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# Synthesis and Characterization of the Pd(II) and Pt(II) Complexes of Trichalcogeno[*n*]ferrocenophanes (*n*=7 and 9). A Dative Fe–Pd or Fe–Pt Bond Formation

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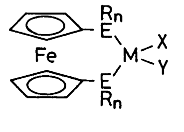
1,7-Dithia-4-selena[7]- and 1,9-dithia-5-selena[9](1,1′)ferrocenophanes were prepared. These compounds, as well as 1,4,7-trithia[7]- and 1,5,9-trithia[9](1,1′)ferrocenophanes, were treated with $(CH_3CN)_4Pd(BF_4)_2$ or $(CH_3CN)_4Pt(BF_4)_2$ to give the corresponding 1/1 complexes in good yield. The spectral data of these complexes confirmed that there exsisted a dative Fe–Pd or Fe–Pt bond in these bimetallic complexes.

Much attention has been focused on the heterobimetallic complexes.[1,2] Such species should be capable of generating unique reactivity by virtue of the close proximity of the adjacent metals. The coordination of the nonbonding $e_{2g}$ electrons of the iron atom in ferrocene to vacant orbitals of a transition metal has also become a topic of interest in recent years. Ferrocene derivatives involving heteroatoms in the 1,1′-positions formed 1/1 complexes (**1**) with various metals.[3] However, it was reported that there was no evidence of an interaction between the iron atom of a ferrocene nucleus and the metal coordinated to the hetero atoms.[4,5] In this connection, Seyferth et al. carried out a reaction of 1,2,3-trithia[3](1,1′)ferrocenophane with tetrakis(triphenylphosphine)palladium(0) to obtain (triphenylphosphine)(1,1′-ferrocenedithiolato-*S,S′,Fe*)palladium(II) (**2a**), which was confirmed by X-ray analysis to have a weak dative Fe–Pd bond.[6,7] A similar Pt(II) complex (**2b**) was also reported.[8] In the same year, Sano et al. reported that the stable metal halide adducts (**3**) of [2](1,1′)ferrocenophane were confirmed by Mössbauer spectroscopy to have a strong bonding interaction between the iron atom and metal halides.[9] On the other hand, thiamacrocyclic compounds are of interest in that these form stable complexes with various transition metals and stabilize an unusual valence of the metal.[10] Since we have already prepared various metal complexes of tetrathia-[*n*]- and trithia[*n*]ferrocenophanes,[11,12] these findings have stimulated us to attempt a reaction of trichalcogeno[*n*]ferrocenophanes with a highly acidic Pd$(BF_4)_2$ or $Pt(BF_4)_2$.[13,14]



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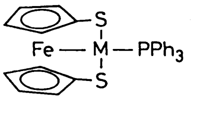
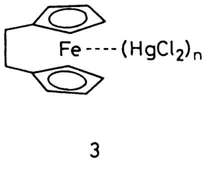


2a : M=Pd

2b : M=Pt



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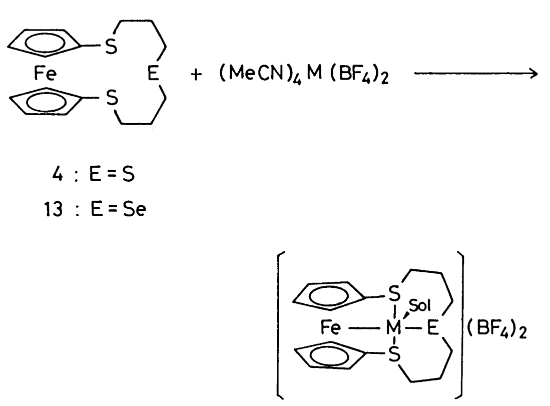
## Results and Discussion

1,5,9-Trithia[9](1,1′)ferrocenophane (**4**)[12] was allowed to react with $(CH_3CN)_4Pd(BF_4)_2$, which was prepared from the reaction of $(CH_3CN)_2PdCl_2$ and $AgBF_4$,[15] in acetone at ambient temperature. Stable dark-brown fine needles (**5a**) were isolated in good yield, which proved by elemental analysis to be a 1/1 complex. A similar reaction of 1,4,7-trithia[7]-(1,1′)ferrocenophane (**6**)[16] with $(CH_3CN)_4Pd(BF_4)_2$ gave a black 1/1 complex (**7a**) and a green powdery 2/1 complex (**8a**) in 74 and 12% yields, respectively. Complexes **5a** and **7a** contained one equivalent of acetone in the crystals. Upon recrystallization from acetonitrile-diethyl ether, the acetone was replaced by acetonitrile. In order to extend the scope of the reaction, each trithia[*n*]ferrocenophane was treated with $(CH_3CN)_4Pt(BF_4)_2$.[15] Only the reaction of the [9]-ferrocenophane (**4**) with $(CH_3CN)_4Pt(BF_4)_2$ in warm acetonitrile under nitrogen gave a stable 1/1 complex (**5b**) as red needles in good yield.



