Bull. Chem. Soc. Jpn., 62, 3492—3497 (1989) [Vol. 62, No. 11

Preparation and Properties of Tetrathia[*n*](1,1′)ferrocenophanes with $Pd(BF_4)_2$. The Metal-Metal Interaction Controlled by the Size of the Thiamacrocycles

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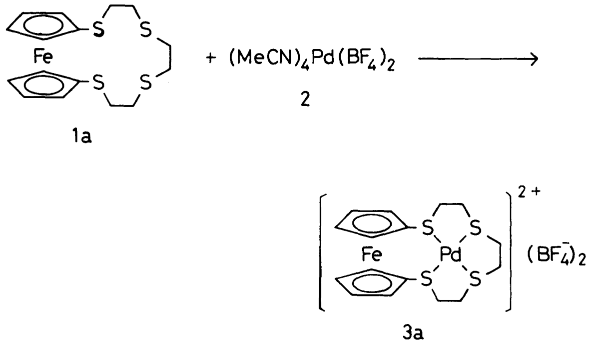
(Received May 25, 1989)

1,4,7,10-Tetrathia[10]-, 1,4,8,11-tetrathia[11]-, 1,5,8,12-tetrathia[12]-, and 1,5,9,13-tetrathia[13](1,1′)ferrocenophanes reacted with $(CH_3CN)_4Pd(BF_4)_2$ to give the corresponding 1/1 complexes in good yield. The ^1H NMR spectra of the Pd(II) complexes were not rigid at room temperature, except for the complex of 1,4,7,10-tetrathia[10](1,1′)ferrocenophane. The ^1H and ^{13}C NMR spectra at low temperature showed that the Pd(II) complex of 1,5,9,13-tetrathia[13]ferrocenophane was a single compound, while the other three complexes were a mixture of two isomers. In the electronic spectra of the above series, the low-energy band shifted to the long-wavelength region and increased its absorbance according to the decrease in the size of the thiamacrocycle.

Recently, numerous studies have been reported about heterobimetallic complexes.[1,2] Such complexes have potential applications in homogeneous catalysis. The presence of another metal in close proximity to the catalytically active metal may offer the possibility of a modification of the catalytic activity. Alternatively, interactions between the two proximate metal centers may lead to unique reactivity. Organometallic ligands are the beneficial starting material for preparing heterobimetallic complexes. We previously reported the syntheses of polythia[*n*]ferrocenophanes[3] as such an organometallic ligand, and some their complexes with transition metals.[4–6] In this paper[7] we describe the synthesis and properties of complexes of tetrathia[*n*](1,1′)ferrocenophanes with $Pd(BF_4)_2$, which is known to have a superior catalytic activity.[8]

A solution of 1,4,7,10-tetrathia[10](1,1′)ferrocenophane (**1a**)[4] in acetonitrile was treated with a solution of $(CH_3CN)_4Pd(BF_4)_2$ (**2**), which was prepared from $(CH_3CN)_2PdCl_2$ and 2 equivalent of $AgBF_2$ in acetone,[9] followed by dilution with anhydrous diethyl ether, gave a 1/1 complex (**3a**) as dark-green needles in 74% yield. In a similar manner, 1,4,8,11-tetrathia[11]- (**1b**), 1,5,8,12-tetrathia[12]- (**1c**), and 1,5,9,13-tetrathia[13](1,1′)ferrocenophanes (**1d**) gave the corresponding 1/1 complexes, **3b**, **3c**, and **3d**, in good yield, respectively. Complex **3b**, alone, contained one equivalent of acetonitrile in the crystal, as shown by elemental analysis. In the IR spectra of these complexes the out-of-plane bending vibration, which was the most diagnostic probe of the oxidation state of ferrocene,[10] was observed at 824, 826, 818, and 818 cm⁻¹ for **3a**, **3b**, **3c**, and **3d**, respectively. The frequencies are a little higher than those of the corresponding free ligands **1a**—**1d**, but considerably lower than those of ferricenium cations (e.g. 846 cm⁻¹ in the ferricenium cation of **1d**). These results suggests that the iron atom of a ferrocenyl moiety is somewhat perturbed by the proximate location of the Pd(II) atom. Particularly, in the complexes **3a** and **3b**, there seems to be a significant interaction between two metal atoms. In this connection, the out-of-plane bending vibration in (triphenylphosphine)(1,1′-ferrocenedithiolato-*S*,*S*′,*Fe*)-palladium(II) (**4**), which is confirmed by X-ray analysis to contain a dative Fe-Pd bond,[11] was observed at 830 and 838 cm⁻¹. In the $Pd(BF_4)_2$ complexes of trithia[*n*](1,1′)ferrocenophanes (n=7 and 9), this band also appeared at 830 and 844 cm⁻¹, respectively.[7] The differences of the frequencies between the Pd(II) complexes (**3a**—**3d**) and the corresponding free ligands (**1a**—**1d**) were 24, 16, 2, and 6 cm⁻¹, respectively. The magnitude of the shifting from the free ligand to the corresponding Pd(II) complex can be assumed to reflect the strength of an interaction between the Pd(II) atom and the Fe atom of a ferrocene nucleus in these complexes, since the coordinating strength of the sulfur atom to the Pd(II) atom seems to be almost the same through the series of the complexes **3a**—**3d**. Therefore, it will be expected that the largest interaction acts in complex **3a** in a series of complexes, **3a**—**3d**.



