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fac-Tricarbonyldichloro(tetrahydrofuran)-ruthenium(II)

Gary M. Gray[a] and Christina H. Duffey[b]

[a] *The Department of Chemistry, The University of Alabama at Birmingham, 242-OB15 UAB Station, Birmingham, AL 35294, USA, and* [b] *The Department of Chemistry, Samford University, Birmingham, AL 35229, USA*

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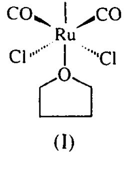
Abstract

In the *fac*-[RuCl$_2$(CO)$_3$(thf)] complex, the Ru^{II} has slightly distorted octahedral coordination geometry with the carbonyl ligands in a facial arrangement and the thf *trans* to one of the carbonyls. The dihedral angle between the least-squares plane of the thf and the least-squares plane through the four ligands *cis* to the thf is 90.56 (23)°. The torsion angles about the Ru^{II}—O(thf) bond indicate that the thf ring nearly bisects the angles between *cis* Cl and carbonyl ligands.

Comment

The complex, *fac*-[RuCl$_2$(CO)$_3$(thf)], (I), first reported in 1989 (Reddy, Whitten, Redmill, Varshney & Gray, 1989), is a useful starting material for the synthesis of *cis,cis,trans*-[RuCl$_2$(CO)$_2$(phosphine)$_2$] complexes. This is particularly true for *cis,cis,trans*-[RuCl$_2$(CO)$_2${Ph$_2$P(CH$_2$CH$_2$O)$_n$CH$_2$CH$_2$PPh$_2$-*P*,*P'*}] metallacrown ethers because the preparation of these complexes requires the simultaneous addition of dilute solutions of [RuCl$_2$(CO)$_3$(thf)] and the ligand (Gray, Varshney & Duffey, 1995). Other Ru^{II} precursors are unsuitable for this reaction because they are generally polymeric and insoluble.



(I)

The *fac*-[RuCl$_2$(CO)$_3$(thf)] complex was initially reported as [RuCl$_2$(CO)$_3$].0.75thf based on elemental analysis (Reddy, Whitten, Redmill, Varshney & Gray, 1989). The fractional stoichiometry seemed unlikely, and one reason for obtaining a crystal structure of the complex was to determine the amount of thf present. Other points of interest in the crystal structure are the coordination geometry at the Ru^{II} center and the conformation of the thf ring.

An *ORTEP*II (Johnson, 1976) drawing of *fac*-[RuCl$_2$(CO)$_3$(thf)] is shown in Fig. 1. The coordination geometry of Ru is slightly distorted octahedral, as indicated by the dihedral angles between the three least-squares planes through the Ru and the atoms coordinated to it (90.7, 89.4 and 92.2°). The carbonyl ligands are in a facial arrangement and the thf is *trans* to one of the carbonyls. The thf ring (O4, C4, C5, C6, C7) has an envelope conformation with O4, C4, C5 and C7 forming the base and C5, C6 and C7 forming the flap. The displacement ellipsoid of C7 of thf is elongated relative to this plane, suggesting that, as expected, the ring is conformationally flexible. The dihedral angles between the least-squares plane of the thf (O4, C4, C5, C6, C7) and the least-squares planes containing the Ru, the thf O atom, one of the *cis* carbonyl C atoms, one of the *cis* Cl ligands and the *trans* carbonyl C atom (Ru, Cl1, O4, C1, C3 35.0°; Ru, Cl2, O4, C2, C3 127.2°) indicate that the thf experiences repulsive interactions with the ligands *cis* to it. This potential strain is relieved by a rotation of the thf around the Ru—O4 bond to move C4 into the space between Cl2 and C1, and C7 into the space between Cl1 and C2. The dihedral angle between the least-squares plane of thf (O4, C4, C5, C6, C7) and that formed by the Ru, the two Cl ligands and the two *cis* carbonyl C atoms (Ru, Cl1, Cl2, C1, C2) is 90.56°. This unusual arrangement is consistent with literature reports of other thf complexes (Sobota, Pluzinski, Utko & Lis, 1988; Sobota, Utko & Szafert, 1994).

