The Preparation of Polythia[*n*](1,1′)ruthenocenophanes. Their Platinum Group Metals Complexes and Their X-Ray Crystal Structures

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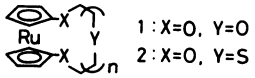
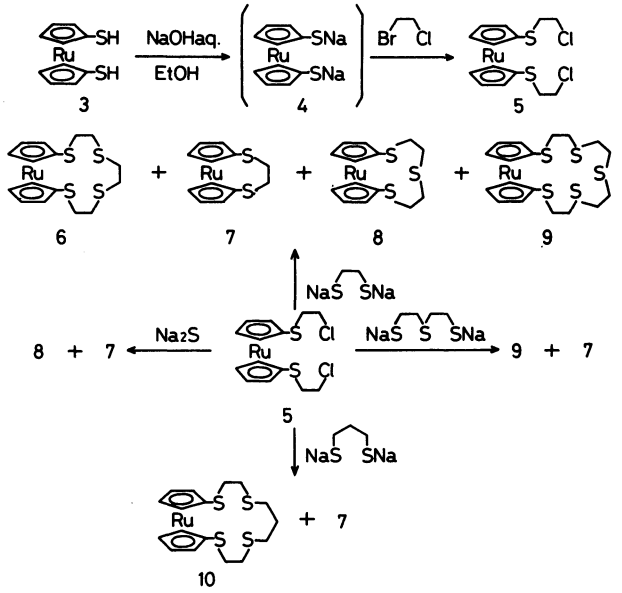
Polythia[*n*](1,1′)ruthenocenophanes were prepared by reaction of 1,1′-bis(2-chloroethylthio)ruthenocene with disodium alkanedithiolates in tetrahydrofuran/ethanol. The ruthenocenophanes efficiently formed 1 : 1 complexes with platinum and palladium dichlorides. X-Ray crystallography of complexes of the 1,4,7,10-tetrathia[*n*](1,1′)ruthenocenophane with $PtCl_2$ and $PdCl_2$ revealed that the Pt (or Pd) atom bonded selectively to the two sulfur atoms at the 4,7-positions among the four sulfur atoms in the bridge of the ligand with a slightly distorted cis square-planar configuration. The conformation of the organic moiety in the 1 : 1 complex is greatly changed from that of the metal-free ligand. Also, the 1 : 1 palladium complex is isomorphous with the 1 : 1 platinum complex.

Although a number of macrocyclic polyethers and their alkali and alkaline earth-metal complexes have already been reported,[1] few complexes of polythia-crown ethers with a platinum group metal are known.[2] We recently suggested[3,4] that the ruthenium atom of the complexes of polyoxa- and dioxapolythia[*n*](1,1′)-ruthenocenophanes (**1** and **2**) with soft cations such as mercury(II) and silver(I) ions interacted with the incorporated metal ions. Therefore, a similar interaction can be expected between the ruthenium atoms of ruthenocenocrown ethers and palladium(II) or platinum(II) ions which are soft cations. In a previous paper,[5] we reported an X-ray analysis of the Pt-complex with 4,7-dithia-1,10-dioxa[10]ruthenocenophane. In this complex, the platinum atom which has a slightly distorted square-planar configuration was selectively coordinated with two sulfur atoms at the 4,7-positions in the bridge. Therefore, the distance between the ruthenium and palladium atoms was too long to allow interaction. Furthermore, we have reported[6] on the syntheses of the polythia[*n*](1,1′)ruthenocenophanes (**6**, **7**, **8**, and **9**) by reactions of 1,1′-bis(2-chloroethylthio)ruthenocene with disodium 1,2-ethanedithiolate. Therefore, we have been interested in the stereochemistry of the complexes formed from polythia-[*n*](1,1′)ruthenocenophanes and *trans*-[$PdCl_2(CH_3CN)_2$] (**11a**) or *cis*-[$PtCl_2(CH_3CN)_2$] (**11b**). Here we report on the syntheses of complexes of polythia[*n*](1,1′)ruthenocenophanes with platinum group metals and their structural studies by spectral and X-ray crystallographic methods.



