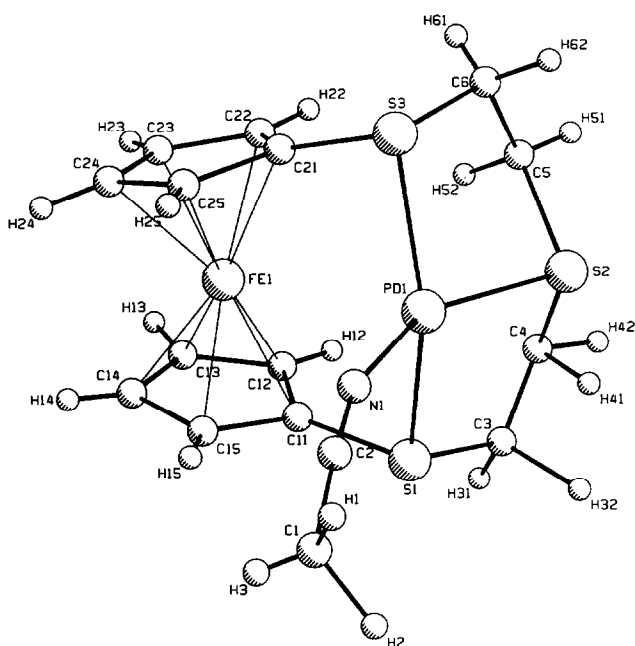


Fig. 3. Structural view of complex 3.

analysis. In complex 3, the Fe–Pd–S(2), Fe–Pd–N, and S(2)–Pd–N angles are 114.93(4), 97.46(8), and 147.29(9)°, respectively, while S(1)–Pd–S(2), S(2)–Pd–S(3), S(1)–Pd–N, and S(3)–Pd–N angles are 90.33(4), 89.27(4), 91.69(9), and 101.78(9)°, respectively. The

TABLE 3. Selected bond distances (Å) and bond angles (°) for 3

Bond distances			
Fe–Pd	3.0962(8)	Pd–S(1)	2.285(1)
Pd–S(2)	2.284(1)	Pd–S(3)	2.303(1)
Pd–N	2.181(3)	Fe–C(11)	2.115(3)
Fe–C(12)	2.082(4)	Fe–C(13)	2.049(4)
Fe–C(14)	2.041(4)	Fe–C(15)	2.064(4)
Fe–C(21)	2.126(4)	Fe–C(22)	2.071(4)
Fe–C(23)	2.047(4)	Fe–C(24)	2.057(4)
Fe–C(25)	2.081(4)	S(1)–C(3)	1.817(5)
S(1)–C(11)	1.748(4)	S(2)–C(4)	1.881(6)
S(2)–C(5)	1.830(5)	S(3)–C(6)	1.824(4)
S(3)–C(21)	1.737(4)	C(2)–N	1.118(5)
Bond angles			
Fe–Pd–S(1)	78.70(3)	Fe–Pd–S(2)	114.93(4)
Fe–Pd–S(3)	79.22(2)	Fe–Pd–N	97.46(8)
S(1)–Pd–S(2)	90.33(4)	S(1)–Pd–S(3)	155.42(4)
S(2)–Pd–S(3)	89.27(4)	S(1)–Pd–N	91.67(9)
S(2)–Pd–N	147.29(9)	S(3)–Pd–N	101.78(9)
C(11)–Fe–C(21)	126.0(1)	C(12)–Fe–C(22)	110.8(2)
C(13)–Fe–C(23)	95.6(2)	C(14)–Fe–C(24)	96.2(2)
C(15)–Fe–C(25)	112.2(2)	Pd–S(1)–C(3)	102.5(2)
Pd–S(1)–C(11)	90.0(1)	C(3)–S(1)–C(11)	106.4(2)
Pd–S(2)–C(4)	99.4(2)	Pd–S(2)–C(5)	97.9(1)
C(5)–S(2)–C(6)	96.6(3)	Pd–S(3)–C(6)	101.6(2)
Pd–S(3)–C(21)	88.4(1)	C(6)–S(3)–C(21)	105.3(2)
Fe–C(11)–S(1)	127.6(2)	Fe–C(21)–S(3)	129.4(2)

