The Conformational Studies of 4,7,10-Trioxa-1,13-dithia[13](1,1′)ruthenocenophane and Its $PdCl_2$ Complex by X-Ray Analyses†

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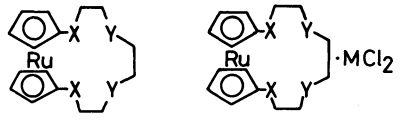
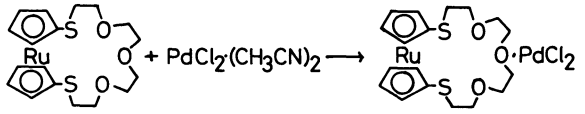
Dichlorobis(4,7,10-trioxa-1,13-dithia[13](1,1′)ruthenocenophane)palladium(II) (**6**) was obtained by the reaction of 4,7,10-trioxa-1,13-dithia[13](1,1′)ruthenocenophane (**5**) with dichlorobis(acetonitrile)palladium(II) in 72% yield. The crystal structures of the complex **6** and its metal free ligand **5** were determined by the X-ray method. The crystal data: **5**, 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, D_c=1.58 g cm^{-3}, μ(Mo $K\alpha$)=10 cm^{-1}. **6**, 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, D_c=1.94 g cm^{-3}, μ(Mo $K\alpha$)=20 cm^{-1}. The Pd atom of **6** bonded to the two 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 1,4,7,10-tetrathia[10](1,1′)ruthenocenophane and its Pt complex. Furthermore, the intramolecular atomic distance (3.697 Å) between the Ru and Pd atoms in **6** suggests the absence of the Ru–Pd dative bond.

Although a number of crown, thiacrown, and azacrown ether complexes of alkali, alkaline earth, 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] Furthermore, few conformational studies of the complexes of metallocenophanes containing polyether and polythiaether moieties with metal ions by X-ray analyses have been carried out,[3–7] although many metallocenophanes have been described.[8–16] 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 connection with the above viewpoints, 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**).[5,6] 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 polyoxa-l,n-dithia[n](1,1′)ruthenocenophanes by the reaction of disodium ruthenocene-1,1′-dithiolate with dihalide.[4] In this paper[17] we report the X-ray analysis of 4,7,10-trioxa-1,13-dithia[13](1,1′)ruthenocenophane (**5**) and its palladium complex **6**.



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

A solution of $PdCl_2\cdot(CH_3CN)_2$ in acetonitrile was reacted with a equimolar amount of **5** in acetonitrile to give 1 : 1 complex **6** in 72% yield. The melting point of the palladium complex **6** was higher than that of the corresponding metal free ligand **5**. The ^{1}H 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 in DMSO, because the complex **6** in the solution seems to take a solvolytic form. The result is consistent with those of [10](1,1′)ruthenocenophanes and their complexes.[5,6] Measurements of the ^{1}H NMR spectra of **6** in less polar solvents such as CD_3CN and $CDCl_3$ were unsuccessful because the low solubility of the complex **6** in such solvents.



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† Dedicated to Professor Michinori Ōki on the occasion of his 60th birthday.

Table 1. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters (Å^2), with Estimated Standard Deviations in Parentheses of **5**

Atom	x	y	z	B_{eq}[25]
Ru	3742.6(3)	6044.6(9)	3954.5(5)	3.08
C(1)	4518(4)	7474(11)	3101(6)	3.91
C(2)	4858(4)	6868(11)	4067(7)	4.11
C(3)	4512(5)	7645(12)	4876(7)	4.62
C(4)	3943(5)	8673(11)	4419(7)	4.97
C(5)	3956(4)	8572(10)	3313(7)	4.16
S(6)	4904(1)	7217(4)	1893(2)	6.09
C(7)	4271(5)	5899(12)	1169(6)	4.99
C(8)	4525(5)	4076(14)	1255(7)	5.79
O(9)	4030(4)	3127(8)	658(5)	6.04
C(10)	4168(5)	1352(13)	696(7)	5.90
C(11)	3509(5)	420(12)	373(7)	5.21
O(12)	3033(3)	653(8)	1165(4)	5.14
C(13)	2332(6)	108(13)	880(8)	6.45
C(14)	1866(5)	529(12)	1717(8)	6.26
O(15)	1736(3)	2333(8)	1734(5)	5.52
C(16)	1426(5)	2829(12)	2651(7)	5.19
C(17)	1303(5)	4702(12)	2628(7)	4.98
S(18)	2086(1)	6088(3)	2599(2)	4.72
C(19)	2698(4)	5021(10)	3456(6)	3.44
C(20)	3207(4)	3835(11)	3166(6)	4.03
C(21)	3579(4)	3322(10)	4119(8)	5.22
C(22)	3297(4)	4124(12)	4974(7)	4.61
C(23)	2752(4)	5217(11)	4577(6)	4.14

