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Preparation and some of the properties of the Pt(II) complexes of tetrathia[*n*](1,1′)ferrocenophanes

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Abstract

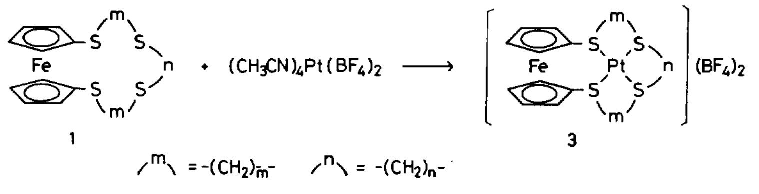
1,4,7,10-Tetrathia[10]-, 1,4,8,11-tetrathia[11]-, 1,5,8,12-tetrathia[12]-, and 1,5,9,13-tetrathia[13](1,1′)-ferrocenophanes reacted with $[Pt(CH_3CN)_4](BF_4)_2$ in refluxing acetonitrile to give the corresponding 1/1 complexes in good yields. The ^1H NMR spectra of the Pt(II) complexes of the latter two ligands are fluxional at room temperature. The ^1H and ^{13}C NMR spectra at low temperature show that the Pt(II) complex of 1,5,9,13-tetrathia[13](1,1′)ferrocenophane is a single compound, but the others are a mixture of two isomers. The ^{195}Pt NMR and other spectral data suggest that there is some interaction between the iron atom of the ferrocene nucleus and the Pt(II) atom coordinated to the sulfur atoms in the complexes and the interaction increases according to the decreasing size of the thiamacrocycle.

Introduction

Thiaferrocenophanes are typical organometallic ligands which are useful starting materials for preparing heterobimetallic complexes. 1,5,8,12-Tetrathia[12]- and 1,5,9,13-tetrathia[13](1,1′) ferrocenophanes, for example, form 1/1 complexes with $Cu(BF_4)_2$ in which the intramolecular redox reaction takes place between the iron atom of the ferrocene moiety and the copper atom coordinated to the sulfur atoms [1]. The thiaferrocenophanes similarly afford 1/1 complexes with Pd(II) in which a certain (probably a type of charge-transfer) interaction controlled by the size of the thiamacrocycle was observed [2,3]. The Pd(II) and Pt(II) complexes of 1,5,9-trithia[9]- and 1,4,7-trithia[7](1,1′)ferrocenophanes which have weak dative Fe–Pd and Fe–Pt bonds, respectively, have also been prepared [2,4]. Here we report on the preparation and ^{195}Pt NMR spectra of the Pt(II) complexes of the tetrathia[*n*]ferrocenophanes.

A solution of 1,4,7,10-tetrathia[10](1,1′)ferrocenophane (**1a**) in dry benzene was refluxed with a solution of $[Pt(CH_3CN)_4](BF_4)_2$ (**2**) in acetonitrile [5]. From the reaction mixture, was isolated a 1/1 complex (**3a**) as red-orange plates in 41% yield. In a similar manner, 1,4,8,11-tetrathia[11]- (**1b**), 1,5,8,12-tetrathia[12]- (**1c**), and 1,5,9,13-tetrathia[13](1,1′)ferrocenophanes (**1d**) gave the corresponding 1/1 complexes, **3b**, **3c**, and **3d**, in moderate yields, respectively. Complexes **3b** contained solvent of crystallization molecules in the crystal, as shown by elemental analysis. Complex **3c** was difficult to crystallize and gave no satisfactory elemental analysis although the spectral data confirmed the structure. It is well-known that the out-of-bending vibration in ferrocene derivatives is the most diagnostic probe of the oxidation state of ferrocene [6]. In the IR spectra, the out-of-bending vibration was observed at 826, 832, 818, and 822 cm^{-1} for **3a**, **3b**, **3c**, and **3d**, respectively. The frequencies of the complexes are higher (by 26, 22, 2, and 10 cm^{-1}, respectively) than those of the corresponding free ligands, but considerably lower than that of the ferrocenium cation (e.g. 846 cm^{-1} for the ferrocenium cation of **1d**). The observed shift to the high frequency is smaller than that in the Pt(II) complexes of 1,5,9-trithia[9]ferrocenophane (40 cm^{-1}) in which a dative Fe–Pt bond is assumed [4]. These results are consistent with the suggestion that there is no dative Fe–Pt bonding in the complexes since the central Pt(II) atom in the thiamacrocycle of complexes **3a–d** is not coordinately unsaturated, but the iron atom of the ferrocenyl moiety in the complexes seems to be perturbed to some extent by the proximate location of the Pt(II) atom. In particular, complexes **3a** and **3b**, seem to show little interaction between the two metal atoms. A similar increase of the out-of-bending vibration with the decreasing size of the thiamacrocycle was also observed in the Pd(II) complexes of tetrathia[*n*](1,1′)ferrocenophanes [2,4]. It is reasonable to suppose that the magnitude of the shift of the out-of-bending vibration from the free ligand to the corresponding Pt(II) complexes may reflect the strength of an Fe–Pt(II) interaction in the complexes.