Pd–N distance (2.181(3) Å) is in the range of a normal Pd^{II}–N distance (2.0–2.2 Å) [27]. These data indicate that complex 3 adopts a distorted tetragonal-pyramidal geometry locating the Fe atom at an apical position. In complex 3, the small ring-size of the [7] ferrocenophane, being insufficient to incorporate the Pd^{II} atom, will not permit a square-planar geometry for the Pd atom any longer. The fairly small Fe–Pd–S(2) angle (114.93°) in 3 compared with the corresponding angle in 2 (156.78°) is the result of the change of configuration due to the smaller size of the thiamacrocycle. The Fe–Pd distance (3.0962(8) Å) in 3 is considerably longer than that in complexes 4a (2.878(1) Å) [7] and 2 (2.827(2) Å). However, the ¹H and ¹³C NMR spectral data suggest the presence of a Fe–Pd dative bond [9] and the S(1)–Pd–S(3) in 3 is 155.42(4)°, being close to the corresponding angle in 1 (164.8°) and 2 (166.1°). So, there apparently remains a Fe–Pd dative bond in 3 although it is very weak. The cause for the weakening of the bond strength in 3 compared with that in 2 is naturally considered to be the change of coordination geometry due to the smaller size of the thiamacrocycle insufficient to incorporate the Pd^{II} atom. A similar and weak dative bond is also observed in the Pd^{II} complexes of 1,7-dithia[2](2,6)-pyridino[2](1,1')ferrocenophane (6) [33] and 1,7-dithia-5-selena[7]ferrocenophane (7) [34].

In brief, the open complex 1 adopts a nearly square-planar geometry, while complex 2 also keeps a square-planar configuration. However, the coordination structure around the Pd^{II} atom in 2 is considerably distorted pyramidally because the cavity of 1,5,9-trithia[9](1,1')ferrocenophane is slightly small compared with the ionic radii of the Pd(II) atom and so acetonitrile interacts weakly with the central metal atom. On the other hand, the Fe and three S atoms in complex 3 is no longer able to coordinate the Pd^{II} atom in a square-planar mode because 1,4,7-trithia[7](1,1')ferrocenophane has much smaller cavity in the thiamacrocycle than 1,5,9-trithia[9](1,1')ferrocenophane. As a result, the central Pd^{II} atom in 3 adopts a tetragonal pyramid geometry in which the thiamacrocycle has a folded conformation and the three S atoms and the N atom of CH₃CN arrange in a basal plane and the Fe atom of the ferrocene moiety constitutes an apical ligand. According to such change of the coordination mode around the Pd^{II} atom, the dative bond between the Fe and Pd^{II} atoms seems to be weakened to much extent probably because of the increased strain which results from forcing the Pd^{II} atom to coordinate to the small thiamacrocycle.

The Fe–M distance (M = Pd or Pt), the E–M–E angle (E = S or P), and the tilt angle of two cyclopentadienyl rings in the ferrocene moiety in complexes 1–7

TABLE 4. Various structural parameters

	Fe–M bond length (Å)	M–E' bond length (Å)	E–M–E angle (°)	Tilt angle (°)
1	2.851(2)	2.249(3)	164.8(1)	21.42
4b	2.935(2)	2.201(3)	165.4(1)	21.0
2	2.827(2)	2.315(3)	166.5(1)	22.20
5	2.877(2)	2.270(3)	155.9(1)	19.6
4a	2.878(1)	2.241(2)	168.60(7)	19.6
3	3.0962(8)	2.284(1)	155.42(4)	19.02
7	3.028(2)	2.401(2)	156.9(2)	19.2
6	3.228(2)	–	153.3(2)	17.8
8	3.810(2)	–	83.9	1.9
9	–	–	97.98(4)	6.2