4 : E=S

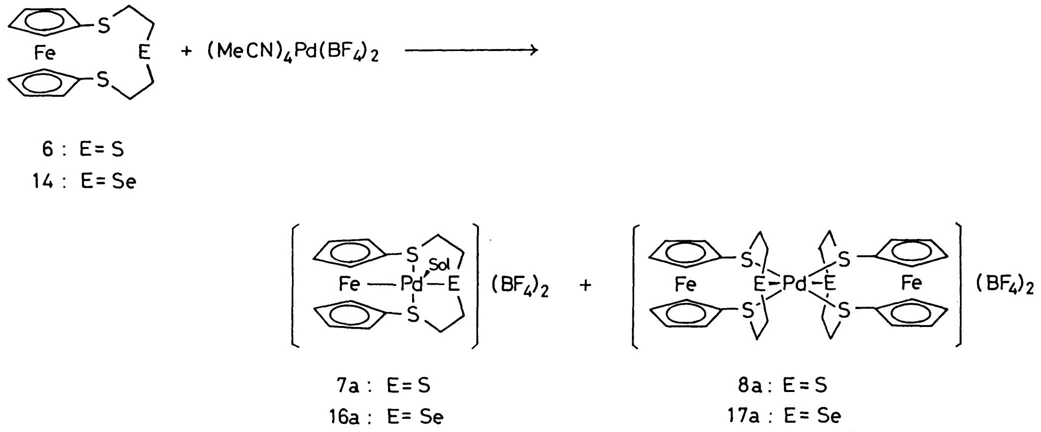
13 : E=Se

5a : E=S, M=Pd

5b : E=S, M=Pt

15a : E=Se, M=Pd

15b : E=Se, M=Pt



Dithiaselena[*n*](1,1′)ferrocenophanes could not be synthesized by the procedure used for preparing trithia[*n*](1,1′)ferrocenophanes. For example, 1,1′-bis(3-chloropropylthio)ferrocene (**9**) reacted with sodium selenide to give no desirable product. This failure seems to be due to the low nucleophilicity of sodium selenide compared with sodium sulfide. Thus, the chloride (**9**) was converted to 1,1′-bis(3-iodopropylthio)ferrocene (**11**) by treating **9** with sodium iodide in refluxing 2-butanone for 24 h. Similarly, 1,1′-bis(2-iodoethylthio)ferrocene (**12**) was obtained in good yield from 1,1′-bis(2-chloroethylthio)ferrocene (**10**). The reaction of the iodide **11** with an aqueous solution of sodium selenide[17] in refluxing THF under high-dilution conditions gave the desired product, 1,9-dithia-5-selena[9](1,1′)ferrocenophane (**13**), although in low yield. The ring closure of the iodide **11** using a thiourea method proceeded successfully to give a more sufficient yield. Thus, **11** was treated with thiourea in refluxing ethanol under high-dilution conditions, followed by the addition of 10% aqueous sodium hydroxide; then, refluxing continued for 4 h to give **13** in 33% yield along with the dimeric compound, 1,9,20,28-tetrathia-5,24-diselena[9,9](1,1′)ferrocenophane in 25% yield. In a similar fashion, 1,7-dithia-4-selena[7](1,1′)ferrocenophane (**14**) was synthesized as red plates in 25% yield from 1,1′-bis(2-iodoethylthio)ferrocene (**12**).

1,9-Dithia-5-selena[9](1,1′)ferrocenophane (**13**) reacted with $(CH_3CN)_4Pd(BF_4)_2$ in acetone to give a 1/1 complex (**15a**) as dark-green needles in good yield. The reaction of 1,7-dithia-4-selena[7](1,1′)ferrocenophane (**14**) with the same Pd(II) salt gave a 1/1 complex (**16a**) and a 2/1 complex (**17a**) in 54 and 31% yields, respectively. A platinum analog (**15b**) was successfully obtained from a treatment of **13** with $(CH_3CN)_4Pt(BF_4)_2$ in warm acetonitrile, but the reaction of the [7]ferrocenophane **14** with the same Pt(II) salt gave no isolable complex.

The out-of-plane bending vibration found in ferrocene at 815 $cm^{-1}$ moves to 851 $cm^{-1}$ in the ferricenium ion and is thus known to be a diagnostic probe for examining the oxidation state of the iron atom of ferrocene derivatives.[18] The frequencies of the Pd(II) complexes, **5a**, **7a**, **15a**, and **16a** (Table 1), were shifted to a higher wavenumber region than those of the corresponding free ligands and the $PdCl_2$ complexes. For example, the out-of-plane bending vibration of **5a** appeared at 844 $cm^{-1}$, while that of the corresponding free lignand and the $PdCl_2$ complex absorbed at 806 and 820 $cm^{-1}$, respectively.[12] Such a large shift of this band in **5a** to high wavenumber region suggests the occurrence of a strong perturbation in the iron atom of a ferrocene nucleus by the Pd(II) atom through the coordinated sulfur atoms and/or a direct Fe-Pd bonding interaction. In this connection, the frequency of the corresponding vibration is observed at 830 and 838 $cm^{-1}$ in the phosphine complex **2a** which is confirmed by X-ray analysis to have a weak dative Fe-Pd bond.[6,7] The platinum complexes, **5b** and **15b**, also exhibited a similar high wavenumber shift of the out-of-plane bending vibration, as shown in Table 1, indicating similar structural features to those in the palladium analogs, **5a** and **15a**. The ring size of the chalcogenomacrocycle moiety in the Pd(II) complexes exerted a significant influence on the out-of-bending vibration. Thus, the frequencies of the [7]ferrocenophane complexes, **7a** and **16a**, were observed at 830 $cm^{-1}$. The relatively low wavenumber frequency in **7a** and **16a** compared with that in **5a** and **15a** may suggest a weaker bonding

Table 1. Infrared (KBr) and Visible Spectral Data ($CH_3CN$)

| Compound | Out of bending vibration/$cm^{-1}$ | $\lambda_{max}$ /nm($\varepsilon$) |
|---|---|---|
| **4**[a] | 806 | 446 (211) |
| **6**[a] | 810 | 462 (349) |
| **13** | 810 | 448 (215) |
| **14** | 810 | 461 (249) |
| **5a** | 844 | 620sh (206), 444 (6240) |
| **7a** | 830 | 812 (2800), 408 (4300) |
| **15a** | 842 | 620sh (274), 448 (8730) |
| **16a** | 830 | 772 (2420), 408 (8410) |
| **5b** | 846 | 500 (309), 372 (5650) |
| **15b** | 844 | 500 (419), 372 (7610) |

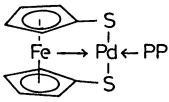
a) From Ref. 11.

interaction in [7]ferrocenophane complexes than that in [9]ferrocenophane complexes.

