

High-valent Paramagnetic Ruthenium(IV) Complexes Containing Multianionic Chelating Ligands as Efficient Catalysts for Alkene Epoxidation; X-Ray Crystal Structure of $2[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)(\text{py})]\cdot\text{Et}_2\text{O}\cdot 2\text{H}_2\text{O}$ [$\text{H}_4\text{chbae} = 1,2\text{-bis}(3,5\text{-dichloro-2-hydroxybenzamido})\text{ethane}$; $\text{py} = \text{pyridine}$]

Chi-Ming Che,^a Wing-Kin Cheng,^a Wa-Hung Leung,^a and Thomas C. W. Mak^b

^a Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

^b Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

The reaction of 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane (H_4chbae) with $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ yielded $[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)_2]$ which in turn gave $[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)(\text{py})]$ ($\text{py} = \text{pyridine}$) upon treatment with pyridine; the $[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)(\text{py})]$ complex has been characterized by magnetic susceptibility measurement ($\mu_{\text{eff.}} = 3.08 \mu_{\text{B}}$) and X-ray crystallography and found to catalyse the epoxidation of alkenes in the presence of iodosylbenzene.

Our approach in developing ruthenium complexes for uses in oxidative reactions has been to explore the co-ordination chemistry of ruthenium in high oxidation states.¹ To our knowledge, stable monomeric Ru^{IV} complexes without terminally bonded oxo ligands are rare.² Collins and co-workers recently showed that the tetra-anionic chelating ligand, H_4chbae [1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane], is capable of stabilizing metal ions in unusual high oxidation states.³ The strong σ -donating properties and the anionic nature of this ligand make it attractive in the study of the high-valent chemistry of ruthenium. In this report, the synthesis, chemical properties, and structural characterization of $[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)(\text{py})]$ ($\text{py} = \text{pyridine}$) are described.

Aerial oxidation of a refluxing methanolic solution of $[\text{Ru}^{\text{II}}(\text{PPh}_3)_3\text{Cl}_2]$, Et_3N , and H_4chbae yielded $[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)_2]$ (1), which upon treatment with pyridine in methanol produced $[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)(\text{py})]$ (2) as a bluish green

microcrystalline solid. The i.r. spectrum of (2) displayed no N–H and O–H stretches in the usual 3000–3500 cm^{-1} region, indicating that the co-ordinated chbae ligand is in the deprotonated form. The optical spectrum of (2) in methanol showed u.v.–visible absorption bands at 250, ~330(br,sh), and 630(br) nm. Magnetic susceptibility measurements indicated a paramagnetic (d_{xy})²(d_{xz})¹(d_{yz})¹ ground state with $\mu_{\text{eff.}} = 3.08 \mu_{\text{B}}$ (crystalline sample, Guoy method) characteristic of the spin-only value for two unpaired electrons; paramagnetic Ru^{IV} oxo complexes with $\mu_{\text{eff.}}$ in the range 2.7–2.9 μ_{B} have previously been reported.¹ Recrystallization of complex (2) from $\text{MeOH-Et}_2\text{O}$ yielded $2[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)(\text{py})]\cdot\text{Et}_2\text{O}\cdot 2\text{H}_2\text{O}$ (3), which was characterized by X-ray crystallography.[†]

In the crystal structure of (3) (Figure 1), the two independent molecules (I and II) of the Ru^{IV} complex (2) are linked by forming acceptor hydrogen bonds, through O(3) of I and O(2) of II, with the bridging water molecule O(7) forming donor hydrogen bonds to O(6) and the ether oxygen atom O(5). Consequently the stoichiometric formula (asymmetric unit) of (3) faithfully represents the structure of this molecular aggregate consolidated by hydrogen bonding. In complex (3) (Figure 1), the Ru^{IV} atom lies in the plane of the equatorial ligand atoms O(1), O(4), N(1), and N(2) of the macrocycle, the two axial bonds making an angle of 172.5(1)°. The molecular dimensions of (2) show that while N(1), N(2), C(7), and C(10) all confirm to sp^2 hybridization, the two amide moieties are not entirely equivalent, presumably owing to uneven steric repulsion of the bulky axial ligands and the effects of hydrogen bonding. As expected, the $\text{Ru}^{\text{IV}}\text{-N}(\text{amide})$ bond lengths, in the range 1.987–2.044(5) Å, are