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters (Å^2), with Estimated Standard Deviations in Parentheses of **6**

Atom	x	y	z	B_{eq}[25]
Ru	9028.3(4)	3395.6(6)	3220.7(6)	2.45
Pd	7464.6(4)	2650.7(5)	466.3(6)	1.80
Cl(1)	7124(2)	4688(2)	−895(2)	3.66
Cl(2)	8373(2)	1860(2)	−1862(2)	3.63
C(1)	7679(5)	4405(7)	3390(8)	2.21
C(2)	8463(5)	5329(7)	2365(9)	2.68
C(3)	9137(6)	5782(8)	3272(10)	3.43
C(4)	8750(6)	5138(8)	4845(9)	3.14
C(5)	7851(6)	4276(8)	4934(8)	2.80
S(6)	6683(1)	3379(2)	2913(2)	2.10
C(7)	5829(5)	4743(8)	2807(9)	3.00
C(8)	4877(6)	3979(10)	2645(10)	4.04
O(9)	4460(4)	3048(7)	3989(7)	4.26
C(10)	3613(7)	2110(12)	3902(14)	5.71
C(11)	3787(7)	534(11)	4059(11)	4.76
O(12)	4502(4)	212(6)	2690(7)	3.85
C(13)	4520(7)	−1351(10)	2623(11)	4.41
C(14)	5354(7)	−1662(9)	1260(11)	4.10
O(15)	6273(5)	−1430(6)	1675(7)	3.94
C(16)	7102(7)	−1353(9)	341(10)	3.96
C(17)	8009(7)	−884(8)	886(10)	3.75
S(18)	7773(1)	706(2)	2002(2)	2.39
C(19)	8931(5)	1288(8)	2323(9)	2.66
C(20)	9736(6)	2176(9)	1280(9)	3.17
C(21)	10442(6)	2543(10)	2157(11)	3.81
C(22)	10080(7)	1878(9)	3697(11)	4.19
C(23)	9140(7)	1085(8)	3828(10)	3.68

The metal free ligand **5** and its Pd complex **6** were further characterized by X-ray crystallographical studies. The final atomic parameters for **5** and **6** are listed in Tables 1 and 2, and bond lengths as well as bond and torsion angles are given in Tables 3 and 4 for **5** and **6**, respectively. The molecular structures of **5** and **6** are illustrated in Fig. 1.

In spite of the steric hindrance due to the two Cp rings the interesting selective coordination of the S(6) and S(18) atoms in **6** on the Pd atom 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 moiety has a slightly distorted cis square-planar configuration. 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**[6] except for the difference of the coordinated site in the macrocyclic ring. 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)[18] and its analogues,[19] and indicates no direct metal–metal interaction between the coordinated palladium atom and the ruthenium atom of the ruthenocene nucleus in the complex **6**. This finding is very different from the result[20] obtained in the 1:1 complex **8** of 1,4,7-trithia[7](1,1′)-ferrocenophane (**7**) with $(CH_3CN)_4 \cdot Pd(BF_4)_2$. Palladium atom was incorporated in the cavity of the macrocyclic moiety of **7** and coordinated by the three sulfur atoms to form the Fe–Pd dative bond. The absence of the Ru–Pd dative bond in **6** attributed to the strong bonding force of the Pd–Cl bond compared with Pd–B bond, because the two Pd–Cl bond length in **6** are 2.303(2) and 2.308(2) Å, respectively, which are consistent with the sum of the covalent radii[21] of Pd and Cl atoms.

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 in 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 and palladium complexes;[5,6] 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.[9,10] However, Cameron et al.[8] reported that the torsion angle in [4](1,1′)ferrocenophane is

