# A New Ruthenium(VI) Oxidant: Preparation, *X*-Ray Crystal Structure, and Properties of $(Ph_4P)[RuO_2(OAc)Cl_2]$

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The title compound has a quasi-trigonal bipyramidal (or alternatively, distorted octahedral) structure with a symmetrically bound acetato ligand and *cis*-dioxo ligands in the trigonal plane, and is an effective oxidant for halides, alcohols, sulphides, and phosphines, functioning catalytically in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidant.

Hypervalent ruthenium oxo complexes are currently of considerable interest because some of them are efficient oxidants for organic substrates and can be made to function catalytically in the presence of suitable co-oxidants.[1–3] We report here a dioxoruthenium(VI) complex with a simple but unusual structure. It is novel in that it will efficiently oxidise activated halides: primary halides to aldehydes and secondary halides to ketones without competing double-bond cleavage; it will similarly oxidise alcohols to the corresponding carbonyls, sulphides to sulphoxides and sulphones, and phosphines to phosphine oxides.

The complex, $(PPh_4)[RuO_2(OAc)Cl_2]\cdot 2AcOH$, was made by passing $RuO_4$ vapour into a solution of $PPh_4Cl$ in glacial acetic acid (analogous propionato and butyrato analogues have been prepared); the title compound is obtained by recrystallisation from dichloromethane–carbon tetrachloride. A more convenient route is by the addition of a solution of $RuO_4$ in carbon tetrachloride (made by Nakata's method[4]) to a slight excess of $PPh_4Cl$ and glacial acetic acid in acetonitrile. The compound is obtained by reducing the volume of the solution followed by recrystallisation as above. Satisfactory microanalyses for the complex were obtained.

**Table 1.** Oxidations with $(PPh_4)[RuO_2(OAc)Cl_2]$.[a]

| Substrate | Product | Yield (%) (catalytic turnover) | Time/ h |
|---|---|---|---|
| Benzyl bromide | Benzaldehyde[c] | 78(19) | 3 |
| Benzyl chloride | Benzaldehyde[b] | 45(12) | 3 |
| *p*-Methoxybenzyl bromide | *p*-Methoxybenzaldehyde[b] | 72(19) | 1 |
| *p*-Methoxybenzyl chloride | *p*-Methoxybenzaldehyde[b] | 53(14) | 1 |
| *p*-Nitrobenzyl bromide | *p*-Nitrobenzaldehyde[c] | 55(15) | 1.5 |
| Geranyl bromide | Geranial[c] | 78(22) | 1.5 |
| Bromodiphenylmethane | Benzophenone[b] | 65(16) | 2 |
| *p*-Anisyl alcohol | *p*-Anisaldehyde[b] | 99(44) | 2 |
| Benzyl alcohol | Benzaldehyde[b] | 55(31) | 2 |
| Cinnamyl alcohol | Cinnamaldehyde[b] | 97(45) | 2 |
| Piperonyl alcohol | Piperonaldehyde[b] | 91(36) | 2 |
| Geraniol | Geranial[c] | 98(26) | 2 |
| Citronellol | Citronellal[c] | 79(30) | 2 |
| α-Tetralol | α-Tetralone[b] | 98(41) | 2 |
| Cyclo-octanol | Cyclo-octanone[b] | 76(36) | 2 |
| Phenyl sulphide | Phenyl sulphoxide[c] | 66(11) | 12 |
| n-Butyl sulphide | n-Butyl sulphoxide[c] | 62(17) | 6 |
|  | n-Butyl sulphone[c] | 31(8) |  |
| Benzyl methyl sulphide | Benzyl methyl sulphone[c] | 69(20) | 2 |
| Triphenylphosphine | Triphenylphosphine oxide[c] | 81(20) | 2 |

[a] General catalytic oxidation procedure. The catalyst (15 mg, 0.025 mmol) was added to a solution of substrate (1 mmol) in the appropriate solvent containing powdered molecular sieves and NMO (200 mg, 1.7 mmol) and stirred for the required length of time, the reaction being followed by TLC. [b] Product characterised and quantified by formation of 2,4-dinitrophenylhydrazone derivative. [c] Product isolated (purified by column chromatography if necessary) and characterised by NMR and IR spectroscopy (melting point recorded where appropriate).

The *X*-ray crystal structure† of the anion is shown in Figure 1. It may be regarded either as a highly distorted octahedron with a bidentate acetate, *trans*-chloro and *cis*-dioxo ligands or, if the acetate is regarded as occupying one co-ordination site, as a trigonal bipyramid with *trans*-chloro ligands. With the latter view, which has been applied previously to complexes containing bidentate acetato ligands,[5] the trigonal bipyramid is virtually undistorted [the ClRuCl angle is 178.1(2)°, O=Ru=O angle 120.2(6)° and the angles between the oxo ligands, ruthenium and the acetate carbon atoms are 119.6(5), and 120.0(6)° respectively]. The Ru=O distances are characteristically short compared with those of the acetato ligand. The complex is then seen to be structurally related to the anion in $K[OsO_2(OAc)_3]\cdot 2AcOH$ which contains one bidentate and two monodentate ligands,[5] but structurally very different from the only other dioxoruthenium acetato complex reported, *trans*-$[RuO_2(OAc)_2py_2]$, in which the O=Ru=O system is linear and the acetato ligands are truly monodentate.[6] It is only the second example of a ruthenium complex containing a *cis*-dioxo unit, the other being $\{(Ph_3P)_2N\}[RuO_2Cl_3]$; *trans*-dioxoruthenate(VI) complexes are much more common![7]