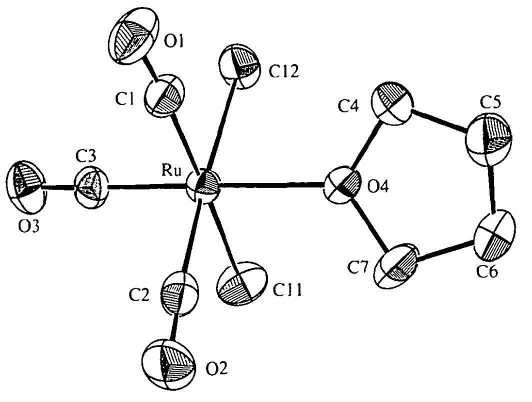


Fig. 1. Drawing of the molecular structure of *fac*-[RuCl$_2$(CO)$_3$(thf)]. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

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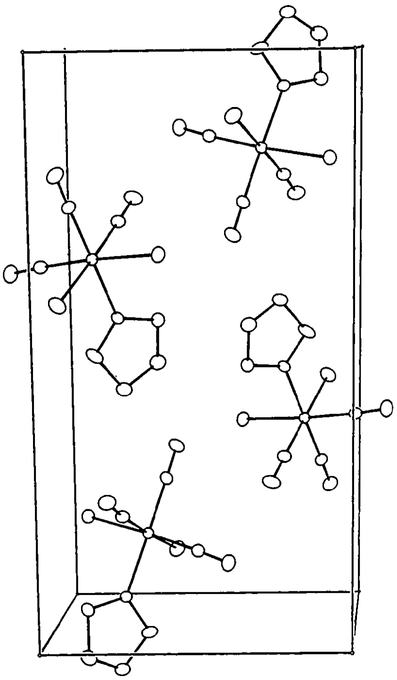

Fig. 2. Drawing of the unit cell of *fac*-[$RuCl_2(CO)_3(thf)$].

Experimental

Crystal data

[$RuCl_2(CO)_3(C_4H_8O)$]
$M_r = 328.12$
Monoclinic
$P2_1/n$
$a = 6.0904 (9)$ Å
$b = 18.414 (4)$ Å
$c = 9.940 (2)$ Å
$\beta = 96.999 (12)°$
$V = 1106.5 (4)$ Å^3
$Z = 4$
$D_x = 1.97$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13–17°$
$\mu = 1.863$ mm^{-1}
$T = 298$ K
Plate
0.46 × 0.16 × 0.055 mm
Light yellow

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.880$, $T_{max} = 0.999$
3399 measured reflections
2618 independent reflections

1591 observed reflections [$I \geq 3\sigma(I)$]
$R_{int} = 0.031$
$\theta_{max} = 27.5°$
$h = -7 \rightarrow 1$
$k = 0 \rightarrow 23$
$l = -12 \rightarrow 12$
3 standard reflections frequency: 120 min intensity decay: 0.3%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.048$
$S = 1.022$
1591 reflections
152 parameters
H atoms placed in calculated positions, riding on heavy atoms
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.521$ e Å^{-3}
$\Delta\rho_{min} = -0.400$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: 5.8363×10^{-8}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ru	0.53801 (7)	0.16693 (3)	0.31093 (5)	2.144 (8)
Cl1	0.2199 (3)	0.1072 (1)	0.3807 (2)	3.97 (4)
Cl2	0.3519 (3)	0.18123 (9)	0.0865 (2)	3.55 (3)
O1	0.9091 (7)	0.2546 (3)	0.2156 (6)	4.3 (1)
O2	0.7658 (9)	0.1349 (3)	0.5940 (5)	4.7 (1)
O3	0.3417 (8)	0.3071 (3)	0.3933 (5)	4.0 (1)
O4	0.6508 (7)	0.0639 (2)	0.2453 (4)	3.06 (9)
C1	0.781 (1)	0.2189 (3)	0.2518 (7)	2.9 (1)
C2	0.687 (1)	0.1489 (3)	0.4891 (6)	2.9 (1)
C3	0.420 (1)	0.2548 (3)	0.3642 (7)	2.8 (1)
C4	0.770 (1)	0.0535 (4)	0.1293 (7)	3.7 (1)
C5	0.849 (1)	−0.0234 (4)	0.1386 (8)	4.6 (2)
C6	0.714 (1)	−0.0603 (4)	0.2354 (8)	4.5 (2)
C7	0.659 (2)	−0.0003 (4)	0.3233 (8)	5.9 (2)