The ^1H NMR spectrum of **3d** (CD_3CN, 400 MHz) was fluxional, indicating the presence of some dynamic process. The static spectrum was obtained at −30 °C, in which the cyclopentadienyl (Cp) ring protons appeared as narrow sextets at δ 4.58 and 4.82 and as narrow quintets at δ 5.14 and 5.19, as shown in Table 1. The ^{13}C NMR spectrum of **3d** at low temperature also showed four carbon signals for the Cp rings at δ 78.86, 77.28, 75.42, 73.81 ppm, along with the signal of the bridge-head carbon at 74.56 ppm, as shown in Table 2. The results confirm the presence of a single conformer for **3d** at low temperature. The unsymmetric pattern of the proton and carbon signals in the ferrocenyl ring seems to reflect the stepped conformation [7] of **3d**, in which the Fe, Pt(II), and two S atoms connected to the Cp rings are not



a : m=n=2 ; b : m=2, n=3 ; c : m=3, n=2 ; d : m=n=3

Fig. 1.

Table 1

The ^{1}H NMR spectral data of complexes **3a**–**3d** in the region of the Cp-ring proton signals

Compound	Temperature	Isomer	Chemical shift (δ) [a]
3a	R.T.	major	5.66(m,2H), 5.23(qu,2H), 4.78(se,2H), 4.43(se,2H)
		minor	5.68(m,2H), 5.46(qu,2H), 4.81(se,2H), 4.35(m,2H)
3b	R.T.	major	5.41(m,2H), 5.31(m,2H), 4.79(m,2H), 4.45(se,2H)
		minor	5.47(m,2H), 5.43(m,2H), 4.77(m,2H), 4.37(se,2H)
3c	80 °C		5.12(s,4H), 4.65(s,4H)
3d	80 °C		5.16(s,4H), 4.69(s,4H)
	−30 °C		5.19(qu,2H), 5.14(qu,2H), 4.82(se,2H), 4.58(se,2H)

[a] qu = quintet, se = sextet.

coplanar. It has previously been shown that in monosubstituted ferrocenyl, the ring protons adjacent to the substituent (i.e. α-protons) give 1 : 2 : 2 : 2 : 1 multiplet pattern, while the internal protons (i.e. β-protons) give a 1 : 1 : 2 : 2 : 1 : 1 pattern [8]. Therefore, the signals at δ 5.14 and 5.19 and those at δ 4.58 and 4.82 were assigned to the α- and β-protons, respectively. The assignment is also confirmed by H,H-COSY measurement, as described previously for the Pd(II) analogs [3].

The metal complexes of ferrocene derivatives containing heteroatoms in the 1,1′-positions can be regarded as analogs of [3](1,1′)ferrocenophanes which involve a bridge reversal process. Orrel and coworkers [9] showed that the ^{1}H and ^{13}C NMR spectra and the presence of two independent dynamic processes, sulfur inversion and bridge reversal, in the PdX_2 and PtX_2 complexes of 1,1′-bis(alkylthio)ferrocenes are strongly temperature-dependent. The proton signals of the Cp rings at δ 4.58 and 4.82 of **3d** in CD_3CN broadened upon warming and coalesced at 50 °C. At 80 °C the Cp ring signals appeared at δ 5.16 and 4.69 as almost sharp singlets, although signals of the methylene protons were still broad. In complex **3d**, the independent sulfur inversion process seems to be impossible, because the coordination of the four sulfur atoms in the thiamacrocycle to the Pt(II) atom imposed the methylene groups on the sulfur atoms at the 1,1′-positions to be always in the same direction. Thus, the remarkable dynamic behavior is probably due to the concurrent occurrence of bridge reversal with *S*-inversion on the sulfur atoms in the 1,1′-posi-

