

The angle between the plane Os(1)–C(11)–Os(2) and the triosmium plane of 103.8 (5)° [102.9 (5)° for molecule II] together with the Os(3)···C(11) contact distance of 3.11 (1) Å [3.097 (9) Å] indicates minimal semi-μ₃ character of the alkylidyne ligand, *cf.* corresponding values for [Os₃(μ-H)(μ₃-CPh)(CO)₁₀] of 78.2° and 2.586 (10) Å (Yeh *et al.*, 1985) and [Os₃(μ-H)(μ₃-CCH₂CHMe₂)(CO)₁₀] of 82.1° and 2.640 (26) Å (Green *et al.*, 1984). Although [Os₃(μ-H)(μ-COCH₃)(CO)₁₀] is structurally undetermined, the related complex [Os₃(μ-H){μ-CN(H)Bu^t}(CO)₁₀] (Adams & Golembeski, 1979), also with a π-donor substituent, has a much greater corresponding interplanar angle of 106°, implying a markedly weaker interaction. These data taken together suggest only a minimal increase in alkylidyne μ₃ character in complex (1) on substitution of μ-H by μ-AuPPh₃, in contrast to previous observations for [CoFe₂(μ-H)(μ₃-COCH₃)(CO)₇(η-C₅H₅)] and the μ-AuPPh₃ analogue (Aitchison & Farrugia, 1986). Moreover, in the [Ru₃(μ-X)(μ-COCH₃)(CO)₁₀] system there is an *increase* in the interplanar angle in going from the hydrido (94.9°) (Churchill, Beanan, Wasserman, Bueno, Rahman & Keister, 1983) to the aurio derivative (av. 101°) (Bateman *et al.*, 1983). These results imply that steric rather than electronic factors are of principal importance in the configurational differences observed, in view of the lack of a consistent pattern.

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Structures of 1,10-(1,1'-Ruthenocenediyl)-1,10-dioxo-4,7-dithiadecane (I) and its PdCl₂ Complex (II)

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Abstract. (I), C₁₆H₂₀O₂RuS₂, *M_r* = 409.6, monoclinic, *C*2/*c*, *a* = 27.393 (4), *b* = 11.966 (2), *c* = 10.375 (2) Å, β = 110.83 (1)°, *V* = 3178.3 Å³, *Z* = 8, *D_x* = 1.71 g cm⁻³, λ(Mo Kα) = 0.7107 Å, μ = 12 cm⁻¹, *F*(000) = 1664, *T* = 297 K, *R* = 0.033 for 2248 observed reflections. (II), C₁₆H₂₀O₂RuS₂.PdCl₂, *M_r* = 586.9, orthorhombic, *P*2₁2₁2₁, *a* = 14.225 (4), *b* = 12.235 (3), *c* = 10.778 (3) Å, *V* = 1877.6 Å³, *Z* = 4, *D_x* = 2.08 g cm⁻³, λ(Mo Kα) = 0.7107 Å, μ = 22 cm⁻¹, *F*(000) = 1152, *T* = 297 K, *R* = 0.055 for

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1355 observed reflections. Conformations of the ruthenocrown ether as the metal-free ligand (I) and in the complex (II) are different. In the complex (II) the PdCl₂ bonds to the two S atoms of the ligand with a *cis* square-planar configuration. The torsion angles of S—C—C—S in (I) and (II) are 161.0 (1) and 58.4 (17)°, respectively. The cyclopentadienyl rings take an eclipsed conformation, but in (II) revolve about one fifth of a turn around the centroidal axis.

Introduction. The present study is part of a research project on synthetic and structural studies of the complexes of metallocenocrown ethers. Although a number of complexes of alkali, alkaline, and transition metals with crown, thiocrown, and azacrown ethers have already been reported, there are few complexes for these crown ethers with platinum-group metals as guests (Metz, Moras & Weiss, 1974; Boyce, Carroy, Lehn & Parker, 1984). The X-ray analysis of the metal-free ligand and its complex can often reveal the changes in the molecular conformation caused by complexation. In this paper, we present the isolation of the palladium complex (II) and X-ray analysis of the metal-free ligand (I) and the complex (II).

