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A novel heterobimetallic complex composed of the imide-bridged [3]ferrocenophane and the tridentate palladium(II) complex

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Abstract

The imide-bridged [3]ferrocenophane, 2-pyridyl-1,1′-ferrocenedicarboximide, served as a monodentate ligand to form the corresponding heterobimetallic complex **4** with the palladium(II) complex bearing the tridentate podand ligand, through displacement of the ancillary acetonitrile. The X-ray crystal-structure determination revealed that the pyridyl nitrogen of the ferrocenophane coordinates to the palladium center with distortion of the ferrocenophane moiety, which lies below the coordination plane of palladium. Such a structure is considered to be present even in solution, resulting in four nonequivalent broad signals of Cp protons in the ^{1}H-NMR spectrum, due to the electronic environment effect of the coordination plane of palladium. A π–π stacking interaction was observed between the benzene ring of the podand moieties and the pyridine ring of the neighboring molecule in the crystal packing of **4**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; [3]Ferrocenophane; Heterobimetallic complex; Tridentate podand ligand

1. Introduction

Ferrocenophanes have attracted much attention due to both their physical properties based on the distortion of two cyclopentadienyl (Cp) rings and their potential utilization as redox-active receptors [1]. Complexation with [*n*]ferrocenophane ligands, in which two Cp rings are bridged intramolecularly by one chain, is expected to induce structural and electronic environmental changes of the ferrocenophane moiety through restriction of the fluxional process of Cp rings. Heterobimetallic complexes composed of [*n*]ferrocenophane ligands and transition metals are of interest in this context [2]. In a previous paper [3], 2-aminopyridine was demonstrated to react with 1,1′-ferrocenedicarboxylic acid chloride to give the novel imide-bridged [3]ferrocenophane (**1**) bearing the pendant 2-pyridyl moiety, in which two Cp rings are staggered and tilted 16.4° with respect to each other. The coordination of the pendant 2-pyridyl moiety of **1** to a metal center is considered to orient the ferrocenophane moiety toward the metal center, which prompted us to investigate the complexation behavior of **1**. Palladium(II) complexes bearing a tridentate podand ligand are envisaged to provide one metal binding site and flexible second-sphere and/or sterically demanding interaction sites based on the podand moieties. The complexation of the imide-bridged [3]ferrocenophane (**1**) with the tridentate palladium(II) complex was investigated in this report.

2. Results and discussion

Amido-*N* ligands, which have σ-donor properties of the deprotonated nitrogen, are well known to afford stable complexes with transition metals. In this respect, the tridentate podand ligand, *N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamide (**2**) [4], is considered to serve as an excellent tridentate ligand possessing σ-donor properties. Two intramolecular NH(amide)···N(pyridine) hydrogen bonds (N(2)···N(1), 2.688 Å; N(3)···N(1), 2.644 Å) and NH(amide)···O(water) hydrogen bonds (N(2)···O(3), 3.053 Å; N(3)···O(3), 3.025 Å) were observed in the crystal structure of **2** (Fig. 1 and Table 1). Treatment of the podand ligand **2** with $Pd(OAc)_2$ in acetonitrile led to the formation of the corresponding palladium(II) complex **3**. The absence of

