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A trichloro-bridged binuclear ruthenium complex with 1,1,1-tris(diphenylphosphinomethyl)ethane

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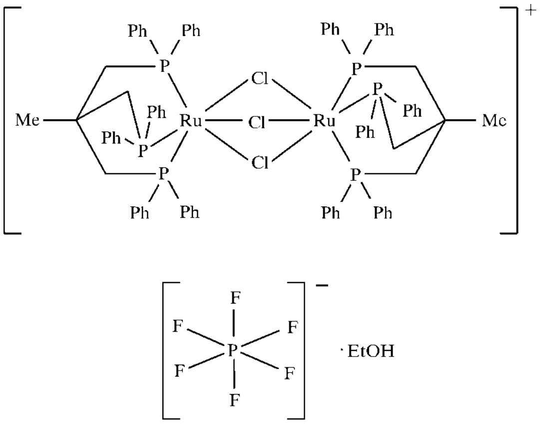
The trichloro-bridged dinuclear $\mathrm{Ru^{II}}$ complex tri-μ-chloro-bis{[1,1,1-tris(diphenylphosphinomethyl)ethane-κ^3P,P',P'']-ruthenium(II)} hexafluorophosphate ethanol solvate, $[\mathrm{Ru_2Cl_3(tripod)_2}]\mathrm{PF_6}\cdot\mathrm{C_2H_6O}$, containing the tripod [1,1,1-tris(diphenylphosphinomethyl)ethane, $\mathrm{C_{41}H_{39}P_3}$] ligand, was unexpectedly obtained from the reaction of $[\mathrm{Ru^{III}Cl_3(tripod)}]$ with 1,4-bis(diphenylphosphino)butane (dppb), followed by precipitation with $\mathrm{NH_4PF_6}$. The magnetic moment of the compound at room temperature indicates that the dinuclear $[\mathrm{Ru_2}(\mu\text{-Cl})_3(\mathrm{tripod})_2]^+$ cation is diamagnetic. A single-crystal X-ray structure determination revealed that the two Ru atoms are bridged by the three Cl atoms. The coordination sphere of each Ru atom is completed by the three P atoms of a tripod ligand. The two $\mathrm{P_3Ru}$ units are exactly eclipsed, while the bridging Cl atoms are staggered with respect to the six P atoms. The Ru$\cdots$Ru distance is 3.3997 (7) Å and the mean Cl—Ru—Cl bond angle is 77.7°.

Comment

Complexes of rhodium and ruthenium with optically active ligands are widely used as catalysts for enantioselective hydrogenation reactions (Chen *et al.*, 1999; Hagiwara *et al.*, 1999). While looking for related complexes suitable as catalysts for oxidation processes, we noted that Ru complexes with arylphosphine ligands are not well described in the literature (Barbaro *et al.*, 1999). In comparison, there are extensive studies of the redox chemistry of oxo and nitrido Ru or Os complexes containing polypyridine, Schiff base or porphyrin ligands (Lebeau *et al.*, 2001). Such complexes are thought to act as oxidants in metal-catalyzed oxidation reactions.

Generally, six-coordinated $\mathrm{Ru^{IV}}$–oxo complexes are prepared starting from the related $\mathrm{Ru^{II}}$–chloro species *via* the corresponding $\mathrm{Ru^{II}}$–aqua complexes, which are finally oxidized (Navarro *et al.*, 1998). In order to extend this synthesis to analogous Ru complexes with phosphine ligands, we attempted to prepare the chloro complex $[\mathrm{Ru(tripod)(dppb)Cl}]\mathrm{PF_6}$ by reaction of $[\mathrm{Ru^{III}Cl_3(tripod)}]$ [tripod is 1,1,1-tris(diphenylphosphinomethyl)ethane; Ott *et al.*, 1985] with dppb [1,4-bis(diphenylphosphino)butane] and subsequent precipitation with $\mathrm{NH_4PF_6}$. However, instead of the expected mononuclear chloro complex, the dinuclear trichloro-bridged ethanol-solvated complex $[\mathrm{Ru_2}(\mu\text{-Cl})_3(\mathrm{tripod})_2]\mathrm{PF_6}\cdot\mathrm{C_2H_6O}$, (I), was obtained in the form of yellow crystals. Obviously, dppb acts here only as a reducing agent, providing two electrons, and does not coordinate to the Ru atom. The identity of the new complex was indicated by multinuclear NMR, IR and UV data, and is confirmed by the results of a single-crystal X-ray structure determination, the results of which are presented here.