In the ^1H NMR spectrum (CD_3CN, 400 MHz) of **3d**, all signals were broadened at room temperature, indicating the presence of a certain dynamic process.

Table 1. ^1H NMR Spectral Data of the Complexes **3a**—**3d** in the Region of the Cp-Ring Proton Signals (400 MHz, CD_3CN)[a]

Compound	Temp	Isomer	Chemical shifts (δ)[b]
3a	R.T.	Major	5.61 (quasi s, 2H), 5.28 (quasi s, 2H), 4.82 (quasi s, 2H), 4.52 (quasi s, 2H)
		Minor	5.91 (broad s, 2H), 5.61 (quasi s, 4H), 5.82 (quasi s, 2H)
3b	−30 °C	Major	5.67 (quin, 2H), 5.54 (quin, 2H), 4.73 (sex, 2H), 4.27 (sex, 2H)
		Minor	5.58 (quin, 2H), 5.37 (quin, 2H), 4.76 (sex, 2H), 4.39 (sex, 2H)
3c	80 °C		5.14 (s, 4H), 4.65 (s, 4H)
3d	80 °C		5.22 (s, 4H), 4.66 (s, 4H)
	−30 °C		5.20 (broad quin, 4H), 4.75 (sex, 2H), 4.52 (sex, 2H)

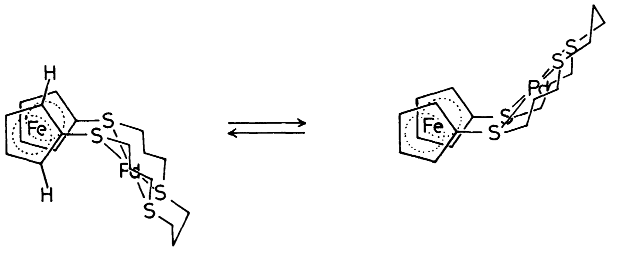
a) The methylene proton signals could not surely assigned because of complexation due to the presence of two isomers. b) quin=quintet, sex=sextet.

Table 2. ^{13}C NMR Spectral Data of the Complexes **3a**—**3d**

Compound	Temp	Isomer	Chemical shifts (δ)
3a	R.T.	Major	86.05,[a] 79.51, 76.17, 75.16, 71.74, 46.29, 43.55, 43.40
		Minor	—,[b] 80.57, 77.10, 75.85, 70.07, 45.63, 43.55, 40.94
3b	−30 °C	Major	83.62,[a] 80.60, 76.10, 75.73, 70.03, 42.71, 42.07, 37.58, 27.18
		Minor	82.28,[a] 80.03, 75.96, 74.67, 70.93, 45.83, 41.59, 37.63, 27.95
3c	−30 °C	Major	79.91, 77.36, 76.77,[a] 75.52, 72.02, 40.05, 38.47, 32.20, 25.68
3d	−30 °C		79.77, 77.53, 75.86, 75.17,[a] 73.12, 38.14, 37.49, 33.06, 25.70, 23.71
	80 °C		79.74, 77.23, 75.84, 75.56,[a] 73.07, 38.39, 37.24, 33.23, 25.82, 23.93

a) This is assigned to be the bridge-head carbon of a ferrocenyl Cp-rings by using the DEPT measurement. b) This signal (which is probably the bridge-head carbon signal) could not be detected.