The $^1$H NMR spectrum of **15a** (400 MHz, $CD_3CN$) showed the ferrocenyl ring protons as narrow sextets at $\delta$ 5.95 and 6.09, and narrow quintets at $\delta$ 3.43 and 3.93. It has been previously shown that in monosubstituted ferrocenyl ring protons adjacent to the substituent (i.e. $\alpha$-protons) give a 1:2:2:2:1 multiplet pattern while internal protons (i.e. $\beta$-protons) give a 1:1:2:2:1:1 pattern.[19] We therefore assigned the signals at $\delta$ 3.43 and 3.93 to the $\alpha$-ring protons and the signals at $\delta$ 5.95 and 6.09 to the $\beta$-ring protons. The facts that in the 2D H,H-COSY experiment for **15a** the signals at $\delta$ 3.43 and 3.93 correlated strongly with the signals at $\delta$ 5.95 and 6.09, respectively, and that the latter signals also correlated strongly with each other, provide conclusive evidence for the assignment described above. It is noteworthy that the $\alpha$-ring protons in complex **15a** appears at a higher field than those of the corresponding free ligand ($\delta$ 4.23) and that the $\beta$-ring protons produce signals at a considerably low field. Generally, the $\alpha$- and $\beta$-protons of the ferrocenyl ring in the complexes coordinated to a metal atom through the heteroatoms at the 1,1′-positions shift to a lower field than those of the corresponding free ligand, and the $\alpha$-protons appear at a lower field than the $\beta$-protons.[5,11,12,20] The low-field shift can be elucidated by the magnetic anisotropy or the inductive effect of the metal halide.[5] The large separation between the $\alpha$- and $\beta$-proton signals of the ferrocenyl ring and the reversal of their chemical shifts observed in complex **15a** appear to be elucidated only by a magnetic anisotropy of a metal-metal bond between the iron atom of the ferrocene moiety and the Pd(II) atom incorporated in the chalcogenomacrocycle. A similar phenomenon concerning the ferrocenyl ring protons is also observed in complexes **2a** and **2b** which have dative Fe-Pd and Fe-Pt bonds in the molecule, respectively.[6–8] Complexes **5a**, **5b**, **7a**, **15b**, and **16a** also showed the same spectral features concerning the ferrocenyl ring protons, suggesting that these ferrocenophane complexes also have a structure containing an iron-metal bond. The replacement of one of the sulfur atoms in complex **5a** for a selenium atom (producing complex **15a**) exerts little influence on the spectral features of the ferrocenyl ring protons. In platinum complexes **5b** and **15b**, the chemical shifts of the $\alpha$- and $\beta$-proton signals of a ferrocenyl ring show no significant change compared with those in palladium complexes **5a** and **15a**. These results seem to indicate that the iron-metal bond in the [9]ferrocenophane complexes is little influenced by the kind of central metal or the kind of coordinating heteroatoms.

In the $^{13}$C NMR spectrum of palladium complex **15a**, the $\alpha$-ring carbons of a ferrocenyl ring were observed at $\delta$ 71.30 and 71.74 and the $\beta$-ring carbons appeared at $\delta$ 85.22 and 86.70. The assignment of these signals of the ferrocenyl ring carbon could be successfully performed by the C,H-COSY experiment. It has been reported that the coordination of $PdCl_2$ to 1,1′-bis(isobutylthio)ferrocene brings about a high-field shift of the bridge-head carbon signal ($\Delta$ 3.4 ppm), though little increase of the separation between the $\alpha$- and $\beta$-carbon signals of a ferrocenyl ring ($\Delta$ 0.8 ppm). On the other hand, complex **15a** showed a similar high-field shift of the bridge-head carbon signal compared to the corresponding free ligand **13** ($\Delta$ 4.6 ppm); however, the separation between the $\alpha$- and $\beta$-carbon signals is considerably increased upon complexation with $Pd(BF_4)_2$ ($\Delta$ ca. 13 ppm). The latter change is mainly due to the large low-field shift of the $\beta$-ring carbon signals of a ferrocenyl ring in complex **15a**. The deshielding of the $\beta$-carbons of a ferrocenyl ring appears to be in part responsible for the low-field shift of the $\beta$-proton signals in the $^1$H NMR spectrum of **15a** described above.

Cowie et al. proposed three canonical forms, I—III, in order to represent the bonding in the phosphine complex **2a**, and supposed that the actual structure may have significant contributions from all three resonance forms.[7] The $^1$H NMR spectra of **5** and **15** can afford some information concerning the structure of the present complexes. The deshielding of the $\beta$-protons compared with the $\alpha$-protons and the large separation between them found in the ferrocenyl moiety of **5** and **15** are similar to those in the ferrocenylmethylium ions [H($\alpha$), $\delta$ 4.72; H($\beta$), 6.23].[21,22] In the latter comounds, the contribution of a fulvene structure is considered for the substituted cyclopentadienyl ring, since the X-ray analysis shows that ferrocenyldiphenylmethylium tetrafluoroborate can be described as a fulvenecyclopentadienyl cation.[23] The similarity of the $^1$H NMR spectral features in **5** and **15** to that in the ferrocenylmethylium ions seems to suggest that the resonance forms corresponding to II and III contributed to the actual structure in complexes **5** and **15** much more than in complex **2a**. As mentioned previously, the $^{13}$C NMR spectra of complex **15a** showed a deshielding of the $\beta$-carbons in the ferrocenyl ring and large separation between $\alpha$- and $\beta$-carbon signals. Similarly, the low-field shift of the $\beta$-carbon signals compared with the $\alpha$-carbon signals of a ferrocenyl ring [C($\alpha$)=$\Delta$ 17.6 ppm and C($\beta$)=$\Delta$ 27.4 ppm) and the large separation between the $\alpha$- and $\beta$-carbon signals ($\delta$ 9.8 ppm) are observed when the carbon chemical shifts in ferrocenylmethylium ions are compared with those in the corresponding alcohols.[24,25] These facts may also support the sugges-