Table 2. *Selected geometric parameters* (Å, °)

Ru—Cl1	2.402 (2)	O2—C2	1.124 (8)
Ru—Cl2	2.390 (2)	O3—C3	1.127 (8)
Ru—O4	2.146 (4)	O4—C4	1.448 (8)
Ru—C1	1.916 (6)	O4—C7	1.411 (9)
Ru—C2	1.918 (6)	C4—C5	1.49 (1)
Ru—C3	1.873 (6)	C5—C6	1.50 (1)
O1—C1	1.111 (8)	C6—C7	1.48 (1)
Cl1—Ru—O4	89.0 (1)	C2—Ru—C3	92.5 (3)
Cl1—Ru—C1	176.9 (2)	Ru—O4—C4	124.7 (4)
Cl1—Ru—C2	87.8 (2)	Ru—O4—C7	124.3 (4)
Cl1—Ru—C3	87.9 (2)	C4—O4—C7	109.9 (5)
Cl2—Ru—O4	86.9 (1)	Ru—C1—O1	173.2 (6)
Cl2—Ru—C1	87.4 (2)	Ru—C2—O2	175.9 (6)
Cl2—Ru—C2	176.4 (2)	Ru—C3—O3	177.5 (5)
Cl2—Ru—C3	90.8 (2)	O4—C4—C5	105.4 (5)
O4—Ru—C1	93.5 (2)	C4—C5—C6	105.7 (6)
O4—Ru—C2	89.7 (2)	C5—C6—C7	102.9 (6)
O4—Ru—C3	176.1 (2)	O4—C7—C6	107.3 (6)
C1—Ru—C2	94.2 (3)		
Cl1—Ru—O4—C4	145.8 (5)	Ru—O4—C4—C5	169.8 (4)
Cl1—Ru—O4—C7	−47.5 (6)	C7—O4—C4—C5	1.4 (7)
Cl2—Ru—O4—C4	55.0 (4)	Ru—O4—C7—C6	172.0 (5)
Cl2—Ru—O4—C7	−138.3 (5)	C4—O4—C7—C6	−19.6 (8)
C1—Ru—O4—C4	−32.3 (5)	O4—C4—C5—C6	16.8 (7)
C1—Ru—O4—C7	134.5 (6)	C4—C5—C6—C7	−27.8 (8)
C2—Ru—O4—C4	−126.5 (5)	C5—C6—C7—O4	29.1 (8)
C2—Ru—O4—C7	40.3 (6)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Program(s) used to solve structure: *MolEN* (Fair, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1187). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraphenylphosphonium *trans*-Aquatetrabromo(carbonyl)osmate(III), *trans*-$[(C_6H_5)_4P][OsBr_4(CO)(H_2O)]$

Matthias Höhling and Wilhelm Preetz

Institut für Anorganische Chemie, Universität Kiel, Olshausenstrasse 40, D-24098 Kiel, Germany. E-mail: sunac024@talos.ac.uni-kiel.de