The static spectrum was obtained at −30 °C, in which the cyclopentadienyl (Cp) ring protons appeared as three pseudosinglests at δ 5.20 (4H), 4.75 (2H), and 4.52 (2H) (The ^1H NMR spectral data was summarized in Table 1). The ^{13}C NMR spectrum of **3d** at low temperature similarly showed the presence of a single conformer. That is, the Cp-ring carbons of a ferrocene moiety produced signals at δ 79.77, 77.53, 75.86, 75.17, and 73.12 (The ^{13}C NMR spectral data was summarized in Table 2). The unsymmetric pattern of the ferrocenyl ring observed in the ^1H and ^{13}C NMR spectra of **3d** seems to reflect the stepped conformation[12] in which the Fe, Pd(II), and two sulfur atoms connected to the Cp rings are not coplanar, since **3d** has been proved by X-ray analysis to have such a stepped conformation.[13] The metal complexes of ferrocene derivatives containing heteroatoms in the 1,1′-positions can be regarded as an analog of [3](1,1′)ferrocenophanes which involves a bridge reversal process. The bridge reversal energy observed in 1,2,3-trichalcogeno[3](1,1′)ferrocenophanes is ca. 80 kJ mol^{-1}, in solution.[14,15] The proton signals of the Cp-rings of **3d** at δ 4.75 and 4.52 broadened upon warming and coallesced at 42 °C. At 80 °C the Cp-ring protons appeared at δ 5.22 and 4.66 as almost sharp signals, although signals of the methylene protons were still somewhat broad. A similar marked temperature dependence in the ^1H and ^{13}C NMR spectra was observed in the $PdCl_2$ complexes of 1,1′-bis(isobutylthio)ferrocenes (**5**),[16] and two independent dynamic processes, sulfur inversion and bridge reversal, were suggested to be involved.[17] In the complex **3d**, the sulfur inversion process seems to be impossible because the four sulfur atoms in the thiamacrocycle coordinate to the Pd(II) atom and, consequently, the methylene groups on the sulfur atoms at the 1,1′-positions are always forced to be in the same direction as that of the Pd(II) atom. Thus, the remarkable dynamic behavior observed in **3d** is probably due to a flipping of the thiamacrocycle moiety coordinated by the Pd(II) atom in which the Pd(II) atom flips from one side of the plane containing the iron atom and two sulfur atoms at the 1,1′-positions to the other. This phenomenon is considered to result from a concurrent occurance of bridge reversal with S-inversion on the sulfur atoms at the 1,1′-positions. From the coalescence temperature (42 °C), $\Delta G^{\neq}$=63.2 kJ mol^{-1} was calculated. This value is comparable with that in the complexes of 1,1′-bis(isobutylthio)ferrocene with palladium halides (**5**).[17] This supports the above elucidation, since it was reported that the bridge reversal was fast and the S-inversion was slow in PdX_2 complexes of 1,1′-bis(alkylthio)ferrocenes.[17] The rate



