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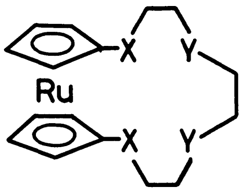
Structures of 4,7,10-Trioxa-1,13-dithia[13](1,1')ruthenocenophane and Its $PdCl_2$ Complex

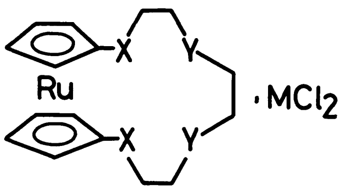
Sadatoshi AKABORI,* Sadao SATO,*† Yoichi HABATA, Kayoko KAWAZOE,†
Chihiro TAMURA,† and Masaru SATO††
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274
†Analytical and Metabolic Reserach Laboratories, Sankyo Co., Ltd., Hiromachi, Shinagawa-ku, Tokyo 140
††Chemical Analysis Center, Saitama University, Urawa, Saitama 338

The X-ray analysis of 4,7,10-trioxa-1,13-dithia[13](1,1')ruthenocenophane and its $PdCl_2$ complex revealed that the Pd atom bonded to the sulfur atoms of the ligand and the torsion angle (69.2°) around the z-axis of the ruthenocenophane nucleus in the metal-free ligand is much larger than the corresponding one (0.4°) in the complex. These results are completely opposite of the case of [10](1,1')-ruthenocenophane and its Pt complex.

Although a number of crown, thiacrown, and azacrown ether complexes of alkali, alkaline, and transition metal ions have already been reported,1) only a few complexes of platinum group metals with the above macrocyclic compounds are known.2) A comparison of the X-ray structures of the metal-free ligand with its metal complex can often reveal changes in the molecular conformation which is caused by complexation. In the previous papers,3,4) we have reported the crystal structures of 1,10-dioxa-4,7-dithia- and 1,4,7,10-tetrathia[10]-(1,1')ruthenocenophanes (**1** and **2**) and their platinum and/or palladium complexes (**3** and **4**). The torsion angle (68°) between the C(1)-S(6) and S(15)-C(16) bond around the z-axis of the ruthenocene nucleus in the palladium complex **4** is much larger than the corresponding one (5.3°) in the metal-free ligand (**2**), although the two Cp rings for these compounds take an eclipsed conformation and the dihedral angles between them are 2.5 and 2.4 for **2** and **4**. Also very similar results were obtained in the cases of [10](1,1')ruthenocenophane (**1**) and its platinum complex (**3**). Furthermore, we have reported on the preparation of 1,n-dithiaoxa[n](1,1')ruthenocenophanes by the reaction of disodium



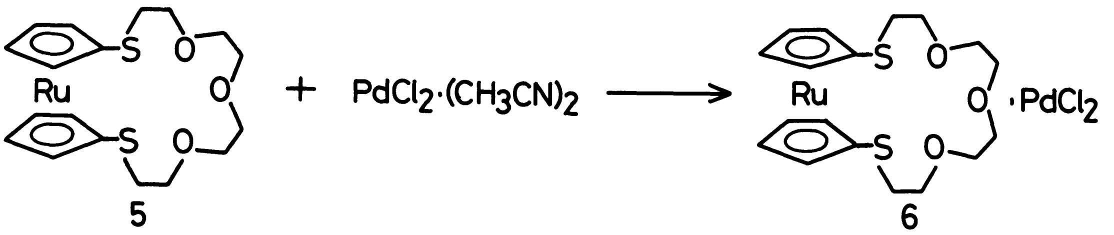
1:X=O, Y=S
2:X=Y=S



3:X=O, Y=S, M=Pd
4:X=Y=S, M=Pt

ruthenocene-1,1'-dithiolate with dihalide.[5)] In this paper we report the X-ray analysis of 4,7,10-trioxa-1,13-dithia[13](1,1')ruthenocenophane **5** and its palladium complex **6**.

A solution of 14 mg (54 mmol) of $PdCl_2 \cdot (CH_3CN)_2$ in 1 ml of acetonitrile was added, dropwise, to a solution of 1 ml of acetonitrile containing 23 mg (51 mmol) of **5**. The resulting precipitates were filtered and washed with a small amount of acetonitrile to give a 1:1 metal complex **6**, mp 200 °C(dec.), in 72% yield.



