November, 1986] © 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 3611—3615 (1986) 3611

The Preparation and Some Properties of 1,4,7-Trithia[7]- and 1,5,9-Trithia[9]ferrocenophanes and Their Copper(I), Silver(I), Mercury(II), and Palladium(II) Complexes

Masaru Sato,* Kaoru Suzuki, and Sadatoshi Akabori†
Chemical Analysis Center, Saitama University, Urawa, Saitama 338
†Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274

(Received May 27, 1986)

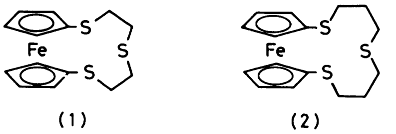
1,5,9-Trithia[9]ferrocenophane was prepared by the reaction of 1,1′-bis(3-chloropropylthio)ferrocene with sodium sulfide. The complexes of 1,5,9-trithia[9]ferrocenophane, along with 1,4,7-trithia[7]ferrocenophane, with copper(I), silver(I), mercury(II), and palladium(II) salts were prepared. Some interaction between the iron atom and the metal atoms coordinated to the thia-crown moiety was suggested from their spectral data in the solution for the complexes of 1,4,7-trithia[7]ferrocenophane with mercury(II) and palladium(II) salts and the complex of 1,5,9-trithia[9]ferrocenophane with silver(I) tetrafluoroborate.

Much attention was focused on the metal–metal interaction existing between metallocenes and metal cations from the viewpoints of biochemical and catalytic interests.[1,2] Ferrocene has been known to form an unstable complex with mercury(II) salts,[3] while [2]Ferrocenophanes, in which the two cyclopentadienyl rings are tilted by 20° because of their shorter bridging, can form more stable 1:1 complexes with mercury(II) chloride[4] and tin(IV) chloride,[5] since a direct metal–metal interaction is present as revealed by their Mössbauer spectra. Recently, dative Fe–Pd and Fe–Pt bonds have been confirmed by X-ray analyses of (1,1′-ferrocenedithiolato-S,S,Fe)(triphenylphosphine) palladium(II)[6] and platinum(II).[7] In regard to these results, we now report on the preparation and various properties of 1,4,7-trithia[7]- (**1**) and 1,5,9-trithia[9]-ferrocenophanes (**2**) and their copper(I), silver(I), mercury(II), and palladium(II) complexes.

Results and Discussion

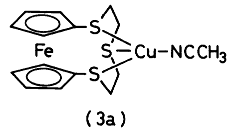
Synthesis of 1,5,9-Trithia[9]ferrocenophane (2). It has been reported that 1,4,7-trithia[7]ferrocenophane was prepared by the reaction of 1,1′-bis(2-chloroethylthio)ferrocene with sodium sulfide.[8] In a similar manner, 1,5,9-trithia[9]ferrocenephane (**2**) was prepared in 53% yield by refluxing a mixture of 1,1′-bis(3-chloropropylthio)ferrocene and sodium sulfide in ethanol–tetrahydrofuran (THF). The structure was determined by an elemental analysis and spectral data. Thus, the molecular formula of **2** was deduced to be $C_{16}H_{20}S_3Fe$ by an elemental analysis and by the mass spectrum (M^+ m/z 364). In the ^{1}H NMR spectrum of **2**, the α- and β-ring protons of the cyclopentadienyl rings (Cp-rings) appeared as a singlet (8H) at δ 4.23, while the methylene protons next to the sulfur atoms resonated as two triplets at δ 3.10 and 2.82 and the other methylene protons as a quintet at δ 2.02. The ^{13}C NMR spectrum of **2** showed a bridge-head carbon as well as α- and β-carbons at 88.8, 71.8, and 68.3 ppm, respectively. Specific spectral behavior observed in the electronic and ^{13}C NMR spectra of 1,4,7-trithia[7]-ferrocenophane (**1**)[9] was not observed in the present ferrocenophane.

