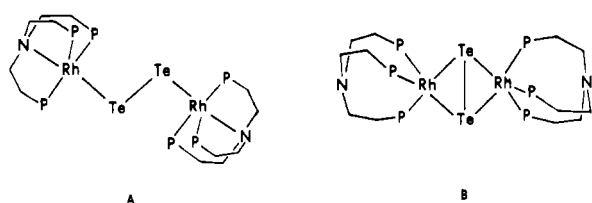


Chart II



Packing diagrams for **2** and **3** are shown in Figure 2.

**Behavior of the Compounds in Solution.** In order to obtain  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the compounds, **1** and **2** were dissolved in  $\text{CD}_2\text{Cl}_2$ . However, **2** decomposes to  $[(\text{pp}_3)\text{RhCl}]$  before any signal can be detected. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** (Figure 3) consists of two doublets [29.68 ppm, 141.0 Hz (A) and 26.41 ppm, 144.4 Hz (B), with 1.3:1 intensity ratio] having similar chemical shifts and coupling constants, which are in the usual range for tripodal polyphosphane-rhodium complexes.<sup>32b</sup> The two doublets present satellites whose intensities are consistent with coupling of the P atoms to tellurium ( $^{125}\text{Te}$ ,  $I = 1/2$ , 7% natural abundance). The coupling constants [ $^2J(\text{P}-\text{Te}) = 152.0$  (A) and 116.0 Hz (B)] are 1 order of magnitude smaller than the  $^1J(\text{P}-\text{Te})$  coupling in compounds containing tellurium directly bonded to phosphorus.<sup>34</sup> A similar decrease in coupling constants, from  $^1J(\text{Te}-\text{H}) = 151$  Hz to  $^2J(\text{Te}-\text{H}) = 16$  Hz, has been found in a rhenium hydrotelluride hydride complex.<sup>19</sup> Satellites due to  $^{125}\text{Te}$  have been recently reported for the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the  $[\text{Cp}(\text{Et}_3\text{P})(\text{CO})\text{Fe}]_2\text{Te}_n$  ( $n = 1, 2$ ) compounds and their  $^2J(\text{P}-\text{Te})$  coupling constants agree with the present ones.<sup>35</sup>

Although the poor solubility of the compound prevented us from running variable-temperature  $^{31}\text{P}\{^1\text{H}\}$  spectra, some considerations are nevertheless possible. The pattern shown in Figure 3 is inconsistent with the solid-state structure of **1**, which requires six equivalent phosphorus atoms in view of the possibility of rotations about the Rh-Te and Te-Te bonds in solution.<sup>36</sup> Also, inequivalent phosphorus atoms on the same  $\text{np}_3$  ligand would produce an  $\text{AB}_2\text{X}$  or  $\text{ABCX}$  spin system, at variance with the features observed for the spectrum. Furthermore, the observed intensity ratio of the two doublets (1.3:1) rules out any inequivalence between the two sets of P atoms belonging to different  $\text{np}_3$  ligands in the same molecule. The features of the spectrum may be accounted for by the presence of two species in solution, having

different geometries. Possible arrangements are as shown in Chart II, where A corresponds to the structure of compound **1** in the solid state and B may be considered as arising from A through an isomerization reaction that involves the detachment of the apical nitrogen donor of the  $\text{np}_3$  ligand. The possibility of such rearrangements is supported by the following considerations: (i) isomerization processes have been observed for compounds where two metal fragments are bound to  $\text{X}_2$  ( $\text{X} = \text{Se},^{37} \text{Te}^{19}$ ) units and consist of a shift of one metal-ligand unit from terminal to side on<sup>37</sup> or vice versa;<sup>19</sup> (ii) a side-on-bridging  $\text{Te}_2$  unit between two  $\text{P}_3\text{Rh}$  fragments has been found in the structure of the compound  $[(\text{triphos})\text{Rh}]_2\text{Te}_2$  containing a tripodal tridentate ligand;<sup>22</sup> (iii) the detachment of the nitrogen atom of the  $\text{np}_3$  ligand, required for the A  $\rightarrow$  B conversion, should easily occur in presence of a predominantly soft set of donor atoms,<sup>38</sup> such as that existing in the present compounds; (iv) the proposed geometry for species B is not in contrast to the stereochemical nonrigidity assumed above as nonrigidity has been observed for the compounds containing a  $\text{Te}_2$  group side-on bonded to two  $\text{M}-\text{L}_3$  fragments, which have been described up to now.<sup>18</sup>