Experimental. A solution of 11 mg (0.042 mmol) of PdCl₂·(CH₃CN)₂ in 1 ml of acetonitrile was added dropwise to a solution of 1 ml of acetonitrile containing 16 mg (0.039 mmol) of (I) (Akabori, Habata & Sato, 1985). The resulting precipitates were filtered and washed with a small amount of acetonitrile to give a pure 1:1 complex (II), m.p. 523 K (dec.), in 78% yield. Analysis: found: C 32.89, H 3.48%; calc. for C₁₆H₂₀O₂RuS₂PdCl₂: C 32.74, H 3.44%. Crystallographic data: Rigaku AFC-5R automated diffractometer, graphite-monochromated Mo K α radiation; lattice constants from least-squares fit of angular settings of 20 reflections within range 15 < 2 θ < 30°; for data collections 2 θ \leq 55°, ω -2 θ scans, intensities of three reflections monitored every 200 reflections, no significant variation; Lp corrections, absorption ignored. (I) Intensity measurement: light-yellow crystal 0.4 × 0.2 × 0.1 mm, 2718 reflections, $\pm h, k, l$ up to 31, 14, 12, 2248 unique reflections with $F_o \geq 2\sigma(F_o)$. Structure analysis: direct methods (MULTAN74; Main, Lessinger, Woolson, Germain & Declercq, 1974); refinement on F with block-diagonal least-squares methods, non-H atoms anisotropic, H atoms (from standard geometry) isotropic, final $R = 0.033$ ($wR = 0.037$, unit weights), $S = 3.4$, $\rho_{\max} = 0.4$ (close to S), $\rho_{\min} = -0.4$ (close to Ru) e Å⁻³ in final difference Fourier synthesis, max. least-squares shift to e.s.d. = 0.01. (II) Intensity measurement: orange crystal 0.4 × 0.05 × 0.05 mm, 1896 reflections, h, k, l up to 16, 14, 12. 1355 unique reflections with $F_o \geq 2\sigma(F_o)$.

Structure analysis: MULTAN74; block-diagonal least squares, non-H atoms anisotropic, H atoms (from standard geometry) isotropic, final $R = 0.055$ [$wR = 0.041$, $w = 1/\sigma(F_o)$], $S = 3.0$, $\rho_{\max} = 0.4$ (close to Pd), $\rho_{\min} = -0.8$ (close to Ru) e Å⁻³ in final difference synthesis, max. least-squares shift to e.s.d. = 0.03,* refinement of the alternative enantiomorph gave $R = 0.056$ [$wR = 0.042$, $w = 1/\sigma(F_o)$]. Atomic scattering factors for all atoms and anomalous-dispersion corrections for Pd, Ru, Cl and S from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic parameters are listed in Table 1. Bond lengths, bond and torsion angles are given in Tables 2 and 3. Perspective views of (I) and (II) are shown in Fig. 1(a). The conformation of the organic ligand moiety differs greatly between the metal-free ligand (I) and the complex (II). Main conformational changes are observed in the torsion angles of the macrocyclic moiety and overlapping patterns between cyclopentadienyl (Cp) rings (Fig. 1b). One interesting feature is the difference in the magnitude of the S—C—C—S torsion angles. For (I) this torsion angle has a value close to 180° while for (II) it is close to 60°. As a result of the *gauche* (\equiv -synclinal) conformation for (II), the two S atoms are in contact with each other [$S \cdots S = 3.192$ (7) Å] and are positioned so that the molecule can function as a bidentate ligand. The Cp rings for both compounds take an eclipsed conformation and the dihedral angles between them are 4.9 (2) and 2.6 (8)° for (I) and (II), respectively. The torsion angle C(1)—Cp1—Cp2—C(16) (Cp1 and Cp2 are the centroids of the Cp rings) in (II) is 70.1°, although that of (I) is only 8.9°. The results suggest that the torsion angle between the two Cp rings in (II) revolves approximately one fifth of a turn around the Cp1—Cp2 axis. The distances of the Ru atom to the best planes of the Cp rings are 1.822 (15) and 1.820 (16) Å for (I), and 1.82 (5) and 1.81 (6) Å for (II), respectively. Mean bond distances from the Ru atom to the ring C atom are 2.195 and 2.18 Å for (I) and (II). These distance values agree well with those of [4](1,1')ruthenocenophane (Ohba, Saito, Kamiyama & Kasahara, 1984) and 4,7,10,13-tetraoxa-1,16-dithia-[16](1,1')ruthenocenophane (Akabori, Munegumi, Habata, Sato, Kawazoe, Tamura & Sato, 1985). The Pd atom in (II) has a slightly distorted *cis* square-planar configuration: the two S atoms of the ligand occupy two positions and the two Cl atoms occupy the other two positions and the dihedral angle between the planes