are summarized in Table 4, along with those in the related complexes. Complexes **1** and **2** have the structural parameters closely similar to those of the previously reported complexes **4a** [7a], **4b** [8], and **5** [11]. The E–M–E angle and the tilt angle in them are quite different from those in the PdCl₂ complexes of 1,1'-bis(isobutylthio)ferrocene **8** [35] and 1,1'-bis(diphenylphosphino)ferrocene **9** [36,37], respectively, which have no metal–metal bonding interaction between the Fe and Pd^{II} atoms. For example, the tilt angle for **1** (21.42°) and **2** (22.20°) is quite close to that for **4a** (19.6°), **4b** (21.0°), and **5** (19.6°), while it is nearly zero for **8** (1.9°) and **9** (6.2°). The E–M–E angle is 83.9° and 97.98° for **8** and **9**, respectively, and is in the range of 155.9–168.60° for **1**, **2**, **4a**, **4b**, and **5**. From these facts it is regarded as a common phenomenon that when a ferrocene molecule is arranged in the proximity of a coordinatively unsaturated Pd^{II} or Pt^{II} atom, a dative bond is formed between the Fe atom in the ferrocenyl moiety and Pd^{II} or Pt^{II} atom, although it has a strong and weak strength. The particular E–M–E (*ca.* 160°) angle and tilt angle (*ca.* 20°) of the Cp rings in the ferrocene ring seem to be a useful index characteristic of complexes having a dative bond.

On the other hand, complexes **3** and **7**, interestingly, adopt the square-pyramidal configuration having the Fe atom in the apical position, probably because of the small cavity of the thiamacrocyclic insufficient to incorporate the Pd^{II} atom in those complexes. It may be worthy to note that the geometry of these complexes is not the square-pyramid having an additional acetonitrile in an apical top but the square-pyramid having the Fe atom in an apical top, since in complex **2** adopting the square-planar geometry acetonitrile interacts weakly with the central Pd^{II} atom at an apical side of the square-planar plane consisting of the Fe and three S atoms. Moreover, complex **6** adopts a strange dimeric structure in which the coordination mode around the Pd^{II} atom is a quasi-octahedral with the Fe atom and the alternative Pd^{II} atoms at two apical positions [33].

This is likely because the steric strain is increased more than that in **3** and **7**. The slightly longer Fe–Pd distance in **6** (3.228 Å) compared with that in **3** (3.0962 Å) seems to stem from the increased steric strain due to the insertion of a pyridine ring into the thiamacrocyclic, while the slightly shorter Fe–Pd distance in **7** (3.028 Å) may result from decreased steric strain due to the longer C–Se bond compared with the S–C bond. These square-pyramidal (**3** and **7**) and quasi-octahedral complexes (**6**) have a significantly long Fe–Pd distance ($\Delta \sim 0.2\text{--}0.4$ Å) compared with that in the square-planar complexes **1**, **2**, **4a**, **4b** and **5**. However, these are considerably shorter than the Fe–Pd distance (3.810(2) Å) in **8** which has no metal–metal interaction [35], even if the difference of the covalent radii (Pd, 1.28; Pt, 1.30 Å) is considered. Moreover, in the ¹H and ¹³C NMR spectra **3**, **6**, and **7** showed the features similar to those observed in the square-planar complexes [9,33]. Also, their S–M–S (153.3–156.9°) and tilt angle (17.8–19.2°) are nearly similar to those in **1**, **2**, **4a**, **4b** and **5** (155.9–168.60° and 19.6–22.20°), respectively. It is, therefore, considered that there also remains a weak bonding interaction between the Fe and Pd^{II} atoms in **3**, **7**, and **6** in spite of the coordination geometry around the Pd^{II} atom different from the square-planar complexes **1**, **2**, **4a**, **4b** and **5**.

