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Complexes of Polythia[n](1,1')ferrocenophanes with $Pd(BF_4)_2$. A Fe-Pd Dative Bond Formation Controlled by the Coordination of the Pd(II) Atom to the Sulfur Atoms of the Thiamacrocycle

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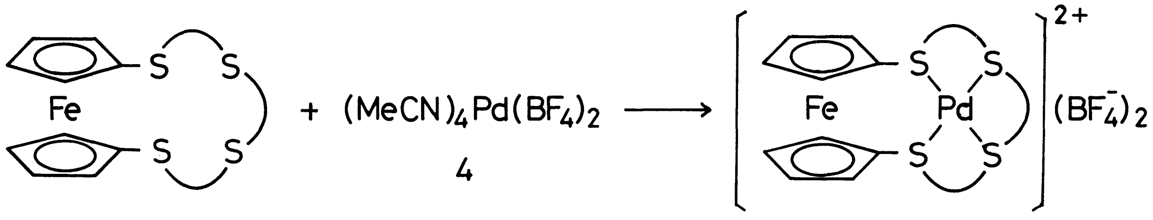
Tetrathia- and trithia[n]ferrocenophanes formed 1:1 complexes with $Pd(BF_4)_2$. The spectral data proved the presence of a Fe-Pd bonding interaction for the Pd(II) complexes of 1,5,9-trithia[9]- and 1,4,7-trithia[7](1,1')ferrocenophanes.

The iron atom of ferrocene is capable of being a Lewis base and a potential coordination site. It has been recently confirmed by the Mössbauer spectra that the $HgCl_2$ adducts of ferrocene1) and [2]ferrocenophane2) have a Fe-Hg bond. Seyferth et al.3) showed the presence of a dative bond in (1,1'-ferrocenedithiolato-S,S',Fe)-(triphenylphosphine)palladium(II) (**1**) by X-ray analysis. Analogous platinum(II) complex (**2**)4) was also reported. We here report the synthesis of the complexes between polythia[n](1,1')ferrocenophanes and $Pd(BF_4)_2$ and the metal-metal interaction controlled by the ring size and the number of sulfur atoms in the thiamacrocycle moiety of the ferrocenothiacrown ligands.

1,4,7,10-Tetrathia[10](1,1')ferrocenophane (**3a**)5) reacted with $(CH_3CN)_4Pd(BF_4)_2$ (**4**), which was prepared from $(CH_3CN)_2PdCl_2$ and $AgBF_4$,6) in acetone-acetonitrile, followed by dilution with anhydrous ether, to give a 1:1 complex (**5a**) as dark green needles in 52% yield. In a similar manner, 1,4,8,11-tetrathia[11]- (**3b**), 1,5,8,12-tetrathia[12]- (**3c**), and 1,5,9,13-tetrathia[13]-ferrocenophanes (**3d**) gave the corresponding 1:1 complexes **5b**, **5c**, and **5d** in moderate or good yield, respectively. The complex **5b** contained one equivalent of acetonitrile in the crystal. The IR spectra of the complexes showed the out of bending vibration, which was the most diagnostic of the oxidation state of ferrocene,7) at 824, 826, 818, and 818 cm^{-1} for **5a**, **5b**, **5c** and **5d**, respectively. The frequencies are somewhat higher than those of the corresponding free ligands and the differences of the frequency between the Pd(II) complexes **5a**-**5d** and the corresponding free ligands **3a**-**d** were 24, 16, 2, and 6 cm^{-1},