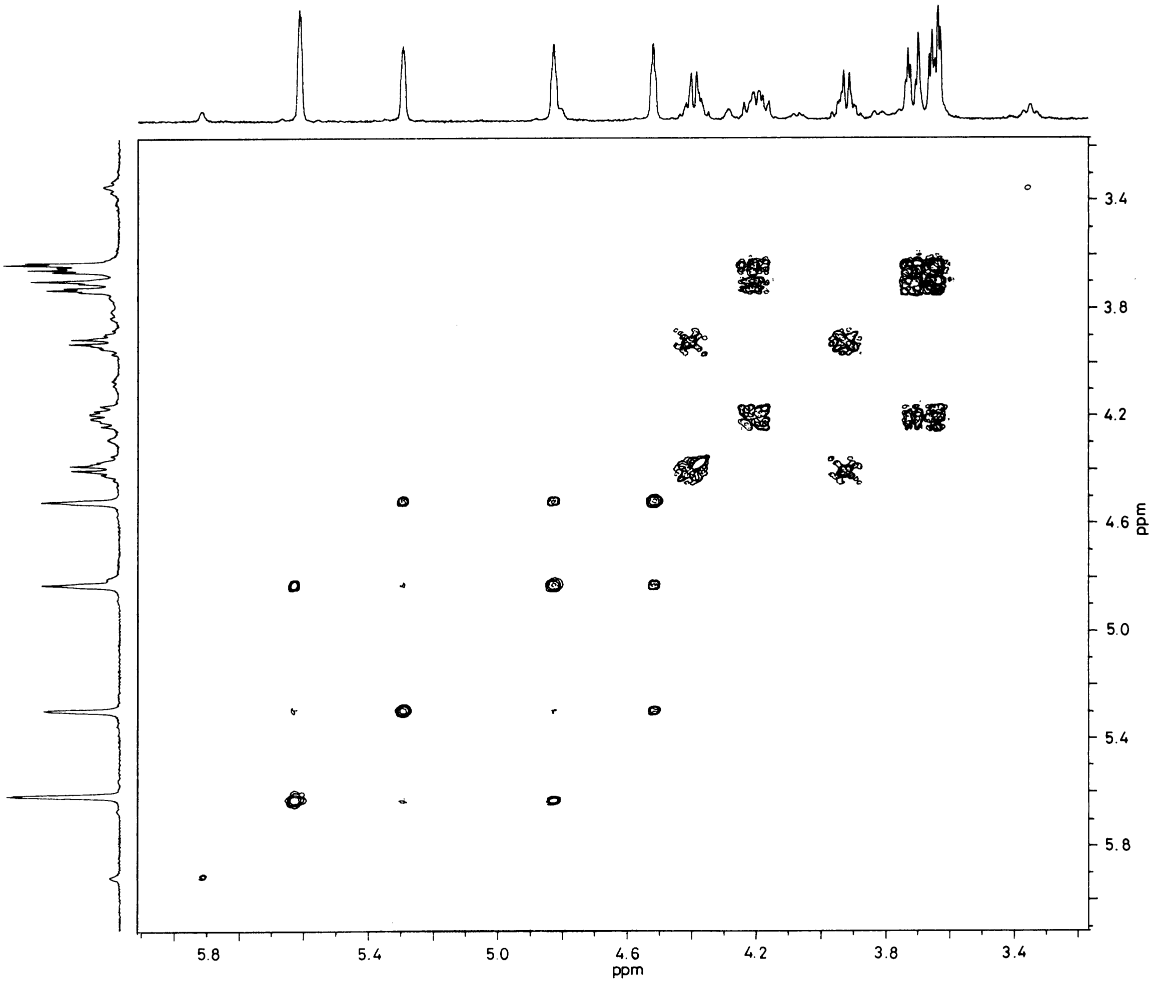


Fig. 1. The H,H-COSY spectrum of the complex **3a**.

of the flipping is, therefore, supposed to be controlled by the rate of S-inversion. The chemical shift of the α- and β-protons of the Cp rings in the ^{1}H NMR spectrum of **3d** is fairly similar to that of **5**.[16] In the latter, the large low-field shift of the α-protons was suggested to be due to a magnetic anisotropy or an inductive effect of the metal halide.[16] A similarity between the complexes **3d** and **5** is also seen in the chemical shift of the ferrocenyl ring carbons in the ^{13}C NMR spectra.

On the other hand, the ^{1}H NMR spectrum of **3a** was static, even at room temperature; moreover, it showed the presence of two isomers in the complex. The isomer ratio of two isomers is established from the integration ratio of the Cp ring proton signals to be about 6:1. In the ^{1}H NMR spectrum of **3a**, the major isomer showed signals of the Cp-ring protons at δ 5.62, 5.29, 4.82, and 4.51. The assignment of these signals to the α- and β-protons of the Cp-rings was successfully performed by the 2D H,H-COSY measurement (Fig. 1). The signals at δ 4.82 and 4.51 correlated intensively with each other and further with the signals at δ 5.62 and 5.29, respectively. This is a clear evidence that the signals at 4.82 and 4.51 can be assigned to the β-protons of the ferrocenyl ring. The remaining signals at 5.62 and 5.29 correspond to the α-protons of the ferrocenyl ring. Thus, the H,H-COSY technique is a more superior method for the assignment of the ferrocenyl ring protons than the *D*-labeling method,[18] if the ring protons are in unsymmetrical circumstances. Here, in order to make a brief explanation, we have tentatively labeled the protons which resonated at δ 5.61, 4.82, 4.52, and 5.28 as H(α), H(β), H(β′), and H(α′) atoms, respectively, on the basis of the H,H-COSY experiment. Interestingly, the chemical shifts of the H(α) and H(β) atoms are in a lower field than those of the H(α′) and H(β′) atoms, especially the signals of the H(α) atom being at a considerably low field (δ 5.61). The difference of the chemical shifts between the H(α) and H(α′) atoms (Δδ 0.33 ppm) is fairly large compared with that in **3d**. This is in good agreement with the adoption of the stepped conformation in **3a**. At the same time, the low-field shift of the H(α) signal seems likely to be explained by the anisotropy of the