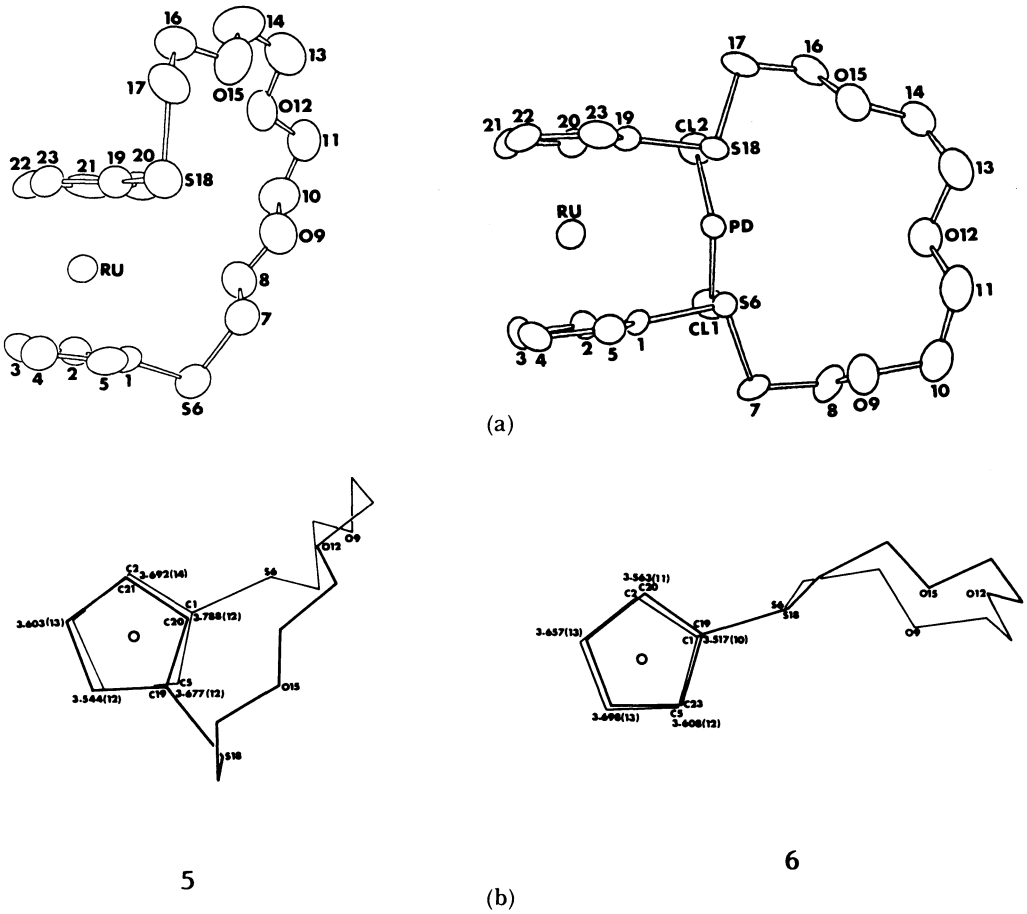

Fig. 1. (a) ORTEP (Johnson, 1965) drawings of molecules **5** and **6** with atom numbering scheme. (b) Projections of the organic ligand moieties on the Cp ring containing the C(1) atom with the C····C distances (Å) between the rings. An open circle denotes the Ru atom.

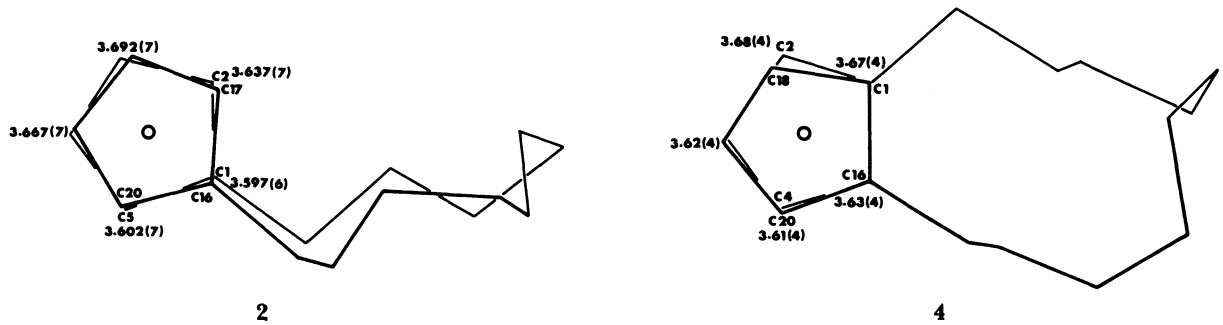

Fig. 2. Projections of the organic ligand moieties on the Cp ring containing the C(1) atom with the C····C distances (Å) between the rings. An open circle denotes the Ru atom (Ref. 5).

