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Copper(I), Silver(I), Mercury(II), and Palladium(II) Complexes of Tetrathia[*n*]ferrocenophanes

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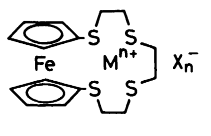
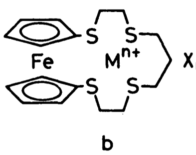
The complexes of a series of macrocyclic tetrathioether ligands containing a ferrocene nucleus in the macrocycle, tetrathia[*n*]ferrocenophanes, with copper(I), silver(I), mercury(II), and palladium(II) salts were prepared and characterized. The stability of complexes seems to depend on the size of the macrocycles in tetrathia[*n*]ferrocenophanes. The interaction between the iron atom of a ferrocene nucleus and the metal ions incorporated in the macrocycles seems to be negligible in these complexes.

Much attention has recently been focused on organo heterobimetallic compounds from the catalytic and biochemical points of view.[1,2] An organometallic ligand can be an important starting material for preparing heterobimetallic complexes. It is well-known that sulfide ligands make stable complexes with soft metals,[3] and many complexes of the macrocyclic thioether with various metal salts were prepared and characterized.[4–9] The iron atom of ferrocene is a potential coordinate site and certain ferrocene derivatives can form complexes with metal salts.[10,11] We prepared a new type of macrocyclic thioether ligand containing a ferrocene nucleus; polythia[*n*]-[12] and oxathia[*n*]ferrocenophanes.[13] The complex of the latter with silver(I) nitrate was isolated and characterized.[13] We now report on the systematic preparation and some properties of the complex of tetrathia[*n*]ferrocenophanes (**1a—d**) with copper(I), silver(I), mercury(II), and palladium(II) salts.



a



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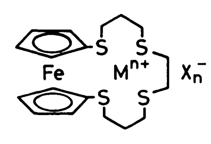
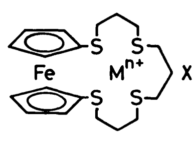


c



d

1. $M^{n+} = X_n^- =$ none
2. $M^{n+} = Cu^+$ $X_n^- = ClO_4^-$
3. $M^{n+} = Ag^+$ $X_n^- = ClO_4^-$
4. $M^{n+} = Hg^{2+}$ $X_n^- = Cl_2^-$
5. $M^{n+} = Pd^{2+}$ $X_n^- = Cl_2^-$

Results and Discussion

Copper(I) Perchlorate Complexes. The addition of anhydrous diethyl ether to a solution of tetrathia[*n*]ferrocenophanes (**1a—d**) and copper(I) perchlorate in acetonitrile afforded the 1:1 complexes (**2a—d**), respectively. The ^{1}H NMR spectra of these complexes (Table 1) shows the proton signals of the Cp-rings at δ ca. 4.4 as a broad singlet or a pair of triplets in acetonitrile-d_3. In the ^{13}C NMR spectra of **2a—d**, the α- and β-carbon signals appeared only as a pair of singlets (Table 2), indicating that complexes

Table 1. ^{1}H NMR Spectral Data of the Ligands **1** and the Complex **2—5** in Acetonitrile-d_3

Compd	Ring-H	SCH$_2$
1a	4.27(s, 8H)	2.85(m, 4H), 3.14(m, 4H), 3.06(s, 4H)
2a	4.42(m, 8H)	2.85—3.25(m, 8H), 3.08 (s, 4H)
3a	4.44(t, 4H), 4.36(t, 4H)	3.13(s, 8H), 3.07(s, 4H)
4a	4.47(s, 8H)	3.4—3.0(m, 8H), 3.20(s, 4H)
5a	4.45(m, 2H), 4.37(m, 6H)	3.8—3.0(m, 12H)a)
1b	4.25(s, 8H)	3.14(m, 4H), 2.85(m, 4H), 2.81(t, 4H)
2b	4.45(m, 8H)	3.2—2.9(m, 8H), 2.84(t, 4H)
3b	4.42(m, 8H)	3.3—2.9(m, 12H)
4b	4.34(bs, 8H)	3.23(m, 4H), 2.88(m, 4H), 2.83(t, 4H)
1c	4.25(s, 8H)	2.92(t, 4H), 2.80(t, 4H), 2.82(s, 4H)
2c	4.59(t, 4H), 4.47(t, 4H)	2.90(t, 4H), 2.72(t, 4H), 3.04(s, 4H)
5c	4.71(m, 2H), 4.28(m, 6H)	3.8(m, 12H)a)
1d	4.24(s, 4H)	2.89(t, 4H), 2.78(t, 4H), 2.62(t, 4H)
2d	4.51(m, 8H)	2.92(m, 12H)
4d	4.32(bs, 8H)	2.99(t, 8H), 2.74(t, 4H)

a) in DMSO-d_6.