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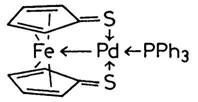

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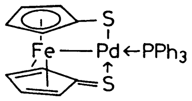

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Table 2. The $^1$H NMR Spectral Data (400 MHz, $CD_3CN$)

| Compound | Ring-H (δ) | Methylene-H(δ) |
|---|---|---|
| **5a** | 3.47 (m, 2H, $H_\alpha$), 4.02 (qu, 2H, $H_\alpha$), 5.98 (se, 2H, $H_\beta$), 6.12 (se, 2H, $H_\beta$) | 2.31 (qu, 2H, $H_3$), 2.52 (qu, 2H, $H_3$), 2.86 (dq, 2H, $H_2$), 3.09 (dq, 2H, $H_4$), 3.47 (m, 2H, $H_2$), 3.61 (dq, 2H, $H_4$) |
| **7a** | 3.65 (m, 2H, $H_\alpha$), 4.23 (m, 2H, $H_\alpha$), 5.29 (m, 2H, $H_\beta$), 5.58 (m, 2H, $H_\beta$), | 2.34 (m, 2H, $H_2$), 3.38 (m, 2H, $H_3$), 3.62 (m, 4H, $H_2$ and $H_3$) |
| **15a** | 3.43 (qu, 2H, $H_\alpha$), 3.93 (qu, 2H, $H_\alpha$), 5.95 (se, 2H, $H_\beta$), 6.09 (se, 2H, $H_\beta$) | 2.22 (m, 2H, $H_3$), 2.67 (m, 2H, $H_3$), 2.90 (m, 2H, $H_2$), 3.03 (m, 2H, $H_4$), 3.54 (m, 2H, $H_2$), 3.57 (m, 2H, $H_4$) |
| **16a** | 3.58 (m, 2H, $H_\alpha$), 4.10 (m, 2H, $H_\alpha$), 5.35 (m, 2H, $H_\beta$), 5.63 (m, 2H, $H_\beta$) | 2.27 (m, 2H, $H_2$), 3.45 (m, 2H, $H_3$), 3.68 (m, 2H, $H_3$), 4.01 (m, 2H, $H_2$) |
| **5b** | 3.66 (s, 2H, $H_\alpha$), 4.16 (m, 2H, $H_\alpha$), 5.95 (m, 2H, $H_\beta$), 6.16 (m, 2H, $H_\beta$) | 2.41 (m, 2H, $H_3$), 2.48 (m, 2H, $H_3$), 3.02 (m, 2H, $H_2$), 3.31 (m, 2H, $H_4$), 3.60 (m, 2H, $H_2$), 3.72 (m, 2H, $H_4$) |
| **15b** | 3.64 (m, 2H, $H_\alpha$), 4.11 (m, 2H, $H_\alpha$), 5.94 (m, 2H, $H_\beta$), 6.16 (m, 2H, $H_\beta$) | 2.48 (m, 4H, $H_3$), 3.07 (m, 2H, $H_2$), 3.21 (m, 2H, $H_4$), 3.68 (m, 4H, $H_2$ and $H_4$) |

The assignment of **5a**, **5b**, and **15b** was done tentatively according to that of **15a** and the proton signals of **7a** was assigned analogously in **16a**.
qu=quintet, se=sextet, dq=double quartet.

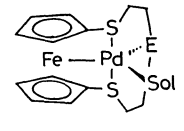
Table 3. The $^{13}$C NMR Spectral Data (100 MHz, $CD_3CN$)

| Compond | Ring-C (δ) | Methylene-C (δ) |
|---|---|---|
| **5a** | 71.63 ($C_\alpha$), 72.24 ($C_\alpha$), 85.01 ($C_b$), 85.65 ($C_\beta$), 87.33 ($C_\beta$) | 28.70 ($C_3$), 34.41 ($C_4$), 36.86 ($C_3$) |
| **7a** | 70.09 ($C_\alpha$), 72.00 ($C_\alpha$), 76.36 ($C_b$) 78.66 ($C_\beta$), 79.47 ($C_\beta$) | 39.89 ($C_3$), 41.31 ($C_2$) |
| **15a** | 71.30 ($C_\alpha$), 71.74 ($C_\alpha$), 82.20 ($C_b$), 85.22 ($C_\beta$), 86.70 ($C_\beta$) | 29.86 ($C_3$), 32.09 (t, $J$=55.1 Hz,[a] $C_4$), 35.23 ($C_2$) |
| **16a** | 69.88 ($C_\alpha$), 72.26 ($C_\alpha$), 75.13 ($C_b$), 79.49 ($C_\beta$), 80.06 ($C_\beta$) | 36.26 (t, $J$=48.5 Hz,[a] $C_3$), 41.31 ($C_2$) |
| **5b** | 70.83 ($C_\alpha$), 72.65 (t, $J$=13.0 Hz, $C_\alpha$), 79.80 ($C_b$), 86.27 ($C_\beta$), 86.98 ($C_\beta$) | 28,03 (t, $J$=86.7 Hz,[b] $C_3$), 35.45 (t, $J$=21.1 Hz,[b] $C_4$), 38.01 (t, $J$=29.6 Hz,[b] $C_2$) |
| **15b** | 70.71 ($C_\alpha$), 72.34 (t, $J$=13 Hz, $C_\alpha$), 77.53 ($C_b$), 86.09 ($C_\beta$), 86.68 ($C_\beta$) | 28.87 (t, $J$=85.1 Hz,[b] $C_3$), 33.42 (p, $J$=29.5,[b] and 53.6Hz, [a] $C_4$), 36.33 (t, $J$=20.6 Hz,[b] $C_2$) |