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 approach the two S atoms more closely and the lobes of lone pair electrons are rotate in the same direction. It was reported that the energy barrier of the rotation around the *z*-axis (Cpl–Ru–Cp2) of ruthenocene is only 3—6 kcal mol^{-1}.[22] 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)–

Table 3. Bond Lengths (Å) and Bond and Torsion Angles (°) in **5**

1	2	3	4	1-2	1-2-3	1-2-3-4
Dithia-crown moiety						
S(6)	C(1)	C(2)	C(3)	1.769(9)	122.5(7)	165.2(4)
S(6)	C(1)	C(5)	C(4)		126.6(7)	−165.7(5)
C(2)	C(1)	S(6)	C(7)			117.2(8)
C(5)	C(1)	S(6)	C(7)			−78.2(9)
C(1)	S(6)	C(7)	C(8)		103.3(4)	−97.3(7)
S(6)	C(7)	C(8)	O(9)	1.798(10)	108.4(7)	−178.3(3)
C(7)	C(8)	O(9)	C(10)	1.518(14)	105.9(8)	−176.9(7)
C(8)	O(9)	C(10)	C(11)	1.390(13)	113.4(8)	160.0(7)
O(9)	C(10)	C(11)	O(12)	1.426(12)	109.4(8)	−69.1(9)
C(10)	C(11)	O(12)	C(13)	1.478(14)	106.8(8)	168.7(7)
C(11)	O(12)	C(13)	C(14)	1.410(11)	113.2(7)	−175.4(7)
O(12)	C(13)	C(14)	O(15)	1.414(12)	109.1(9)	73.0(10)
C(13)	C(14)	O(15)	C(16)	1.469(15)	110.1(9)	−167.1(8)
C(14)	O(15)	C(16)	C(17)	1.446(13)	111.5(7)	180.0(7)
O(15)	C(16)	C(17)	S(18)	1.405(12)	109.3(8)	−63.0(10)
C(16)	C(17)	S(18)	C(19)	1.497(14)	117.8(7)	−39.3(8)
C(17)	S(18)	C(19)	C(20)	1.836(10)	101.3(4)	93.9(8)
C(17)	S(18)	C(19)	C(23)			−85.5(8)
S(18)	C(19)	C(20)	C(21)	1.759(8)	125.5(6)	179.8(5)
S(18)	C(19)	C(23)	C(22)		125.2(6)	179.0(4)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.445(12)	107.2(8)	2.3(10)
C(2)	C(3)	C(4)	C(5)	1.404(13)	107.9(8)	−2.0(11)
C(3)	C(4)	C(5)	C(1)	1.438(13)	108.7(8)	0.9(10)
C(4)	C(5)	C(1)	C(2)	1.429(12)	106.7(7)	0.5(10)
C(5)	C(1)	C(2)	C(3)	1.406(12)	109.5(7)	−1.8(10)
C(19)	C(20)	C(21)	C(22)	1.405(11)	105.3(8)	1.7(11)
C(20)	C(21)	C(22)	C(23)	1.434(13)	111.0(9)	−2.0(12)
C(21)	C(22)	C(23)	C(19)	1.402(14)	107.0(8)	1.4(11)
C(22)	C(23)	C(19)	C(20)	1.411(13)	107.5(8)	−0.4(10)
C(23)	C(19)	C(20)	C(21)	1.451(12)	109.3(7)	−0.7(10)

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.

Experimental

The decomposition point has not been corrected. ^{1}H NMR spectra were obtained on a JEOL FX-90Q spectrometer with TMS as an internal standard.

Materials. 4,7,10-Trioxa-1,13-dithia[13](1,1′)ruthenocenophane (**5**) was prepared according to the previously reported method.[4]

Dichlorobis(acetonitrile)palladium(II) was prepared according to methods described in the literature.[23]

Dichloro(4,7,10-trioxa-1,13-dithia[13](1,1′)ruthenocenophane)palladium(II) (**6**). A solution of 14 mg (54 mmol) of dichlorobis(acetonitrile)palladium(II) in 1 cm^3 of acetonitrile was added, dropwise, to a solution of 1 cm^3 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** in 72% yield. Mp 200 °C (decomp).

Found: C, 34.26; H, 3.84. Calcd for $C_{18}H_{24}O_3S_2RuPdCl_2$: C, 34.27; H, 3.84.

X-Ray Crystallography. Crystals of dimensions 0.4×0.2×0.1 mm for the metal free ligand **5** and 0.4×0.3×0.15 mm for the Pd-complex **6** were used for X-ray crystallography. Crystal data are as follows: **5**, $C_{18}H_{24}O_3S_2Ru$, M_w=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, D_x=1.58 g cm^{-3}, μ(Mo $K\alpha$)=10 cm^{-1}. **6**, $C_{18}H_{24}O_3S_2RuPdCl_2$, M_w=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, D_x=1.94 g cm^{-3}, μ(Mo $K\alpha$)=20 cm^{-1}.