Table 2

The ^{13}C NMR spectral data of complexes **3a**, **3b**, and **3d**

Compound	Temperature	Isomer	Chemical shifts (ppm, Hz)
3a	R.T.	major	86.26, 78.40(s + d, J = 30.5), 75.34, 73.59, 71.48, 47.23, 43.97(s + d, J = 17.6), 43.46(s + d, J = 19.3)
		minor	– 79.62, 76.74, 75.27, 71.05, 45.17, 44.50, 40.84
3b	R.T.	major	81.26(s + d, J = 23.1), 79.27(s + d, J = 31.2), 75.62, 74.62(s + d, J = 9.2), 71.93, 44.98, 40.61(s + d, J = 15.3) 38.17(s + d, J = 14.8), 28.21
		minor	81.90, 79.66(s + d, J = 31.3), 75.80, 75.33, 71.43, 43.09, 41.50(s + d, J = 14.6), 38.20, 27.44
3d	−30 °C		78.86, 77.28, 75.42, 74.56, 73.81, 37.29, 37.13, 33.17, 25.95, 24.20(s + d, J = 18.9)

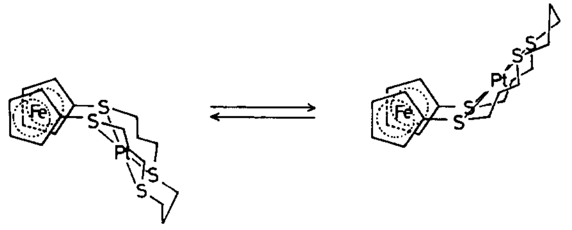


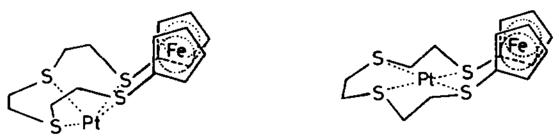
Fig. 2.

tions (i.e. a flipping motion of the thiamacrocycle moiety coordinated by the Pt(II) atom). From the coalescence temperature (50 ° C), $\Delta G^{\neq} = 64.9$ kJ/mol was calculated. This value is comparable with that in the $PtCl_2$ complexes of 1,1′-bis(isobutylthio)ferrocene (65.0 kJ/mol) [9] and that in the Pd(II) analog of **1d** (63.2 kJ/mol) [3].

The ^1H NMR spectra of **3a** and **3b**, on the other hand, were static and almost static at room temperature, respectively. Moreover, they showed the presence of two isomers in the complexes. The isomer ratio of the two isomers was estimated from the integration ratio of the Cp-ring proton signals to be 10 : 1 for **3a** and 2 : 1 for **3b**. The ^1H NMR spectrum of **3c** was broadened at room temperature and moreover the completely static spectrum could not be obtained only at −40 ° C. The low-temperature NMR spectrum of **3c** also indicated the presence of two isomers.

The ^1H NMR spectrum of the major isomer of **3a**, for example, showed signals of the Cp-ring protons at δ 5.66, 5.23, 4.78, and 4.43. The averaging process for the signals of the Cp-ring protons in complexes **3a–c** on warming was very complicated because of the presence of two isomers. No completely-averaged spectra could be obtained for **3a–c** not even on warming at 80 ° C. From the temperature at which the spectrum becomes static, the dynamic motion decreases in the following order: **3a** < **3b** < **3d** < **3c**, the order being almost consistent with the decrease in ring size of the thiamacrocycle. It is noteworthy this order is also consistent with that of the increase in the Fe–Pt(II) interaction observed in the IR study.