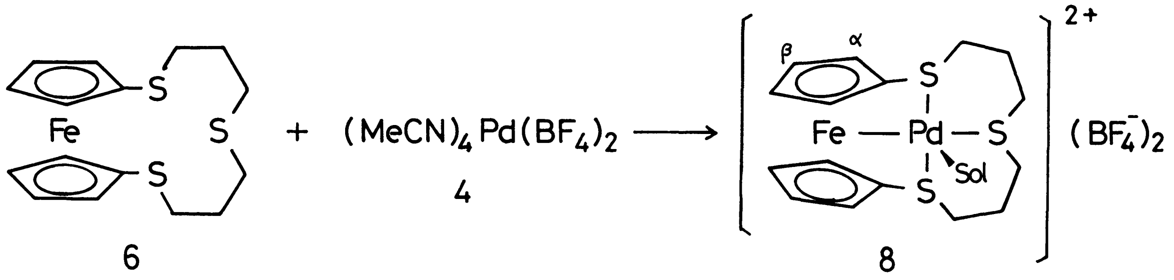


3a-d

5a-d

respectively. The out of vending vibration was observed at 830 and 838 cm^{-1} in the phosphine complex **1**, and at 846 cm^{-1} in the ferricenium cation of **3d**.[8] These results suggest that there may be a little interaction between the iron atom of the ferrocene moiety and the incorporated Pd(II) atom, especially in the complexes **5a-b**. In the ^{1}H-NMR spectrum of **5a**, the Cp ring protons all shifted down-field as compared with those of the free ligand **3a** and appeared separately as four multiplets at δ 5.68, 5.34, 4.87, and 4.57. This suggests that the electron density of the ferrocene ring in **5a** is decreased by the coordination through the sulfur atoms to a strong Lewis acidic $Pd(BF_4)_2$[9] and the Pd(II) atom is forced out of the basal plane made by the four sulfur atoms to form an unsymmetric circumstance toward the ferrocene ring protons. The complex **5b** showed a similar pattern to that of **5a** for the Cp ring proton signals of a ferrocene moiety. The ^{1}H-NMR spectrum (90 MHz, CD_3CN) of **5d** showed the Cp ring protons as a triplet and a broad multiplet at δ 5.26 and 4.78 in the down-field compared with those of the ligand **3d**, respectively. This symmetric pattern of the Cp ring protons is explained by the incorporation of the Pd(II) atom into the center of the thiamacrocycle or a fast interconversion of the unsymmetric structures as seen in **5a**. The Cp ring protons in **5c** resonated essentially in a similar manner to that of **5d**. The indication from the ^{1}H-NMR spectra that the complexes **5a** and **5b** has a rigid and unsymmetric structure and the large down-field shift (δ 1.41-0.30 ppm) of the Cp ring protons compared with that ($\Delta\delta$ 0.46-0.03 ppm) of the corresponding $PdCl_2$ complexes[10] may suggest a certain interaction between the iron atom of a ferrocene moiety and the Pd(II) atom coordinated to the sulfur atoms of the thiamacrocycle. As described above, the IR and ^{1}H-NMR spectra of **5a** and **5b** is clearly different from those of **5c** and **5d**. Furthermore, a broad absorption band was observed near 600 nm in the electronic spectra of **5a-5d** and it showed a bathochromic shift according with the decreasing ring size of the thiamacrocycle moiety: **5a**, 670 nm (ε 499); **5b**, 612 nm (ε 245); **5c**, 604 nm (ε 376); **5d**, 572 nm (ε 113). As a similar absorption was observed in the complex of 1,4,7-trithiacyclononane with $Pd(BF_4)_2$ but its intensity is weak (575 nm, ε 50),[11] this absorption band rather seems to relate with the metal-metal interaction in the complexes **5a-d**. From these facts, the strength of the metal-metal interaction is likely supposed to be controlled by the size of the thiamacrocycle moiety of the free ligands **3a-d**.

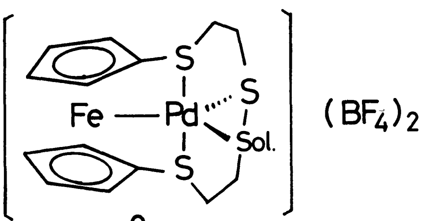
1,5,9-Trithia 9 ferrocenophane (**6**)[12] reacted in acetone with $(CH_3CN)_4Pd(BF_4)_2$ to precipitate a 1:1 complex (**8**) as dark brown fine needles in 73% yield. When 1,4,7-trithia[7]ferrocenophane (**7**) was treated similarly, a black 1:1 complex (**9**) and a green powdery 2:1 complex (**10**) were isolated in 74 and 12% yields, respectively. The complexes **8** and **9** contained one equivalent of acetone in the crystal. On



recrystallization of them from acetonitrile-ether the complexes contain acetonitrile in place of acetone. In the ^{13}C-NMR spectra of **8** and **9**, the downfield shift of the methylene carbons next to the sulfur atoms, compared with the free ligand **6** and **7**, was observed [3.0 and 3.3 ppm in **8**, and 5.7 and 7.0 in **9**], indicating the coordination of all the three sulfur atoms to the Pd(II) atom in both **8** and **9**. In the IR spectra of **8** and **9**, the out of bending vibration appeared at 844 and 830 cm^{-1}, respectively. These frequencies were shifted to a higher wave-number region than those of the free ligands **6** and **7** (806 and 810 cm^{-1}) and the corresponding $PdCl_2$ complexes (820 and 828 cm^{-1})$^{12)}$ and were close to the corresponding frequency (830 and 838 cm^{-1}) of the phosphine complex **1** in which a Fe-Pd dative bond was confirmed by X-ray analysis.$^{3)}$ However, they are in a lower wave-number region than those of the corresponding ferricenium cations (846 and 846 cm^{-1}).$^{8)}$ These facts suggest that in the complexes **8** and **9** there is a strong bonding interaction similar to that in **1** between the iron atom of the ferrocene nucleus in the ligands and the Pd(II) atom coordinated to the sulfur atoms in the thiamacrocycle moiety.