**Conclusions.** Rhodium compounds containing the end-on-coordinated ditellurium unit are synthesized from easily accessible reagents and easy manipulation. The Rh-Te-Te-Rh zigzag skeleton is highly reactive, suggesting that such compounds could behave as sources of tellurium fragments for the synthesis of new tellurium-containing compounds. The Te-Te distances in the present compounds are typical of Te-Te single bonds in  $\text{Te}_2$  dimetal derivatives. A difference in such bond lengths of 0.07 Å between compounds **2** and **3** is essentially due to different packing in the solid. This reveals how sensitive the Te-Te distance may be to various factors. This feature, combined with the documented possibility of octet expansion on Te,<sup>39</sup> adds interest to the chemistry of heavy main-group elements such as Te.

**Registry No.** **1**, 123726-12-5; **2**, 123726-14-7; **3**, 123726-13-6;  $[\text{RhCl}(\text{cod})]_2$ , 12092-47-6; Te, 13494-80-9;  $(\text{Bu}_4\text{N})\text{BH}_4$ , 33725-74-5.

**Supplementary Material Available:** Full details of the crystal data and crystallographic data collections (Table SI), thermal parameters for **1-3** (Tables SII-SIV), bond distances (Tables SV-SVII) and angles (Tables SVIII-SX) for **1-3**, and hydrogen atom coordinates (Tables SXI-SXIII) for **1-3** (23 pages); listings of observed and calculated structure factors (58 pages). Ordering information is given on any current masthead page.

(34) Kuhn, N.; Schumann, H. *J. Chem. Soc., Dalton Trans.* **1987**, 541.

(35) Steigerwald, M. L. *Chem. Mater.* **1989**, *1*, 52.

(36) Dahlenburg, L.; Mirzaei, F. *Inorg. Chim. Acta* **1985**, *97*, L1.

(37) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Hecht, C. *J. Organomet. Chem.* **1986**, *314*, 295.

(38) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Inorg. Chem.* **1983**, *22*, 2196.

(39) Bogan, L. E.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1985**, *24*, 3722.

Contribution from the Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

## Oxidation Chemistry of Ruthenium-Salen Complexes

Wa-Hung Leung and Chi-Ming Che\*

Received November 29, 1988

The synthesis of  $[\text{Ru}^{\text{III}}(\text{salen})(\text{X})(\text{Y})]^n$  [ $n = -1$ ,  $(\text{X})(\text{Y}) = (\text{CN})_2$ ;  $n = 0$ ,  $(\text{X})(\text{Y}) = (\text{PPh}_3)(\text{PBu}_3)$ ,  $(\text{PPh}_3)(\text{py})$ ;  $n = 1$ ,  $(\text{X})(\text{Y}) = (\text{PPh}_3)(\text{N}_3)$ ,  $(\text{PPh}_3)(\text{TsO})$  ( $\text{TsO} = \text{tosylate anion}$ )] from  $[\text{Ru}^{\text{III}}(\text{salen})(\text{PPh}_3)(\text{Cl})]$  is described. These ruthenium(III) complexes are dark green air-stable solids. Their cyclic voltammograms display reversible  $\text{Ru}(\text{IV})/\text{Ru}(\text{III})$  and  $\text{Ru}(\text{III})/\text{Ru}(\text{II})$  couples with  $E^\circ$  ranging from 0.37 to 0.76 V and -0.47 to -1.06 V vs  $\text{Ag}/\text{AgNO}_3$  (0.1 M), respectively. At room temperature, they catalyze oxidation of alkenes by  $\text{PhIO}$ . With norbornene and cyclooctene, epoxides are formed. For arenes, oxidative cleavage of  $\text{C}=\text{C}$  bond is the major reaction pathway. The mechanism of the catalytic oxidation is discussed.

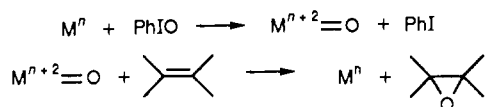
### Introduction

The use of metal-salen [salen =  $N,N'$ -ethylenebis(salicylide-aminate) anion] complexes to catalyze oxidation of hydrocarbons by oxygen atom donors has been receiving much attention in recent years. This area is highlighted by the works of Kochi and co-workers on the oxidation chemistry of salen complexes of

chromium,<sup>1</sup> manganese,<sup>2</sup> and nickel.<sup>3</sup> The isolation of the reactive  $[\text{Cr}^{\text{V}}(\text{salen})\text{O}]^{1a}$  by these workers indicates that the pathways

(1) (a) Siddall, T. L.; Miyaura, N.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1185. (b) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606.