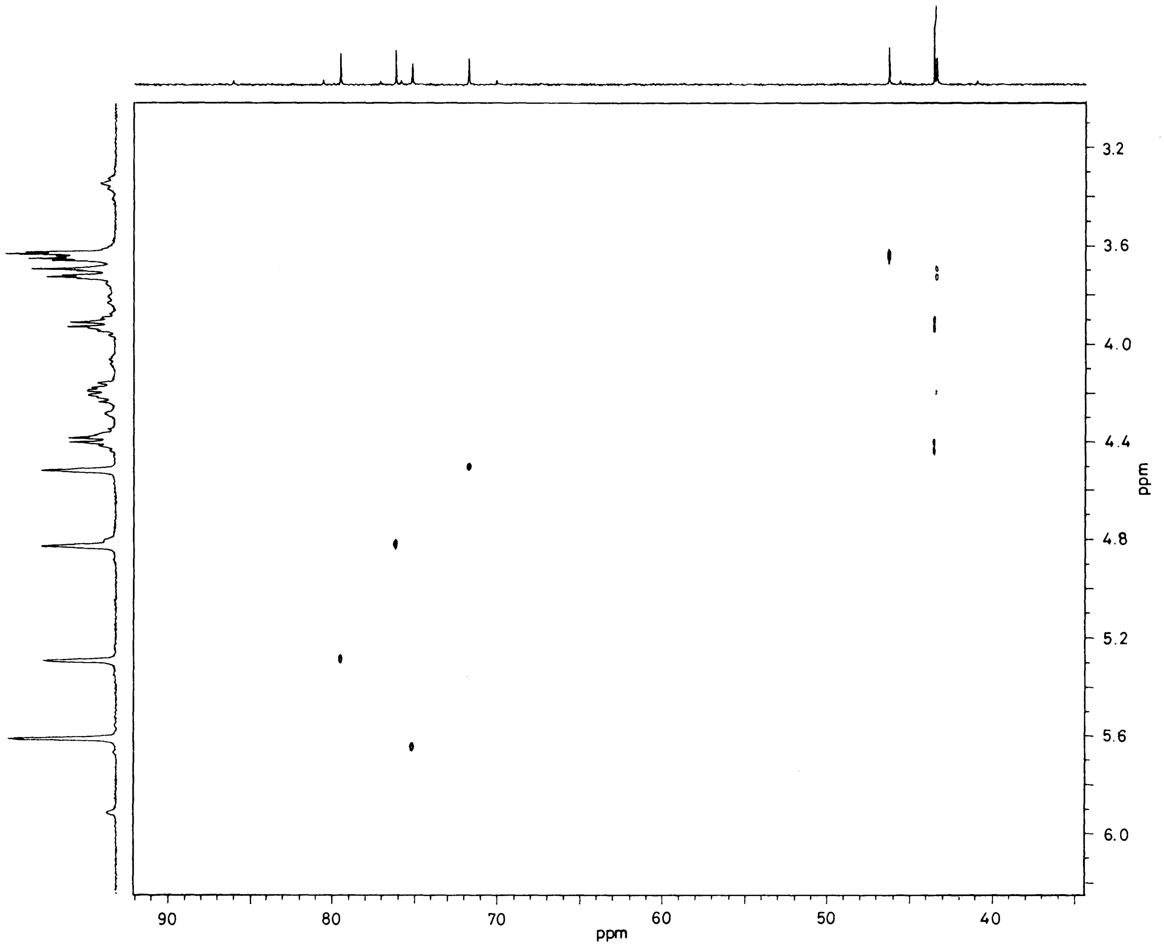
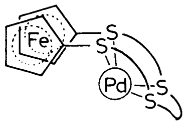


Fig. 2. The C,H-COSY spectrum of the complex **3a**.

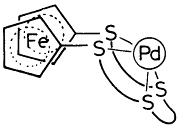
lone pair of the sulfur atom connected to the Cp-rings, since the lone pair of the sulfur atom is placed nearly parallel to the H(α) atom on the basis of the molecular model of **3a**. The assignment of the ferrocenyl ring carbons in the major isomer of **3a** was accomplished by the C,H-COSY experiment (Fig. 2). The carbon signals at δ 79.51 and 75.16 correlated to the α-proton signals at δ 5.28 and 5.61, respectively. The carbon signals at δ 76.17 and 71.74 showed good correlation to the β-proton signals at δ 4.82 and 4.52, respectively. Using the labelling described above, the carbon signals at δ 75.16, 76.17, 71.74, and 79.51 were assigned to the C(α), C(β), C(α'), and C(β') atoms, respectively. It is interseting that the lowest field signal in the ^{13}C NMR spectrum of the major isomer of **3a** is the signal of the C(α') atom, while the signals of the H(α) atom appear at lowest field in the ^{1}H NMR spectrum. This may suggest that a certain interaction due to the metal atom incorporated in the thiamacrocycle exerts an influence on the ferrocenyl ring carbons.