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42769 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

formed by S(9)—Pd—S(12) and Cl(1)—Pd—Cl(2) is 2.2 (2)°. The Pd—Cl distances 2.321 (6), 2.313 (6) Å appear normal although the Pd—S distances 2.272 (5), 2.274 (5) Å are slightly short compared with those found in similar *cis* square-planar palladium(II) complexes: 2.313 (2), 2.316 (3) and 2.302 (2), 2.305 (2) Å in *cis*-dichloro(1,10-dithia-4,7,13,16-cyclooctadecane)-palladium(II) (Metz *et al.*, 1974), 2.310 (3), 2.318 (3) and 2.298 (3), 2.295 (3) Å in dichloro(1,2-dicyclohexyl-1,2-bis(diethylamino)-1,2-dithioxodi-λ⁵-phosphane)palladium(II) (Legros & Troy, 1983). The bond angles around the Pd atom range from 88.2 (2) to 93.2 (2)°.

There are only van der Waals interactions between adjacent molecules. The shortest intermolecular distances are 3.401 (7) Å for O(6)···C(11)(*x*, 1−*y*, $\frac{1}{2}$ +*z*) and 3.267 (14) Å for S(12)···O(15)($\frac{1}{2}$ −*x*, 1−*y*, $-\frac{1}{2}$ +*z*) for (I) and (II), respectively.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å²) for (I) and (II)