The assignment of the signals in **5a** and **5b** was undergone according to those in **15a** and **15b**. The signals in **7a** were assigned analogously in **16a**.
a) $^{13}$C-$^{77}$Se coupling constant. b) $^{13}$C-$^{195}$Pt coupling constant.

tion described above.

The $^1$H NMR spectra of the [7]ferrocenophane complexes, **7a** and **16a**, showed the same pattern of ring protons in a ferrocenyl moiety with that found in the [9]ferrocenophane complexes, as shown in Table 2. The separation between the α- and β-proton signals is somewhat small compared with that found in the [9]ferrocenophane complexes. This may partly reflect the decrease in the deshielding in the β-carbons of the ferrocenyl ring in complexes **16a**, as seen in the $^{13}$C NMR spectrum (Table 3). The β-carbon resonances in **16a** shift by ca. 6 ppm to a higher field than those in **15a**. These facts seem to suggest that there also exsists an Fe-Pd bond in the [7]ferrocenophane complexes, although it is somewhat weak compared with that in the [9]ferrocenophane complexes. A remarkable feature was observed in the region of the methylene protons of the $^1$H NMR spectra of the [7]ferrocenophane complexes, **7a** and **16a**. One of the protons attached to C(2) resonated at δ 4.01, the position of which is in a 0.47 ppm lower field than the corresponding proton in the [9]ferrocenophane complex, **15a**. The other proton attached to C(2) appeared at δ 2.27, the chemical shift of which is in a 0.63 ppm higher field than the corresponding proton in **15a**. This can probably be explained by the constrained structure of **16a**, in which one of the protons attached to C(2) is greatly imposed to be in the deshielding zone and the other in the shielding zone of ferrocene.[26] In such strained complexes, **7a** and **16a**, the Fe-Pd(II)-S angle can be no longer 180° because of the small ring size of the thiamacrocycle; thus, that the Pd(II) atom cannot assume a regular square-planar coordination. In these complexes, the distinct distortion from a square-planar (probably to a trigonal-bipyramidal coordination as shown in **18**) seems to



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occur in terms of a strong coordination of solvent molecules. The weakening of the Fe–Pd bond in the [7]ferrocenophane complexes seems to be probably due to a structural deformation, as mentioned above.

The visible spectrum of the [9]ferrocenophane complex, **5a**, exhibited one strong absorption at 444 nm ($\varepsilon$ 6240) and one weak shoulder at 620 nm ($\varepsilon$ 206), while the free ligand **4** showed an absorption maximum at 446 nm ($\varepsilon$ 211). The square-planer $Pd(BF_4)_2$ complexes of 2,6,10,14-tetrathiapentadecane[15] and 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane[27] showed no absorption above 380 nm.[28] Therefore, either of the two absorptions seems to relate to the Fe–Pd bonding interaction. A similar absorption pattern, as seen in **5a**, was also observed in the phosphine complex, **2a**, which has a dative Fe–Pd bond, although the absorption peaks somewhat shift to a long-wavelength region.[6,7] As shown in Table 1, the replacement of one sulfur atom of trithiamacrocycle in complexes **5** for a selenium atom had no influence on the electronic absorption of the [9]ferrocenophane complexes, while the absorption maxima in the Pt analog **5b** shifted to a short-wavelength compared with those in the Pd analog, **5a** [Δ ca. 70 nm]. A similar blue shift was observed in the phosphine complex, **2b**. The electronic spectra of the [7]ferrocenophane complexes, **7a** and **16a**, were considerably different from those of the [9]ferrocenophane complexes, **5a** and **15a**, respectively. The most remarkable difference was, for example, the appearance of a large and broad band at 812 ($\varepsilon$ 2800) in **7a**. A similar band near 800 nm was also observed in the oxidized 1,5,7-trithia[7]ferrocenophane [$\lambda_{max}$ 850 nm ($\varepsilon$ 1150) and 752 nm ($\varepsilon$ 955)]. This may suggest that complex **7a** contains a contribution from the ferricenium cation structure, which is generated through an intramolecular redox reaction, as seen in similar copper complexes.[29] However, this is not the fact, since **7a** afforded a clear $^1H$ NMR spectrum. The absorption in the long-wavelength region may be caused by the distorted coordination manner described above.

The Mössbauer spectral data of complexes **5a** and **7a**, along with those of the related complexes, are summarized in Table 4. The QS value of **5a** is similar to that of the corresponding free ligand **4**, while a considerably large QS value was obtained in the $HgCl_2$ adducts (**3**) of [2](1,1′)ferrocenophane.[9] This may suggest that there is no substantial metal-metal bonding interaction between the Fe atom in the ferrocene moiety and the Pd(II) atom coordinated to the thiamacrocycle. However, only a small decrease of the QS value was obtained in the bisthiolate complex **2a**, in which a weak Fe–Pd dative bond was confirmed by X-ray analysis.[6,7] It may also be worth noting that an increased IS value was observed, especially at low temperature, in complexes **2a**, **5a**, and **7a**, in which a metal-metal bonding interaction was assumed. Anyway, at the present stage, no definite conclusion seems to be derived from the Mössbauer parameter.