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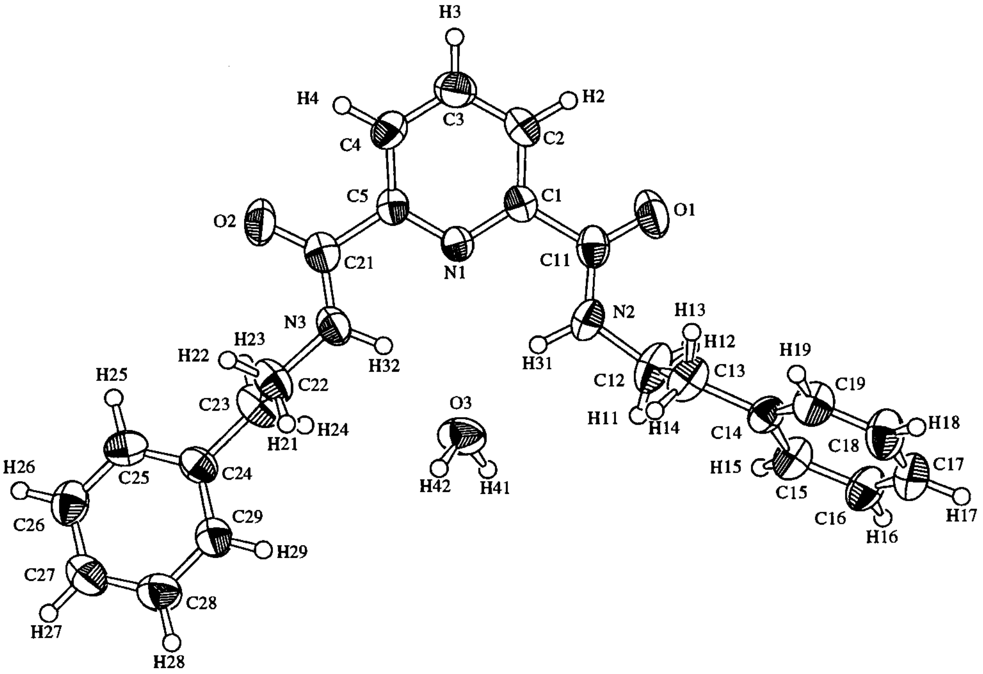
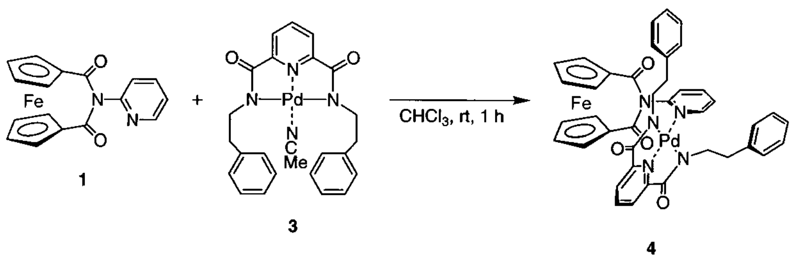


Fig. 1. ORTEP view of the X-ray crystal structure of **2** (40% probability ellipsoids).

the amide protons in ^{1}H-NMR confirmed that the podand ligand **2** coordinates in a deprotonated form. The X-ray crystal structure of **3** indicates a sligthly distorted square-planar geometry at palladium substituted with two amide nitrogens of **2** (N(2)–Pd–N(3), 161.4°) as shown in Fig. 2. The two deprotonated amido moieties and the pyridine ring are coplanar to form the five-membered chelate rings with extended conjugation [5]. The C(1)–C(11)–N(2) and C(5)–C(21)–N(3) angles in the five-membered chelate rings decreased slightly upon complexation (**2**: C(1)–C(11)–N(2), 114.8°; C(5)–C(21)–N(3), 114.3°; **3**: C(1)–C(11)–N(2), 113.3°; C(5)–C(21)–N(3), 112.6°). The open coordination site is occupied by the ancillary acetonitrile with a Pd–N(4) distance of 2.014 Å and N(1)–Pd–N(4) angle of 179.5°, suggesting a utility of **3** as a metalloreceptor through metal coordination [6]. Selected bond distances and bond angles are listed in Table 2.

The coordination behavior of the imide-bridged [3]ferrocenophane ligand (**1**) was investigated by use of an interchangeable coordination site of **3**. The ancillary acetonitrile was displaced by the reaction of **1** with **3** to give the 1:1 palladium complex **4** in 90% yield (Scheme 1). The structure of the isolated complex **4** was elucidated by ^{1}H-NMR (Fig. 3). Interestingly, Cp protons appeared as four nonequivalent broad signals at 4.92, 4.75, 4.54, and 4.44 ppm, three of which were observed at higher field as compared with those of **1** at room temperature. Combined ^{1}H–^{1}H COSY and NOE experiments conducted at 223 K established that four signals of Cp protons all belong to the same Cp. From these results, magnetically nonequivalent Cp protons of **4** are probably explained by the electronic environment effect of the coordination plane of palladium with extended conjugation composed of the two deprotonated amido moieties and the pyridine ring. The uncomplexed [3]ferrocenophane (**1**) exhibited only two Cp signals that persisted from 298 to 193 K, demonstrating the very low energy barrier in the torsional twist of the Cp rings of **1**. If fluxional processes of Cp rings were frozen



Scheme 1.