B _{eq} according to Hamilton (1959).				
	<i>x</i>	<i>y</i>	<i>z</i>	B _{eq}
Molecule (I)				
Ru	4175.4 (2)	1749.6 (3)	3737.3 (4)	2.27
C(1)	4516 (2)	3306 (5)	4872 (5)	2.6
C(2)	4760 (2)	3054 (5)	3890 (6)	3.3
C(3)	5010 (2)	1991 (6)	4262 (6)	4.0
C(4)	4912 (2)	1587 (6)	5449 (6)	3.9
C(5)	4594 (2)	2391 (5)	5814 (5)	3.2
O(6)	4289 (2)	4275 (3)	5047 (4)	3.2
C(7)	4187 (2)	5081 (5)	3976 (5)	3.1
C(8)	3890 (2)	6013 (5)	4360 (6)	3.4
S(9)	3752 (1)	7218 (1)	3239 (2)	3.8
C(10)	3129 (2)	6838 (5)	1940 (6)	3.9
C(11)	3184 (2)	6149 (5)	760 (6)	3.4
S(12)	2600 (1)	5392 (1)	−213 (1)	3.1
C(13)	2597 (2)	4333 (4)	1032 (5)	3.0
C(14)	3002 (2)	3439 (4)	1153 (5)	2.8
O(15)	2982 (1)	2669 (3)	2186 (4)	3.0
C(16)	3332 (2)	1816 (4)	2440 (5)	2.5
C(17)	3632 (2)	1449 (4)	1641 (5)	2.6
C(18)	3873 (2)	421 (5)	2229 (6)	3.6
C(19)	3744 (2)	194 (5)	3420 (6)	3.8
C(20)	3413 (2)	1066 (4)	3569 (6)	3.1
Molecule (II)				
Pd	2225 (1)	2859 (1)	−214 (1)	2.0
Cl(1)	1077 (3)	4017 (4)	−999 (5)	2.8
Cl(2)	1578 (4)	1331 (4)	−1144 (5)	3.5
Ru	414 (1)	2789 (1)	4069 (1)	1.9
C(1)	1679 (12)	1756 (13)	4109 (16)	1.9
C(2)	879 (12)	1083 (15)	4354 (18)	2.8
C(3)	484 (15)	1541 (16)	5484 (17)	3.6
C(4)	1036 (12)	2455 (15)	5874 (17)	3.0
C(5)	1778 (11)	2602 (14)	5002 (16)	2.3
O(6)	2342 (9)	1600 (9)	3189 (11)	2.2
C(7)	2085 (13)	874 (12)	2197 (16)	1.8
C(8)	2927 (13)	620 (15)	1386 (17)	2.8
S(9)	3398 (4)	1774 (4)	512 (5)	2.7
C(10)	3959 (12)	2631 (16)	1683 (17)	3.2
C(11)	4041 (13)	3780 (15)	1148 (18)	2.9
S(12)	2915 (3)	4314 (4)	731 (5)	2.6
C(13)	2326 (13)	4378 (14)	2223 (16)	2.2
C(14)	1566 (12)	5258 (12)	2092 (16)	1.7
O(15)	937 (9)	5220 (10)	3160 (12)	2.6
C(16)	284 (11)	4395 (13)	3243 (16)	1.6
C(17)	137 (13)	3601 (16)	2299 (16)	2.6
C(18)	−653 (13)	2960 (18)	2656 (19)	3.7
C(19)	−979 (11)	3448 (15)	3803 (21)	3.6
C(20)	−401 (12)	4308 (12)	4113 (18)	2.2

Table 2. Bond lengths (Å), and bond and torsion angles (°) for (I)

1	2	3	4	1–2	1–2–3	1–2–3–4
Dithiacrown moiety						
O(6)	C(1)	C(2)	C(3)	1.358 (6)	128.7 (5)	171.0 (5)
O(6)	C(1)	C(5)	C(4)		121.7 (4)	−171.1 (5)
C(2)	C(1)	O(6)	C(7)			13.3 (8)
C(5)	C(1)	O(6)	C(7)			−174.1 (5)
C(1)	O(6)	C(7)	C(8)		116.6 (3)	174.6 (4)
O(6)	C(7)	C(8)	S(9)	1.422 (6)	105.6 (3)	175.2 (3)
C(7)	C(8)	S(9)	C(10)	1.514 (7)	115.3 (5)	89.0 (5)
C(8)	S(9)	C(10)	C(11)	1.806 (6)	101.8 (3)	−86.6 (5)
S(9)	C(10)	C(11)	S(12)	1.818 (5)	113.3 (5)	161.0 (1)
C(10)	C(11)	S(12)	C(13)	1.527 (8)	113.6 (5)	−71.1 (5)
C(11)	S(12)	C(13)	C(14)	1.803 (5)	100.3 (2)	−75.2 (4)
S(12)	C(13)	C(14)	O(15)	1.813 (6)	111.4 (4)	178.1 (2)
C(13)	C(14)	O(15)	C(16)	1.513 (6)	107.3 (2)	−178.8 (4)
C(14)	O(15)	C(16)	C(17)	1.428 (6)	114.6 (2)	−14.9 (8)
C(14)	O(15)	C(16)	C(20)			171.2 (4)
O(15)	C(16)	C(17)	C(18)	1.361 (5)	129.0 (6)	−170.6 (5)
O(15)	C(16)	C(20)	C(19)		121.6 (3)	171.9 (5)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.435 (6)	107.1 (4)	0.9 (7)
C(2)	C(3)	C(4)	C(5)	1.432 (8)	108.2 (3)	0.8 (8)
C(3)	C(4)	C(5)	C(1)	1.435 (8)	108.5 (4)	−2.2 (7)
C(4)	C(5)	C(1)	C(2)	1.436 (7)	106.8 (3)	2.8 (7)
C(5)	C(1)	C(2)	C(3)	1.432 (8)	109.3 (3)	−2.3 (7)
C(16)	C(17)	C(18)	C(19)	1.428 (6)	106.9 (3)	−3.1 (7)
C(17)	C(18)	C(19)	C(20)	1.426 (7)	108.4 (3)	1.2 (7)
C(18)	C(19)	C(20)	C(16)	1.427 (8)	108.5 (4)	1.1 (7)
C(19)	C(20)	C(16)	C(17)	1.426 (7)	106.9 (3)	−3.1 (7)
C(20)	C(16)	C(17)	C(18)	1.429 (7)	109.2 (3)	3.8 (7)