Copper(I) Complexes. A solution of **1** and $(CH_3CN)_4CuBF_4$ was refluxed in acetonitrile for 1 h and then diluted with diethyl ether to give the copper(I) complex **3a** in good yield. The copper(I) perchlorate complex **3b** was similarly obtained by a reaction of **1** with $(CH_3CN)_4CuClO_4$ in acetonitrile. An elemental analysis showed that **3a** was a 1:1 complex of **1** with $CuBF_4$, containing one equivalent of acetonitrile in the crystal. The IR spectrum of **3a** showed the absorption characteristic of a coordinated



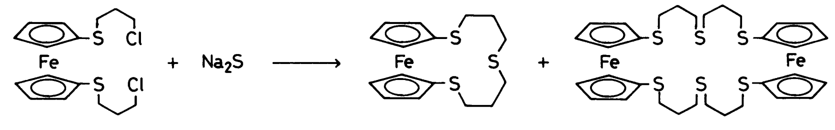
(1) (2)

Fig. 1.



(3a)

Fig. 3.



(2)

Fig. 2.

cyano group at 2256 cm^{-1}. From the IR spectrum of the perchlorate complex **3b**, it appears that an intermediate between a free and covalently bounded perchlorate anion was present owing to the appearance of three well-defined maxima in the region between 1200 and 1000 cm^{-1}.[10] Upon considering a stereo-model of **1** it was found that the size of the ferrocenothiacrown ring is too small to allow the inclusion of the Cu(I) ion (r_{ion} 0.96 Å)[11] into the center of the trithia-macrocycle. Moreover, it was confirmed by an X-ray analysis that the Cu(I) ion in the 1,4,8,11-tetrathiacyclotetradecane with $CuClO_4$ had a tetrahedral configuration.[12] From these facts and the IR spectra, it is suggested that the copper(I) ion in complex **3** is coordinated by the three sulfur atoms of ligand **1** and the nitrogen atom of acetonitrile or the oxygen atom of a perchlorate anion in the crystal of complex **3**. On the other hand, in the ^{1}H NMR spectrum of **3a**, the signals of the Cp-rings and the methylene protons appeared as multiplets centered at δ 4.37 and 3.13, respectively, indicating the presence of a symmetrical structure. This view was supported by the ^{13}C NMR spectrum of **3a**, which showed only three Cp-ring carbon signals at 91.1 (C_b), 69.8 (C_α), and 69.0 (C_β). The appearance of symmetrical signals for the Cp-rings in a solution of **3** seems to be due to a rapid dissociative equilibrium to afford an averaged spectra. Small changes in the IR, ^{13}C NMR ($\Delta\delta$ −1.9 and +0.2 ppm in α- and β-carbons, respectively), and electronic spectral data [hypsochromic shift ($\Delta\lambda$ 14 nm) and a decreased absorbance ($\Delta\varepsilon$ 155) in the 440 nm-band] when going from the free ligand **1** to the metal complex **3a** may suggest that the ferrocene moiety of complex **3** is little influenced by the Cu(I) ion coordinated to the sulfur atoms of the thia-crown moiety. Such a small perturbation was also observed in the tetrathia[*n*]ferrocenophane series.[13]

Table 1. Visible Spectral Data of **1**—**9** in Acetonitrile

Compd	$\lambda_{\max}$ (ε)
1	462 (349)
3a	448 (194)
3b	448 (211)
4	450 (246)
6	458 (280)
8	558 (403), 410 (832)
2	446 (211)
5	448 (226)
7	449 (170)
9	552 (809), 388 (2200)

Ag(I) Complexes. A solution of **1** in acetonitrile was added to a solution of silver(I) tetrafluoroborate in acetonitrile; the solution was then diluted with anhydrous diethyl ether to give the 1:1 complex **4** in good yield. In a similar manner, the 1:1 complex **5** was obtained from **2** and $AgBF_4$. An elemental analysis confirmed that **5** contained one equivalent of acetonitrile in its crystal form. The IR spectrum showed a C≡N stretching vibration at 2260 cm^{-1}. In the ^{1}H NMR (Table 2) and the electronic spectra (Table 1), negligible differences were observed between ligand **1** and complex **4**. In the ^{13}C NMR spectrum of **4**, rather small up-field shifts of the α- ($\Delta\delta$ 2.1) and β-carbons ($\Delta\delta$ 0.2) of the Cp-rings were observed. These spectral data suggest two possible coordinations: (i) the silver(I) ion is coordinated to only the sulfur atom (S-4) farthest from the ferrocene nucleus of ligand **1**; (ii) complex **4** is in a rapid equilibrium with the free ligand **1** and $AgBF_4$ in acetonitrile. In any case, the interaction between the ferrocene nucleus and the Ag(I) ion in **4** was negligible. Also, complex **5** exhibited similar features regarding the electronic spectrum, but showed a specific behavior regarding the ^{1}H NMR spectrum. That is, the H-3 and H-7 signals appeared at δ 2.83 as multiplets and the H-4 and H-6 signals at δ 1.74 as multiplets. These chemical shifts are nearly comparable with the corresponding values of the free ligand **2**. However, the signals of the Cp-ring protons