Scheme I



for the PhIO epoxidation of olefins catalyzed by metal-salen complexes and the analogous metalloporphyrins could be similar, as shown in Scheme I. Scheme I is reminiscent of Groves's oxygen-rebound mechanism of catalytic oxidation with metalloporphyrins.<sup>4</sup>

We have been interested in the oxidation chemistry of oxo-ruthenium-salen complexes, as a result of Groves's recent work on *trans*-dioxo(tetramesitylporphinato)ruthenium(VI)<sup>5</sup> and also because of the periodic relationship of ruthenium with its iron congener. However, the chemistry of ruthenium-salen complexes is not well explored.<sup>8</sup> Because dianionic salen ligand is known to stabilize metal complexes in high oxidation states,<sup>1a,6</sup> it is not surprising that ruthenium-salen complexes with oxidation states higher than III should be easily accessible. As part of our continuing program on the design of ruthenium catalysts for organic oxidation, we describe here the results of a study on the synthesis, electrochemistry, and catalytic oxidative reactions of ruthenium-salen complexes.

### Experimental Section

**Materials.** Ruthenium trichloride was purchased from Strem. The H<sub>2</sub>salen ligand was prepared by condensation of salicylaldehyde and ethylenediamine in ethanol. [Ru<sup>II</sup>(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>]<sup>7</sup> and [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(Cl)]<sup>8</sup> were prepared by literature methods. All reagents and solvents of syntheses were reagent grade.

**Physical Measurements.** UV-visible spectra were obtained on a Shimadzu UV-240 spectrophotometer. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 577 spectrophotometer. Gas chromatography was performed on a Varian Model 940 gas chromatograph equipped with a flame-ionization detector. Quantification of gas chromatographic components was done on a Shimadzu CR-3A electronic integrator. The 90-MHz <sup>1</sup>H NMR spectra were obtained by the use of a JEOL FX90Q spectrometer using tetramethylsilane as the internal reference. Elemental analyses were performed by the Microanalytical Unit of the Australian Mineral Development Laboratory.

**Electrochemistry.** Acetonitrile (HPLC, Mallinkrodt) was distilled from KMnO<sub>4</sub> and CaH<sub>2</sub>. Dichloromethane (AR, Ajax) was washed with concentrated sulfuric acid and distilled from CaH<sub>2</sub>. Tetraethylammonium tetrafluoroborate ((TEA)BF<sub>4</sub>, Southwestern analytical reagent) was dried in vacuo at 100 °C. Cyclic voltammetry was performed on a Princeton Applied Research Model 173/179 potentiostat/digital coulometer, and a Model 175 universal programmer. The working electrode was a glassy-carbon electrode. The reference electrode was an Ag/AgNO<sub>3</sub> electrode (0.1 M in CH<sub>3</sub>CN). In all cases, ferrocene was added as internal reference.

**Syntheses.** [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(N<sub>3</sub>)]. To a methanolic solution of [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(Cl)] (250 mg) was added an excess of NaN<sub>3</sub> (500 mg). The solution was refluxed for 15 min. The microcrystalline solid formed was filtered and washed with water and methanol. It was further recrystallized from methanol/ether (yield ≈ 60%). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>; λ<sub>max</sub>/nm (log ε): 800 (3.53), 500 (3.91), 360 (3.90). IR (cm<sup>-1</sup>): ν(N<sub>3</sub>) 2000. Anal. Calcd: C, 59.7; H, 4.70; N, 9.95. Found: C, 59.8; H, 4.33; N, 9.72.

[Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(TsO)] (TsO = Tosylate Anion). [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(PPh<sub>3</sub>)(Cl)] (250 mg) was refluxed with silver *p*-toluenesulfonate (200 mg) in water/acetone (1:3) for 1 h. After removal of silver chloride, a dark microcrystalline solid was formed gradually. It was then filtered

and recrystallized in methanol/ether (yield ≈ 25%). UV-vis (MeOH; λ<sub>max</sub>/nm (log ε): 740 (3.53), 505 (3.14), 345 (4.09). Δ<sub>M</sub> (MeOH) = 5.2 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd: C, 61.5; H, 4.50; N, 3.50. Found: C, 61.3; H, 4.78; N, 3.54.

[Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(py)]ClO<sub>4</sub>. [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(Cl)] (250 mg) was refluxed with silver *p*-toluenesulfonate (220 mg) in methanol for 1 h. After removal of silver chloride, it was refluxed with pyridine (0.1 mL) for 1 h. It was cooled to room temperature and added to an excess of LiClO<sub>4</sub>. The green crude product was filtered and recrystallized in acetonitrile/ether (yield ≈ 40%). UV-vis (CH<sub>3</sub>CN; λ<sub>max</sub>/nm (log ε): 740 (3.50), 500 (3.26), 345 (3.91). Δ<sub>M</sub> (CH<sub>3</sub>CN) = 132 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd: C, 60.0; H, 4.21; N, 5.00; Cl, 4.40. Found: C, 57.7; H, 4.04; N, 5.39; Cl, 4.40.

[Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(P<sup>n</sup>Bu<sub>3</sub>)]ClO<sub>4</sub>. It was prepared by a procedure similar to that used for [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(py)]ClO<sub>4</sub> but with tri-*n*-butylphosphine used instead of pyridine (yield ≈ 33%). UV-vis (CH<sub>3</sub>CN; λ<sub>max</sub>/nm (log ε): 820 (3.24), 440 sh (2.88), 355 (3.92), 280 sh (3.84), 235 (2.37). Δ<sub>M</sub> (CH<sub>2</sub>Cl<sub>2</sub>) = 155 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd: C, 55.2; H, 7.56; N, 3.22. Found: C, 55.2; H, 7.52; N, 3.57.

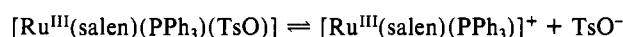
Na[Ru<sup>III</sup>(salen)(CN)<sub>2</sub>]. [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(Cl)] (250 mg) was refluxed with NaCN (40 mg) in methanol for 1 h. The solution was evaporated to dryness and chromatographed on a column of neutral alumina with methanol as the eluant. The product was recrystallized in methanol/ether (yield ≈ 50%). The [NBu<sub>4</sub>]<sup>+</sup> salt was prepared by adding [NBu<sub>4</sub>]Cl to an aqueous solution of Na[Ru<sup>III</sup>(salen)(CN)<sub>2</sub>]. UV-vis (MeOH; λ<sub>max</sub>/nm (log ε): 700 (2.94), 490 (2.94), 380 (3.86), 370 (3.86). IR (cm<sup>-1</sup>): ν(C≡N) 2080. Δ<sub>M</sub> (MeOH): 73.3 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd: C, 45.7; H, 3.86; N, 11.4. Found: C, 45.8; H, 3.56; N, 11.6.

**Catalytic Oxidation of Alkanes by Iodosylbenzene.** All hydrocarbon substrates were purified by standard procedures<sup>9</sup> and distilled before use. Dichloromethane was purified as described earlier. Iodosylbenzene was prepared by hydrolysis of iodosylbenzene diacetate (Aldrich) in sodium hydroxide solution. In a typical run, ruthenium catalyst (0.002 mmol), alkene (10 mmol), and PhIO (0.4 mmol) were stirred at room temperature in dichloromethane (1 mL) for 4 h. The end of the reaction was indicated by the disappearance of solid PhIO. After addition of an internal standard, an aliquot was taken for GLC analysis. The oxidized products were analyzed either on a 1/8 in. × 6 ft 10% Carbowax 20M on Chromosorb W column or a 1/8 in. × 6 ft 5% SE 30 on Chromosorb W column. Stilbene oxides were determined by an NMR method using 1,1-diphenylethylene as the internal standard. All catalytic oxidations were carried out under nitrogen atmosphere.

### Results

There are few reports on the ruthenium-salen complexes.<sup>7,8</sup> [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(Cl)], which is the starting material for the syntheses, was prepared by the reaction of [Ru<sup>II</sup>(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] with H<sub>2</sub>salen under aerobic conditions.<sup>8</sup> As earlier noted by West and co-workers,<sup>8</sup> the coordinated chloride of [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(Cl)] is labile and easily undergoes substitution in the presence of Ag(I). Substitution of the coordinated PPh<sub>3</sub> by other ligands such as N<sub>3</sub><sup>-</sup> and py (pyridine) proves to be difficult. However, with CN<sup>-</sup>, [Ru<sup>III</sup>(salen)(CN)<sub>2</sub>]<sup>-</sup> can be prepared in high yield.