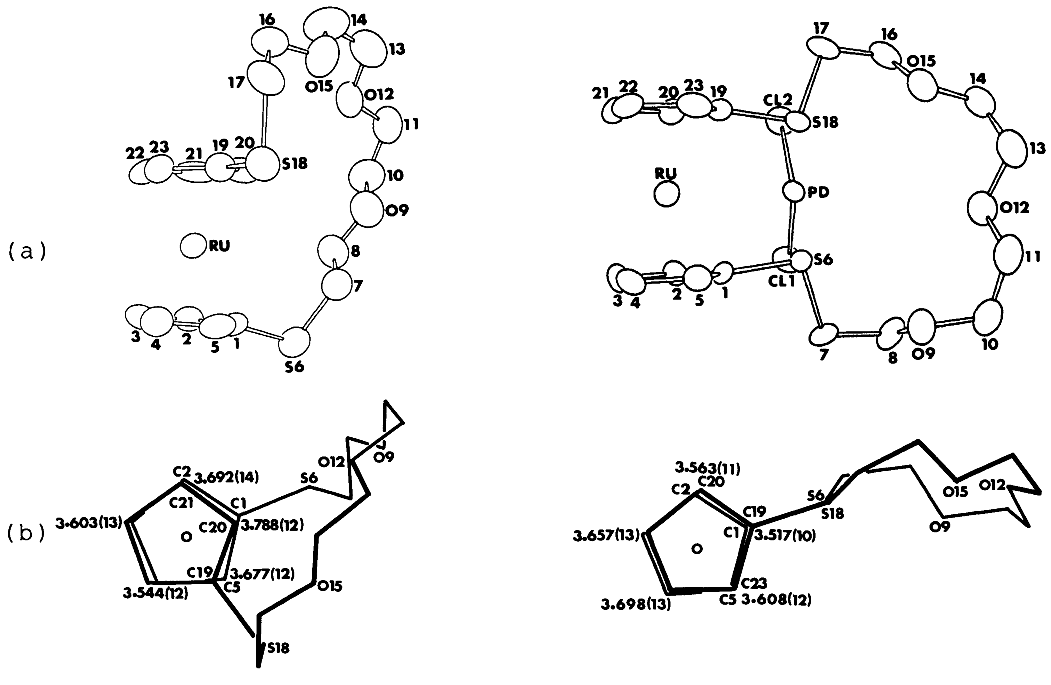
The ^1H-NMR spectrum of **5** in DMSO-d_6 showed a pair of triplets corresponding to the α - and β-ring protons of the ruthenocene nucleus at δ 4.64 (J=1.7 Hz, 4H) and 4.77(J=1.7 Hz, 4H), in addition to a singlet at δ 3.75 (OCH_2CH_2O, 8H) and two triplets at δ 2.85 (J=6.6 Hz, SCH_2, 4H) and 3.60 (J=6.6 Hz, OCH_2, 4H). These results suggest that **5** in the solution takes a symmetrical structure which differs from its conformation in the solid state as described below. Furthermore, the differences in the chemical shifts between all the protons of **5** and **6** were not observed because the complex **6** in the solution seems to take a solvolytic form with DMSO. The result is consistent with those of [10](1,1')ruthenocenophane and its complex.[3,4)]

Crystal data: The metal-free ligand **5**, $C_{18}H_{24}O_3S_2Ru$, Mw=456.3, monoclinic, $P2_1/a$, a=18.783(2), b=7.895(1), c=12.892(1) Å, β=93.53(1)°, U=1908.2 $Å^3$, Z=4, Dc=1.58g·cm^{-3}, μ(MoKα)=10 cm^{-1}. The palladium complex **6**, $C_{18}H_{24}O_3S_2RuPdCl_2$, Mw=630.9, triclinic, $P\bar{1}$, a=13.956(2), b=9.174(1), c=8.770(1) Å, α=86.61(1), β=75.54(1), γ=94.37(1)°, U=1080.6$Å^3$, Z=2, Dc=1.94g·cm^{-3}, μ(MoKα)=20 cm^{-1}.

The intensities of the independent reflections ($Fo \geq 2\sigma(Fo)$) of 2511 and 3129 were collected on a Rigaku AFC-5R diffractometer using MoKα radiation. The structures were resolved by the heavy atom method and refined by block-diagonal least-squares to final R values of 0.054 and 0.039 for **5** and **6**, respectively. The molecular structures of **5** and **6** are illustrated in Fig. 1.

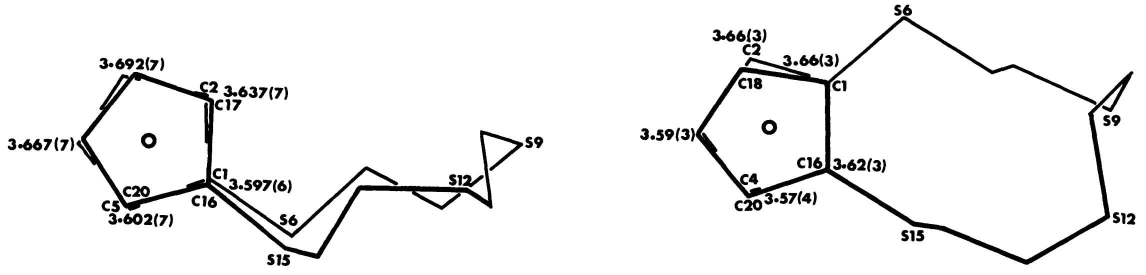
In the case of **6**, the interesting selective coordination of the Pd atom on the S(6) and S(18) atoms in spite of the steric hindrance due to the two Cp rings suggests that the Pd atom has a higher complexation ability on the S atoms than the O atoms. The Pd atom bonded to the two S atoms of the oxathiacrown ether has a slightly distorted cis square-planar environment. The dihedral angle between the planes defined by S(6)-Pd-S(18) and Cl(1)-Pd-Cl(2) is 4.1(1)°. The coordination geometry of the Pd atom is similar to that found in the platinum complex of [10]ruthenocenophane **4**[4)] except for the difference of the coordinated site in the macrocyclic ring. The Pd-Cl (2.303(2) and 2.308(2) Å) and Pd-S bond (2.314(2) and 2.303(2) Å) distances are consistent with the sum of covalent radii, respectively . The intramolecular atomic distance between the Ru and Pd atoms is 3.697(1) Å. This value is much longer than that of the Ru-Pd dative bond, (2.692(1) Å), in (1,1'-ruthenocenedithiolato--S,S',Ru)(triphenylphosphine)palladium (II)[6] and indicates no direct metal-metal interaction between the coordinated palladium atom and the ruthenium atom of the ruthenocene nucleus in the complex **6**.