The electrochemical property of complexes **1**, **2** and **3** were examined by cyclic voltammetry. The results are summarized in Table 5, along with that of **8** and [1,1'-bis(methylthio)ferrocene-*S,S'*]PtCl₂ (**10**). Complexes **8** and **10** show one irreversible cathodic wave at a low-potential region and one quasi-reversible wave at a high-potential region. The latter was assigned to the wave due to the redox of the ferrocenyl part [35]. However, **1** and (triphenylphosphine) [1,1'-bis(isobutylthio)ferrocene-*S,S'*,*Fe*]Pd(BF₄)₂ (**11**) involving a dative bond showed no wave at a high-potential region, probably because the corresponding anodic wave shifted above 1.1 V (measurement above 1.1 V was

TABLE 5. Redox potentials in dichloromethane (Ag/AgCl)^a

	<i>E</i> _{pc} (1)	<i>E</i> _{pc} (2)	<i>E</i> _{pa} (2)
1	–0.85	–	–
11	–0.55	–	–
2	–0.46	–	–
3	–0.28	+0.75	+0.88
6 ^b	–0.47	+0.60	+0.67
8	–1.02	+0.67	+0.79
	–0.89 ^c		+0.86 ^c
10	–1.73	+0.65	+0.79
	–1.50 ^c		+0.93 ^c

^a 0.5 M Et₄NClO₄, working electrode: glassy carbon.

^b Measured in CH₃CN because it is insoluble in CH₂Cl₂.

^c From ref. 35.

impossible under these conditions). Also, the cathodic wave at a low-potential region shifted to a higher-potential side ($\Delta = 0.47$ V for the Pd series and $\Delta = 0.88$ V for the Pt series). These results seem to be interpreted by assuming that the dative bond involved in **1** and **11** decreases the electron density on the Fe atom of the ferrocenyl moiety and increases that on the Pd or Pt atom in the complexes. The features observed above seem to give some instructive information about the nature of the dative bond in the Pd^{II} complexes of polythia[*n*]ferrocenophanes (**2** and **3**). That is, a quasi-reversible wave at a high-potential region is observed in **3** and **6**, while the corresponding wave is not observed in **2**. This suggests that the dative bond in **3** and **6** is, if anything, very weak, compared with that in **2**. The X-ray analysis of these complexes supports this suggestion: the bond distance in **2** is 2.827(2) Å, while those in **3** and **6** are 3.0962(8) and 3.228(2) Å, respectively.

3. Experimental details

Complexes **1**, **2**, and **3** were prepared according to the procedures reported previously [9,10]. Recrystallization from acetone/diethyl ether (for **1**) or acetonitrile/diethyl ether (for **2** and **3**) by a diffusion method gave single crystals sufficient for X-ray analysis.

All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo K α radiation and a 12 kW rotating anode generator.

3.1. Structure determination of **1**

Crystal data of **1**: C₃₃H₃₅B₂OF₈PS₂FePt, Fw = 967.28, triclinic, *P*1 (#2): *a* = 12.947(3) Å, *b* = 12.960(7) Å, *c* = 11.596(2) Å; α = 101.20(3)°, β = 108.94(2)°, γ = 94.87(3)°; *V* = 1782(1) Å³; *Z* = 2; *D*(calcd) = 1.802 g cm⁻³; μ (Mo K α) = 45.93 cm⁻¹; *T* = 296 K; Crystal size 0.400 × 0.400 × 0.100 mm.

The data was collected using the ω -2 θ scan technique to a maximum 2 θ value of 50.2°. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range 33.16 < 2 θ < 37.73°. Of the 6684 reflections which were collected, 6341 were unique (*R*_{int} = 0.039). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 5136 observed reflections (*I* > 3.00 σ (*I*)) and 374 variable parameters and converged with un-

weighted and weighted agreement factors of *R* = 0.057 and *R*_w = 0.072. The standard deviation of an observation of unit weight was 1.68.

3.2. Structure determination of **2**

Crystal data of **2**: C₁₈H₂₃B₂NF₈S₃FePd, Fw = 685.42, monoclinic, *P*2₁/*c* (no. 14): *a* = 8.149(6) Å, *b* = 17.803(6) Å, *c* = 16.947(4) Å; β = 98.91(4)°; *V* = 2429(2) Å³; *Z* = 4; *D*(calcd) = 1.874 g cm⁻³; μ (Mo K α) = 16.45 cm⁻¹; crystal size of 0.250 × 0.250 × 0.200 mm.