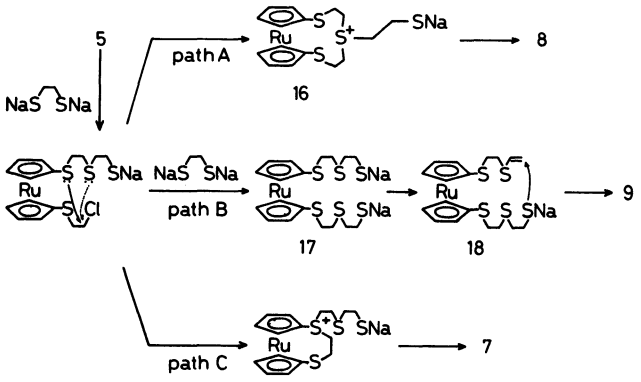
Syntheses of Polythia[*n*](1,1′)ruthenocenophanes. In order to obtain the starting material of polythia-[*n*](1,1′)ruthenocenophanes (**6—10**), ruthenocene-1,1′-dithiol (**3**),[6] which was prepared by the reduction of trithia[3](1,1′)ruthenocene, was reacted with 1-bromo-2-chloroethane in the presence of sodium hydroxide to give 1,1′-bis(2-chloroethylthio)ruthenocene (**5**) in 67% yield. A new series of polythia[*n*](1,1′)ruthenocenophanes were synthesized by the reaction of an equimolar amount of **5** with the disodium salt of 1,2-ethanedithiol and/or its homologs in several solvents. The best results were achieved when highly diluted conditions were realized by the combination of a slow addition and a high reaction temperature and when tetrahydrofuran (THF)–aqueous ethanol was used as the solvent. For example, the reaction of **5** with disodium 1,2-ethanedithiolate gave 1,4,7,10-tetrathia[10](1,1′)-ruthenocenophane (**6**) in 9.8% yield together with trace amounts of the unexpected 1,4-dithia[4](1,1′)ruthenocenophane (**7**), 1,4,7-trithia[7](1,1′)ruthenocenophane (**8**), and 1,4,7,10,13-pentathia[13](1,1′)ruthenocenophane (**9**).



Similarly, **5** reacted with disodium 1,3-propanedithiolate, the disodium salt of bis(2-mercaptoethyl) sulfide, and sodium sulfide to give 1,4,8,11-tetrathia[11](1,1′)ruthenocenophane (**10**) (15%), **9** (23%), and **8** (15%) as the main products, respectively. Furthermore, in addition to the normal products, an unexpected product **7**

Table 1. ^{1}H NMR Spectral Data of **6**, **9**, and Their Palladium(II) and Platinum(II) Complexes (DMSO-d_6)

Compd	α-Protons	β-Protons	Methylene protons
6	4.64 (t, J=1.8 Hz, 4H)	4.81 (t, J=1.8 Hz, 4H)	3.10—2.79 (m, 12H)
12a	4.95 (s, 2H), 4.88 (s, 2H)	4.71 (t, J=1.8 Hz, 4H)	3.48—2.91 (m, 12H)
12b	5.02—4.85 (m, 4H)	4.71 (t, J=1.8 Hz, 4H)	3.44—2.91 (m, 12H)
9	4.65 (t, J=1.8 Hz, 4H)	4.79 (t, J=1.8 Hz, 4H)	3.03—2.74 (m, 16H)
13a	5.20—4.78 (m, 4H)	4.68 (broad-s, 4H),	3.48—2.84 (m, 16H)
13b	5.27—4.46 (m, 4H)	4.65 (broad-s, 4H)	3.75—2.59 (m, 16H)



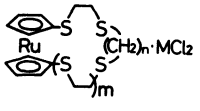
Scheme 1.

was also isolated in all cases. The structures of these products were established by their ^{1}H NMR and mass spectroscopic data and elemental analyses. A possible mechanism for the unexpected formation of **7**, **8**, and **9** in the reaction of **5** with disodium 1,2-ethanedithioate is proposed in Scheme 1. The formation of **7** can be rationalized in terms of the formation of the intermediate sulfonium ion **15** (path C) followed by dealkylation. The formation mechanisms of **8** and **9** can be interpreted similarly as follows (paths A and B): Dealkylation of **16** gives **8**, and elimination of SH^- from **17** gives the vinyl sulfide intermediate (**18**) followed by cyclization to give **9**. Also, a similar propagation reaction mechanism has been observed in the reaction of bis(2-chloroethyl) ether with sodium sulfide,[7] and the reaction of disodium 1,2-ethanedithiolate with 1,1′-bis(2-chloroethoxy)ferrocene[8] and 1,1′-bis(2-chloroethylthio)ferrocene.[9]

Palladium(II) and Platinum(II) Chloride Complexes of 6, 9, and 10. A solution of the ruthenocenothiacrown ether (**6**, **9**, and **10**) in acetonitrile was reacted with an equimolar amount of $MCl_2(CH_3CN)_2$ (**11a**: M=Pd or **11b**: M=Pt) in acetonitrile to give 1:1 complexes in 47—89% yields. The melting and decomposition points of these palladium and platinum complexes were higher than those of the corresponding metal-free ligands. As shown in Table 1 and Fig. 1, all of the α-protons of the ruthenocene nucleus and the methylene protons of complexes **12** and **13** were shifted downfield, and the signal shape of the α-protons became extremely complex. For example, the α- and the methylene protons of **12a**, compared with metal-free ligand **6**, shifted downfield by ca. +0.31—+0.24 and

Fig. 1. ^{1}H NMR spectra of **6** and **12a**.