Table 2. ^{1}H NMR Spectral Data of **1**—**9** in CD_3CN

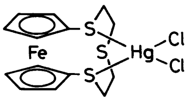
Compd	Ring-H	SCH_2	CH_2
1	4.33(t, J=1.3 Hz, 4H), 4.25(t, J=1.3 Hz, 4H)	3.5—2.9(A_2B_2 pattern, 8H)	
3a	4.37(m, 8H)	3.13(m, 8H)	
3b	4.37(m, 8H)	3.14(s, 8H)	
4	4.37(broad s, 8H)	3.18(m, 8H)	
6[a)]	ca. 5.3 (extremely broad, 12H)	2.81(m, 4H)	
8[b)]	4.81(m, 2H), 4.60(m, 2H), 4.43(m, 4H)	3.0—3.7(m, 8H)	
2	4.23(s, 8H)	3.10(t, J=7.1 Hz), 2.82(t, J=6.8 Hz, 4H)	2.02(m, 4H)
5	ca. 6.3 (extremely broad, 8H)	2.83(m, 4H)	1.74(m, 4H)
7[c)]	4.32(broad s, 8H)	3.23(t, J=7.4 Hz, 4H), 2.85(t, J=6.8 Hz, 4H)	2.04(m, 4H)
9[b)]	4.85(m, 1H), 4.50(m, 3H), 4.28(m, 4H)	2.7—3.3(m, 8H), 1.9—2.5(m, 4H)	

a) at 70 °C, b) in DMSO-d_6, c) at 60 °C.

and H-2 and H-8 shifted down-field (δ ca. 6.3) and collapsed to become extremely broad. This phenomenon can be understood as resulting from the scanty appearance of the unpaired electrons on the Cp-ring carbons as well as the C-2 and C-8 by means of a partial electron transfer from the iron atom of the ferrocene nucleus to the coordinated Ag(I) ion in intermediate **5a**, which may lie in the rapid equilibrium (Scheme 1). In a solution of **5** in acetonitrile, at least, the silver(I) ion seemed to be incorporated into the center of the thia-crown or located near the iron atom of the ferrocene nucleus of **5**.

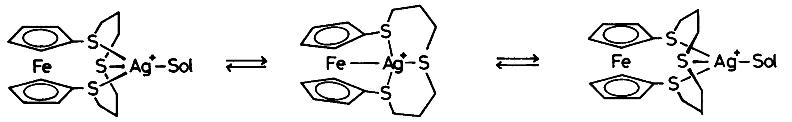
Hg(II) Complexes. A solution of mercury(II) chloride in anhydrous diethyl ether was added to a solution of **1** in anhydrous diethyl ether to give the 1 : 1 complex **6** as dark-red crystals in good yield. In the same manner, a 1 : 1 complex **7** was obtained from **2** and $HgCl_2$ as red-orange cubes in good yield. As can be seen in Tables 1 and 3, the electronic and IR spectra of **6** and **7** are similar to those of the free ligands **1** and **2**, respectively. The octahedral coordination of the Hg(II) ion in a 1 : 1 complex of 1,4,8,11-tetrathiacyclotetradecane with $HgCl_2$ was suggested from its IR spectrum;[14] an X-ray analysis has confirmed that the coordination about the Hg(II) atom is approximately tetrahedral in the 1 : 2 complex of 1,4,8,11-tetrathiacyclotetradecane with $HgCl_2$.[15] The Hg(II) ion (r_{ion} 1.10 Å)[10] does not seem to be incorporated into the smaller thia-macrocycle of **6** and **7** than that of 1,4,8,11-tetrathiacyclotetradecane. Therefore, a structure in which the Hg(II) atom coordinates to only the sulfur atoms attached to a ferrocene nucleus in the thia-maclocycle is suggested. In the ^{1}H NMR spectrum (70 °C) of **7** in acetonitrile-d_3, the Cp-ring protons appeared as a symmetrically broad singlet and shifted down-field (Δδ 0.09), suggesting the same reason given for the Ag(I) complexes. On the other hand, the ^{1}H NMR spectrum (60 °C) of **6** in CD_3CN showed features that were similar to those observed in a silver(I) complex **5**: The Cp-ring protons and H-2 and H-6 collapsed and shifted down-field (δ ca. 6.3). This suggests some type of interaction between the iron atom and the Hg(II) atom coordinated to the thia-macrocycle moiety in the solution, as described for complex **5**.