All the Ru(III)-salen complexes are air-stable dark green solids, which are soluble in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN. Their IR spectra show the absence of ν(O-H) stretch at 3000–3500 cm<sup>-1</sup> but intense bands at 1500–1600 cm<sup>-1</sup> attributed to ν(C=N) and ν(C=C) stretches. Their UV-visible spectra display characteristic broad absorption near 700 nm, which probably arises from a p<sub>π</sub>(phenoxide) → d<sub>π</sub>(Ru<sup>III</sup>) charge-transfer transition. For [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(TsO)], the coordinated TsO group is labile and dissociates off in solution.



Conductivity measurement established that [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(TsO)] exists as a 1:1 electrolyte in methanol with measured Δ<sub>M</sub> of 77 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

Oxidation of [Ru<sup>III</sup>(salen)(CN)<sub>2</sub>]<sup>-</sup> with [Ce<sup>IV</sup>(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> in methanol gave a bluish green solid, which immediately precipitated out from the solution. Attempts to obtain an analytical pure sample of this compound were unsuccessful because this species is virtually insoluble in any solvent. Its IR spectrum in the 1600–1700-cm<sup>-1</sup> region is similar to that for Na[Ru<sup>III</sup>(salen)-

(2) Srinivasan, K.; Michand, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.

(3) Koola, J. D.; Kochi, J. K. *Inorg. Chem.* **1987**, *26*, 908.

(4) (a) Groves, J. T.; McClusky, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 859.

(b) Nemo, T. E.; Myers, R. S.; Groves, J. T. *Ibid.* **1979**, *101*, 1032.

(5) (a) Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984**, *23*, 3846. (b) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790.

(6) (a) Arshankaw, S. I.; Pozanjak, A. C. *Z. Anorg. Allg. Chem.* **1981**, *481*, 201. (b) Che, C. M.; Cheng, W. K.; Mak, T. C. W. *Inorg. Chem.* **1985**, *23*, 703. (c) Che, C. M.; Cheng, W. K.; Mak, T. C. W. *Ibid.* **1988**, *27*, 250.

(7) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.

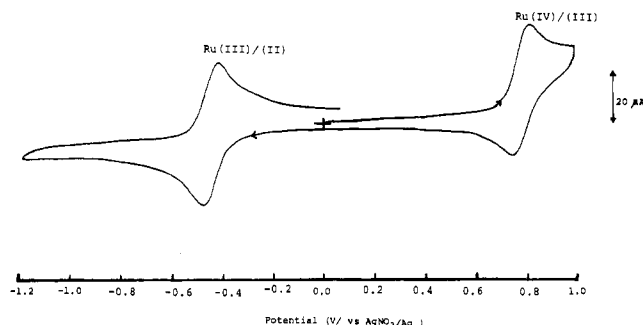
(8) Murray, K. S.; van den Berga, A. M.; West, B. O. *Aust. J. Chem.* **1978**, *31*, 203.

(9) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1980.

**Table I.** Electrochemical Data for Ruthenium–Salen Complexes

complex	$E^\circ$ , <sup>a</sup> V vs Ag/AgNO <sub>3</sub>	
	redn	oxidn
[Ru <sup>III</sup> (salen)(PPh <sub>3</sub> )(Cl)] <sup>b</sup>	-0.52	0.49
[Ru <sup>III</sup> (salen)(PPh <sub>3</sub> )(py)]ClO <sub>4</sub> <sup>c</sup>	-0.47	0.76
[Ru <sup>III</sup> (salen)(PPh <sub>3</sub> )(N <sub>3</sub> )] <sup>b</sup>	-0.64	0.48
[Ru <sup>III</sup> (salen)(PPh <sub>3</sub> )(P <sup>n</sup> Bu <sub>3</sub> )]ClO <sub>4</sub> <sup>c</sup>	-0.47	<i>d</i>
[Ru <sup>III</sup> (salen)(PPh <sub>3</sub> )(TsO)] <sup>c</sup>	-0.65	0.76
[NBu <sub>4</sub> ][Ru <sup>III</sup> (salen)(CN) <sub>2</sub> ] <sup>c</sup>	-1.06	0.37

<sup>a</sup> Potentials measured at scan rate = 100 mV s<sup>-1</sup>. <sup>b</sup> 0.1 M [Et<sub>4</sub>N]BF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> as the supporting electrolyte. <sup>c</sup> 0.1 M [Et<sub>4</sub>N]BF<sub>4</sub> in CH<sub>3</sub>CN as the supporting electrolyte. <sup>d</sup> Irreversible.



**Figure 1.** Cyclic voltammogram of [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(py)]ClO<sub>4</sub> in acetonitrile at a glassy-carbon electrode. Scan rate = 100 mV s<sup>-1</sup>.