(I)

The crystal structure of (I) consists of discrete $[\mathrm{Ru_2}(\mu\text{-Cl})_3(\mathrm{tripod})_2]^+$ cations and $[\mathrm{PF_6}]^-$ anions and contains one molecule of ethanol in the molecular unit (Fig. 1). Each Ru atom is coordinated by three bridging Cl atoms and by the three P atoms of the tripod ligand in a slightly distorted octahedral environment. In the dinuclear unit, two such octahedra share a common face, with the bridging Cl atoms occupying its edges. The two $\mathrm{P_3Ru}$ fragments are exactly eclipsed, while the bridging Cl atoms are staggered with respect to the six P atoms (Fig. 2).

The bond distances and angles of the dinuclear cation in (I) compare well with those of the corresponding tetraphenylborate salt reported by Rhodes *et al.* (1988), indicating only a small counter-ion effect. The Ru—P [2.246 (1)–2.272 (1) Å] and Ru—Cl distances [2.445 (1)–2.478 (1) Å] in the hexafluorophosphate, (I), are slightly shorter than those found for the tetraphenylborate. The Ru—Cl—Ru bond angles of about 87° are larger than those calculated for an ideal cofacial bioctahedral geometry (75.0°). Accordingly, the Cl—Ru—Cl bond angles of about 78° are smaller than the ideal value of 90°. This results in an elongation of the bioctahedron along the Ru$\cdots$Ru axis and thus in a longer Ru$\cdots$Ru distance [3.3997 (7) Å] than would be expected for a regular face-sharing bioctahedron, excluding a bond interaction between the two Ru atoms. The P—Ru—P bond angles range between

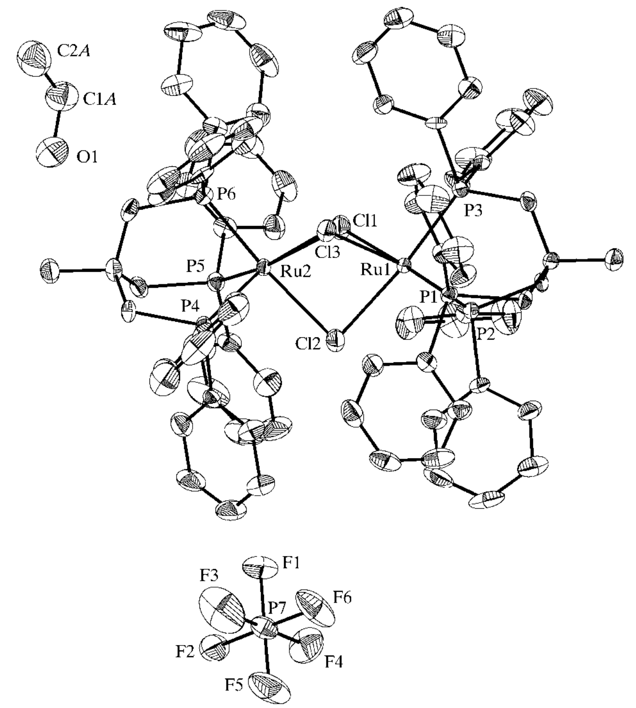


Figure 1
A view of the components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

86.35 (4) and 89.59 (4)°, and are comparable with the angles found in complexes with tridentate phosphine ligands (Pal & Pal, 2001) and smaller than those in related complexes with monodentate phosphine ligands (Higham *et al.*, 1998; Laing & Pope, 1976; Rhodes *et al.*, 1988).

As is generally found for tripod complexes, the bond lengths and angles of the tripod ligand in (I) deviate only slightly from those observed for the free ligand (Bianchini *et al.*, 1982). The tetracoordinated P atoms display a distorted tetrahedral coordination, with Ru—P—C_{aryl} = 113.24 (12)–122.23 (15), Ru—P—C_{alkyl} = 112.28 (13)–115.10 (14), C_{alkyl}—P—C_{aryl} = 100.16 (19)–105.64 (19) and C_{aryl}—P—C_{aryl} = 97.34 (17)–99.33 (19)°. The bond lengths and angles in the hexafluorophosphate anion are as expected.