2a—**d** have a symmetrical structure. However, it was confirmed by an X-ray analysis[14] that the Cu(I) atom had a tetrahedral coordination in the complex of 1,4,8,11-tetrathiacyclotetradecane with copper(I) perchlorate, although it was supposed[15] to be located in the central hole of a complex of 1,5,9,13-tetrathiacyclohexadecane with copper(I) tetrafluoroborate. Therefore, the appearance of symmetrical signals for the Cp-rings in the NMR spectra of **2a**—**d** seems to be due to a rapid dissociative equilibrium since in more coordinatable solvents (e.g. dimethyl-d_6 sulfoxide) complexes are completely dissociated to give NMR spectra of the corresponding free ligands. The IR spectra of **2a**—**d** (Table 3) showed a strong and broad band at 1140—1060 cm^{-1} and a sharp medium-strength band at about 620 cm^{-1}, indicating that there was only an uncoordinated perchlorate anion in the complexes.[16] A C–S–C medium-strength stretching vibration mode of the free ligand **1a**—**d** appeared near 680 cm^{-1}, but disappeared in **2b**—**d**. This suggests a considerably strong coordination of sulfur atoms to the copper(I) atom. In the ^{13}C NMR spectra (Table 2), complexes **2** showed a down-field shift of the α- and β-ring carbon signals, compared with the corresponding free ligands. The electronic spectra of **2** (Table 4) showed a hypsochromic shift and a decreased absorbance of the 440 nm band, assigned to the d–d transition.[17] These spectral data may suggest

Table 2. ^{13}C NMR Spectral Data of **1**—**4** in CD_3CN (22.5 MHz, ppm)

Compd	C_b[a]	C_α	C_β	Others
1a	87.3	73.0	70.2	39.2, 33.9, 32.5
2a	—	74.9	71.7	40.4, 36.2, 35.2
3a	82.9	73.5	71.8	36.2, 32.9, 32.5
1b	87.4	72.9	70.2	38.0, 33.2, 32.3, 31.0
2b	—	78.2	72.7	40.6, 35.4, 32.6, 24.6
3b	82.4	75.0	71.9	37.5, 35.1, 33.6
1c	86.6	73.7	70.2	35.9, 33.4, 31.3, 30.7
2c	—	77.6	73.0	41.2, 35.3, 32.1, 26.1
1d	86.4	73.7	70.2	36.0, 31.9, 31.8, 31.4, 30.7
2d	—	76.5	73.1	40.7, 35.4, 35.1, 25.9, 25.6

a) C_b means a bridge-head carbon.

Table 3. IR Spectral Data of **2**—**5** (KBr disk)

Compd	Frequency/cm^{-1}
2a[a]	3054m, 2860m, 1410s, 1384w, 1262s, 1140—1060vs, 1023s, 881m, 821s, 813s, 703w, 682w, 618s, 505s, 493s
2b	3050w, 2872w, 1412s, 1385w, 1256s, 1140—1065vs, 1027s, 885m, 817s, 621s, 502s, 484s
2c	3078m, 2906s, 1413s, 1385m, 1255m, 1140—1070vs, 1024s 888s, 813s, 623s, 503s, 480s
2d	3038m, 2866s, 1412s, 1384w, 1250s, 1150—1060vs, 1022s, 942m, 887m, 812s, 623s, 502s
3a	3046w, 2886m, 1412s, 1385m, 1257s, 1150—1065vs, 1024s, 882m, 810s, 684m, 623s, 512s, 493s, 480s
3b	3074w, 2902m, 1411s, 1383w, 1256s, 1145—1070vs, 1023s, 883m, 814s, 695w, 623s, 498s
4a[a]	3080w, 2920m, 1415s, 1385w, 1258m, 1195m, 1164m, 1130m, 1023s, 882m, 810s, 683, 516s, 492s, 480s
4b	3052w, 2880m, 1407s, 1380m, 1264m, 1256m, 1067m, 1062m, 1023s, 889m, 819s, 758m, 693w, 522s, 499s, 480s
4d[a]	3050w, 2870s, 1432s, 1427s, 1300m, 1254s, 1168m, 1162m, 1029s, 1024s, 892m, 885m, 817s, 812s, 519s, 503s, 484m
5a[a]	3076w, 2942m, 2886m, 1415s, 1403s, 1390m, 1280m, 1262m, 1218m, 1200m, 1165m, 1054m, 1031s, 1024s, 918s, 854s, 828s, 800s, 688w, 512s, 503s, 478s, 327m, 316m
5c[a]	3038w, 2866s, 1410s, 1332w, 1295m, 1253m, 1162m, 1024s, 925w, 890m, 882m, 815s, 512s, 493s, 470m, 340m, 320m