Palladium(II) Complexes. Compound **1** reacted with dichlorobis(acetonitrile)palladium(II) in hot acetonitrile to give the 1 : 1 complex **8** as black crystalline powder in good yield. Compound **2**, on the other hand, gave two products: black crystals **9** and black violet powder **10** in a similar manner. The former was confirmed to be a 1 : 1 complex by an elemental analysis. The IR spectra of **8**—**10** showed absorption at 330—315 cm^{-1}, the region for *cis*-$PdCl_2$ moieties.[16] The ^{1}H NMR spectrum of **8** in DMSO-d_6 showed three multiplets at δ 4.81 (2H), 4.61 (2H), and



(6)

Fig. 4.



Scheme 1.

Table 3. IR Spectral Data of **1**—**10** (KBr disk)

Compd	ν_{max}/cm^{-1}
1	3100, 2924, 1418(s), 1160, 1050, 1024, 890, 846, 810(s), 524, 502, 472(s)
3a	3088, 3060, 2944, 2912, 2256(w), 1424(s), 1414(s), 1158, 1140—1030(vs), 940(w), 890(s), 840(s), 806(s), 540, 512, 490, 480
3b	3084, 3060, 2944, 2912, 1414(s), 1144(vs), 1116(vs), 1082(vs), 1030, 890(s), 940, 840, 832, 816, 804, 624(s), 540, 510, 488, 480
4	3092, 2924, 2904, 1430(s), 1420(s), 1160, 1120—1030(vs), 892, 806(s), 526(s), 498, 480
6	3096, 2924, 1416(s), 1160, 1032, 1020, 884(w), 808(s), 508(s), 474(s)
8	3084, 2924, 1432, 1414, 1406, 1162, 1154, 1032, 1020, 888, 820(s), 526, 488, 480, 342(w), 306(s)
2	3088, 2920, 2900, 1430(s), 1420(s), 1264, 1160, 1026, 892, 806(s), 798(s), 526(s), 498(s), 480(s)
5	3088, 2920, 2260(vw), 1418(s), 1160, 1120—1020(vs), 892, 882, 810(s), 526(s), 514(s), 496, 482
7	3120, 3100, 2924, 1412(s), 1262, 1158, 1026(s), 890, 880, 812(s), 514(s), 480(s)
9	3076, 2984, 2948, 1444(m), 1436(m), 1386, 1030, 1020, 880, 840, 828(s), 818(s), 520(s), 490, 476(s), 338, 320(s), 298
10	3088, 2924, 1620, 1416(s), 1254, 1164, 1030(s), 888, 826(s), 516(s), 480(s), 358, 319

Table 4. Mössbauer Parameters of **2**—**9**

Compd	*IS*	*QS*
2	0.43	2.36
3	0.44	2.31
4	0.43	2.33
5	0.44	2.34
6	0.47	2.44
7	0.46	2.39
8	0.45	2.29
9	0.42	2.34

(**8**) (**9**)

Fig. 5.

4.43 (m, 4H) for the Cp-ring protons, indicating a strong coordination of $PdCl_2$ to the sulfur atoms at 1 and 7 positions on one side of the thiamacrocycle in **1** and no intervention of the dissociative equilibrium in the solution observed in the Cu(I), Ag(I), and Hg(II) complexes. On the other hand, in the ^1H NMR spectrum of **9** in DMSO-d_6, the Cp-ring protons appeared at δ 4.85 (m, 1H), 4.50 (m, 3H), and 4.28 (m, 4H). This pattern of the Cp-ring protons can probably be rationalized by the coordination of a $PdCl_2$ moiety to the sulfur atoms at 1 (or 9) and 5 positions in **9**. Compounds **8** and **9** were very insoluble in most organic solvents. As the complexes of 1,1′-bis(alkylthio)ferrocene with $PdCl_2$ are soluble in a polar solvent,[17] a possibility that the present $PdCl_2$ complexes have a polymeric structure cannot be ruled out. Complex **10** gave an unsatisfactory elemental analysis as a 1 : 1 complex and a rather broad IR spectrum, suggesting a polymeric product.