Table 3. Bond lengths (Å), and bond and torsion angles (°) for (II)

1	2	3	4	1–2	1–2–3	1–2–3–4
Dithiacrown moiety						
O(6)	C(1)	C(2)	C(3)	1.38 (2)	126.6 (15)	174.1 (16)
O(6)	C(1)	C(5)	C(4)		121.3 (15)	−174.0 (14)
C(2)	C(1)	O(6)	C(7)			17 (2)
C(5)	C(1)	O(6)	C(7)			−167.9 (14)
C(1)	O(6)	C(7)	C(8)		116.5 (13)	−169.9 (13)
O(6)	C(7)	C(8)	S(9)	1.44 (2)	110.9 (14)	−66.2 (18)
C(7)	C(8)	S(9)	C(10)	1.52 (3)	115.5 (13)	71.4 (15)
C(8)	S(9)	C(10)	C(11)	1.824 (19)	104.4 (9)	−159.0 (10)
S(9)	C(10)	C(11)	S(12)	1.83 (2)	107.6 (13)	58.4 (17)
C(10)	C(11)	S(12)	C(13)	1.52 (3)	111.4 (14)	63.5 (15)
C(11)	S(12)	C(13)	C(14)	1.79 (2)	101.9 (9)	155.4 (10)
S(12)	C(13)	C(14)	O(15)	1.815 (19)	105.9 (12)	169.0 (7)
C(13)	C(14)	O(15)	C(16)	1.53 (3)	109.8 (14)	−75.1 (19)
C(14)	O(15)	C(16)	C(17)	1.46 (2)	119.3 (14)	−4 (3)
C(14)	O(15)	C(16)	C(20)			−173.4 (15)
O(15)	C(16)	C(17)	C(18)	1.38 (2)	123.6 (16)	−173.9 (16)
O(15)	C(16)	C(20)	C(19)		126.1 (17)	172.9 (17)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.43 (3)	103.9 (16)	0 (2)
C(2)	C(3)	C(4)	C(5)	1.45 (3)	109.6 (17)	1 (2)
C(3)	C(4)	C(5)	C(1)	1.43 (3)	108.2 (16)	−1 (2)
C(4)	C(5)	C(1)	C(2)	1.43 (3)	106.3 (15)	2 (2)
C(5)	C(1)	C(2)	C(3)	1.42 (2)	112.0 (15)	−1 (2)
C(16)	C(17)	C(18)	C(19)	1.42 (3)	107.4 (17)	3 (2)
C(17)	C(18)	C(19)	C(20)	1.43 (3)	104.9 (18)	−1 (3)
C(18)	C(19)	C(20)	C(16)	1.45 (3)	109.3 (19)	−1 (3)
C(19)	C(20)	C(16)	C(17)	1.38 (3)	108.8 (18)	3 (2)
C(20)	C(16)	C(17)	C(18)	1.36 (3)	109.6 (16)	−3 (2)
Pd coordination						
Cl(1)	Pd	Cl(2)		2.321 (6)	93.2 (2)	
Cl(2)	Pd	S(9)		2.313 (6)	88.2 (2)	
S(9)	Pd	Cl(1)		2.272 (5)	177.4 (2)	
S(12)	Pd	Cl(1)		2.274 (5)	89.4 (2)	
S(9)	Pd	S(12)			89.2 (2)	
S(12)	Pd	Cl(2)			177.4 (2)	