The ^{1}H NMR spectra of **3b** and **3c** were broadened at room temperature, similarly to that of **3d**. The static spectrum of **3b** was obtained at 0 °C, and showed the presence of two isomers, as can be seen in the case of complex **3a** (Table 1). The ratio of the major to minor isomers was estimated from the integration ratio of the signals at δ 4.27 and 4.39 to be ca. 2.2 for **3b**. The averaging process of the proton signals in **3b** on warming was very complex because of the presence of two isomers; **3b** gave no completely averaged spectra, even on warming at 80 °C. The dynamic behavior of the ^{1}H NMR spectrum dependent on the temperature was further complicated for complex **3c**. Two pseudo singlets for the Cp-ring protons of **3c** were observed at δ 5.14 and 4.65 at 80 °C. However, even on cooling at −40 °C (limiting low temperature for acetonitrile) no static spectrum was obtained, although the ^{13}C NMR spectrum of **3c** at −40 °C gave a definite spectrum only for the major isomer (Table 2). Judging from the temperature affording the static spectrum and the spectrum at 80 °C, the flipping motion of the thiamacrocycle moiety coordinating the Pd(II) atom increases in the following order: **3a**<**3b**<**3d**≲**3c**, the order being in accord with the increase of the ring size in the thiamacrocycle. It is worthy to note that this order is also consistent with that of the decrease of the Fe(II)–Pd(II) interaction obtained from the IR study. Therefore, we feel justified in assuming that the interaction between the iron atom of the ferrocene moiety and the Pd(II) atom incorporated in the thiamacrocycle may lock the flipping motion of the thiamacrocycle moiety towards the ferrocenyl part in the complexes **3a**—**3d**. The chemical shift of the bridge-head carbon of ferrocenyl rings of the series **3a**—**3d** was shifted down-field from δ 75.17 in **3d** to δ 86.05 in **3a** according to the decrease in the size of the thiamacrocycle, although the other ring carbons were little changed. This seems unlikely to be due to a conjugate interaction between the sulfur lone pair and the π-orbital of the ferrocenyl rings, since there was observed no significant difference in the chemical shift between a flexible molecule at 80 °C (δ 75.56) and a fixed molecule at −30 °C (δ 75.17) in **3d**. This down-field shift (described above) probably stems from the change in the coordination mode of a Pd(II) atom to the thiamacrocycle part (vide infra).

It was proven by X-ray analysis[13] that complex **3d** had a stepped conformation and that the Pd(II) atom was located in the center of a square planar consisting of four sulfur atoms of the thiamacrocycle moiety. This is consistent with the ^{1}H and ^{13}C NMR spectra of complex **3d** in solution at −30 °C. On the other hand, the NMR data of complexes **3a**—**3c** showed the presence of two isomers at low temperature. We suppose that the Pd(II) atom in the complexes can not fit sufficiently in the center of the cavity of the thiamacrocycle moiety, because of the small size of the cavity, contrary to complex **3d**. Consequently, the Pd(II) atoms in the complexes **3a**—**3c** deviate up or down from the plane of the thiamacrocycle moiety, resulting in two isomers. Although the structure of the major and minor isomers is not decided from the ^{1}H and ^{13}C NMR spectral data, a consideration of the steric hindrance between the Pd(II) atom coordinated to the sulfur atoms in the thiamacrocycle and the α-protons of the ferrocene ring leads to the assignment of the major isomers to a configuration that the Pd(II) atom is deviated to the outer side of the plane of the thiamacrocycle away from the ferrocene moiety (**3B**).



3A



3B

In the minor isomers of **3a**—**3c**, the decrease of the size of the thiamacrocycle increases the steric hindrance (described above), and at the same time increases the deviation of the Pd(II) atom from the plane consisting of the four sulfur atoms in the thiamacrocycle moiety. The latter change may shrink somewhat the distance between the Pd(II) atom and the iron atom of the ferrocene moiety, and may increase an interaction between both metals (**3A**). This suggestion appears to be supported by the behavior of the electronic spectra.