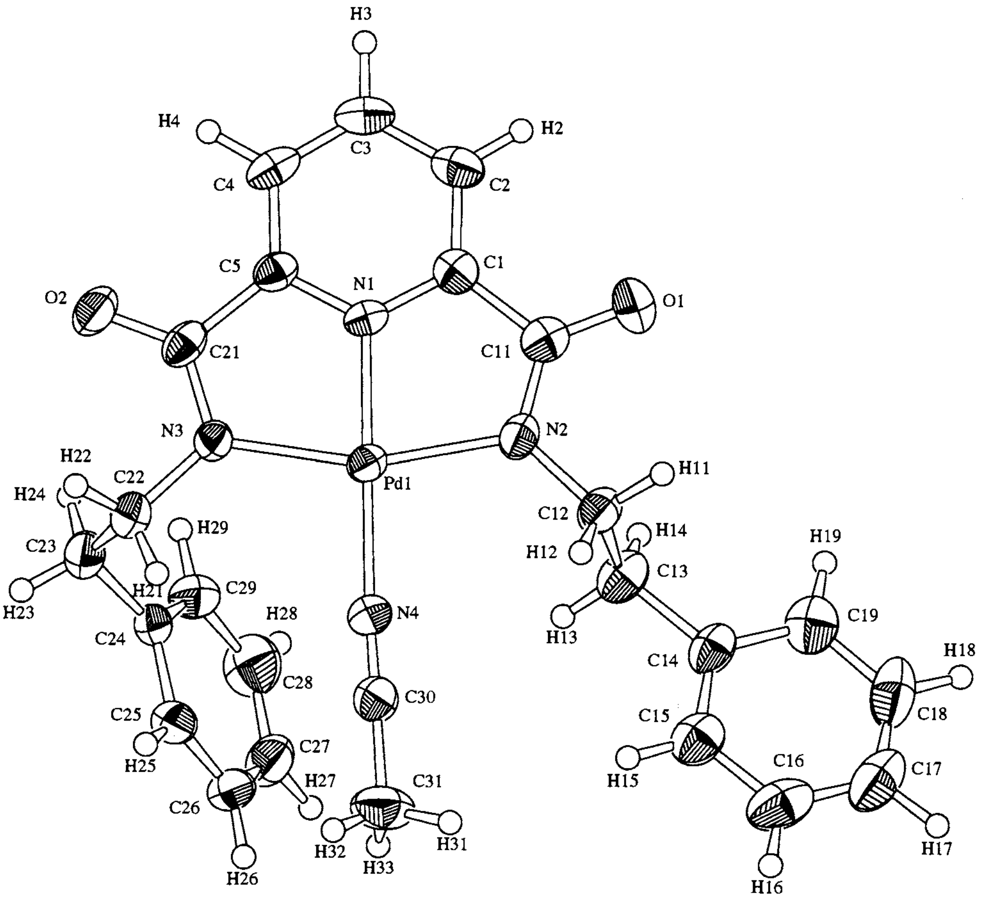


Fig. 2. ORTEP view of the X-ray crystal structure of **3** (40% probability ellipsoids).

Table 1
Crystallographic data for **2**–**4**

	2	**ff3**	**4**
Formula	$C_{23}H_{23}N_3O_2{\cdot}H_2O$	$C_{25}H_{24}N_4O_2Pd$	$C_{40}H_{33}N_5O_4$-$FePd{\cdot}CHCl_3$
Molecular weight	391.47	518.89	929.36
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	9.478(2)	9.406(3)	22.482(4)
b (Å)	11.134(1)	19.849(4)	13.420(3)
c (Å)	19.743(2)	12.220(2)	9.331(2)
α (°)			111.02(2)
β (°)	95.16(1)	92.51(2)	114.02(1)
γ (°)			108.04(2)
V (Å^3)	2075.1(4)	2279.2(8)	2028(1)
Z	4	4	2
$D_{\mathrm{calc.}}$ (g cm^{-3})	1.253	1.512	1.521
μ (Mo–K$_\alpha$) (cm^{-1})	0.84	8.44	10.45
T (°C)	23	23	23
λ (Mo–K$_\alpha$) (Å)	0.71069	0.71069	0.71069
R [a]	0.058	0.045	0.056
R_w [b]	0.029	0.037	0.069

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

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

at a lower temperature, eight Cp signals would be expected in the case of **4**. On lowering the temperature from 298 to 193 K, however, four Cp resonances were sharpened to four multiplets, indicating that torsional twist of the Cp rings of **4** is neither static even at 193 K and the rotation of C(43)–N(5) bond might be frozen. On the other hand, the upfield shift of the pyridyl proton on C(47) atom was detected throughout the temperature-lowering process. The swing of the pyridyl moiety about the palladium center is suggested to be frozen at the lower temperature to locate the pyridyl proton on C(47) atom above the coordination plane of palladium. Notably, the signals attributable to the methylene protons on C(12) and C(13) exhibited nonequivalent resonances in the region 3.74–3.68, 2.74–2.66, and 2.15–2.07 ppm at room temperature, although those of **3** are magnetically equivalent and in the expected form of a triplet. These results indicate that the free rotation of the podand moieties of **3** is restrained by the coordination of the sterically hindered [3]ferrocenophane (**1**).