+0.38—+0.12 ppm, respectively, and the signal shape of the α-protons varied to two singlets from a triplet (J= 1.8 Hz). However, the β-protons of **12a** shifted upfield only a little (by −0.10 ppm). From the ^{1}H NMR spectral data, it is suggested that the palladium (or platinum) ion was coordinated with sulfur atoms outside of the polythia macrocyclic plane, so the structures of complexes **12** and **13** may be unsymmetrical. The far-IR spectra of **6** and **9** and their palladium and platinum complexes (**12** and **13**) were recorded using a CsI disk. These results are listed in Table 2. In complexes **12** and **13**, the Cp-Ru-Cp ring tilting and Cp-Ru stretching bands were slightly shifted to a lower frequency by ca. 10—20 cm^{-1}, respectively. In addition, new absorptions appeared at 2960 cm^{-1}, and 325 and 310 cm^{-1}, which were assigned to the C-H stretching vibrations of the Cp rings and *cis*-MCl_2 (M=Pd or Pt) stretching vibrations, respectively. The absorption bands at 325 and 310 cm^{-1} are in good agreement with the range reported for *cis*-MCl_2 (M=Pd or Pt) vibrations. These results suggest that the reaction of the ruthenocenocrown ethers with *trans*-$[PdCl_2(CH_3CN)_2]$ (**11a**) and *cis*-$[PtCl_2(CH_3CN)_2]$ (**11b**) gives only a cis-isomer.



12a: m=1, n=2, M=Pd
12b: m=1, n=2, M=Pt
13a: m=2, n=2, M=Pd
13b: m=2, n=2, M=Pt
14a: m=1, n=3 M=Pd
14b: m=1 n=3 M=Pt

Table 2. IR Spectral Data[a] of **6**, **9**, and Their Palladium(II) and Platinum(II) Complexes (cm^{-1})

Compd	ν(C-H)			ν(C-C)		δ(C-H)	π(C-H)	Ring tilt	ν(Ru-Cp)	ν(M-Cl)	
6	3080		2910	1410		1025	808	450	382		
12a	3080	2960	2920	1410	1400(sh)[b]	1020	805	430	370	325(sh)	313
12b	3080	2960	2920	1420	1400(sh)	1020	805	432	370	325(sh)	312
9	3080		2920	1415		1025	817	450	395		
13a	3080	2960	2910	1410		1020	810	435	385	325(sh)	310
13b	3080	2950(sh)	2910	1410		1020	810	435(sh)	385	320(vw)[c]	610(vw)

a) CsI disk. b) Shoulder. c) Very weak.

Table 3. Fractional Atomic Coordinates (×10⁴) and Thermal Parameters (Å²)

	Atom	x	y	z	B_{eq}[a]
Molecule **6**	Ru	1685.7(3)	4150.9(3)	4087.7(6)	1.96
	C(1)	1151(3)	2261(4)	3590(8)	2.2
	C(2)	381(3)	2697(4)	1935(8)	2.5
	C(3)	10(3)	3447(4)	3437(9)	2.9
	C(4)	546(4)	3490(4)	6019(9)	3.0
	C(5)	1253(3)	2758(4)	6121(8)	2.7
	S(6)	1852(1)	1334(1)	2585(2)	3.0
	C(7)	1125(4)	−89(4)	2863(10)	2.9
	C(8)	1280(4)	−322(4)	5530(11)	3.9
	S(9)	2227(1)	−1129(1)	6682(3)	4.6
	C(10)	3428(4)	−264(5)	6404(11)	4.1
	C(11)	3890(5)	817(5)	8394(10)	4.2
	S(12)	5170(1)	1611(1)	8355(3)	5.1
	C(13)	4856(4)	2239(5)	5522(11)	3.8
	C(14)	4353(4)	3228(4)	5824(9)	3.4
	S(15)	3973(1)	3737(1)	2836(2)	3.0
	C(16)	3224(3)	4662(3)	3564(8)	2.2
	C(17)	2496(3)	5054(4)	1706(8)	2.5
	C(18)	2098(4)	5862(4)	3012(9)	2.8
	C(19)	2562(4)	5964(4)	5629(9)	3.0
	C(20)	3256(3)	5222(4)	5994(8)	2.5
Molecule **12b**	Pt	5884.3(8)	3119.2(3)	6547.9(11)	2.22
	Cl(1)	4197(6)	3026(2)	3235(8)	4.3
	Cl(2)	7180(6)	3590(2)	8796(8)	4.1
	Ru	2305(2)	4493.4(6)	1903(2)	2.6
	C(1)	942(20)	3941(7)	2608(29)	2.8
	C(2)	139(18)	4285(8)	1419(31)	3.9
	C(3)	348(23)	4746(8)	2392(33)	4.0
	C(4)	1209(27)	4680(8)	4051(31)	4.6
	C(5)	1647(23)	4190(9)	4249(27)	3.7
	S(6)	697(6)	3341(2)	2077(9)	3.6
	C(7)	2107(19)	3055(8)	3637(27)	3.1
	C(8)	3386(18)	3036(8)	2876(27)	2.8
	S(9)	4657(5)	2653(2)	4369(7)	2.6
	C(10)	5853(20)	2545(7)	2908(26)	2.7
	C(11)	6744(20)	2968(7)	2734(26)	2.9
	S(12)	7584(5)	3150(2)	5005(7)	2.7
	C(13)	8083(19)	3770(8)	4705(28)	3.3
	C(14)	7115(18)	4095(7)	3403(28)	2.5
	S(15)	5451(6)	4119(2)	4079(8)	3.2
	C(16)	4533(20)	4435(8)	2140(30)	3.6
	C(17)	3838(21)	4221(8)	458(28)	3.2
	C(18)	3084(22)	4615(9)	−560(30)	4.4
	C(19)	3275(21)	5021(8)	459(32)	3.8
	C(20)	4138(22)	4923(7)	2121(30)	3.3

a) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

The metal free ligand **6** and its Pt complex **12b** were further characterized by X-ray crystallographic studies. The final atomic parameters are listed in Table 3, and bond lengths as well as bond and torsion angles are given in Tables 4 and 5 for **6** and **12b**, respectively. Perspective views of **6** and **12b** are shown in Fig 2.

For **6** the C-C bond lengths and C-C-C bond angles of the two Cp rings are in the range of 1.413(7)—

Table 4. Bond Lengths (l/Å), and Bond and Torsion Angles (ϕ/°) for **6**

1	2	3	4	1-2	1-2-3	1-2-3-4
Tetrathia-crown moiety						
S(6)	C(1)	C(2)	C(3)	1.750(5)	128.4(4)	175.4(3)
S(6)	C(1)	C(5)	C(4)		123.7(4)	−175.6(2)
C(2)	C(1)	S(6)	C(7)			22.5(5)
C(5)	C(1)	S(6)	C(7)			−162.0(4)
C(1)	S(6)	C(7)	C(8)		99.9(2)	169.8(4)
S(6)	C(7)	C(8)	S(9)	1.813(5)	109.7(4)	−175.7(1)
C(7)	C(8)	S(9)	C(10)	1.504(8)	112.4(4)	72.7(5)
C(8)	S(9)	C(10)	C(11)	1.808(6)	101.8(3)	72.0(5)
S(9)	C(10)	C(11)	S(12)	1.827(6)	113.3(4)	173.6(1)
C(10)	C(11)	S(12)	C(13)	1.510(9)	112.8(4)	74.6(5)
C(11)	S(12)	C(13)	C(14)	1.812(6)	104.6(3)	58.6(5)
S(12)	C(13)	C(14)	S(15)	1.806(6)	117.0(4)	−96.3(4)
C(13)	C(14)	S(15)	C(16)	1.511(8)	114.8(4)	−74.3(5)
C(14)	S(15)	C(16)	C(17)	1.822(6)	101.7(2)	84.7(5)
C(14)	S(15)	C(16)	C(20)			−98.0(4)
S(15)	C(16)	C(17)	C(18)	1.755(5)	127.9(4)	177.9(2)
S(15)	C(16)	C(20)	C(19)		124.6(4)	−178.1(2)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.435(6)	108.1(4)	0.4(6)
C(2)	C(3)	C(4)	C(5)	1.425(7)	108.1(4)	0.1(6)
C(3)	C(4)	C(5)	C(1)	1.413(7)	108.7(4)	−0.5(6)
C(4)	C(5)	C(1)	C(2)	1.433(7)	107.4(4)	0.7(6)
C(5)	C(1)	C(2)	C(3)	1.432(7)	107.7(4)	−0.7(6)
C(16)	C(17)	C(18)	C(19)	1.434(7)	108.1(4)	0.0(6)
C(17)	C(18)	C(19)	C(20)	1.434(7)	108.0(4)	−0.2(6)
C(18)	C(19)	C(20)	C(16)	1.426(7)	108.2(4)	0.4(6)
C(19)	C(20)	C(16)	C(17)	1.425(7)	108.3(4)	−0.4(6)
C(20)	C(16)	C(17)	C(18)	1.435(6)	107.5(4)	0.3(5)