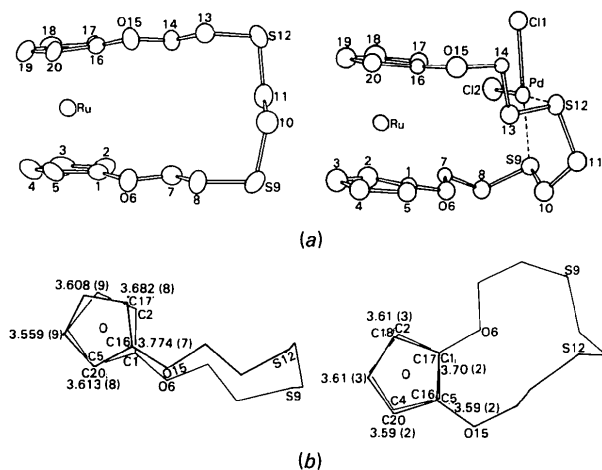


Fig. 1. (a) ORTEP (Johnson, 1965) drawings of the molecules [1] on the left with atom-numbering scheme. (b) Projections of the organic ligand moieties on the Cp ring containing the C(1) atom with the C...C distances (Å) between the rings. An open circle denotes the Ru atom.

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Structural Identification of a Purple Product (5,6-Dihydro-10-hydroxy-6-methyl-4*H*-dibenzo[*de,g*]quinoline-8,11-dione) of the Reaction of Froehde Reagent and Morphine

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Abstract. The single-crystal X-ray structure of a purple material isolated from the chloroform extraction of the reaction of morphine and Froehde reagent in aqueous sulfuric acid has been identified as $C_{17}H_{13}NO_3$, 5,6-dihydro-10-hydroxy-6-methyl-4*H*-dibenzo[*de,g*]quinoline-8,11-dione. $M_r = 279.29$, monoclinic, $P2_1/n$, $a = 18.591$ (12), $b = 7.774$ (4), $c = 8.762$ (5) Å, $\beta = 96.60$ (5)°, $V = 1258.0$ (13) Å³, $Z = 4$, $D_x = 1.474$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.951$ cm⁻¹, $F(000) = 584$, room temperature, final $R = 5.8\%$ for 1528 reflections with $I > 3\sigma(I)$. The morphine molecule undergoes a rearrangement to the apomorphine skeleton by breaking an ether linkage; after further dehydration a hydroxyquinone system is formed in place of the phenolic morphine ring to give a highly conjugated product. The molecule shows coplanarity of the aromatic rings. The quinone ring has typical bond lengths.

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Introduction. Color reactions of morphine and its derivatives, of cholesterol, and of other biologically significant compounds with a variety of test reagents have been used extensively for rapid screening of unknown compounds in clinical and forensic situations (Clarke, 1978). A number of tests are available. Most reagents involve complex inorganic ions with the inorganic element present in its highest valence state, dissolved in concentrated sulfuric acid: for example, the Froehde (ammonium molybdate), the Mecke (selenous acid), and the Mandelin (ammonium vanadate) reagents (Stewart & Stohlman, 1961; Fulton & Nebraska, 1928). The principal reaction is believed to be oxidation–reduction with the reagent oxidizing the drug in some specific way.

The chemistry of the progressive color changes which occur with time for the morphine alkaloids is very complex and not fully understood. Akin to the color reaction of cholesterol with ferric ion in concentrated sulfuric acid solution (Burke, Diamondstone,

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