Further structural information of **4** was obtained by the single-crystal X-ray structure determination (Fig. 4). The important bond distances and bond angles of **4** are summarized in Tables 2 and 3. The pyridyl nitrogen

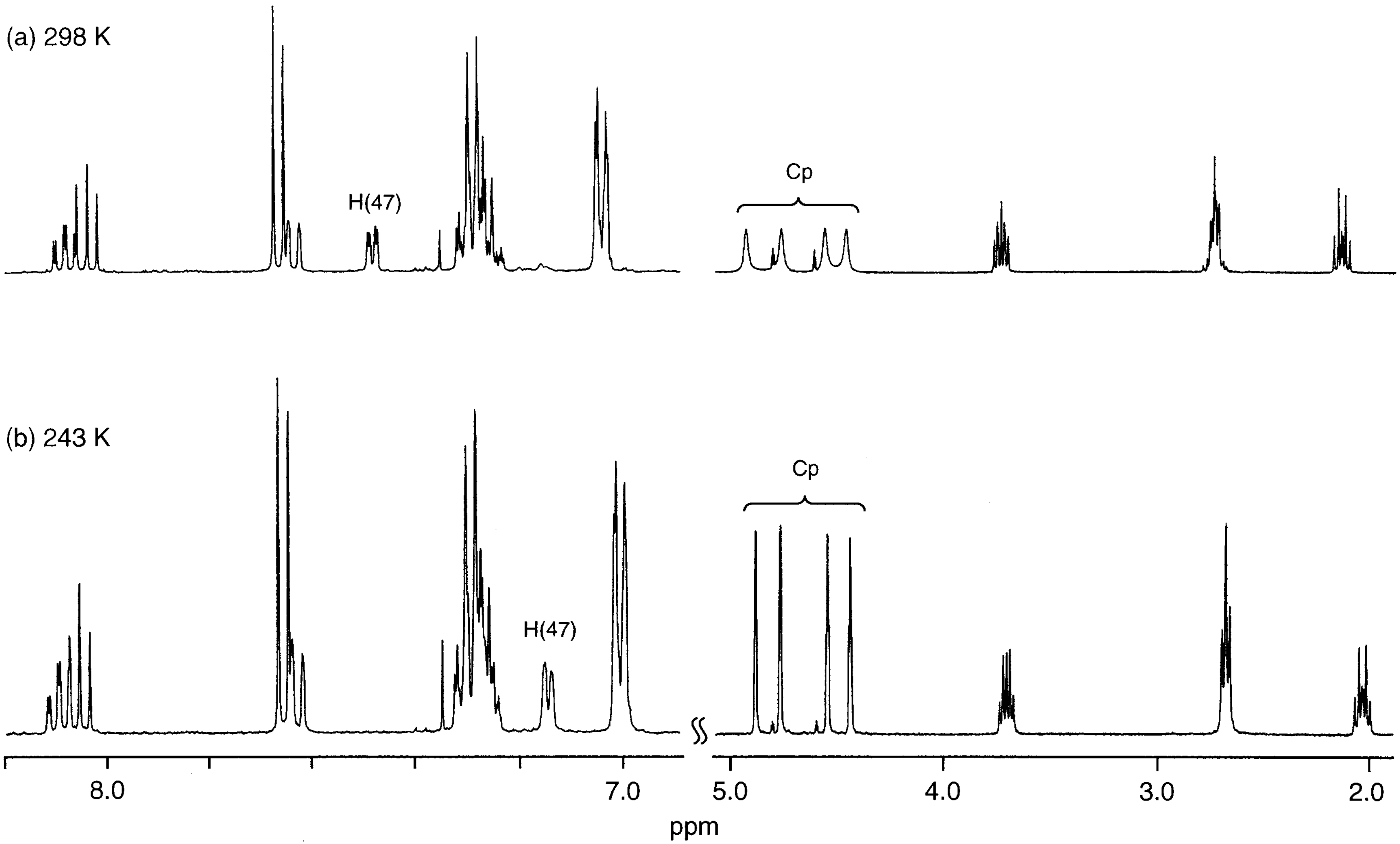


Fig. 3. ^{1}H-NMR spectra of **4** in CD_2Cl_2 at (a) 298 K; (b) 243 K.