Table 4. The Mössbauer Spectral Data

| Compound | Conditions | IS/mm s$^{-1}$ | QS/mm s$^{-1}$ |
|---|---|---|---|
| **4** | R.T. | 0.43 | 2.36 |
| **4**$^+$ $BF_4^-$ | R.T. | 0.45 | 0.72 |
| **5a** | R.T. | 0.49 | 2.36 |
|  | Liq. $N_2$ | 0.57 | 2.39 |
| **7a** | R.T. | 0.50 | 2.10 |
| **2a** | R.T. | 0.48 | 1.99 |
|  | Liq. $N_2$ | 0.53 | 2.03 |

## Experimental

The melting point was measured by using a differential scanning calorimeter (SEIKO DSC-20). The IR spectra were taken by a Hitachi 750-20 Infrared Spectrometer. The electronic spectra were measured by a Shimadzu UV-2000 Spectrometer. The $^1H$ and $^{13}C$ NMR spectra were taken by a Bruker AM 400 or GEOL FX-90Q Spectrometer, using TMS as an internal standard.

1,1′-Bis(3-chloropropylthio)ferrocene,[16] 1,1′-bis(2-chloroethylthio)ferrocene,[16] 1,5,9-trithia[9](1,1′)ferrocenophane (**4**),[12] 1,4,7-trithia[7](1,1′)ferrocenophane (**6**),[16] dichlorobis(acetonitrile)palladium(II) and -platinum(II)[15] were prepared according to the literature. Silver(I) tetrafluoroborate and selenourea were commercially available.

**(1,5,9-trithia[9](1,1′)ferrocenophane-*S,S′,S″,Fe*)palladium(II) Tetrafluoroborate (5a).** To a solution of dichlorobis(acetonitrile)palladium(II) (0.16 g, 0.6 mmol) in dry acetone (15 cm$^3$) was added silver(I) tetrafluoroborate (0.25 g, 1.3 mmol). The mixture was stirred for 1 h and the resulting silver(I) chloride was filtered off. To the filtrate, 1,5,9-trithia[9](1,1′)ferrocenophane (**4**) (0.22 g, 0.6 mmol) was added and then the solution was stirred for 1 h. The resulting brown crystals were collected by filtration to give the title compound (**5a**) containing one equivalent of acetone as dark-brown needles (0.30 g, 73%), mp 250 °C. Found: C, 32.33; H, 3.72%. Calcd for $C_{16}H_{20}B_2F_8S_3FePd \cdot C_3H_6O$: C, 32.48; H, 3.73%. The complex was recrystallized from acetonitrile–diethyl ether to give **5a** containing one equivalent of acetonitrile as black needles, mp 250 °C. Found: C, 31.64; H, 3.41; N, 1.89%. Calcd for $C_{16}H_{20}B_2F_8S_3FePd \cdot C_2H_3N$: C, 31.54; H, 3.38; N, 2.04%.

**(1,4,7-Trithia[7](1,1′)ferrocenophane-*S,S′,S″,Fe*)palladium(II) Tetrafluoroborate (7a).** A mixture of dichlorobis(acetonitrile)palladium(II) (0.26 g, 1 mmol) and silver(I) tetrafluoroborate (0.40 g, 2.1 mmol) was stirred for 1 h at room temperature and then filtered to remove the resulting silver(I) chloride. To the filtrate diluted with dry acetone (50 cm$^3$) was added a solution of 1,4,7-trithia[7](1,1′)-ferrocenophane (**6**) (0.34 g, 1 mmol) in dry acetone (50 cm$^3$) dropwise for a period of 30 min. The mixture was stirred for 1 h and then filtered. A green powder (55 mg, 12%) of bis(1,4,7-trithia[7](1,1′)ferrocenophane-*S,S′,S″*)palladium(II) tetrafluoroborate (**8a**) was obtained. Mp 250 °C. Found: C, 34.95; H, 3.53%. Calcd for $C_{28}H_{32}B_2F_8S_6Fe_2Pd$: C, 35.30; H, 3.39%. IR (KBr): 3120, 2976, 1418, 946, 900, 888, 824, 538, 528, 504, and 488 cm$^{-1}$. VIS ($CH_3CN$): $\lambda_{max}$ 380sh and 784 nm (log$\varepsilon$ 2.7). $^1$H NMR (90 MHz, $CD_3CN$): $\delta$=3.32—3.92 (m, 16H, $CH_2S$), 4.50 (m, 12H, ring-H), and 4.65 (m, 4H, ring-H). The filtrate was evaporated under reduced pressure and then the residue was dissolved in acetone (5 cm$^3$). The resulting solution was diluted with dry diethyl ether (2.5 cm$^3$) and kept in a freezer to give the title complex **7a** containing one equivalent of acetone as fine black needles, mp 250 °C. Found: C, 30.49; H, 3.38%. Calcd for $C_{14}H_{16}B_2F_8S_3FePd\cdot C_3H_6O$: C, 30.27; H, 3.29%.