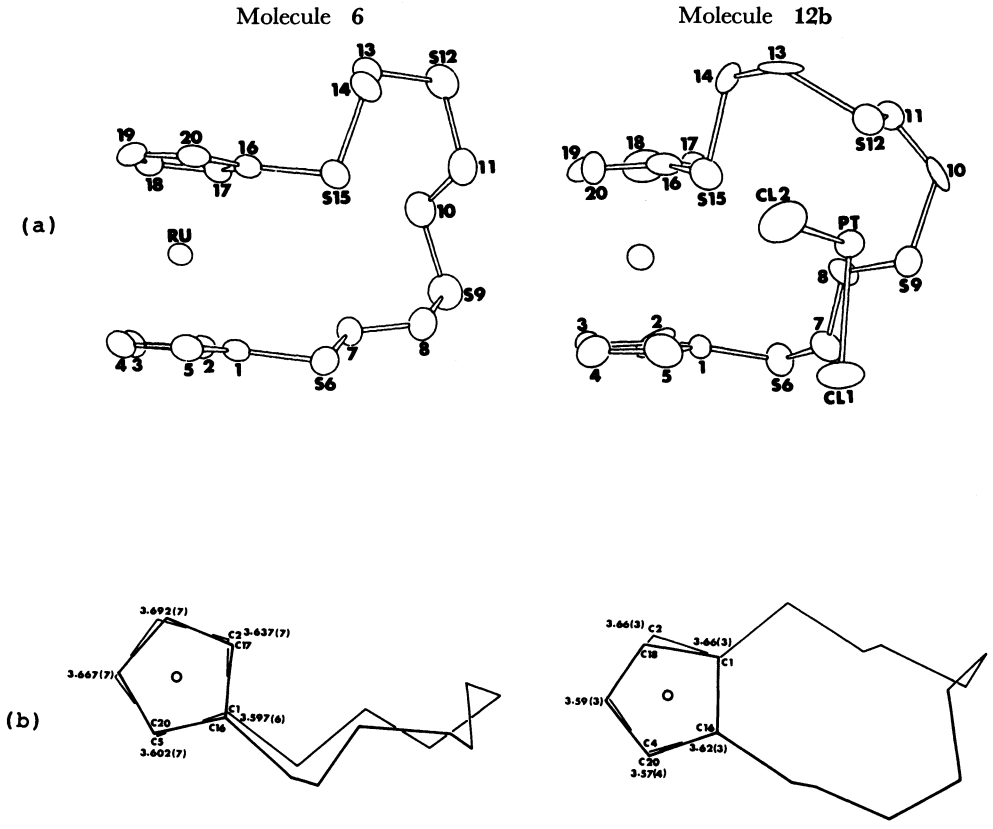


Fig. 2. (a) ORTEP (Johnson, 1965) drawings of molecules with atom numbering scheme. (b) Projections of the organic ligand moieties on the Cp ring containing the C(1) atom are also given with the C···C distance (A) between the rings. An open circle denotes Ru atom.

Table 5. Bond Lengths (l/Å) and Bond and Torsion Angles (ϕ/°) for **12b**

1	2	3	4	1-2	1-2-3	1-2-3-4
Tetrathia-crown moiety						
S(6)	C(1)	C(2)	C(3)	1.74(2)	118.5(17)	168.6(10)
S(6)	C(1)	C(5)	C(4)		132.6(17)	−165.5(15)
C(2)	C(1)	S(6)	C(7)			169.6(18)
C(5)	C(1)	S(6)	C(7)			−24.0(3)
C(1)	S(6)	C(7)	C(8)		103.3(11)	−86.8(18)
S(6)	C(7)	C(8)	S(9)	1.81(2)	111.5(16)	−170.6(3)
C(7)	C(8)	S(9)	C(10)	1.50(3)	108.1(15)	164.5(15)
C(8)	S(9)	C(10)	C(11)	1.85(2)	100.2(10)	74.2(17)
S(9)	C(10)	C(11)	S(12)	1.80(2)	113.2(14)	54.2(19)
C(10)	C(11)	S(12)	C(13)	1.50(3)	107.7(14)	−159.4(14)
C(11)	S(12)	C(13)	C14)	1.81(2)	103.6(10)	39(2)
S(12)	C(13)	C(14)	S(15)	1.84(2)	119.9(16)	57(2)
C(13)	C(14)	S(15)	C(16)	1.52(3)	109.0(15)	−171.3(16)
C(14)	S(15)	C(16)	C(17)	1.83(2)	97.2(10)	87(2)
C(14)	S(15)	C(16)	C(20)			−106(2)
S(15)	C(16)	C(17)	C(18)	1.79(2)	125.4(17)	171.6(13)
S(15)	C(16)	C(20)	C(19)		125.3(17)	−171.4(11)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.44(3)	106(2)	−1(3)
C(2)	C(3)	C(4)	C(5)	1.48(3)	109(2)	2(3)
C(3)	C(4)	C(5)	C(1)	1.37(4)	110(2)	−3(3)
C(4)	C(5)	C(1)	C(2)	1.44(4)	107(2)	2(3)
C(5)	C(1)	C(2)	C(3)	1.46(3)	108(2)	−1(3)
C(16)	C(17)	C(18)	C(19)	1.44(3)	104(2)	−2(3)
C(17)	C(18)	C(19)	C(20)	1.46(3)	110(2)	1(3)
C(18)	C(19)	C(20)	C(16)	1.36(4)	109(2)	1(3)
C(19)	C(20)	C(16)	C(17)	1.39(3)	108(2)	−3(2)
C(20)	C(16)	C(17)	C(18)	1.43(3)	108(2)	3(2)
Pt coordination						
Cl(1)	Pt		Cl(2)	2.316(7)	91.0(2)	
Cl(2)	Pt		S(9)	2.315(7)	179.0(2)	
S(9)	Pt		Cl(1)	2.249(5)	89.5(2)	
S(12)	Pt		Cl(1)	2.239(6)	175.2(2)	
S(9)	Pt		S(12)		89.7(2)	
S(12)	Pt		Cl(2)		89.7(2)	