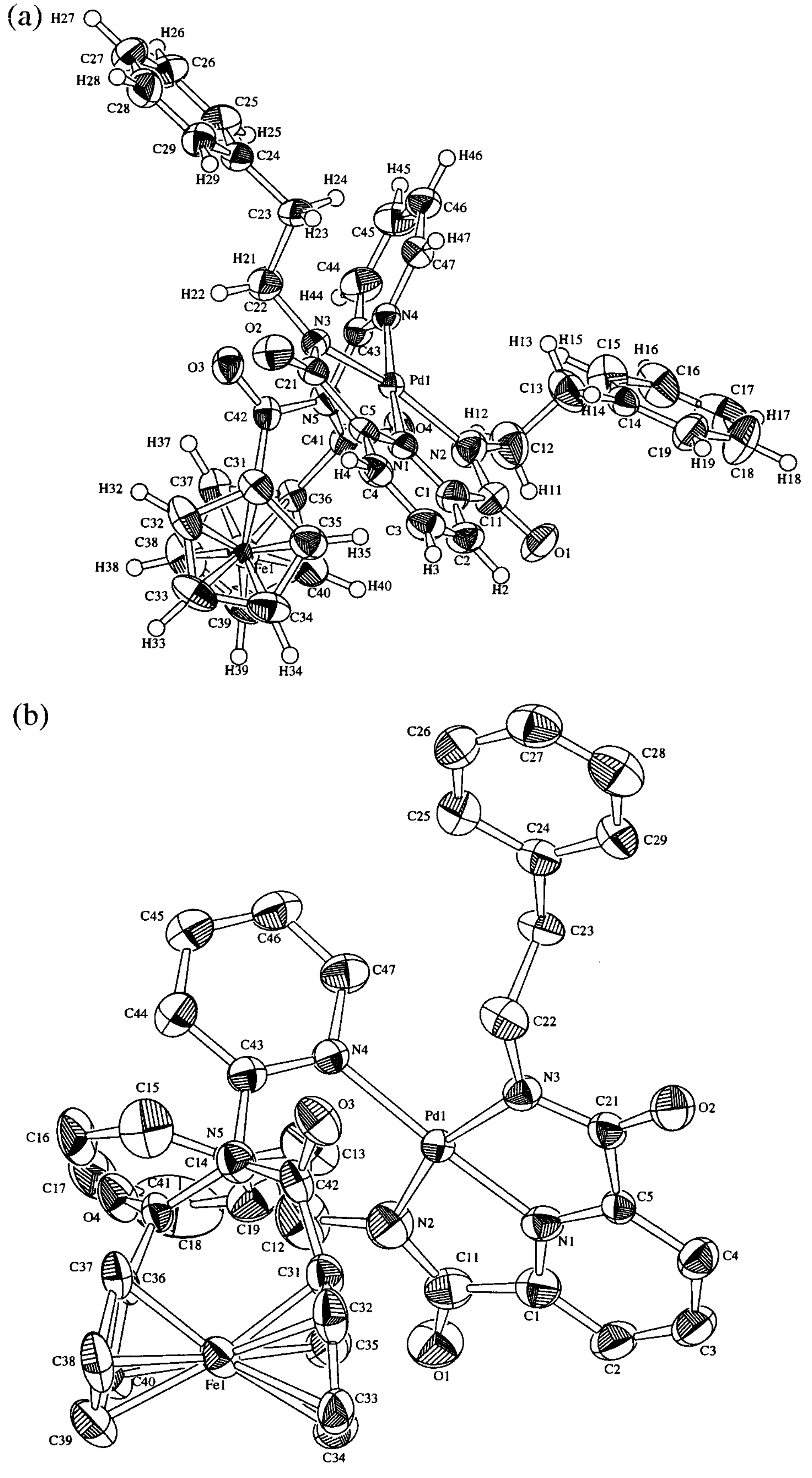


Fig. 4. ORTEP view of the X-ray crystal structure of **4** (40% probability ellipsoids). (a) Top view; (b) side view. Hydrogen atoms are omitted for clarity.