The ^{1}H-NMR spectra (300 MHz, acetone-d_6) of **8** and **9** showed a dramatic change in the region of the Cp ring protons, compared with that of complexes **5a-d**. The β-protons of the ferrocene ring in **8** shifted largely down-field and the α-protons shifted up-field compared with those of the free ligand **6**. That is, the β-protons appeared as a pair of triple doublets (J=2.9 and 1.4 Hz) at δ 6.13 and 5.99, and the α-protons appeared as a pair of double triplets (J=2.9 and 1.4 Hz) at δ 4.01 and 3.48. Such a large separation of the chemical shifts of the α- and β-protons of the Cp rings in the ferrocene nucleus of **8** seems to be explained$^{4)}$ only by the anisotropy of the metal-metal bond between the Fe atom of a ferrocene nucleus and the Pd(II) atom coordinated to the sulfur atoms in the thiamacrocycle, because the similar large separation was observed in **1**$^{3)}$ and its Pt analogs **2**.$^{4)}$ That is, the Pd(II) atom in **8** seems to be sitting inside the thiamacrocycle in order to make a dative Fe-Pd bond and to adopt a square-planar coordination. However, both α- and β-protons of **8** consisted of two separate signals. In agreement with this, the ^{13}C-NMR spectrum (22.5 MHz, CD_3CN) of **8** showed two pairs of the Cp ring carbon signals [85.1, 83.1, 72.3, and 71.6 ppm]. These results indicate that the complex **8** is unsymmetrical concerning the plane made by the S(1)-Fe-S(9) atoms and the Pd(II) atom is somewhat forced out of the basal plane made by the three sulfur atoms and the iron atom of the ferrocene nucleus. This is also supported by the fact that the methylene protons appeared as three pairs; δ 3.62 and 3.48 (ddd, J=13.9, 8.4, and 1.7 Hz), 3.09 and 2.86 (ddd, J=13.4, 7.7, and 3.0 Hz), and 2.54 and 2.31 (m, CH_2).

The similar large separation of the chemical shifts of the α- and β-protons of the ferrocene ring was also observed in the ^{1}H-NMR spectrum of **9**. The α-protons appeared as a pair of triple doublets (J=2.9 and 1.4 Hz) at δ 5.62 and 5.34, while the β-protons appeared as a pair of double triplets (J=2.9 and 1.4 Hz) at 4.30 and 3.76. The presence of the dative Fe-Pd bond is likely supposed by the separation of the chemical shifts between the α- and β-protons of the ferrocene ring similarly as described above, but the magnitude of the separation in



9

9 is smaller by ca. 1.0 ppm than that in **8**, suggesting a weaker Fe-Pd bonding in the former. The thiamacrocycle moiety in **9** also seems to adopt a rigid conformation, because the methylene protons, which appeared as a symmetrical A_2B_2 pattern at δ 3.0-3.5 (90 MHz, $CDCl_3$) in **7**, showed an unsymmetrical signal pattern [δ 2.44 (broad dd, 2H), 3.39 (dt, J= 13.2 and 3.6 Hz, 2H), and 3.39 (m, 4H)]. The signal at δ 2.44 is probably assigned to the proton on the carbons next to the sulfur atoms attached to the ferrocene nucleus. The abnormal shift of the present proton singal to the upper field seems to be due to that the proton is imposed to be in the shielding zone (over the Cp rings of ferrocene)[13)] because of the rigid conformation of the thiamacrocycle moiety. The Pd(II) atom in **9** can sit no longer in the center of the thiamacrocycle moiety in **7** because of its small ring size, so that the Pd(II) atom cannot take a regular square-planar coordination by the three sulfur atoms of the thiamacrocycle moiety and the iron atom of the ferrocene moiety. In this complex, the distinct distortion from a square-planar (probably to a bipyramidal coordination) seems to take place in terms of a strong coordination of solvent (acetonitrile or acetone), although the dative Fe-Pd bond still remains.

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