1.435(6) Å and 107.4(4)—108.7(4)° with average values of 1.429 Å and 108.0°, respectively. These average bond lengths and angles are in good agreement with those of ruthenocene.[11] In macrocyclic units, each average bond length of S-Csp^2, S-Csp^3, Csp^3-Csp^3 was 1.753, 1.816, and 1.508 Å; this is in agreement with each expected value. In the Cp moiety for **12b**, the bond lengths are in the range of 1.36(4)—1.48(3) Å with an average of 1.43 Å. Although the average value of the bond lengths is in good agreement with that of the metal-free ligand **6**, the bond lengths of C(3)-C(4), C(18)-C(19), and C(19)-C(20) are slightly shorter and C(2)-C(3), C(5)-C(1), and C(17)-C(18) are slightly longer than those found in the metal-free ligand **6**. The bond angles in the Cp rings are ranged over 104(2)—110(2)° with an average value of 108°. The difference (6°) of the bond angle is much larger than that (1.3°) in the free ligand **6**. The above results suggest a deformation of the Cp ring in the complex due to complexation. The Pt atom, which is complexed by the two S atoms of the tetradentate macrocyclic moiety, has a slightly distorted cis square-planar environment; the two S atoms at the 9- and 12-positions of the ligand occupy the other two cis positions. These results are consistent with those obtained from the IR spectral data. The Pt-S bond lengths are 2.249(5) and 2.239(7) Å. The bond lengths are slightly shorter than the sum of the covalent radii (2.32 Å)[12] and suggest that there is little π-bonding in the Pt-S bond. The Pt-Cl bond lengths have an average value of 2.315 Å, almost equal to the sum of the covalent radii, 2.28 Å. The interestingly selective coordination of the Pt atom to the S(9) and S(12) atoms is attributable to a steric hindrance of the two Cp rings to the S(6) and S(15) atoms. Moreover, the conformations of the organic ligand moiety differ greatly between ligand **6** and complex **12b**. The two Cp rings for both compounds take an eclipsed conformation and the dihedral angles between them are 2.5(2) and 2.4(10)° for **6** and **12b**, respectively. However, as shown in Fig. 1, the torsion angle (68°) between the C(1)-S(6) and S(15)-C(16) bonds around the z-axis of the ruthenocene nucleus in the complex **12b** is much larger than the corresponding one (5.3°) in the free ligand **6**. These results are quite similar to those obtained in 1,10-dioxa-4,7-dithia[10](1,1')ruthenocenophane.[5] Furthermore, X-ray crystal data, which are presented in the experi-

mental section, showed the two compounds (**12a** and **12b**) to be isostructural.

Experimental

The melting and decomposition points have not been corrected. The ^{1}H NMR spectra were obtained on a JEOL FX-90Q spectrometer with TMS as an internal standard. The mass spectra were measured on a Hitachi M80 mass spectrometer. The electronic spectra were recorded on a Hitachi 330 spectrometer. The IR spectra were taken by using a JASCO DS-701G Diffraction Grating Infrared Spectrometer in CsI pellets.

Materials. Ruthenocene,[13] 1-bromo-2-chloroethane,[14] dichlorobis(acetonitrile) complexes of palladium(II) and platinum(II)[10] were prepared according to previously reported methods. The synthesis of ruthenocene-1,1′-dithiol (**3**) was carried out as described previously.[4] All other solvents and reagents used were reagent grade.

1,1′-Bis(2-chloroethylthio)ruthenocene (5). 1-Bromo-2-chloroethane (25 g, 176 mmol) was added to a mixture of **3** (2.3 g, 7.0 mmol) and sodium hydroxide (0.70 g, 18 mmol) in ethanol (170 cm^3) containing water (5 cm^3). After the mixture was stirred for 4 h at room temperature, the reaction mixture was concentrated in vacuo and the residual solid was chromatographed on activated alumina (dichloromethane as eluent). The yellow fraction was collected and concentrated in vacuo. Recrystallization of the residual solid from benzene gave **5** as pale-yellow powder in 67% yield. Mp 92.5—93 °C. Found: C, 40.30; H, 3.80%. Calcd for $C_{14}H_{16}Cl_2S_2Ru$: C, 40.00; H, 3.84%. ^{1}H NMR ($CDCl_3$) δ=4.75 (t, J=1.8 Hz, 4H), 4.65 (t, J=1.8 Hz, 4H), 3.66 (t, J=6.1 Hz, 4H), 2.90 (t, J=6.1 Hz, 4H). MS (60 eV) m/z 421 (M$^+$).