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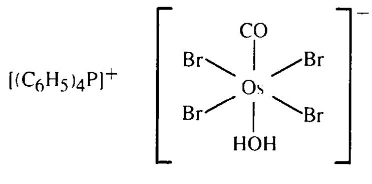
Abstract

The X-ray structure determination of tetraphenylphosphonium *trans*-aquatetrabromo(carbonyl)osmate(III), *trans*-$[(C_6H_5)_4P][OsBr_4(CO)(H_2O)]$, at 293 K has revealed slightly distorted octahedral coordination of the osmium(III) atom, with H_2O *trans* to the almost linear carbonyl group. The distances are 1.795 (10) for Os—C, 2.181 (6) for Os—O*w* and 1.164 (9) Å for C—O; among the Os—Br bond lengths two are shorter [2.4692 (8) and 2.4753 (10) Å] and two are longer [2.5042 (8) and 2.5072 (8) Å]. Centrosymmetric dimers of the complex anions are formed by intermolecular hydrogen bonding between the coordinated water molecule and the two Br ligands that form longer bonds to the central atom.

Comment

We are currently studying the mutual influences of different ligands in octahedral complexes on their spectroscopic and structural properties. The halogenocarbonyl compounds of osmium(III) of the types $[OsX_5(CO)]^{2-}$ (X = Cl, Br, I) and *trans*-$[OsX_4(CO)_2]^-$ (X = Br, I) have been synthesized and well characterized by vibrational spectroscopy (Cleare & Griffith, 1970; Johannsen & Preetz, 1977*a*) and in some cases by X-ray structure determination (Berngardt *et al.*, 1993*a*,*b*, 1994). The related aqua complexes of the type *trans*-$[OsX_4(CO)(H_2O)]^-$ are formed by hydrolysis of the monocarbonylates (Johannsen & Preetz, 1977*b*; Bottomley, Lin & White, 1978). The substitution of the Br ligand *trans* to CO causes a shift of the carbonyl stretching frequency from 1949 to 1989 cm^{-1} (10 K, KBr disc) in the title compound, (1).



(1)

(1) crystallizes in space group $P\bar{1}$ with all atoms located in general positions. The complex anion, which is represented in Fig. 1 with its labelling scheme, has almost $mm4$ (C_{4v}) local symmetry.

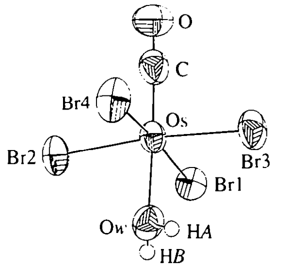


Fig. 1. View of the *trans*-$[OsBr_4(CO)(H_2O)]^-$ anion showing 50% probability ellipsoids. H atoms are drawn as spheres of arbitrary size.

The Os—C distance in (1) of 1.795 (10) Å is slightly shorter than that in $K_2[OsBr_5(CO)]$, (2) [1.84 (2) Å; Berngardt *et al.*, 1994], and significantly shorter than those in *trans*-$(Bu_4N)[OsBr_4(CO)_2]$, (3) [1.90 (3) and 1.91 (4) Å; Berngardt *et al.*, 1993*a*]. On the other hand, the Os—O*w* distance [2.181 (6) Å] in (1) is somewhat longer than the sum of the covalent radii of osmium and oxygen (2.03 Å; Pauling, 1960). These results are consistent with a decreasing *trans* influence of the ligands in the order CO > Br > H_2O. The effect on the C—O distances [1.164 (9) in (1), 1.16 (3) in (2), and 1.14 (4) and 1.21 (4) Å in (3)] is uncertain, due to lower accuracy of determination. The Os—C, Os—O*w* and C—O distances in (1) are in good agreement with the corresponding averaged distances in *trans*-$[(C_6H_5)_4P][OsCl_4(CO)(H_2O)]$, (4) (2.19, 1.81 and 1.16 Å; Gorbunova *et al.*, 1994), and the carbonyl stretching frequencies are virtually equal [1987 in (4),

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