Mössbauer Spectra. ^{57}Fe Mössbauer spectral data can give useful information about the state of an iron atom in various complexes. The IS and *QS* values of the free ligand **2** and the metal complexes **4**—**9** are summarized in Table 4. A large change in the *QS* value was observed in complexes of [2]ferrocenophanes with mercury(II)[4] and tin(IV) chlorides,[5] in which a direct interaction between the iron atom of a ferrocene nucleus and the metal atoms was suggested on the basis of their Mössbauer spectra. The negligible change observed here is within the limits of the difference in the packing mode of the crystal, suggesting that the metal atoms coordinated to the polythia-crown moiety in the trithia[*n*]ferrocenophanes **1** and **2** exert little interaction on the iron atom of a ferrocene nucleus in the solid state. A similar change was also observed in the metal complexes of tetrathia[*n*]ferrocenophanes[13] and the complex of 1,1′-bis(diphenylphosphino)ferrocene with $HgCl_2$.[18]

Experimental

The melting points are uncorrected. The IR spectra were taken on a Hitachi 270-50 Infrared Spectrometer. The ^1H and ^{13}C NMR spectra were measured on a JEOL FX-90Q Spectrometer, TMS being chosen as the standard material. The electronic spectra were taken on a Hitachi 340 spectrometer. The Mass spectra were measured on a Hitachi M-80B spectrometer.

Materials. 1,4,7-Trithia[7]ferrocenophane (**1**) was previously reported.[8] Mercury(II) chloride, silver(I) tetrafluoroborate, and copper(II) tetrafluoroborate hydrate were commercially available. Tetrakis(acetonitrile)copper(I) perchlorate[19] and dichlorobis(acetonitrile)palladium(II)[20] were prepared according to methods described in the literature.

1,5,9-Trithia[9]ferrocenophane (2). Sodium sulfide nonahydrate (3.6 g, 15 mmol) was dissolved in ethanol (650 cm^3). To the solution was added a solution of 1,1′-bis(3-chloropropylthio)ferrocene[8] (2.0 g, 5 mmol) in tetrahydrofuran (120 cm^3). The mixture was refluxed for 24 h under a nitrogen atmosphere. After evaporation under reduced pressure, the residue was dissolved in water. The mixture was extracted with benzene and the extract was dried over anhyd sodium sulfate. After evaporation under reduced pressure, the residue was chromatographed on silica gel by the elution of hexane-toluene (1:1) and, subsequently, toluene. The following products were separated.

1,5-Dithia[5]ferrocenophane.[9] Yield 28 mg (1.9%).

1,5,9-Trithia[9]ferrocenophane (2). Red orange crystals, mp 69—70 °C (recrystallization from cyclohexane). Yield 0.96 g (53%). Found: C, 52.74; H, 5.74%. Calcd for $C_{16}H_{20}S_3Fe$: C, 52.74; H, 5.53%. MS: *m/z* 364 (M^+). ^{13}C NMR ($CDCl_3$) 87.5 (C_b), 71.2 (C_α), 67.7 (C_β), 33.9 (SCH_2), 31.1 (SCH_2), and 29.6 (CH_2).

1,5,9,21,25,29-Hexathia[9.9]ferrocenophane. Yellow orange needles, mp 102—103 °C (recrystallization from benzene). Yield 0.32 g (8.6%). Found: C, 52.77; H, 5.60%. Calcd for $C_{32}H_{40}S_6Fe_2$: C, 52.74; H, 5.53%. MS: *m/z* 728 (M^+). IR (KBr): 3080, 1418, 1190, 1022, and 810 cm^{-1}. ^1H NMR ($CDCl_3$) δ=4.34 (t, J=1.6 Hz, 4H), 4.28 (t, J=6.8 Hz, 4H), 2.74 (t, J=6.8 Hz, 4H), 2.63 (t, J=7.5 Hz, 4H), and 1.83 (p, 4H).

