General Synthesis of Dioxoruthenium(vi) Complexes. Structure and Reactivity of *trans*-Dioxobis(acetato)bis(pyridine)ruthenium(vi)

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The two step conversion of $RuCl_3$ into a new general class of dioxoruthenium(vi) complexes is characterized by *X*-ray crystallography of *trans*-$(O)_2Ru(py)_2(OAc)_2$ (py = pyridine) and by its utilization in oxygen atom transfer to triphenylphosphine and alkene donors.

Metal catalysis of various organic oxidations is effectively promoted by ruthenium complexes acting *via* their high oxidation states, presumably ruthenium-(iv), -(v) and -(vi).[1—4] Among these, our interest has been directed to dioxoruthenium(vi) complexes owing to the possibility of effecting direct oxygen atom transfer.[5] Unfortunately only a single complex of this genre has been structurally characterized.[6] The limited number of dioxoruthenium(vi) complexes which are known are not easily prepared, and certainly not by a synthetic procedure of general applicability.[6—10]

We report the two-step synthesis and structural characterization of a general class of dioxoruthenium(vi) complexes of which the first member is *trans*-dioxobis(acetato)bis(pyridine)-ruthenium(vi) (**1**). Thus $RuCl_3$ hydrate was easily converted in the first step into barium ruthenate which was isolated as the brick-red, insoluble $BaRuO_3(OH)_2$ in ~80% yield.[1] However it can be readily converted in a second step into the bright yellow, highly soluble complex (**1**) by the addition of acetic acid and pyridine (py) to a suspension of $BaRuO_3(OH)_2$ in acetonitrile at 0 °C. This synthetic method is general and various other analogues were easily prepared from related carboxylic acids and pyridine bases, including $(O)_2Ru(py)_2(O_2CPr^n)_2$, $(O)_2Ru(py)_2(O_2CPh)_2$, $(O)_2Ru(4\text{-}Mepy)_2\text{-}(OAc)_2$, and $(O)_2Ru(py)_2(O_2CCF_3)_2$. Although the α,α'-bipyridine derivative was apparently too transient, we hope that other polypyridine complexes of dioxoruthenium(vi) will be isolable.

All the dioxoruthenium(vi) complexes related to (**1**) were diamagnetic and characterized by an intense band at ~840 cm^{-1} in their i.r. spectra, diagnostic of the *trans*-dioxoruthenium moiety.[1,6,8] The electronic spectrum of (**1**) consisted of a weak, vibronically structured absorption band at $\lambda_{max.}$ ~400 nm characteristically present in other *trans*-dioxoruthenium(vi) complexes.[11] Such a structural assignment was

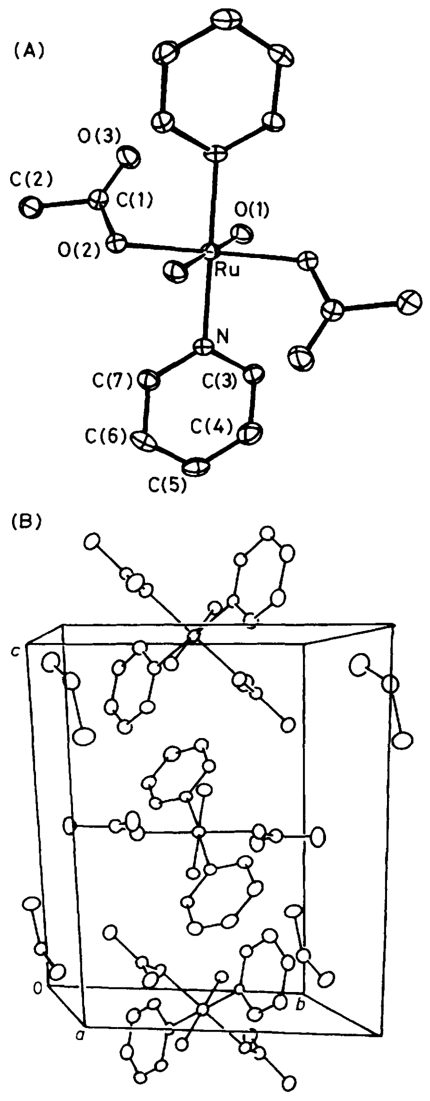

Figure 1. ORTEP diagrams of (A) nonhydrogen atoms in complex (**1**) showing the *trans*-dioxoruthenium unit with an O=Ru^{VI} bond length of 1.726(1) Å and (B) unit cell showing the presence of two independent molecules.

confirmed by a single crystal *X*-ray structure determination† of (**1**) obtained from the slow diffusion of n-pentane into a dichloromethane solution at −20 °C. The ORTEP diagram in Figure 1(A) shows the ruthenium(VI) to be coordinated to a pair of *trans*-pyridine ligands and a pair of *trans*-σ-acetato ligands. The linear *trans*-dioxoruthenium moiety completes the regular octahedral co-ordination about the ruthenium centre. Indeed the presence of a crystallographic centre of inversion defines the anti-coplanar acetato ligands as well as the coplanar pyridines. Slight differences in the dihedral angles of the latter relative to the *trans*-dioxoruthenium(VI) axis lead to two independent molecules in the unit cell (Figure 1B). Most importantly, the oxo-ruthenium bond distance of 1.726(1) Å is longer than those reported recently for the cationic macrocyclic analogues $(O)_2Ru(16\text{-tmc})^{2+}$ [1.705(7) Å] and $O_2Ru(15\text{-tmc})^{2+}$ [1.718(5) Å] (16-tmc = 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane; 15-tmc = 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacyclopentadecane).[6]

In accord with this increased O=Ru^{VI} bond distance, preliminary studies indicate that (**1**) is capable of oxygen atom transfer to various donors. Thus triphenylphosphine was rapidly and quantitatively converted into its oxide. The stoicheiometry for oxygen atom transfer in equation (1) is tentative since the reduced ruthenium product which was isolated as a green solid has not yet been successfully purified by crystallization.

$$\underset{(\mathbf{1})}{(O)_2Ru(py)_2(OAc)_2} + PPh_3 \rightarrow OPPh_3 + ORu(py)_2(OAc)_2 \quad (1)$$

Cyclohexene was slowly (16 h) converted by (**1**) into cyclohexenone in 40% yield together with small amounts of cyclohexene oxide. Although added acetate [as $(Ph_3\text{-}P)_2\text{-}N^+OAc^-$] had little effect on this oxidation, the conversion into cyclohexenone was complete within 3 h in the presence of 1 equiv. of added pyridine. This oxidation is likely to proceed by prior allylic insertion of an oxygen atom into cyclohexene,[12] since cyclohexenol was rapidly and quantitatively converted into cyclohexenone by (**1**) under comparable conditions. The oxidation of other alkenes such as hexenes and styrenes appeared to be slow and is under further investigation.

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† *Crystal Data* for (**1**): $RuC_{14}H_{16}N_2O_6\cdot CH_2Cl_2$, M = 494.3, triclinic, space group $P\bar{1}$, a = 8.359(2), b = 9.599(4), c = 13.431(8) Å, α = 89.68(5), β = 74.20(5), γ = 69.52(3)°, U = 966 Å^3, Z = 2, D_c = 1.70 g cm^{-3}, Enraf Nonius CAD 4 diffractometer, Mo-K_α (λ = 0.71073 Å), μ = 11.06 cm^{-1}, 2038 observed reflections with $I < 3\sigma(I)$ refined to R = 0.021 (R_w = 0.023). 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.