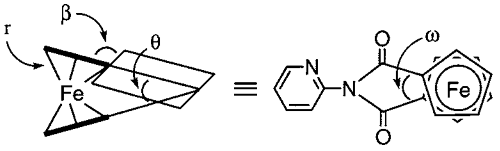
Table 2
Selected bond distances (Å) and angles (°) for **2**–**4**

	2	**3**	**4**
Bond distances			
Pd–N(1)	–	1.924(3)	1.922(7)
Pd–N(2)	–	2.023(3)	2.013(7)
Pd–N(3)	–	2.024(3)	2.037(7)
Pd–N(4)	–	2.014(3)	2.061(7)
C(1)–C(11)	1.515(4)	1.479(6)	1.50(1)
C(5)–C(21)	1.498(3)	1.514(6)	1.49(1)
C(11)–O(1)	1.228(3)	1.246(5)	1.233(10)
C(21)–O(2)	1.226(3)	1.240(4)	1.249(9)
C(11)–N(2)	1.321(4)	1.341(5)	1.35(1)
C(21)–N(3)	1.326(3)	1.338(5)	1.35(1)
Bond angles			
N(1)–Pd–N(2)	–	80.8(1)	81.0(3)
N(1)–Pd–N(3)	–	80.6(1)	80.4(3)
N(1)–Pd–N(4)	–	179.5(1)	175.4(3)
N(2)–Pd–N(3)	–	161.4(1)	161.4(3)
N(2)–Pd–N(4)	–	98.7(1)	98.2(3)
N(3)–Pd–N(4)	–	99.9(1)	100.4(3)
C(11)–N(2)–Pd	–	114.0(3)	114.8(6)
C(21)–N(3)–Pd	–	115.2(3)	114.5(6)
C(1)–C(11)–N(2)	114.8(3)	113.3(4)	112.8(8)
C(5)–C(21)–N(3)	114.3(3)	112.6(4)	113.0(8)
N(1)–C(1)–C(11)	116.5(3)	114.4(4)	113.3(8)
N(1)–C(5)–C(21)	116.6(3)	113.2(4)	113.4(8)

Table 3
Selected bond distances (Å) and angles (°) for **4**

Bond distances			
Fe–C(31)	1.965(9)	Fe–C(40)	2.042(9)
Fe–C(32)	2.048(9)	C(31)–C(42)	1.47(1)
Fe–C(33)	2.09(1)	C(36)–C(41)	1.50(1)
Fe–C(34)	2.06(1)	C(41)–O(4)	1.198(10)
Fe–C(35)	2.006(10)	C(42)–O(3)	1.207(10)
Fe–C(36)	1.957(9)	C(41)–N(5)	1.41(1)
Fe–C(37)	2.006(9)	C(42)–N(5)	1.44(1)
Fe–C(38)	2.08(1)	C(43)–N(5)	1.42(1)
Fe–C(39)	2.08(1)	Fe–Pd	5.24
Bond angles			
C(31)–C(42)–N(5)	117.8(9)	C(41)–N(5)–C(42)	125.7(7)
C(31)–C(42)–O(3)	123.6(9)	C(41)–N(5)–C(43)	117.6(7)
O(3)–C(42)–N(5)	118.5(9)	C(42)–N(5)–C(43)	115.3(7)
C(36)–C(41)–N(5)	117.1(8)	C(43)–N(4)–Pd	125.8(6)
C(36)–C(41)–O(4)	122.6(8)	C(47)–N(4)–Pd	115.5(6)
O(4)–C(41)–N(5)	120.3(9)		

Table 4
Selected strucural parameters



	1	**4**
β (°)[a]	34.6, 45.7	32.7, 49.5
r (Å)[b]	2.036	2.033
θ (°)[c]	16.4	16.2
ω (°)[d]	35.5	33.3

[a] The dihedral angle between the plane of Cp ring and C(ipso)-CO(bridging).

[b] The average distance of the iron from the ring carbons.

[c] The dihedral angle between two Cp rings.

[d] The dihedral angle between the two planes of Fe-C(ipso)-C(carbonyl).

of **1**, which was slightly deviated from the square-planar coordination plane (N(1)–Pd–N(4), 175.4°), coordinated to the palladium center at the interchangeable coordination site of **3**. The dihedral angle between the least-square planes of the pyridine ring of **1** and Pd–N(1)–N(2)–N(3) was found to be 75.7°. It is noteworthy that the coordination of the pyridyl nitrogen locates the ferrocenophane moiety below the coordination plane of palladium, being consistent with the spectroscopically nonequivalent Cp protons of **4** in ^{1}H-NMR.