1,4,7-Trithia[7](1,1′)ruthenocenophane (8). A mixture of **5** (0.31 g, 0.74 mmol) and sodium sulfide (0.22 g, 0.92 mmol) in THF–ethanol (1:4) (158 cm^3) was refluxed under nitrogen for 10 h. The reaction mixture was cooled, evaporated in vacuo and the residual solid was dissolved in dichloromethane (100 cm^3). After the insoluble material was filtered off, the filtrate was evaporated and then the residual solid was chromatographed on silica-gel TLC (benzene as eluent). The fourth (main) fraction was collected and evaporated. Recrystallization of the residual solid from hexane gave **8** as pale-yellow needles in 15% yield. Mp 154.0—154.6 °C. Found: C, 44.10; H, 4.20%. Calcd for $C_{14}H_{16}S_3Ru$: C, 44.07; H, 4.24%. ^{1}H NMR ($CDCl_3$) δ=4.83 (t, J=1.8 Hz, 4H), 4.61 (t, J=1.8 Hz, 4H), 3.22—2.88 (m, 8H). MS (60 eV) m/z 382 (M$^+$). From the third fraction, **7** was obtained in 9.8% yield. Mp 225.6—226.5 °C. Found: C, 44.56; H, 3.76%. Calcd for $C_{12}H_{12}S_2Ru$: C, 44.84; H, 3.77%. ^{1}H NMR ($CDCl_3$) δ= 5.06 (t, J=1.8 Hz, 4H), 4.57 (t, J=1.8 Hz, 4H), 3.14 (s, 4H). MS (60 eV) m/z 322 (M$^+$).

1,4,7,10-Tetrathia[10](1,1′)ruthenocenophane (6). **5** (0.58 g, 1.4 mmol) in THF (100 cm^3) and a mixture of sodium hydroxide (0.50 g, 13.0 mmol) and 1,2-ethanedithiol (0.50 g, 5.3 mmol) in 98% ethanol (100 cm^3) were added dropwise to the refluxing mixture of THF (200 cm^3) and ethanol (200 cm^3) in the same rate for a period of 3 h, and further refluxed for 14 h. The reaction mixture was cooled and evaporated, and the residue was extracted with three 50 cm^3 portions of chloroform. After the extracts were combined, the resulting solution was washed with water, dried and evaporated in vacuo. The residual oil was chromatographed on activated alumina (benzene as eluent). The third (main) fraction was collected and evaporated. Recrystallization of the residual solid from benzene gave **6** as pale-yellow needles in 9.8% yield. Similarly, trace amounts of **7**, **8**, and **9** were obtained from the first, second and fourth fractions, respectively. **6**: Mp 138.6—139.0 °C. Found: C, 44.48; H, 4.60%. Calcd for $C_{16}H_{20}S_4Ru$: C, 43.50; H, 4.57%. ^{1}H NMR ($CDCl_3$) δ=4.62 (t, J=1.8 Hz, 4H), 4.77 (t, J=1.8 Hz, 4H), 3.10 (s, 4H), 3.21—2.75 (m, 8H). MS (60 eV) m/z 441 (M$^+$). **9**: Mp 93.5—94.0 °C. Found: C, 42.82; H, 4.74%. Calcd for $C_{18}H_{24}S_5Ru$: C, 43.08; H, 4.83%. ^{1}H NMR ($CDCl_3$) δ=4.75 (t, J=1.8 Hz, 4H), 4.61 (t, J=1.8 Hz, 4H), 3.15—2.71 (m, 16H). MS (60 eV) m/z 501 (M$^+$). The structures of **7** and **8** were confirmed by comparison with the melting points, R_f values of TLC and the spectral data of the authentic samples.

1,4,7,10,13-Pentathia[13](1,1′)ruthenocenophane (9). Bis-(2-mercaptoethyl) sulfide (1.5 cm^3, 11 mmol) was reacted with **5** (0.80 g, 1.9 mmol) in the presence of sodium hydroxide (0.80 g, 20 mmol) under the same conditions described above. The reaction mixture was worked up according to the previously described procedure and chromatographed on activated alumina (benzene as eluent). The second (main) fraction was collected and evaporated. Recrystallization of the residual solid from hexane gave **9** as white needles in 27% yield. Also, **7** was obtained from the first fraction. The structures of these compounds were confirmed by comparison with the melting points, R_f values of TLC and the spectral data of the authentic samples.

1,4,8,11-Tetrathia[11](1,1′)ruthenocenophane (10). A mixture of 1,3-propanedithiol (0.55 g, 5.1 mmol) and **5** (0.50 g, 1.2 mmol) in THF (30 cm^3) was added to absolute ethanol (170 cm^3) containing sodium hydroxide (0.51 g, 13 mmol) at a refluxing temperature. After refluxing for 2 h, the reaction mixture was cooled, evaporated in vacuo and extracted with three 50 cm^3 portions of chloroform. The extracts were combined, washed with 10% of aq sodium hydroxide solution and concentrated, and then the residual solid was chromatographed on activated alumina (benzene as eluent). From the second (main) fraction, **10** was obtained in 15% yield. Mp 121.6—122.2 °C. Found: C, 45.03; H, 4.95%. Calcd for $C_{17}H_{22}S_4Ru$: C, 44.80; H, 4.88%. ^{1}H NMR ($CDCl_3$) δ=4.79 (t, J=1.8 Hz, 4H), 4.63 (t, J=1.8 Hz, 4H), 3.20—2.62 (m, 12H), and 2.08 (q, J=7.6 Hz, 2H). MS (60 eV) m/z 455 (M$^+$). Also, a trace amount of **7** was isolated from the first fraction.