a) A CsI disk was used.

Table 4. Electronic Spectral Data of the Ligands **1** and the Complexes **2**—**4** in Acetonitrile

Ligands Metal salts		**1a**	**1b**	**1c**	**1d**
None		442 nm (ε 223)	443 nm (ε 196)	443 nm (ε 191)	443 nm (ε 190)
$CuClO_4$	(2)	440 (ε 137)	434 (ε 129)	430 (ε 122)	434 (ε 139)
$AgClO_4$	(3)	438 (ε 195)	437 (ε 185)	—	—
$HgCl_2$	(4)	442 (ε 140)	447 (ε 140)	—	445 (ε 170)[a]

a) The 1 : 2 complex.

that for complex **2**, Cu(I) atoms coordinate to the sulfur atoms attached to ferrocene nuclei, although the definite structure is unknown at present. As a result, the electron density on a sulfur atom is decreased, resulting in a down-field shift of Cp-ring carbons and a change in the 440 nm band. In complex **2a**, the down-field shift of the Cp-ring carbons in the ^{13}C NMR spectrum and the hypsochromic shift of the 440 nm band in the electronic spectrum was rather small, compared with those of **2b**—**d**. This suggests that the coordination mode described above may be somewhat different in **2a**.

Silver(I) Perchlorate Complexes. When a solution of the ligand **1a** and silver(I) nitrate in acetonitrile was diluted with anhydrous diethyl ether, a 1:1 complex was precipitated. The 1:1 complexes (**3a** and **3b**) of the tetrathiaferrocenophanes **1a** and **1b** with silver(I) perchlorate were similarly isolated by the reaction of **1a** and **1b** with silver(I) perchlorate, respectively. However, the reaction of **1c** and **1d** with silver(I) salts gave no stable complex. Thus, the complex formation of tetrathia[*n*]ferrocenophanes with silver(I) salt depends on the size of the thiacrown ether rings. Although some complexes of oxathiacrown ethers with silver(I) nitrate were known,[13,18] the corresponding thiacrown ether complexes are rare. 1,4,8,11-Tetrathiacyclotetradecane has been shown to give the 1:1 and 1:2 complexes with silver(I) perchlorate, though their structures were not confirmed.[19] The absorption for the C–S–C stretching vibration of **3a** and **3b** appeared at about 690 cm^{-1} with decreased intensity compared with that of the corresponding free ligand, suggesting a weak coordination of the sulfur atom to the silver(I) atom in these complexes. In the electronic spectra of **3a** and **3b**, the absorption band near 440 nm, characteristic of a ferrocene nucleus, showed a hypsochromic shift and a decreased absorbance, the extent of which were rather small compared with those of the Cu(I) complexes (vide supra). A similar trend has been observed in the AgNO$_3$-added solution of oxathia[*n*]-[13] and polythia[*n*]ferrocenophanes in acetonitrile.[12] Thus, the complexation of silver(I) atoms in the complexes **3a** and **3b** appears to be loose. In the ^{1}H NMR spectrum of **3a**, the Cp-ring protons of the ferrocene nucleus appears as a pair of triplets at δ 4.44 and 4.36 (J=1.7 Hz) and the methylene protons resonates as two singlets at δ 3.13 and 3.07. The proton signals for the Cp-rings and the methylene groups in **3b** appears at δ 4.42 and 3.3—2.9 as multiplets, respectively. Similar spectra were also obtained upon the addition of silver(I) nitrate to a solution of **1a**—**d** in CD$_3$CN-CD$_3$NO$_2$ (1:4), suggesting that **1c** and **1d** also formed similarly 1:1 complexes **3c** and **3d** in the solution although they could not be isolated. The size of a silver(I) ion (1.26 Å) is too large to be incorporated into the central hole of the polythia-macrocycle in the ligands **1a** and **1b**. Thus, complexes **3a** and **3b** must have an unsymmetrical structure. Therefore, the symmetrical pattern of the ring proton signals observed in the ^{1}H NMR spectra, which suggests a symmetrical structure of complex **3**, seems due to a rapid dissociative equilibrium in the solution described in the copper(I) complexes. In the ^{13}C NMR spectra of **3a** and **3b** (Table 2), the bridge-head carbon signal is shifted up-field and the α- anf β-ring carbon signals down-field, compared with those in the corresponding ligands. This also seems to support a loose coordination of silver(I) atoms to the thiacrown moiety of ligands **1**.