(1,4,7-Trithia[7]ferrocenophane)copper(I) Perchlorate (3b). To a solution of **1** (34 mg, 0.1 mmol) in hot anhyd acetonitrile (2 cm^3) was added tetrakis(acetonitrile)copper(I) perchlorate (33 mg, 0.1 mmol). After tetrakis(acetonitrile)-copper(I) perchlorate had been dissolved, the solution was filtered. The filtrate was diluted with anhyd diethyl ether (5 cm^3) to form orange crystals. After the mixture had been kept for 2 h in a refrigerator, the crystals were collected by filtration. Orange needles. Yield 36 mg (72%). This compound was very explosive on heating. ^{13}C NMR ($CDCl_3$) 69.8 (C_α), 69.2 (C_β), 37.0 (SCH_2), and 34.9 (SCH_2).

(1,4,7-Trithia[7]ferrocenophane)copper(I) Tetrafluoroborate (3a). Copper(II) tetrafluoroborate hydrate (18 mg, 0.075 mmol) and excess copper powder were refluxed in anhyd acetonitrile (5 cm^3) for 1 h under nitrogen and then the mixture was filtered. To the filtrate was added **1** (50 mg, 0.15 mmol) and the mixture was refluxed for 0.5 h. After being cooled to room temperature, the solution was diluted with anhyd diethyl ether (20 cm^3) to form orange crystals. The mixture was kept overnight in a refrigerator, and the resulting crystals were collected by filtration. Orange needles (63 mg, 86.4%), mp ~230 °C (decomp). Found: C, 36.56; H%, 3.53%. Calcd for $C_{14}H_{16}BF_4S_3FeCu \cdot CH_3CN$: C, 36.42; H, 3.63%. ^{13}C NMR (CD_3CN) 91.1 (C_b), 69.8 (C_α), 69.0 (C_β), 36.9 (SCH_2), and 35.0 (SCH_2).

(1,4,7-Trithia[7]ferrocenophane)silver(I) Tetrafluoroborate (4). To a hot solution of **1** (34 mg, 0.1 mmol) in acetonitrile (2 cm^3) was added to a hot solution of silver(I) tetrafluoroborate (20 mg, 0.1 mmol) in acetonitrile (1 cm^3). The resulting solution was filtered and the filtrate was diluted with anhyd diethyl ether (10 cm^3). The solution was kept overnight in a refrigerator. The title compound **4** (43 mg, 81%) was obtained as yellow orange needles, mp 195 °C (decomp). Found: C, 31.61 H, 2.99%. Calcd for $C_{14}H_{16}BF_4S_3FeAg$: C, 31.67; H, 3.04%. ^{13}C NMR (CD_3CN) 91.3 (C_b), 69.6 (C_α), 68.6 (C_β), 35.3 (SCH_2), and 32.5 (SCH_2).

(1,5,9-Trithia[9]ferrocenophane)(acetonitrile)silver(I) Tetrafluoroborate (5). To a solution of **2** (100 mg, 0.27 mmol) in anhyd acetonitrile (7 cm^3) was added a solution of silver(I) tetrafluoroborate (53 mg, 0.27 mmol) in anhyd acetonitrile (3 cm^3). The resulting dark red-brown solution was filtered and then diluted with anhyd diethyl ether (35 cm^3). After the solution had been kept in a refrigerator, the resulting crystals were collected by filtration. The complex **5** (108 mg, 66%) was obtained as yellow plates, mp 115 °C (decomp). Found: C, 36.06; H, 3.97%. Calcd for $C_{16}H_{20}BF_4FeAg \cdot C_2H_3N$: C, 36.03; H, 3.86%.

Dichloro(1,4,7-Trithia[7]ferrocenophane)mercury(II) (6). To a solution of **1** (68 mg, 0.2 mmol) in anhyd diethyl ether (4 cm^3) was added a solution of mercury(II) chloride (55 mg, 0.2 mmol) in anhyd diethyl ether (4 cm^3). The solution was stirred for 15 min. The resulting crystals were collected by filtration. Light orange crystals (104 mg, 85%), mp 121 °C (decomp). Found: C, 28.02; H, 2.58%. Calcd for $C_{14}H_{16}Cl_2S_3FeHg$: C, 27.67; H, 2.65%.