The data was collected at a temperature of 2 ± 1°C using the ω -2 θ scan technique to a maximum 2 θ value of 50.0°. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range 29.37 < 2 θ < 29.96°. Of the 4762 reflections which were collected, 4433 were unique (*R*_{int} = 0.050). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2031 observed reflections (*I* > 3.00 σ (*I*)) and 307 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.058 and *R*_w = 0.042. The standard deviation of an observation of unit weight was 1.96.

3.3. Structure determination of **3**

Crystal data of **3**: C₁₆H₁₉B₂NF₈S₃FePd, Fw = 657.37, monoclinic, *P*2₁/*c* (#14): *a* = 8.094(3) Å, *b* = 16.470(3) Å, *c* = 16.877(3) Å; β = 103.44(2)°; *V* = 2188.4(9) Å³; *Z* = 4; *D*(calcd) = 1.995 g cm⁻³; μ (Mo K α) = 18.21 cm⁻¹; *T* = 296 K; Crystal size 0.700 × 0.300 × 0.100 mm.

The data was collected using the ω -2 θ scan technique to a maximum 2 θ value of 50.0°. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range 29.63 < 2 θ < 29.98°. Of the 4302 reflections which were collected, 4003 were unique (*R*_{int} = 0.026). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by Fourier difference synthesis and were isotropically refined. The final cycle of full-matrix least-squares refinement was based on 2818 observed reflections (*I* > 3.00 σ (*I*)) and 366 variable parameters and converged with unweighted and

weighted agreement factors of $R = 0.031$ and $R_w = 0.026$. The standard deviation of an observation of unit weight was 1.85.

3.4. Cyclic voltammetry

Redox potentials were measured by cyclic voltammetry in a solution of 0.05 M tetrabutylammonium perchlorate (TBPA) in dichloromethane or acetonitrile (dried over phosphorous pentoxide and distilled from calcium hydride) under nitrogen at 25°C, using a standard three-electrode cell on a CV-27 Cyclic Voltammograph (Bioanalytical Systems). All potentials were measured vs. Ag/Ag⁺ (TBAP/acetonitrile) electrode by using glassy carbon as a working electrode and the scan rate was 100 mV s⁻¹.