It was confirmed by X-ray diffraction that the Pd(II) complex of **1d** has a stepped conformation, the Pd(II) atom is located in the center of a square-planar formed by the four S atoms of the thiamacrocycle moiety. The chelate ring containing the Pt(II) atom has a quasi-chair form [10]. From the NMR spectral behavior it is reasonable to suppose that the Pt(II) complex **3d** has a structure similar to that of the Pd(II) complex. In the complexes **3a–c**, the Pt(II) atom is not properly seated in the center of the cavity of the thiamacrocycle part, when the thiamacrocycle part in the complexes maintains a *syn*-conformation, because of the smaller size of the cavity in **1a–c** compared with that in **1d**. Consequently, the Pt(II) atom is deviated to the outer side of the plane of thiamacrocycle away from the ferrocene moiety in order to avoid severe interference with one of the α-protons of the ferrocene moiety, as shown in Fig. 3 for **3a**. For the complexes which have ethylene bridges between the two sulfur atoms, an *anti*-isomer (Fig. 3) may also exist. So, the region of the aliphatic protons in the ^1H NMR spectrum of complex **3a** was analyzed by use of homo-decoupling, NOE, H,H-COSY, and C,H-correlation measurements. Only six multiplets were observed for the aliphatic protons, indicat-



Syn-confomer

Anti-confomer

Fig. 3. Conformational isomers of **3a**.

ing that the molecule of **3a** had a symmetrical plane through the two metals and perpendicular to the C(5)–C(6) bond. It was clear from the NOE and C,H-correlation measurements that the proton signal at δ 4.40 is coupled only to the proton signal at δ 3.96, and both protons are connected to the same carbon C(5), respectively. The signal at δ 4.40 shows a ddd pattern (J 12.0, 5.4, and 2.0 Hz), suggesting that the C(5)–C(6) ethylene bridge has a distorted eclipsed conformation. On the other hand, the signals from two pairs of two protons at the C(2) and C(3) atoms appeared at δ 3.98 and 3.66, and 3.86 and 3.59, respectively. The assignment is based on the fact that 12% enhancement was observed for the α-proton at δ 5.63 on irradiation of the multiplet at δ 3.98 in the NOE measurements, and the protons that resonated at δ 3.98 and 3.66 are connected to the same carbon as proved by the C,H-correlation measurement. The ddd pattern at 3.98 has the coupling constants J 14.6, 12.4, and 4.6 Hz, and the double triplet at δ 3.59 consists of the coupling constants J 14.6 and 3.7 Hz. These suggest that one of the protons at the C(2) atom is co-planar with one of the protons at the C(3) atom, so that the torsion angle S(1)–C(2)–C(3)–S(4) is almost 120°. Therefore, the main isomer of **3a** must be an *anti*-conformer. In order to make cavity for the Pt(II) atom, the cyclopentadienyl (Cp) rings of the ferrocene moiety may need to tilt a little towards each other. Such a deformation may increase interaction between the two metals, because the increased tilting enhances the basicity of the Fe atom of ferrocene [11]. The deformation also seems to reduce the distance between the Pt(II) atom and the Fe atom of the ferrocene moiety, which somewhat increases the interaction between the two metals.

The electronic spectrum of **3d** shows broad and weak absorptions at 435 nm (ϵ 129 as well as a more intense shoulder at 329 nm (ϵ 557). The free ligand **1d** shows an absorption maximum at 443 nm (ϵ 190) [11], while the Pt(II) complex of the open-chain tetrakis(thioether), 2,6,10,14-tetrathiapentadecane, which is regarded as having a square-planar coordination, shows no absorption above 370 nm [5]. We suggest that the weak absorption band at 435 nm observed for complex **3d** is probably due to an interaction between the iron atom of the ferrocene nucleus and the Pt(II) atom incorporated into the thiamacrocycle moiety, which in turn may be caused by the charge-transfer from the HOMO of the Fe atom to the LUMO of the Pd(II) atom. The absorption showed a bathochromic shift according to the decreased size of the thiamacrocycle in the series **3a–d** as follows: **3a**, 512 (ϵ 126) > **3b**, 457 (131) > **3c**, 443 (268) > **3d**, 435 nm (129). As described above, the decreased size of the thiamacrocycle seems to increase the tilting angle of the Cp rings of the ferrocene nucleus, enhancing the basicity of the Fe atom of the ferrocene nucleus and the distance between two metals may also decrease slightly in the same order in the preferred conformer. The bathochromic shift observed, is probably due to an

Table 3

The ^{195}Pt NMR spectra data (85.877 MHz, CD_3CN)