Palladium(II) and Platinum(II) Complexes (12, 13, and 14) of Polythia[n](1,1′)ruthenocenophanes: General Procedure. Dichloro(1,4,7,10-tetrathia[10](1,1′)ruthenocenophane)platinum(II) (12b). **11** (35.6 mg, 0.102 mmol) in acetonitrile (5 cm^3) was slowly added to gently refluxing acetonitrile solution (10 cm^3) containing **6** (44.9 mg, 0.102 mmol). The resulting crystals were collected by filtration and washed with small amounts of acetonitrile to give **12b** in 51% yield as pale-yellow needles. Mp 257 °C (decomp). Found: C, 27.16; H, 2.85%. Calcd for $C_{16}H_{20}Cl_2S_4RuPt$: C, 27.19; H, 2.70%.

Dichloro(1,4,7,10-tetrathia[10](1,1′)ruthenocenophane)palladium(II) (12a). Yield (89%). Mp 248 °C (decomp). Found: C, 31.05; H, 3.26%. Calcd for $C_{16}H_{20}Cl_2S_4RuPd$: C, 30.98; H, 2.99%.

Dichloro(1,4,7,10,13-pentathia[13](1,1′)ruthenocenophane)palladium(II) (13a). Yield (79%). Mp 211—212 °C. Found: C, 31.39; H, 3.62%. Calcd for $C_{18}H_{24}Cl_2S_5RuPd$: C, 31.83; H, 3.56%.

Dichloro(1,4,7,10,13-pentathia[13](1,1′)ruthenocenophane)-

platinum(II) (13b). Yield (49%). Mp 218—218.5°C. Found: C, 28.16; H, 3.15%. Calcd for $C_{18}H_{24}Cl_2S_5RuPt$: C, 28.06; H, 2.95%.

Dichloro(1,4,8,11-tetrathia[11](1,1')ruthenocenophane)palladium(II) (14a). Yield (73%). Mp 207—209°C. Found: C, 32.26; H, 3.50%. Calcd for $C_{17}H_{22}Cl_2S_4RuPd$: C, 32.29; H, 3.47%.

Dichloro(1,4,8,11-tetrathia[11](1,1')ruthenocenophane)platinum(II) (14b). Yield (47%). Mp 212—213°C. Found: C, 28.29; H, 3.07%. Calcd for $C_{17}H_{22}Cl_2S_4RuPt$: C, 28.15; H, 2.83%.

X-Ray Crystallography. Crystals of dimensions 0.4×0.15×0.1 mm for the metal-free ligand (**6**), 0.3×0.2×0.1 mm for the Pd-complex **12a**, and 0.4×0.1×0.05 mm for the Pt-complex **12b** were used for the X-ray crystallography. Crystal data are as follows: **6**, $C_{16}H_{20}S_4Ru$, MW=441.7. Triclinic, $P\bar{1}$, a=13.828 (2), b=11.890 (2), c=5.587 (2) Å, α=95.53 (2), β=105.39 (2), γ=102.22 (1)°, U=853.1 Å^3, Z=2, Dx=1.72 g·cm^{-3}, μ(Mo $K\alpha$)=1.4 mm^{-1}. **12a**, $C_{16}H_{20}Cl_2S_4RuPd$, MW=619.0, monoclinic, $P2_1/n$, a=9.925(4), b=28.148 (8), c=7.489 (3) Å, β=102.20 (3)°, U=2044.5 Å^3, Z=4, Dx=2.01 g·cm^{-3}, μ(Mo $K\alpha$)=2.3 mm^{-1}. **12b**, $C_{16}H_{20}Cl_2S_4RuPt$, MW=707.7, monoclinic, $P2_1/n$, a=9.912 (6), b=28.142 (9), c=7.521 (3) Å, β=102.08 (4)°, U=2053.3 Å^3, Z=4, Dx=2.29 g·cm^{-3}, μ(Mo $K\alpha$)=8.3 mm^{-1}.

An X-ray structural analysis was carried out on compounds **6** and **12b**, because **12a** was isostructural with **12b** as can be seen from each crystal data. Intensity data for 2θ=50° were recorded on a Rigaku AFC-5R with graphite-monochromatized Mo $K\alpha$ radiation. A Total of 3017 (**6**) and 3606 (**12b**) independent reflections were corrected for Lorentz and polarization factors but not for absorption. Both structures **6** and **12b** were solved by a combination of the heavy-atom technique and direct methods using MULTAN,[15] and refined by block diagonal least-squares methods. The positions of the hydrogen atoms were estimated using standard geometry. The final refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms were lowered R values 0.031 (R_w=0.034, w=1.0, 2646 observed reflections with $F_o \geq 2\sigma(F_o)$) and 0.070 (R_w=0.055, $w=1/\sigma(F_o)$, 2528 observed reflections with $F_o \geq 2\sigma(F_o)$) for **6** and **12b**, respectively. Anomalous dispersion corrections were applied to the scattering factors of Pt, Ru, Cl, and S.[16]

Parameters for hydrogen atoms and the thermal parameters for non-hydrogen atoms (observed and calculated) as well as structure factors are kept at the Chemical Society of Japan (Document No. 8642).

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