The conformation of the organic ligand moiety of the complex **6** differs greatly from that of the metal-free ligand **5**. The main conformational changes are reflected in the overlapping patterns between the two Cp rings and the torsion angles of the macrocyclic moiety. The Cp rings take an eclipsed conformation, in which the dihedral angles between them are 5.5(4) and 4.4(3)° for **5** and **6**, respectively. The torsion angle C(1)-Cp1-Cp2-C(19) (Cp1 and Cp2 are the centroids of the Cp rings) in **5** is 69.2°, although that in **6** is only 0.4°. As shown in Fig. 2, these results are just the opposite of the cases of [10](1,1')ruthenocenophanes and their platinum group metal complex;[3,4] the metal-free ligand **2** has a small torsion angle (5.3°), while the torsion angle of its platinum complex is a large one (68°). The torsion angles in [3](1,1')- and [4](1,1')ruthenocenophanes are 14.8(2) and 1.7(2)°, respectively.[7] However, Cameron et al[8]



Molecule **5** Molecule **6**

Fig.1. (a)**ORTEP** drawings of molecules with atom numbering scheme. (b)Projections of the organic ligand moieties on the Cp ring containing the C(1) atom with the C---C distance(Å) between the rings. An open circle denotes Ru atom. Selected bond lengths (Å), and bond and torsion angles (°) (First numerical values for **5**, and second for **6**). C(1)-S(6) 1.769(9), 1.769(7), S(6)-C(7) 1.798(10), 1.807(8), C(17)-S(18) 1.836(10), 1.810(10), S(18)-C(19) 1.759(8), 1.758(8); S(6)-C(1)-C(2) 122.5(7), 128.3(5), S(6)-C(1)-C(5) 126.6(7), 122.2(5), C(1)-S(6)-C(7) 103.3(4), 102.6(4), S(6)-C(7)-C(8) 108.4(7), 108.3(6), C(16)-C(17)-S(18) 117.8(7), 109.0(7), C(17)-S(18)-C(19) 101.3(4), 104.2(4), S(18)-C(19)-C(20) 125.5(6), 128.1(6), S(18)-C(19)-C(23) 125.2(6), 122.5(6); C(1)-S(6)-C(7)-C(8) -97.3(7), -171.7(5), S(6)-C(7)-C(8)-O(9) -178.3(3), 63.4(9), O(15)-C(16)-C(17)-S(18) -63.0(10), -49.2(9), C(16)-C(17)-S(18)-C(19) -39.3(11), -172.0(6).



Molecule **2** Molecule **4**

Fig. 2. Projections of the organic ligand moieties of 1,4,7,10-tetrathia-[10](1,1')ruthenocenophane and its Pd complex on the Cp ring containing the C(1) atom. The C---C distances (Å) between the rings are given. An open circle denotes Ru atom (Ref. 4).

reported that the torsion angle in [4](1,1')ferrocenophane is approximately 36°. Therefore the conformational stability around the z-axis of the ruthenocene nucleus in the metal-free ligands is attributable to the ring size of the macrocyclic rings. The large rotational angle (69.2°) between the two Cp rings in the metal-free ligand **5** causes the two S atoms attached to each Cp ring to separate by more than 4.5 Å from each other, and this distance is too long to form the complex. In order to form the complex **6**, it is necessary to rotate the two S atoms more closely so their lobes of lone pair electrons are in the same direction. It was reported that the energy barrier of the rotation around the z-axis (Cp1-Ru-Cp2) of ruthenocene is only 3-6 kcal/mol.[9] Therefore, the energy of the rotation around the z-axis of the ruthenocene nucleus is compensated by the conformational changes of the macrocyclic moiety. Indeed the three torsion angles, C(1)-S(6)-C(7)-C(8), S(6)-C(7)-C(8)-O(9) and C(16)-C(17)-S(18)-C(19), in **6** are remarkably changed by the complexation, compared with those of the corresponding metal-free ligand **5** as shown in Fig. 1.

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