The electronic spectrum of **3d** showed broad and weak absorption at 572 nm (ε 113), as well as intensive absorptions at 330 sh (15700) and 296 nm (ε 17000). The free ligand **1d** showed an absorption maximum at 443 nm (ε 190), while the $Pd(BF_4)_2$ complex with the open-chain tetrakis(thioether), 2,6,10,14-tetrathiapentadecane, which is considered to have a square-planar coordination, showed no absorption above 370 nm.[9] Furthermore, the Pd(II) complex of 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane, which contains square-planar configuration of the four thioether donor atoms, also showed an absorption only at 373 nm (ε 2175) in the region above 300 nm,[19,20] although weak absorption at 620 nm (ε 55) was observed in bis(1,4,7-trithiacyclononane)palladium(II) tetrafluoroborate, which was confirmed by X-ray analysis to contain a weak interaction between the Pd(II) atom and the apical thioether donor atom.[21,22] We suppose, therefore, that the absorption band at 572 nm observed in complex **3d** may be concerned with an interaction between the iron atom of the ferrocene nucleus and the Pd(II) atom incorporated into the thiamacrocycle moiety. The absorption at 572 nm showed a bathochromic shift and an increase in absorbance according to the decreasing size of the thiamacrocycle in the series **3a**—**3d**: **3d**, 572 (ε 113) <**3c**, 604 (376) <**3b**, 612 (245) <**3a**, 670 (499). As mentioned above, the distance between the Pd(II) atom incorporated in the thiamacrocycle moiety and the iron atom of the ferrocene ring decrease potentially according to the size of the thiamacrocycle through series **3a**—**3d**. The observed bathochromic shift, therefore, may be due to an increasing Fe–Pd interaction in the complexes. However, we cannot rule out the possibility that the shift stems from an increasing deviation of the Pd(II) atom from the thiamacrocycle plane because the hole size is insufficient for a good fit.

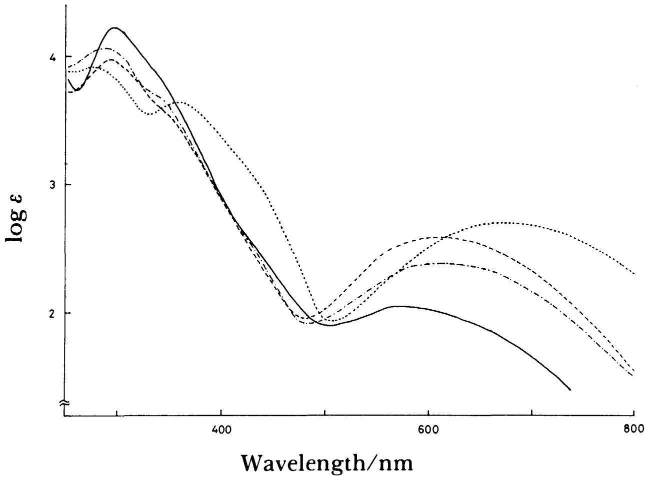


Fig. 3. The electronic spectra of the complex **3a** (·····), **3b** (—-—-), **3c** (----), and **3d** (—).

Finally, we reported the preparation of the $Pd(BF_4)_2$ complexes of 1,5,9-trithia[9]- and 1,4,7-trithia[7](1,1′)-ferrocenophanes.[7,23] In these complexes, a bonding interaction between the Fe atom of the ferrocene nucleus and the Pd(II) atom incorporated into the thiamacrocycle is confirmed by the spectroscopic data. The complexes are rigid, even at high temperature, in contrast with complexes **3b**—**3d** and showed a greater frequency of out-of-plane bending than that of complexes **3a**—**3d**. The rigidness of the molecule and the high out-of-plane bending vibration are considered to stem from the presence of the Fe–Pd dative bond in these complexes. From a comparison with these results, it is clear that these is no bonding interaction but, rather, a certain (probably charge-transfer type of) interaction in the present complexes of the tetrathia[*n*](1,1′)ferrocenophanes; the interaction is controlled by the size of the thiamacrocycle moiety.

Experimental

The IR spectra were taken on a Hitachi 270—50 Infrared Spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM400 Spectrometer, TMS being chosen as the standard material. The electronic spectra were taken on a Shimadzu UV2100 Spectrometer.

Tetrathia[*n*]ferrocenophanes were prepared as described in a previous paper.[3] Dichlorobis(acetonitrile)palladium(II) was prepared according to a method from the literature.[9]

(1,4,7,10-Tetrathia[10]ferrocenophane)palladium(II) Tetrafluoroborate (3a). General Procedure. Dichlorobis(acetonitrile)palladium(II) (26 mg, 0.1 mmol) was added to a solution of silver tetrafluoroborate (40 mg, 0.2 mmol) in acetone (5 cm^3). The solution was refluxed for 1 h. The resulting precipitates (AgCl) were filtered off and the filtrate was evaporated under reduced pressure. To a solution of the residue in acetonitrile (2 cm^3) was added a solution of 1,4,7,10-tetrathia[*n*]ferrocenophane (**1a**) (40 mg, 0.1 mmol) in acetonitrile (5 cm^3). The resulting green solution was diluted with anhyd diethyl ether (16 cm^3). The solution was kept overnight in refrigerator. Filtration gave dark green plates, mp ca. 180 °C (decomp). Found: C, 28.71; H, 3.11%. Calcd for $C_{16}H_{20}B_2F_8S_4FePd$: C, 28.41; H, 2.98%.