**1,1′-Bis(3-iodopropylthio)ferrocene (11).** A mixture of sodium iodide (2.24 g, 14.9 mmol) in methyl ethyl ketone (40 cm$^3$) was refluxed for 1 h under nitrogen. To the resulting solution was added 1,1′-bis(3-chloropropylthio)ferrocene (2.00 g, 4.96 mmol). The mixture was then refluxed for 8 h under nitrogen and cooled to room temperature. The mixture was filtered and the precipitate was washed with methyl ethyl ketone (20 cm$^3$). The filtrate and the washing were combined and washed with water (60 cm$^3$), 5% sodium thiosulfate solution (20 cm$^3$), 5% sodium hydrogencarbonate (20 cm$^3$), and water (20 cm$^3$), and then dried over anhyd $MgSO_4$. The solution was evaporated under reduced pressure and the residue was chromatographed on silica gel by elution of hexane-toluene (2 : 1). The title compound (**11**) was obtained as yellow plates (2.66 g, 91%) after recrystallization from ethanol-hexane, mp 49.5—51.5 °C. Found: C, 32.65; H, 3.44%. Calcd for $C_{16}H_{20}I_2S_2Fe$: C, 32.79; H, 3.44%. MS (75 eV): $m/z$ 586 (M$^+$, 100%). IR (KBr): 3076, 2952, 1448, 1422, 1390, 1318, 1238, 1166, 1022, 900, 824, 724, 572, 528, 512, and 456 cm$^{-1}$. $^1$H NMR (90 MHz, $CDCl_3$): $\delta$=1.98 (p, $J$=6.8 Hz, 4H, $CH_2$), 2.66 (t, $J$=6.8 Hz, 4H, $SCH_2$), 3.25 (t, $J$=6.8 Hz, 4H, $CH_2I$), and 4.27 (m, 8H, ring-H).

**1,1′-Bis(2-iodoethylthio)ferrocene (12).** To a solution of sodium iodide (4.07 g, 27.2 mmol) in methyl ethyl ketone (40 cm$^3$), prepared as described above, was added 1,1′-bis(2-chloroethylthio)ferrocene (1.50 g, 4.00 mmol). The mixture was refluxed for 16 h under nitrogen. After the reaction had been completed, the resulting yellow crystals were collected by filtration. The filtrate was washed with water (80 cm$^3$), 10% sodium thiosulfate solution (20 cm), 5% sodium hydrogencarbonate solution (20 cm$^3$), and water (40 cm$^3$), and then dried over anhyd $MgSO_4$. After evaporation, the residue was chromatographed on silica gel by elution of hexane-toluene (1 : 1). The title compound (**12**) was obtained as yellow plates (mp 136—139 °C). The yield was 1.62 g (72.6%) in all. Found: C, 30.13; H, 2.89%. Calcd for $C_{14}H_{16}I_2S_2Fe$: C, 30.31; H, 2.90%. MS (75 eV): $m/z$ 558 (M$^+$, 100%). IR (KBr): 3076, 1414, 1162, 896, 816, 726, 566, 504, and 454 cm$^{-1}$. $^1$H NMR (90 MHz, $CDCl_3$): $\delta$=2.96 (dd, $J$=6.6 and 1.8 Hz, 4H, $SCH_2$), 3.20 (dd, $J$=6.6 and 1.8 Hz, 4H, $SCH_2$), 3.20 (dd, $J$=6.7 and 1.8 Hz, 4H, $CH_2I$), and 4.30 (m, 8H, ring-H).

**1,9-Dithia-5-selena[9](1,1′)ferrocenophane (13).** A mixture of 1,1′-bis(3-iodopropylthio)ferrocene (**11**) (1.00 g, 1.7 mmol) and selenourea (0.21 g, 1.7 mmol) in ethanol (50 cm$^3$) was refluxed under nitrogen for 4 h. To the solution diluted with ethanol (800 cm$^3$) was added 10% aqueous sodium hydroxide (1.8 cm$^3$) under refluxing; the solution was then refluxed for 4 h. After evaporation, the residue was dissolved in benzene (100 cm$^3$). The solution was washed with water (60 cm$^3$) and dried over anhyd $MgSO_4$. The solution was then condensed under reduced pressure and chromatographed on silica gel by elution of hexane-toluene (2 : 1) to give the title compound (**13**) as red crystals (0.26 g, 37%) after recrystallization from ethanol-hexane, mp 62.0—62.5 °C. Found: C, 47.02; H, 4.94%. Calcd for $C_{16}H_{20}S_2SeFe$: C, 46.73; H, 4.90%. IR (KBr): 3092, 2928, 1418, 1290, 1222, 1158, 1024, 882, 810, 516, and 472 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=2.16 (p, $J$=6.9 Hz, 4H, $CH_2$), 2.89 (t, $J$=6.7 Hz, 4H, $CH_2Se$), 3.09 (t, $J$=7.0 Hz, 4H, $CH_2S$), and 4.22 (s, 8H, ring-H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$=23.30 (t, $J$=62.4 Hz, $SeCH_2$), 30.47 ($CH_2$), 34.85 ($SCH_2$), 67.88 ($C_\beta$), 71.37 ($C_\alpha$), and 86.87 ($C_b$).