Compound	Temperature	Chemical shifts (ppm) [a]	
		Major isomer	Minor isomer
3a	R.T.	−2726	−2590
3b	R.T.	−2819	−2753
3c	−40 °C	−2699	−2667
3d	−30 °C	−2440	
4	R.T.	−3171	
5	R.T.	−3346	
3S9–Pt [b]	R.T.	−2503	

[a] Saturated solution of Na_2PtCl_4 in D_2O was chosen as the standard. [b] 3S9–Pt = bis(1,5,9-trithiacyclononane)platinum(II) tetrafluoroborate.

increased Fe–Pt interaction in the complexes, although the tilting of the Cp rings of ferrocene results in a small bathochromic shift [12].

The ^{195}Pt NMR spectral data of complexes **3a–d**, along with those of the related compounds, were summarized in Table 3 In complex **3d**, only one signal of ^{195}Pt nucleus was observed at −2440 ppm, relative to the standard (Na_2PtCl_6), indicating that **3d** is a single compound. On the other hand, complexes **3a–c** gave two signals. For example, **3a** produced signals at −2819 and −2753 ppm. The findings are in agreement with the result from the ^{1}H and ^{13}C NMR spectra that **3a** consists of two isomers. The Pt(II) complexes of 1,4,7-trithiacyclononane [13] gave the signal of the ^{195}Pt nucleus at −2503 ppm and the chemical shift was similar to that found for **3d**. The ^{195}Pt resonance in the Pt(II) complex of 1,5,9-trithia[9](1,1′)ferrocenophane (**4**), in which a dative Fe–Pt bond was assumed [4], appeared at −3171 ppm, was found at considerably higher field than that of **3d** (−2440 ppm). These data suggest that there is no significant interaction between the Fe atom of a ferrocene moiety and the Pt(II) atom incorporated in the thiamacrocycle. The resonances due to ^{195}Pt nucleus in complexes **3a–c** were intermediate between two extremes, suggesting that there is some interaction between the Fe and Pt(II) atoms. It is noteworthy that the ^{195}Pt resonance of the major isomer always appears at higher field than that of the minor isomer in complexes **3a–c**, and the difference of the chemical shift between the major and the minor isomers decreases in the order: **3a** > **3b** > **3c**. This seems to indicate that the major isomer (the *anti*-conformer) involves larger interaction between two metals than the minor isomer (syn-conformer). This seems to be consistent with the suggestion made above that in the *syn*-conformer the Pt(II) atom is probably deviated far away from the ferrocene nucleus and in the *anti*-conformer the incorporation of the Pt(II) atom into the cavity of the thiamacrocycle may cause the tilting of the Cp rings of the ferrocene nucleus, resulting in the increase of the interaction between two metals. However, we cannot rule out the possibility that the change of the ^{195}Pt chemical shift and the bathochromic shift observed in the visible spectra may depend merely on the change in the stereochemistry of coordination around the Pt(II) atom through the complexes **3a–d**.

In summary, the Pt(II) complexes of tetrathia[n](1,1′)ferrocenophanes were prepared. The free ligands (**1d**) which have a cavity large enough to incorporate the

Pt(II) atom in the thiamacrocycle afforded a single complex, **3d**, while others (**1a–c**) gave a complex present as two isomers.

Complexes **3d** and **3c** were sufficiently fluxional and complexes **3a** and **3b** are completely or almost static. The free energy of activation in the dynamic process of **3d** was calculated to be 64.9 kJ/mol. The spectral data indicate that there is some interaction between the Fe atom and the Pt(II) atoms, the magnitude of which is controlled by the size of the thiamacrocycle in the complexes.

Experimental

The IR spectra were taken on Hitachi 270-50 Infrared Spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM400 Spectrometer, TMS was the internal standard. The electronic spectra were taken on a Shimadzu UV2000 Spectrometer.

Materials. Tetrathia[*n*](1,1′)ferrocenophanes were prepared by a method described in a previous paper [14]. Dichloro(acetonitrile)platinum(II) was prepared by a procedure described previously [5].

(1,4,7,10-Tetrathia[10](1,1′)ferrocenophane)platinum(II) tetrafluoroborate.