The staggered orientation of two Cp rings (33.3°) was slightly released although the dihedral angle (16.2°) between the least-squares planes of two Cp rings was not affected so much by complexation with **1** (35.5 and 16.4°, respectively). The structural parameters of **4** are summarized in Table 4. There are two distinct β-angles, defined as the angle between the plane of the Cp ring and C(*ipso*)–CO(bridging) bond: 32.7° for C(31)–C(32)–C(33)–C(34)–C(35) and C(31)–C(42)O(3) and 49.5° for C(36)–C(37)–C(38)–C(39)–C(40) and C(36)–C(41)O(4). The location of the ferrocenophane moiety below the coordination plane of palladium is likely to require the rotation of C(31)–C(42)O(3) bond possibly due to the steric or electronic interaction, which leads to the rotation of the opposite C(36)–C(41)–O(4) bond giving the above-mentioned dihedral angle between two Cp rings.

Notably, the benzene ring of the podand moieties almost faces the pyridine ring of the neighboring molecule in the crystal packing of **4** (Fig. 5). The distance between the benzene and pyridine rings was ca. 3.6 Å, suggesting a π–π stacking interaction. The dihedral angle between the least-square planes of the benzene and pyridine rings was 5.73°, which is reasonable for a face-to-face interaction.

The electrochemical properties of **4** were studied by cyclic voltammetry. A reversible oxidation wave of the Fc|Fc$^+$ couple was observed at $E_{1/2}$ value of 1.03 V versus Ag|Ag$^+$. The ferrocenophane complex **4** showed a cathodic shift of 10 mV in comparison with the uncomplexed ferrocenophane **1** ($E_{1/2} = 1.04$ V), indicating a cathodic perturbation of the ferrocenophane redox couple via the complexation. This result is consistent with the above-mentioned upfield shift of Cp protons based on the location of the ferrocenophane moiety below the coordination plane of palladium.

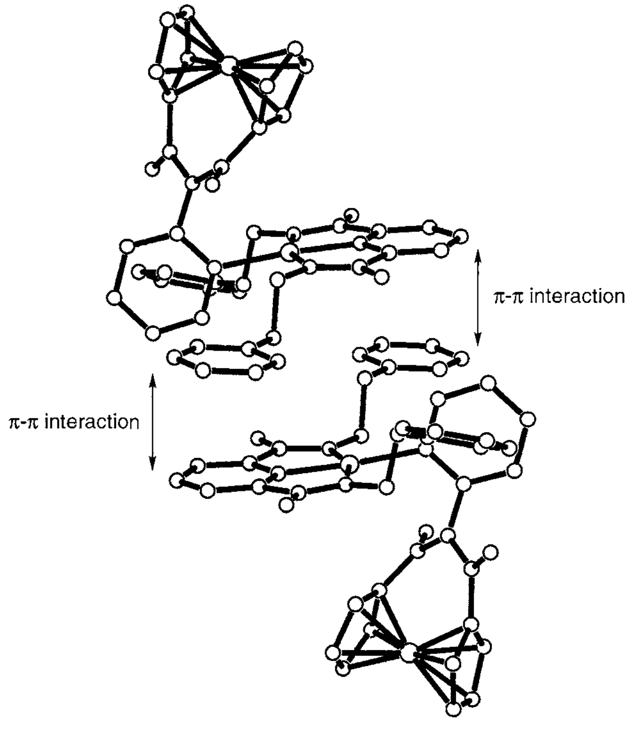


Fig. 5. Molecular packing of **4**.

In conclusion, the imide-bridged [3]ferrocenophane (**1**) forms the heterobimetallic complex with the tridentate palladium(II) complex composed of the two deprotonated amido moieties and the pyridine ring through the coordination of the pendant 2-pyridyl moiety of the imide linkage. The coordination of the pendant 2-pyridyl moiety of **1** to the palladium center locates the ferrocenophane moiety below the coordination plane of palladium with extended conjugation to influence the structural and electronic environmental changes of the ferrocenophane moiety.

3. Experimental

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Melting points were determined on a Yanagimoto micromelting point apparatus and were uncorrected. Infrared spectra were obtained with a Perkin–Elmer model 1605 FT-IR. ^{1}H-NMR spectra were recorded on a JEOL JNM-GSX-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. ^{13}C-NMR spectra were recorded on a JEOL JNM-GSX-400 (100 MHz) spectrometer and a Varian Unity Inova 600 (150 MHz) spectrometer. Mass spectra were run on a JEOL JMS-DX303HF mass spectrometer.