References

- J. Kotz and D. Pedrotty, *Organomet. Chem. Rev. (A)*, **4** (1969) 479.
- R.M.G. Roberts, J. Silver and I.E.G. Morrison, *J. Organomet. Chem.*, **209** (1981) 385.
- M. Watanabe, H. Ichikawa, I. Motoyama and H. Sano, *Bull. Chem. Soc. Jpn.*, **56** (1983) 3291.
- A.N. Nesmeyanov, E.G. Prevalova, K.I. Grandberg, D.A. Lemenovskii, T.V. Baukova and O.B. Afanassova, *J. Organomet. Chem.*, **65** (1974) 131.
- A.N. Nesmeyanov, Yu.T. Struchkov, N.N. Sedova, V.G. Andrianov, Yu.V. Volgin and V.A. Sazonova, *J. Organomet. Chem.*, **137** (1977) 217.
- A.N. Nesmeyanov, N.N. Sedova, Yu.T. Struchkov, V.G. Andrianov, E.N. Stakheeva and V.A. Sazonova, *J. Organomet. Chem.*, **153** (1978) 115.
- (a) D. Seyferth, B.W. Hames, T.G. Rucker, M. Cowie and R.S. Dickson, *Organometallics*, **2** (1983) 472; (b) M. Cowie and R.S. Dickson, *J. Organomet. Chem.*, **326** (1987) 269.
- S. Akabori, T. Kumagai, T. Shirashige, S. Sato, K. Kawazoe, C. Tamura and M. Sato, *Organometallics*, **6** (1987) 526.
- M. Sato, K. Suzuki and S. Akabori, *Chem. Lett.*, (1987) 2239; M. Sato, H. Asano, K. Suzuki, M. Katada and S. Akabori, *Bull. Chem. Soc. Jpn.*, **62** (1989) 3829.
- M. Sato, M. Sekino and S. Akabori, *J. Organomet. Chem.*, **344** (1988) C31; M. Sato, M. Sekino, M. Katada and S. Akabori, *J. Organomet. Chem.*, **377** (1989) 327.
- M. Sato, H. Shigeta, M. Sekino and S. Akabori, *J. Organomet. Chem.*, **458** (1993) 199.
- M.I. Bruce, P.A. Humphrey, O.B. Shawkataly, M.R. Snow, E.R.T. Tiekink and W.R. Cullen, *Organometallics*, **9** (1990) 2910.
- W.R. Cullen, S.J. Rettig and T.-C. Zheng, *Organometallics*, **11** (1992) 277.
- L. Pauling, *The nature of the chemical bond*, Cornell University Press, New York, 1960, Chapter 7.
- C. Bellitto, A. Flamini and P.F. Zanazzi, *Inorg. Chem.*, **19** (1980) 3632.
- F.W. Einstein and J. Trotter, *J. Chem. Soc. A*, (1967) 824.
- A.J. Blake, R.O. Gould, A.J. Lavery and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, **25** (1986) 274.
- A.J. Blake, R.O. Gould, A.J. Holder, T.I. Hyde, A.J. Lavery, M.O. Odulate and M. Schröder, *J. Chem. Soc., Chem. Commun.*, (1987) 118.
- C. Briant, G.R. Huges, P.C. Minshall and D.M.P. Mingos, *J. Organomet. Chem.*, **202** (1980) C18.
- J. Howard and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1973) 1740.
- P.L. Bellon., M. Manassevo, F. Porta and M. Sansoni, *J. Organomet. Chem.*, **80** (1974) 139.
- A. Sorivanti, G. Carturan, U. Belluco, N.B. Pahor, M. Calligaris and L. Randaccio, *Inorg. Chim. Acta*, **20** (1976) L3.
- C.G. Biefeld, H.A. Eich, R.H. Grubbs, *Inorg. Chem.*, **12** (1973) 2166.
- B. Crociani, M. Nicolini, D.A. Clemente and G. Bandoli, *J. Organomet. Chem.*, **49** (1973) 249.
- M. Bonamico, G. Dessy, V. Fares, M.V. Russo and L. Scaramuzza, *Cryst. Struct. Commun.*, **6** (1977) 39.
- N. Won, K. Iwai, M. Katada, H. Sano, M. Sato and S. Akabori, *56th Annual Meeting of Chem. Soc. Jpn.*, p. 851, 1988.
- P.M. Maitlis, *The organic chemistry of palladium*, Academic Press, New York, Vol. 1, 1971.
- K. Wieghardt, H.-J. Kuppers, E. Raabe and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, **25** (1986) 1101.
- A.J. Blake, A.J. Holder, T.I. Hyde, Y.V. Roberts, A.J. Lavery and M. Schröder, *J. Organomet. Chem.*, **323** (1987) 261.
- A.J. Blake, A.J. Holder, T.I. Hyde and M. Schröder, *J. Chem. Soc., Chem. Commun.*, (1987) 987.
- P. Meakin and J.P. Jesson, *J. Am. Chem. Soc.*, **96** (1974) 5751; J.P. Jesson and P. Meakin, *J. Am. Chem. Soc.*, **96** (1974) 5760.
- J.W. Collier, F.G. Mann, D.G. Watson and H.R. Watson, *J. Chem. Soc.*, (1964) 1803.
- M. Sato, H. Asano and S. Akabori, *J. Organomet. Chem.*, **452** (1993) 105.
- Y. Yokomori and Y. Ohashi, *39th Symposium of Coord. Chem., Japan*, 1989, p. 769.
- B. McCulloch, D.L. Ward, J.D. Woolins and C.H. Brubacker, Jr., *Organometallics*, **4** (1985) 1425.
- I.R. Butler, W.R. Cullen, T.-J. Kim, S.J. Rettig and J. Trotter, *Organometallics*, **4** (1985) 972.
- T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, *J. Am. Chem. Soc.*, **106** (1984) 158.