**1,7-Dithia-4-selena[7](1,1′)ferrocenopahne (14).** A mixture of 1,1′-bis(2-iodoethylthio)ferrocene (**12**) (0.10 g, 0.18 mmol) and selenourea (25 mg, 0.20 mmol) in tetrahydrofuran (30 cm$^3$) was refluxed for 3 h under nitrogen. To the solution diluted with tetrahydrofuran (70 cm$^3$) was added 10% aqueous sodium hydroxide (1.5 cm$^3$) under refluxing; the solution was then refluxed for 1 h. After evaporation, the residue was disolved in benzene (50 cm$^3$). The solution was washed with water (50 cm$^3$) and dried over anhyd $MgSO_4$. After evaporating the solvent, the residue was chromatographed on silica gel by elution of hexane-toluene (2 : 1) to give the title compound (**14**) as red-orange plates (16 mg, 24%) after recrystallization from hexane-toluene, mp 116.5 °C. Found: C, 44.07; H, 4.27%. Calcd for $C_{14}H_{16}S_2SeFe$: C, 43.88; H, 4.21%. IR (KBr): 3096, 3080, 2916, 1416, 1380, 1260, 1160, 1050, 1022, 890, 846, 810, 526, 504, and 474 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=3.17 (dd, $J$=7.2 and 6.0 Hz, 4H, $CH_2Se$), 3.46 (dd, $J$=7.2 and 6.0 Hz, 4H, $CH_2S$), 4.26 (t, $J$=1.8 Hz, 4H, $H_\alpha$), and 4.31 (t, $J$=1.8 Hz, 4H, $H_\beta$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$=24.91 (t, $J$=67.9 Hz, $SeCH_2$), 37.99 ($SCH_2$), 67.87 ($C_\beta$), 71.29 ($C_\alpha$), and 89.24 ($C_b$).

**(1,9-Dithia-5-selena[9](1,1′)ferrocenopahane-*S,S′,Se,Fe*)palladium(II) Tetrafluoroborate (15a).** A mixture of dichlorobis(acetonitrile)palladium(II) (26 mg, 0.1 mmol) and silver(I) tetrafluoroborate (40 mg, 0.2 mmol) in acetone (2 cm$^3$) was stirred for 1 h at room temperature and then filtered to remove the resulting silver(I) chloride. To the filtrate was added a solution of 1,9-dithia-5-selena[9](1,1′)ferrocenophane (41 mg, 0.1 mmol) in dry acetonitrile (5 cm$^3$); the solution was then stirred for 1 h at room temperature. The solution was evaporated under reduced pressure and the residue was then dissolved in acetonitrile (5 cm$^3$). The resulting dark-brown solution was diluted with dry diethyl ether and kept in a freezer overnight to give the title compound (**15a**) containing one equivalent of acetonitrile as black needles, mp 250 °C. Found: C, 29.76; H, 3.24; N, 1.94%. Calcd for $C_{16}H_{20}B_2F_8S_2SePd\cdot C_2H_3N$: C, 29.52; H, 3.16; N, 1.91%.

**(1,7-Dithia-7-selena[7](1,1′)ferrocenophane-*S,S′,Se,Fe*)palladium(II) Tetrafluoroborate (16a).** To a solution of palladium(II) tetrafluoroborate [prepared as described above and then diluted with dry acetone (20 cm$^3$)], a solution of 1,7-dithia-4-selena[7](1,1′)ferrocenophane (38 mg, 0.1 mmol) in dry acetone (10 cm$^3$) was added dropwise for a period of 10 min. After the solution was stirred for 1 h the resulting crystals were filtered. A green powder (16 mg, 31%) of bis(1,7-dithia-4-selena[7](1,1′)ferrocenophane-*S,S′*)palladium(II) tetrafluoroborate (**17a**) was obtained. Mp 250 °C. Found: C, 32.37; H, 3.02%. Calcd for $C_{28}H_{32}B_2F_8S_4Se_2Fe_2Pd$: C, 32.13; H, 3.08%. IR (KBr): 3116, 2996, 2944, 1416, 1258, 1084, 926, 886, 830, 528, 486, and 456 cm$^{-1}$. After the filtrate was evaporated under reduced pressure, the residue was dissolved in dry acetonitrile (5 cm$^3$). The resulting solution was diluted with dry diethyl ether (5 cm$^3$) and kept in a freezer overnight to give the title compound (**16a**) containing one equivalent of acetonitrile as black fine needles, mp 250 °C. Found: C, 27.44; H, 2.74; N, 2.37%. Calcd for $C_{14}H_{16}B_2F_8S_2SeFePd \cdot C_2H_3N$: C, 27.28; H, 2.71; N, 1.98%.

**(1,5,9-Trithia[9](1,1′)ferrocenophane-*S,S′,S″,Fe*)-platinum Tetrafluoroborate (5b).** A mixture of dichlorobis(acetonitrile)platinum(II) (35 mg, 0.1 mmol) and silver(I) tetrafluoroborate (40 mg, 0.2 mmol) in dry acetonitrile (5 cm$^3$) was refluxed for 2 h under nitrogen. To the resulting mixture was added a solution of 1,5,9-trithia[9](1,1′)-ferrocenophane (36 mg, 0.1 mmol) in dry acetonitrile (5 cm$^3$). The mixture was refluxed for 1 h and then filtered to remove silver(I) chloride. The filtrate was evaporated under reduced pressure; then, the residue was dissolved in dry acetone-acetonitrile (4:1 v/v, 5 cm$^3$). The resulting solution was filtered and the filtrate was diluted with dry diethyl ether (2 cm$^3$) to give the title compound **5b** as red needles (53 mg, 73%), mp 250 °C. Found: C, 26.42; H, 2.76%. Calcd for $C_{16}H_{20}B_2F_8S_3FePt$: C, 26.21; H, 2.75%.

**(1,9-Dithia-5-selena[9](1,1′)ferrocenophane-*S,S′,Se,Fe*)-platinum(II) Tetrafluoroborate (15b).** This compound was prepared from 1,9-dithia-5-selena[9](1,1′)ferrocenophane (41 mg, 0.1 mmol) according to the procedure described above. The title compound (**15b**) was obtained as red needles (55 mg, 70%), mp 250 °C. Found: C, 24.27; H, 2.54%. Calcd for $C_{16}H_{20}B_2F_8S_2SeFePt$: C, 24.63; H, 2.58%.

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