Intensity data for $2\theta \leq 50°$ were recorded on a Rigaku AFC-5R with graphite-monochromatized Mo $K\alpha$ radiation. A total of 3362 (**5**) and 3424 (**6**) independent reflections were corrected for Lorentz and polarization factors but not for absorption. Both structures **5** and **6** were solved by the heavy-atom method, 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 nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms were lowered R values 0.054 (R_w=0.049, $w=1/\sigma(F_o)$, 2511 observed reflections with $F_o \geq 2\sigma(F_o)$) and 0.039 (R_w=0.049, $w=1/\sigma(F_o)$, 3129 observed reflections with $F_o > 2\sigma(F_o)$) for **5** and **6**, respectively. Anomalous dispersion corrections were applied to the scattering factors of Pd, Ru, Cl, and S.[24]

List of structural factors, anisotropic thermal parameters and H-atom coordinations are kept at the Chemical Society of Japan (Document No. 8792)

Table 4. Bond Lengths (Å) and Bond and Torsion Angles (°) in the Complex **6**

1	2	3	4	1-2	1-2-3	1-2-3-4
Dithia-crown moiety						
S(6)	C(1)	C(2)	C(3)	1.769(7)	128.3(5)	−173.8(4)
S(6)	C(1)	C(5)	C(4)		122.2(5)	174.6(3)
C(2)	C(1)	S(6)	C(7)			−80.4(7)
C(5)	C(1)	S(6)	C(7)			106.3(6)
C(1)	S(6)	C(7)	C(8)		102.6(4)	−171.7(5)
S(6)	C(7)	C(8)	O(9)	1.807(8)	108.3(6)	63.4(9)
C(7)	C(8)	O(9)	C(10)	1.496(13)	109.0(7)	−172.3(7)
C(8)	O(9)	C(10)	C(11)	1.386(12)	114.6(8)	118.6(9)
O(9)	C(10)	C(11)	O(12)	1.429(14)	111.7(9)	−69.0(11)
C(10)	C(11)	O(12)	C(13)	1.488(16)	108.8(9)	−166.6(8)
C(11)	O(12)	C(13)	C(14)	1.420(12)	110.3(7)	−174.1(7)
O(12)	C(13)	C(14)	O(15)	1.442(12)	109.2(8)	76.4(9)
C(13)	C(14)	O(15)	C(16)	1.504(14)	109.3(8)	−165.7(7)
C(14)	O(15)	C(16)	C(17)	1.423(12)	112.3(7)	171.7(6)
O(15)	C(16)	C(17)	S(18)	1.420(12)	107.2(8)	−49.2(9)
C(16)	C(17)	S(18)	C(19)	1.503(14)	109.0(7)	−172.0(6)
C(17)	S(18)	C(19)	C(20)	1.810(10)	104.2(4)	82.6(8)
C(17)	S(18)	C(19)	C(23)			−106.8(7)
S(18)	C(19)	C(20)	C(21)	1.758(8)	128.1(6)	170.7(4)
S(18)	C(19)	C(23)	C(22)		122.5(6)	−171.4(3)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.414(10)	107.1(7)	−0.5(10)
C(2)	C(3)	C(4)	C(5)	1.430(12)	107.9(7)	0.7(10)
C(3)	C(4)	C(5)	C(1)	1.423(12)	109.0(7)	−0.6(10)
C(4)	C(5)	C(1)	C(2)	1.414(12)	106.7(7)	0.2(9)
C(5)	C(1)	C(2)	C(3)	1.433(10)	109.3(6)	0.2(9)
C(19)	C(20)	C(21)	C(22)	1.422(11)	107.1(7)	0.7(11)
C(20)	C(21)	C(22)	C(23)	1.425(12)	108.3(8)	−0.3(11)
C(21)	C(22)	C(23)	C(19)	1.402(14)	109.1(8)	−0.3(11)
C(22)	C(23)	C(19)	C(20)	1.425(14)	106.5(8)	0.7(10)
C(23)	C(19)	C(20)	C(21)	1.426(12)	108.9(7)	−0.9(10)
Pd coordination						
Cl(1)	Pd	Cl(2)		2.303(2)	90.4(1)	
Cl(2)	Pd	S(6)		2.308(2)	174.2(1)	
S(6)	Pd	Cl(1)		2.314(2)	93.8(1)	
S(18)	Pd	Cl(1)		2.303(2)	175.6(1)	
S(6)	Pd	S(18)			81.9(1)	
S(18)	Pd	Cl(2)			93.8(1)	

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