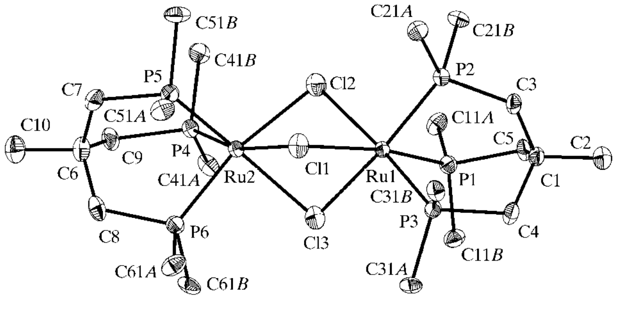


Figure 2
A view of the dinuclear $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]^+$ cation of (I). For clarity, H atoms have been omitted and only the *ipso* C atoms of the phenyl rings are shown. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

In a typical reaction, the dppb ligand (0.071 g, 0.17 mmol) in ethanol (30 ml) was added slowly to a solution of $[RuCl_3(tripod)]$ (0.125 g, 0.15 mmol) in acetonitrile (150 ml). The mixture was refluxed for 3 h, during which time the initially deep-green solution gradually changed colour to yellow. After removal of the solvent, 5 drops of a saturated solution of NH_4PF_6 in ethanol were added to precipitate the products. The precipitate was filtered off, washed with diethyl ether (2 × 10 ml) and dried under vacuum to give (I) as a yellow crystalline solid. Single crystals suitable for an X-ray structure determination were obtained by crystallization from acetone.

Crystal data

$[Ru_2Cl_3(C_{41}H_{39}P_3)_2]PF_6{\cdot}C_2H_6O$
M_r = 1748.79
Monoclinic, *Cc*
a = 13.069 (3) Å
b = 25.602 (5) Å
c = 22.991 (5) Å
β = 92.66 (3)°
V = 7684 (3) Å^3
Z = 4
D_x = 1.512 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5000 reflections
θ = 1.8–25.9°
μ = 0.71 mm^{-1}
T = 293 (2) K
Block, yellow
0.20 × 0.12 × 0.09 mm

Data collection

Stoe IPDS area-detector diffractometer
φ scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1997)
T_{min} = 0.908, T_{max} = 0.959
26 982 measured reflections
14 149 independent reflections
11 740 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 25.9°
$h = -15 \rightarrow 16$
$k = -31 \rightarrow 31$
$l = -28 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.057
S = 0.89
14 149 reflections
933 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0176P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}
Absolute structure: Flack (1983), 6746 Friedel pairs
Flack parameter = 0.725 (17)

Table 1
Selected geometric parameters (Å, °).

Ru1—P1	2.2469 (11)	Ru2—P4	2.2617 (12)
Ru1—P3	2.2682 (12)	Ru2—P6	2.2635 (11)
Ru1—P2	2.2719 (11)	Ru2—P5	2.2657 (11)
Ru1—Cl3	2.4449 (12)	Ru2—Cl1	2.4717 (12)
Ru1—Cl2	2.4553 (13)	Ru2—Cl2	2.4738 (11)
Ru1—Cl1	2.4650 (12)	Ru2—Cl3	2.4776 (12)
Ru1···Ru2	3.3997 (7)		
P1—Ru1—P3	89.55 (4)	P6—Ru2—P5	87.37 (4)
P1—Ru1—P2	86.35 (4)	Cl1—Ru2—Cl2	77.96 (4)
P3—Ru1—P2	86.97 (4)	Cl1—Ru2—Cl3	77.31 (4)
Cl3—Ru1—Cl2	77.62 (4)	Cl2—Ru2—Cl3	76.67 (4)
Cl3—Ru1—Cl1	78.04 (4)	Ru1—Cl1—Ru2	87.05 (4)
Cl2—Ru1—Cl1	78.44 (4)	Ru1—Cl2—Ru2	87.21 (4)
P4—Ru2—P6	89.24 (4)	Ru1—Cl3—Ru2	87.36 (4)
P4—Ru2—P5	88.82 (5)		

H atoms were treated as riding, with C—H distances in the range 0.93–0.97 Å and an O—H distance of 0.82 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O)$.

m440 Won K. Seok *et al.* • $[Ru_2Cl_3(C_{41}H_{39}P_3)_2]PF_6{\cdot}C_2H_6O$ *Acta Cryst.* (2003). C**59**, m439–m441

Data collection: *IPDS* (Stoe & Cie, 1997); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1146). Services for accessing these data are described at the back of the journal.

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