(1,4,8,11-Tetrathia[11]ferrocenophane)palladium(II) Tetrafluoroborate (3b). Blue black crystals, mp ca. 115 °C (decomp). Found: C, 31.30; H, 3.50; N, 1.95%. Calcd for $C_{17}H_{22}B_2F_8S_4FePd \cdot CH_3CN$: C, 31.20; H, 3.44; N, 1.95%.

(1,5,8,12-Tetrathia[12]ferrocenophane)palladium(II) Tetrafluoroborate (3c). Blue black crystals, mp ca. 195 °C (decomp). Found: C, 30.97; H, 3.45%. Calcd for $C_{18}H_{24}B_2F_8S_4FePd$: C, 30.69; H, 3.43%.

(1,5,9,13-Tetrathia[13]ferrocenophane)palladium(II) Tetrafluoroborate (3d). Blue black needles, mp 250 °C. Found: C, 32.02; H, 3.81%. Calcd for $C_{19}H_{26}B_2F_8S_4FePd$: C, 31.76; H, 3.65%.

References

1) M. I. Bruce, *J. Organomet. Chem.*, **242**, 147 (1983); **283**, 339 (1985).

2) G. L. Geoffroy and D. A. Roberts, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford (1982), Chap. 40.

3) M. Sato, H. Watanabe, S. Ebine, and S. Akabori, *Chem. Lett.*, **1982**, 1753: M. Sato, S. Tanaka, S. Ebine, and S. Akabori, *Bull. Chem. Soc. Jpn.*, **57**, 1929 (1984).

4) M. Sato, S. Tanaka, S. Akabori, and Y. Habata, *Bull. Chem. Soc. Jpn.*, **59**, 1515 (1986).

5) M. Sato, K. Suzuki, and S. Akabori, *Bull. Chem. Soc. Jpn.*, **59**, 3611 (1986).

6) M. Sato, S. Akabori, M. Katada, I. Motoyama, and H. Sano, *Chem. Lett.*, **1987**, 1847.

7) A. Preliminary report: M. Sato, K. Suzuki, and S. Akabori, *Chem. Lett.*, **1987**, 2239.

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

9) F. R. Hartley, S. G. Murry, and C. A. McAuliffe, *Inorg. Chem.*, **18**, 1394 (1979).

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

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

12) J. J. Bishop and A. Davison, *Inorg. Chem.*, **10**, 826 (1971).

13) N. Won, K. Iwai, M. Katada, H. Sano, M. Sato, and S. Akabori, in preparation.

14) A. Davison and J. C. Smart, *J. Organomet. Chem.*, **174**, 321 (1978).

15) E. W. Abel, M. Booth, and K. G. Orrell, *J. Organomet. Chem.*, **208**, 213 (1981).

16) B. McCulloch, D. L. Ward, J. D. Woolins, and C. H. Brubaker, Jr., *Organometallics*, **4**, 1425 (1985).

17) K. G. Orrell, V. Sik, C. H. Brubaker, and B. McCulloch, *J. Organomet. Chem.*, **276**, 267 (1984).

18) D. W. Slocum and C. R. Ernst, *Tetrahedron Lett.*, **1972**, 5217, and the literature therein.

19) G. Reid, A. J. Blake, T. I. Hyde, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, **1988**, 1397.

20) There is also in the literature 22a the description that the $Pd(BF_4)_2$ complex of 1,4,8,11-tetrathiacyclotetradecane shows no absorption near 600 nm.

21) K. Wieghardt, H.-J. Küppers, E. Raabe, and C. Kruger, *Angew. Chem., Int. Ed. Engl.*, **25**, 1101 (1986).

22) a) A. J. Blake, A. J. Holder, T. I. Hyde, Y. V. Roberts, A. J. Lavery, and M. Schröder, *J. Organomet. Chem.*, **323**, 261 (1987): b) A. J. Blake, A. J. Holder, T. I. Hyde, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, **1987**, 987.

23) M. Sato, H. Asano, K. Suzuki, M. Katada, and S. Akabori, *Bull. Chem. Soc. Jpn.*, to be submitted.