Mercury(II) Chloride Complexes. It is well-known that a soft mercury(II) salt forms a wide range of complexes with thioethers,[3] particularly a stable complex with thiacrown ether.[20,21] When an ethereal solution of mercury(II) chloride was added to a solution of **1a** in diethyl ether, the stable 1:1 complex **4a** was isolated in good yield. Similarly, the 1:1 complex **4b** was prepared. However, in a similar manner, **1c** gave no stable complex and **1d** gave the stable 1:2 complex **4d** with mercury(II) chloride. Thus, the complex formation of tetrathia[*n*]ferrocenophanes with mercury(II) chloride depends on the size of the thiacrown ether ring. In complexes of the thioethers with mercury(II) chloride, of which the crystal structure were determined by X-ray analysis, the coordination about the mercury(II) atom was approximately tetrahedral in the most cases. For example, the coordination mode of a mercury(II) atom in the 1:2 complex of 1,4,8,11-tetrathiacyclotetradecane with mercury(II) chloride is a distorted tetrahedral,[22] while an octahedral coordination is suggested from its IR spectrum in the 1:1 complex of 1,4,8,11-tetrathiacyclotetradecane with mercury(II) chloride.[20] The 1:1 complexes **4a** and **4b** show no blue shifts in their electronic spectra, although their absorbances decrease to a considerable degree. Regarding their ^{1}H NMR spectra of **4a** and **4b**, a broading of the singlet as well as a small down-field shift (0.1—0.2 ppm) of the Cp-ring protons was observed; but non-symmetrization of the Cp-ring proton signals was not recognized. These spectral data suggests that in **4a** and **4b** the mercury(II) atoms coordinate only to sulfur atoms far away from the ferrocene nucleus of **1a** and **1b**. This may be due to a rather large ion radius (r_{ion}=1.10 Å)[23] that cannot be fitted to the central hole of the ligands **1a** and **1b**. The additional HgCl$_2$ in the 1:2 complex **4d** is probably bonded to the mercury(II) atom coordinated to the sulfur atoms of the macrocycle through the bridging chloro atoms, because the ^{1}H NMR spectrum of **4d** was very similar with those of **4a** and **4b**.

Palladium(II) Chloride Complexes. The addition of a solution of dichlorobis(acetonitrile)palladium(II) in acetonitrile to a solution of **1a** and **1c** in acetonitrile gave the stable 1:1 complexes **5a** and **5c**, respectively. Unstable complexes were obtained from **1b** and **1d** by a similar procedure, but could not be characterized. The isolated complexes **5a** and **5c** were very insoluble in almost organic solvents. The ^{1}H NMR spectrum (dimethyl-d_6 sulfoxide) of **5a** showed broad signals at δ 4.45 and 4.37 (1:2), suggesting an unsymmetrical structure of complex **5a**. By contrast, the ring protons in dichloro[1,1′-(bis(isobutylthio)ferrocene)]palladium[24] appears as a symmetric pattern at δ 5.28 and 4.42. In the far-IR spectra of **5a**, the absorption at 327 and 316 cm^{-1} is in the range reported for *cis*-$PdCl_2$ moieties,[25] indicating a monomeric structure, where the Pd atom coordinated to the two sulfur atoms far from the ferrocene nucleus, because of the steric hindrance of large $PdCl_2$ moiety. However, the polymeric structure in which the Pd atom builds a bridge across two ferrocenophanes also cannot be ruled out. Recently, the X-ray analysis of the complex of 1,4,7,10-tetrathia[10]ruthenocenophane with palladium(II) chloride was reported and confirmed that the two sulfur atoms far from a ruthenocene nucleus coordinated to the palladium(II) atom.[26] Therefore, **5a** is suggested to have the same coordination mode with the above complex.