General Procedure. 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 ml) was refluxed for 2 h under nitrogen. To the resulting mixture was added a solution of 1,4,7,10-tetrathia[10](1,1′)ferrocenophane (400 mg, 0.1 mmol) in dry benzene (5 ml). The mixture was refluxed for 1 h and then filtered to remove silver(I) chloride. The filtrate was evaporated under reduced pressure and then the residue was dissolved in dry acetone-acetonitrile (1 : 2 v/v, 3 ml). The resulting solution was filtered and the filtrate was diluted with dry diethyl ether (2 ml) to give the title compound as red plates (48 mg, 41%), m.p. 294 °C. Found: C, 25.36; H, 2.66%. $C_{16}H_{20}B_2F_8S_4FePt$ calcd.: C, 25.11; H. 2.63% IR (KBr): 3120, 3004, 2964, 1434, 1418, 1286, 888, 826, and 520 cm^{-1}. VIS (CH_3CN): 512 nm (ϵ 126).

(1,4,8,11-Tetrathia[11](1,1′)ferrocenophane)platinum(II) tetrafluoroborate

Orange needles (43 mg, 55%), m.p. 295 °C. The crystal contains one equivalent of acetonitrile as solvent of crystallization. Found: C, 27.53; H, 2.86; N, 1.71%. $C_{17}H_{22}B_2F_8S_4FePt \cdot C_2H_3N$ calcd.: C, 27.82; H, 3.07; N, 1.70%. IR (KBr): 3096, 3060, 2948, 2908, 1626, 1422, 1298, 832, and 522 cm^{-1}. VIS (CH_3CN): 457 nm (ϵ 131).

(1,5,8,12-Tetrathia[12](1,1′)ferrocenophane)platinum(II) tetrafluoroborate

Red solids (63% yield). IR (KBr): 3080, 2956, 1622, 1410, 1294, 818, and 506 cm^{-1}. VIS (CH_3CN): 443 nm (ϵ 268).

(1,5,9,13-Tetrathia[13](1,1′)ferrocenophane)platinum(II) tetrafluoroborate

Orange crystals (24 mg, 22%), m.p. 258 °C. Found: C, 28.46; H, 3.51%. $C_{19}H_{26}B_2F_8S_4FePt$ calcd.: C, 28.27; H, 3.27%. IR (KBr): 3092, 2916, 1630, 1432, 1296, 966, 886, 822, and 524 cm^{-1}. VIS (CH_3CN): 435 nm (ϵ 129).

References

1 M. Sato, S. Akabori, M. Katada, I. Motoyama, and H. Sano, Chem. Lett., (1987) 1847.
2 M. Sato, K. Suzuki, and S. Akabori, Chem. Lett., (1987) 2239.
3 M. Sato and S. Akabori, Bull. Chem. Soc. Jpn., 62 (1989) 3492.
4 M. Sato, H. Asano, K. Suzuki, M. Katada, and S. Akabori, Bull. Chem. Soc. Jpn., 62 (1989) 3828.
5 F.R. Hartley, S.G. Murry, and C.A. McAuliffe, Inorg. Chem., 18 (1979) 1394.
6 J.A. Kramer and D.N. Hendrickson, Inorg. Chem., 19 (1980) 3330.
7 J.J. Bishop and A. Davison, Inorg. Chem., 10 (1971) 826.
8 I.R. Butler, W.R. Cullen, F.G. Herring, N.R. Jagannathan, F.W.B. Einstein, and R. Jones, Inorg. Chem., 25 (1986) 4534.
9 K.G. Orrel, V. Sik, C.H. Brubacker, and B. McCulloch, J. Organomet. Chem., 276 (1984) 267.
10 N. Won, K. Iwai, M. Katada, H. Sano, M. Sato, and S. Akabori, The 56th Annual Meeting of Chem. Soc. Jpn., (1988) I-851.
11 H.L. Lentzner and W.E. Watts, Tetrahedron, 27 (1971) 4343.
12 T.H. Barr and W.E. Watts, Tetrahedron, 24 (1968) 6111.
13 A.I. Blake, R.O. Gould, A.J. Holder, T.I. Hyde, A.J. Lavery, M.O. Odulate, and M. Schloder, J. Chem. Soc., Chem. Commun., (1987) 118.
14 M. Sato, S. Tanaka, S. Ebine, and S. Akabori, Bull. Chem. Soc. Jpn., 57 (1984) 1929.