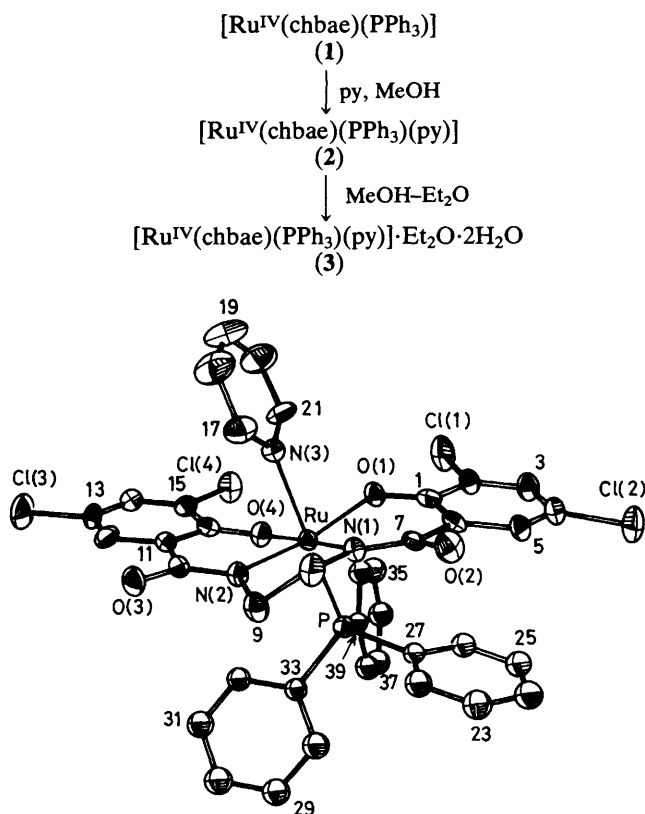


Figure 1. Perspective view of the structure of the $[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)(\text{py})]$ unit of (3), a common atom labelling scheme being used for both independent molecules I and II.

[†] Crystal data for (3): $2\text{C}_{39}\text{H}_{28}\text{N}_3\text{Cl}_4\text{O}_4\text{PRu}\cdot\text{C}_4\text{H}_{10}\text{O}\cdot 2\text{H}_2\text{O}$, $M = 1863.19$, triclinic, space group $P\bar{1}$, $a = 10.626(2)$, $b = 16.535(4)$, $c = 23.552(6)$ Å, $\alpha = 100.36(2)$, $\beta = 92.69(2)$, $\gamma = 95.34(1)^\circ$, $U = 4044(1)$ Å³, $Z = 2$, $D_c = 1.530 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 7.33 \text{ cm}^{-1}$. Crystal size $0.24 \times 0.20 \times 0.18 \text{ mm}$. Intensity data: Nicolet R3m diffractometer, Mo-K α radiation ($\lambda = 0.71069$ Å), ω - 2θ scan mode, $2\theta_{\text{max.}} = 45^\circ$, 10 137 unique reflections, 7695 observed [$|F_o| > 3\sigma(|F_o|)$]. Empirical absorption correction by fitting pseudo ellipsoid to ψ -scan data, mean $\mu_r = 0.08$, transmission factors 0.800–0.836. The structure was solved by the heavy-atom method and refined to $R_F = 0.055$, $R_{wF} = 0.059$ using SHELXTL.⁴ The phenyl rings were treated as rigid groups with individual isotropic thermal parameters for the C atoms. All other non-hydrogen atoms were refined anisotropically. The methyl groups were also handled as rigid groups, and the ring and methylene H atoms were generated geometrically and allowed to ride on their respective parent C atoms; fixed isotropic thermal parameters were assigned to all H atoms. The water H atoms could not be located from the final difference map (residual extrema +0.63 to -0.50 $e \text{ \AA}^{-3}$). 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.

Table 1. Oxidation of organic substrates catalysed by $[\text{Ru}^{\text{IV}}(\text{chbae})(\text{PPh}_3)(\text{py})]$.

Substrate	Product	t/h	Total % yield ^a	Total turnover
Cyclohexene	Cyclohexene oxide (10.3%)	6	21.6	96
	Cyclohex-2-en-1-one (11.3%)			
Styrene	Styrene oxide	6	7.3	58

^a Based on PhIO; this does not include loss of PhIO due to self-decomposition in CH_2Cl_2 solution in the absence of catalyst.

significantly shorter than the $\text{Ru}^{\text{II}}\text{-N}(\text{sp}^3)$, $\text{Ru}^{\text{III}}\text{-N}(\text{sp}^3)$, and $\text{Ru}^{\text{IV}}\text{-N}(\text{sp}^3)$ distances involving saturated amine ligands: *e.g.* 2.144(4) Å in $[\text{Ru}(\text{NH}_3)_6]\text{I}_2$,⁵ 2.104—2.117(3) Å in *cis*- $[\text{Ru}(\text{14aneN}_4)\text{Cl}_2]\text{Cl}$,⁶ and 2.085—2.141(5) Å in *trans*- $[\text{Ru}(\text{tmc})(\text{O})(\text{MeCN})](\text{PF}_6)_2$ ^{2a} (14aneN₄ = 1,4,8,11-tetra-azacyclotetradecane; tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane).

Complex (2) acts as an efficient catalyst for alkene epoxidation by iodosylbenzene (PhIO). In a typical experiment, a mixture of PhIO (200 mg), the organic substrate (1 ml), and (2) (1 mg) in CH_2Cl_2 (1 ml) were stirred for 6 h at room temperature. PhIO was transformed into PhI and the organic products were identified by *g.c.*-mass spectrometry (see Table 1); in the absence of the catalyst only a trace of the organic product was found. With cyclohexene, both the C-H and C=C bonds were attacked. The mechanism of the oxidative reaction is not yet known; however, the possibility of a $\text{Ru}^{\text{VI}}=\text{O}$ reactive intermediate *via* a $\text{Ru}^{\text{IV}} + \text{PhIO} \rightarrow \text{Ru}^{\text{VI}}=\text{O} + \text{PhI}$ pathway⁷ opens up an interesting area of oxidation chemistry of ruthenium with the use of polyanionic chelating ligands.

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