Mössbauer Spectra. The *IS* and *QS* values in ^{57}Fe Mössbauer spectra (300° K) of the free ligands **1** and the metal complexes **2**—**5** are summarized in Table 5. The Mössbauer parameters are little changed in going from the free ligands to the metal complexes. A similar small change was also observed in the complex of 1,1′-bis(diphenylphosphino)ferrocene with mercury(II) chloride.[27] A large change in the *QS* value observed in the complex of [2]ferrocenophanes with mercury(II) chloride[10] and tin(IV) chloride,[11] suggests the direct interaction between the iron atom of a ferrocene nucleus and the metal atoms. The relatively small change observed here seems to indicate that the metal atoms incorporated in the polythia-macrocycle has no strong interaction with the iron atom of a ferrocene nucleus.

Table 5. Mössbauer Parameters of **1**—**5**

Compd	*IS*	*QS*
1a	0.46	2.38
1c	0.42	2.39
2a	0.41	2.37
2b	0.41	2.37
3a	0.43	2.34
3b	0.42	2.36
4a	0.45	2.35
4b	0.45	2.32
4d	0.45	3.29
5a	0.42	2.33
5c	0.44	2.32

Experimental

Melting points are uncorrected. The electronic spectra were measured on a Hitachi 340 spectrometer. The IR spectra were measured on a JASCO IR-2 spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer, TMS being chosen as an internal standard.

Materials. Tetrathia[*n*]ferrocenophanes were prepared as described in a previous paper.[12] Mercury(II) chloride and silver(I) perchlorate were commercially available. Tetrakis(acetonitrile)copper(I) perchlorate[28] and dichlorobis(acetonitrile)palladium(II)[29] were prepared according to the literature.

(1,4,7,10-Tetrathia[10]ferrocenophane)copper(I) Perchlorate (2a). General Procedure. To a solution of 1,4,7,10-tetrathia[10]ferrocenophane (**1a**) (40 mg, 0.1 mmol) in hot acetonitrile (2.5 cm^3) was added a solution of tetrakis(acetonitrile)copper(I) perchlorate (33 mg, 0.1 mmol) in acetonitrile (2.5 cm^3). The solution was refluxed for 15 min and then diluted with anhydrous diethyl ether (15 cm^3) to form yellow crystals. After the mixture was kept for 2 h in a refrigerator, the crystals were collected by filtration. Yellow leaflets (37 mg, 66%), mp 200 °C (decomp). Found: C, 34.63; H, 3.83%. Calcd for $C_{16}H_{20}ClO_4S_4FeCu$: C, 34.35; H, 3.61%.

(1,4,8,11-Tetrathia[11]ferrocenophane)copper(I) Perchlorate (2b). Yellow leaflets (68%), mp 208 °C (decomp). Found: C, 35.34; H, 3.92%. Calcd for $C_{17}H_{22}ClO_4S_4FeCu$: C, 35.61; H, 3.87%.

(1,5,8,12-Tetrathia[12]ferrocenophane)copper(I) Perchlorate (2c). Yellow crystals (75%), mp ≈214 °C (decomp). Found: C, 37.10; H, 4.16%. Calcd for $C_{18}H_{24}ClO_4S_4FeCu$: C, 36.80%; H, 4.16%.

(1,5,9,13-Tetrathia[13]ferrocenophane)copper(I) Perchlorate (2d). Yellow plates (55%), mp ≈204 °C (decomp). Found: C, 38.16; H, 4.45%. Calcd for $C_{19}H_{26}ClO_4S_4FeCu$: C, 37.93; H, 4.36%.