3.1. Syntheses

*3.1.1. Palladium complex **3***

A mixture of **2** (18.7 mg, 0.05 mmol) and $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) in acetonitrile (5.0 ml) was stirred under argon at room temperature (r.t.) for 2 h. After evaporation of the solvent, the palladium complex **3** was isolated in 96% yield (24.9 mg) as yellow crystals by recrystallization from acetonitrile. M.p. 165–167°C (uncorrected). IR (KBr): 1590 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, CD_3CN, 298 K): δ 8.01 (t, 1H, $J = 7.7$ Hz, Py), 7.56 (d, 2H, $J = 7.7$ Hz, Py), 7.33–7.19 (m, 10H, Ph), 3.40 (t, 4H, $J = 7.3$ Hz, CH_2), 2.78 (t, 4H, $J = 7.3$ Hz, CH_2). ^{13}C-NMR (100 MHz, CD_3CN, 298 K): δ 170.8 (C=O), 153.9 (Py), 142.4 (Py), 141.7 (Ph), 130.0 (Ph), 129.2 (Ph), 126.8 (Ph), 124.9 (Py), 49.1 (CH_2), 37.7 (CH_2). MS (FAB): *m/z*: 478 ($[M–CH_3CN]^+ + 1$). Anal. Calc. for $C_{25}H_{24}N_4O_2Pd$: C, 57.87; H, 4.66; N, 10.80 Found: C, 57.83; H, 4.75; N, 10.76%.

*3.1.2. Ferrocenophane complex **4***

A mixture of the imide-bridged [3]ferrocenophane (**1**) (16.6 mg, 0.05 mmol) and the palladium complex **3** (25.9 mg, 0.05 mmol) in dichloromethane (2.0 ml) was stirred under argon at r.t. for 1 h. The reaction mixture was filtered and concentrated. The ferrocenophane complex **4** was isolated in 90% yield (36.4 mg) as orange crystals by recrystallization from chloroform–hexane. M.p. 184–187°C (dec.). IR (KBr) 1707 (C=O), 1679 (C=O), 1583 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.04 (td, 1H, $J = 7.9$, 1.8 Hz, Py), 8.00 (t, 1H, $J = 7.8$ Hz, Py), 7.63 (t, 2H, $J = 7.8$ Hz, Py), 7.60 (ddd, 1H, $J = 7.9$, 1.1, 0.5 Hz, Py), 7.45 (ddd, 1H, $J = 5.4$, 1.8, 0.5 Hz, Py), 7.29–7.20 (m, 7H, Ph and Py), 7.02–6.99 (m, 4H, Ph), 4.92 (br s, 2H, Cp), 4.75 (br s, 2H, Cp), 4.54 (br s, 2H, Cp), 4.44 (br s, 2H, Cp), 3.74–3.68 (m, 2H, CH_2), 2.74–2.66 (m, 4H, CH_2), 2.15–2.07 (m, 2H, CH_2). ^{13}C-NMR (150 MHz, $CDCl_3$, 298 K): δ 170.6 (C=O), 170.5 (C=O), 154.1 (Py), 152.8 (Py), 151.9 (Py), 141.3 (Ph), 140.6 (Py), 140.4 (Py), 129.4 (Ph), 128.3 (Ph), 127.5 (Py), 125.8 (Ph), 124.7 (Py), 124.2 (Py), 75.9 (Cp), 75.9 (*ipso* Cp), 75.7 (Cp), 73.3 (Cp), 73.1 (Cp), 48.4 (CH_2), 35.9 (CH_2). MS (FAB): *m/z*: 810 $[M^+ + 1]$. Anal. Calc. for $C_{40}H_{33}N_5O_4FePd \cdot H_2O$: C, 58.02; H, 4.26; N, 8.46. Found: C, 58.42; H, 4.11; N, 8.54%.

3.2. Electrochemical experiments

The cyclic voltammetry measurements were performed on a BAS CV-50W voltammetry analyzer in deaerated dichloromethane containing 0.1 M $^nBu_4NClO_4$ as a supporting electrolyte at 25°C with a three-electrode system consisting of a highly polished glassy carbon working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag|AgCl reference electrode (BAS) with scan rate 100 mV s^{-1}. Potentials are reported versus aqueous Ag|AgCl and are not corrected for the junction potential. For a 1.0 mM dichloromethane solution of ferrocene as an internal standard, the $E_{1/2}$ value was 0.51 with 0.13 V peak separation.

3.3. X-ray structure analysis

The measurement was made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo–K_α radiation and a rotating anode generator. The data were collected at a temperature of 23 ± 1°C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 55.1°. The structure of **2** was solved by direct methods and expanded using Fourier techniques. The structures of **3** and **4** were solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 1.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136004 for **2**, CCDC-136005 for **3**, and CCDC-136006 for **4**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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