Dichloro(1,5,9-trithia[9]ferrocenophane)mercury(II) (7). To a solution of **2** (200 mg, 0.55 g) in anhyd diethyl ether (25 cm^3) was added a solution of mercury(II) chloride (136 mg, 0.5 mmol) in anhyd diethyl ether (20 cm^3). The solution was refluxed for 30 min and then kept overnight in a refrigerator. The title compound **7** (257 mg, 81%) was obtained as red fine crystals, mp 115—116 °C (decomp). Found: C, 30.29; H, 3.46%. Calcd for $C_{16}H_{20}Cl_2FeHg$: C, 30.22; H, 3.17%.

Dichloro(1,4,7-trithia[7]ferrocenophane)palladium(II) (8). To a solution of **1** (36 mg, 0.1 mmol) in hot acetonitrile (5 cm^3) was added a solution of dichlorobis(acetonitrile)-palladium(II) (26 mg, 0.1 mmol) in hot acetonitrile (5 cm^3). The solution was kept for 1 h at room temperature. The resulting crystals were collected by filtration. Greenish black crystals (41 mg, 80%), mp~300 °C. Found: C, 32.95; H, 3.15%. Calcd for $C_{14}H_{16}Cl_2S_3FePd$: C, 32.74; H, 3.15%.

Dichloro(1,5,9-trithia[9]ferrocenophane)palladium(II) (9). To a solution of **2** (180 mg, 0.5 mmol) in hot acetonitrile (20 cm^3) was added a solution of dichlorobis(acetonitrile)-palladium(II) (130 mg, 0.5 mmol). The solution was kept overnight in a refrigerator. The resulting violet fine powder (**10**) was collected by filtration. Yield: 105 mg (39%). Mp ~250 °C. Found: C, 33.77; H, 3.65%. Calcd for $(C_{16}H_{20}Cl_2S_3FePd)_n$: C, 35.48; H, 3.72%.

The filtrate was kept for several days in a freezer. The resulting black-brown crystals were filtered and washed with acetonitrile. Yield 102 mg (38%). Mp 235 °C (decomp). Found: C, 35.71; H, 3.72%. Calcd for $C_{16}H_{20}Cl_2S_3FePd$: C, 35.48; H, 3.71%.

We thank Prof. Izumi Motoyama and Prof. Motomi Katada for measurement of Mössbauer spectra. The present work was supported by a Grant-in-Aid for Science Research (No. 61540362) from the Ministry of Education, Science and Culture.

References

1) M. I. Bruce, *J. Organomet. Chem.*, **242**, 147 (1983).

2) W. R. Cullen and J. D. Woollins, *Coord. Chem. Rev.*, **39**, 1 (1981).

3) R. M. G. Roberts, J. Silver, and I. G. Harrison, *J. Organomet. Chem.*, **209**, 385 (1981).

4) M. Watanabe, H. Ichikawa, I. Motoyama, and H. Sano, *Bull. Chem. Soc. Jpn.*, **56**, 3291 (1983).

5) M. Watanabe, H. Ichikawa, I. Motoyama, and H. Sano, *Chem. Lett.*, **1983**, 1009.

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

7) S. Akabori, T. Kumagai, T. Shirashige, S. Sato, K. Kawazoe, C. Tamura, and M. Sato, unpublished data.

8) 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).

9) M. Sato, S. Tanaka, S. Ebine, K. Morinaga, and S. Akabori, *J. Organomet. Chem.*, **282**, 247 (1985).

10) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, **1961**, 3091.

11) F. A. Cotton and G. Willkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York (1966), p. 44.

12) E. R. Dockal, L. L. Diaddario, M. D. Glick, and D. B. Rorabacker, *J. Am. Chem. Soc.*, **99**, 4530 (1977).

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

14) D. Sevdic and H. Meider, *J. Inorg. Nucl. Chem.*, **39**, 1409 (1977).

15) N. W. Alcock, N. Herron, and P. Moore, *J. Chem. Soc., Dalton Trans.*, **1978**, 394.

16) G. E. Coats and C. Parkins, *J. Chem. Soc.*, **1963**, 421.

17) B. McCulloch, D. L. Ward, J. D. Woolins, and C. H. Brubacker, Jr., *Organometallics*, **4**, 1428 (1985).

18) K. P. Mann, W. H. Morrison, and D. N. Hendrickson, *Inorg. Chem.*, **13**, 1180 (1974).

19) P. Hemmerich and C. Sigwart, *Experimentia*, **19**, 488 (1963).

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