(1,4,7,10-Tetrathia[10]ferrocenophane)silver(I) Nitrate. To a solution of **1a** (400 mg, 1 mmol) in hot acetonitrile (20 cm^3) was added silver(I) nitrate (170 mg, 1 mmol). After heating for 15 min, the resulting crystals were filtered and washed with hot acetonitrile. Orange crystals (400 mg, 70%), mp ≈180 °C (decomp). ^{1}H NMR (CMSO-d_6) δ=4.46 (s, 8H), 3.18 (s, 8H) and 3.12 (s, 4H). IR (KBr): 2900, 1620, 1380, 1300, 1160, 1020, and 800 cm^{-1}. Found: C, 33.98%; H, 3.56; N, 2.74%. Calcd for $C_{16}H_{20}NO_2S_4FeAg$: C, 34.02; H, 3.56; N, 2.47%.

(1,4,7,10-Tetrathia[10]ferrocenophane)silver(I) Perchlorate (3a). General Procedure. To a solution of **1a** (40 mg, 0.1 mmol) in acetonitrile (10 cm^3) was added silver(I) perchlorate (21 mg, 0.1 mmol). The solution was evaporated up. The yellow oily residue was dissolved in acetonitrile (1 cm^3) and then diluted with anhydrous ether (ca. 2 cm^3). The solution was kept for overnight in a refrigerator. The crystals formed were filtered. Yellow rods (50 mg, 83%), mp ≈190 °C (decomp). Found: C, 32.08; H, 3.42%. Calcd for $C_{16}H_{20}ClO_4S_4FeAg$: C, 31.83; H, 3.34%.

(1,4,8,11-Tetrathia[11]ferrocenophane)silver(I) Perchlorate (3b). Yellow needles (88%), mp 185 °C (decomp). Found:

C, 33.05; H, 3.72%. Calcd for $C_{17}H_{22}ClO_4S_4FeAg$: C, 33.05; H, 3.56%.

Dichloro(1,4,7,10-tetrathia[10]ferrocenophane)mercury(II) (4a). General Procedure. To a solution of **1a** (50 mg, 0.13 mmol) in anhydrous ether (25 cm^3) was added a solution of mercury(II) chloride (35 mg, 0.13 mmol) in anhydrous ether (5 cm^3). The solution was refluxed for 15 min and then kept for overnight at room temperature. The resulting crystals were collected by filtration. Yellow leaflets (60 mg, 69%), mp ≈210 °C (decomp). Found: C, 28.77; H, 3.02%. Calcd for $C_{16}H_{20}Cl_2S_4FeHg$: C, 28.77; H, 3.02%.

Dichloro(1,4,8,11-tetrathia[11]ferrocenophane)mercury(II) (4b). Yellow fine needles (92%), mp 147 °C (decomp). Found: C, 30.11; H, 3.17%. Calcd for $C_{17}H_{22}Cl_2S_4FeHg$: C, 29.94; H, 3.25%.

Tetrachloro(1,5,9,13-tetrathia[13]ferrocenophane)dimercury(II) (4d). Yellow powdery crystals (46%), mp 151 °C (decomp). Found: C, 23.75; H, 2.97%. Calcd for $C_{19}H_{26}Cl_4S_4FeHg_2$: C, 23.25; H, 2.67%.

Dichloro(1,4,7,10-tetrathia[10]ferrocenophane)palladium (II) (5a). General Procedure. To a solution of **1a** (40 mg, 0.1 mmol) in acetonitrile (5 cm^3) was added a solution of dichlorobis(acetonitrile)palladium(II) (26 mg, 0.1 mmol). The solution was kept overnight at room temperature. The resulting crystals were collected by filtration. Brown needles (49 mg, 86%), mp ≈205 °C (decomp). Found: C, 33.80; H, 3.60%. Calcd for $C_{16}H_{20}Cl_2S_4FePd$: C, 33.50; H, 3.51%.

Dichloro(1,5,8,12-Tetrathia[12]ferrocenophane)palladium (II) (5c). Red brown fine crystals (87%), mp ≈185 °C (decomp). Found: C, 36.07; H, 3.91%. Calcd for $C_{18}H_{24}Cl_2S_4FePd$: C, 35.92; H, 4.02%.

^{1}H and ^{13}C NMR Spectra of the Complex of 1 with Silver(I) Nitrate. ^{1}H and ^{13}C NMR spectra were measured upon the addition of silver(I) nitrate (1.2 equiv) to a solution of **1a—d** in CD_3CN-CD_3NO_2 (1:4). The spectral data obtained were similar to those of **3a** and **3b** shown in Tables 1 and 2.

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