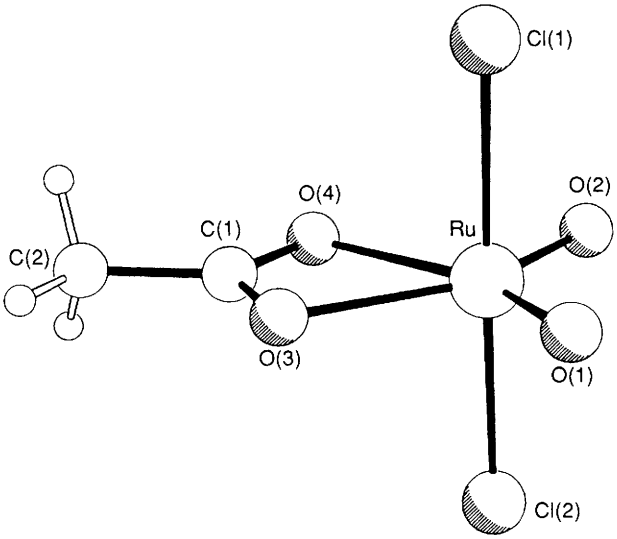

**Figure 1.** The molecular structure of $(PPh_4)[RuO_2Cl_2(OAc)]$. Selected bond lengths (Å) and angles (°); Ru–Cl(1) 2.37, Ru–Cl(2) 2.38, Ru–O(1) 1.64, Ru–O(2) 1.71, Ru–O(3) 2.12, Ru–O(4) 2.19 (Avg esd = 0.01 Å); O(1)–Ru–O(2) 120.2, O(1)–Ru–O(3) 88.9, O(1)–Ru–O(4) 150.4, O(2)–Ru–O(3) 149.7, O(2)–Ru–O(4) 89.1, O(3)–Ru–O(4) 60.6 (Avg esd = 0.5°); Cl(1)–Ru–Cl(2) 178.1(2).

The vibrational spectra of $(PPh_4)[RuO_2(OAc)Cl_2]$ in the solid state show bands at 872 and 889 cm$^{-1}$ (Raman) and 866 and 891 cm$^{-1}$ (IR) assigned to the symmetric and antisymmetric stretches of the *cis*-$RuO_2$ unit respectively; in $CH_2Cl_2$ solution the profile of the IR spectrum is similar to that of the solid-state spectrum, suggesting retention of the solid-state structure in solution [$\nu_s$ ($RuO_2$) 866 cm$^{-1}$, $\nu_{as}$ ($RuO_2$) 886 cm$^{-1}$]. Likewise, the IR bands at 1584 and 1475 cm$^{-1}$, typical

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† *Crystal data*: $C_{26}H_{23}Cl_2O_4PRu$, $M$ = 602.4, monoclinic, $a$ = 16.823(4), $b$ = 7.725(2), $c$ = 20.576(5) Å, $\beta$ = 98.93(2)°, $V$ = 2642 Å$^3$, space group $Cc$, $Z$ = 4, $D_c$ = 1.51 g cm$^{-1}$, $\mu$ = 77 cm$^{-1}$. Data were measured on a Nicolet R3m diffractometer with Cu-$K_\alpha$ radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy-atom method and refined anisotropically using absorption corrected data to give $R$ = 0.050, $R_w$ = 0.047 for 1618 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 116°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

of bidentate acetato ligands,[8] are little changed in the solution spectrum (1588 and 1485 $cm^{-1}$).

The complex is an efficient two-electron oxidant at room temperature, both stoicheiometrically and, in the presence of NMO as a co-oxidant, catalytically. In MeCN, in the presence of powdered molecular sieves, primary halides are oxidised to aldehydes and secondary halides to ketones in relatively good yields and with turnovers (mol of product : mol of catalyst) of the order of 20. Few reagents are able to accomplish this in such a simple one-step reaction.[9] Probably the most similar of the known reagents for halo-carbon oxidation are the chromium (VI) reagents, but these cannot be rendered catalytic.[10] In a scaled-up oxidation benzyl bromide (5 g) was converted to benzaldehyde (49% yield) in 3 h by $(PPh_4)[RuO_2(OAc)Cl_2]$ (0.075 g) representing a catalytic turnover of 115; and such turnovers may be obtained with other halides. The reagent also efficiently oxidises alcohols to aldehydes and ketones; these latter oxidations are more efficiently carried out in $CH_2Cl_2$. Using the same method sulphides are oxidised to sulphoxides and sulphones, and phosphines to phosphine oxides. The results for such reactions are given in Table 1.

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