(CN)<sub>2</sub>] indicating that the salen ligand remains unchanged in the oxidation reaction. It is basically diamagnetic with a measured  $\mu_{\text{eff}} = 0.7 \mu_{\text{B}}$ . We suggest it to be [Ru(salen)(CN)<sub>2</sub>].

Table I summarizes the electrochemical data of ruthenium–salen complexes. In general, these complexes show one oxidative and one reductive couple; a typical cyclic voltammogram of [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(py)]<sup>+</sup> in CH<sub>3</sub>CN is shown in Figure 1. Except for [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(P<sup>n</sup>Bu<sub>3</sub>)]ClO<sub>4</sub>, the redox couples in each case are reversible with current ratios ( $i_{\text{pa}}/i_{\text{pc}}$ ) and peak-to-peak separations ( $\Delta E_{\text{p}}$ ) characteristic of a reversible one-electron-transfer process ( $i_{\text{pa}}/i_{\text{pc}} \approx 1$  and  $\Delta E_{\text{p}} \approx 60\text{--}80$  mV for scan rates of 50–200 mV s<sup>-1</sup>). As the salen ligand is electrochemically inactive in the potential range concerned (+1.0 to -1.5 V), the two couples are assigned to the metal-centered Ru(III)/Ru(II) and Ru(IV)/Ru(III) couples. In accordance with this assignment, the redox potentials were found to vary with the nature of the axial ligands (Table I) and decrease in the order (X)(Y) = (PPh<sub>3</sub>)(py)  $\sim$  (PPh<sub>3</sub>)(TsO) > (PPh<sub>3</sub>)(P<sup>n</sup>Bu<sub>3</sub>) > (PPh<sub>3</sub>)(Cl) > (PPh<sub>3</sub>)(N<sub>3</sub>) > (CN)<sub>2</sub> for both Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples. This order roughly correlates with the decrease in the charges on the metal complexes. The similar  $E^\circ$  values for [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(py)]<sup>+</sup> and [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(TsO)] are likely due to the fact that the latter complex exists as [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(CH<sub>3</sub>CN)]<sup>+</sup> in acetonitrile solution. The range of potentials spanned is 400 mV for the Ru(IV)/Ru(III) and 600 mV for the Ru(III)/Ru(II) couples, suggesting that the axial ligands have a profound effect on the redox properties of the ruthenium–salen system. Oxidation of [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(P<sup>n</sup>Bu<sub>3</sub>)]<sup>+</sup> is irreversible; presumably, oxidative dissociation of the phosphine ligand occurs at the Ru(IV) center.

**Catalytic Oxidation of Alkenes by Iodosylbenzene.** Ruthenium(III)–salen complexes are able to catalyze oxidation of alkenes by iodosylbenzene; the results are summarized in Table II. Negligible amounts of oxidized product was detected when either the ruthenium catalyst or PhIO was absent. For norbornene and cyclooctene, epoxides were formed. In the oxidation of cyclohexene, allylic oxidation products such as cyclohexenone and cyclohexenol were also detected. Epoxidation of *cis*-stilbene was nonstereoretentive and resulted in a mixture of *cis*- and *trans*-stilbene oxides (in a ratio of 4:1). Significant amount of benzaldehyde, which is due to oxidative cleavage of C=C bond, was produced in the oxidation of arenes. Ru(III)–salen complexes could not catalyze hydroxylation of saturated alkanes such as

**Table II.** Catalytic Oxidation by PhIO with Ru(III)–Salen Complexes<sup>a</sup>

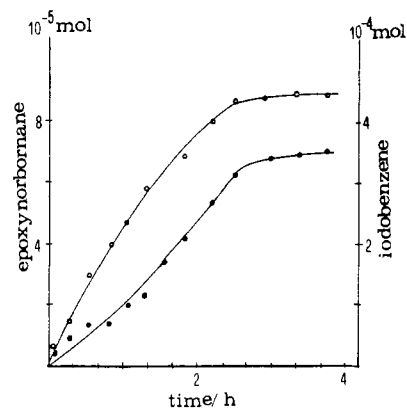
substrate	product (% yield) <sup>b</sup>
styrene	styrene oxide (6) benzaldehyde (22)
cyclohexene	cyclohexene oxide (9) <sup>c</sup>
cyclooctene	cyclooctene oxide (29)
<i>trans</i> -stilbene	benzaldehyde (35) <i>trans</i> -stilbene oxide (12)
<i>cis</i> -stilbene	benzaldehyde (30) <i>cis</i> -stilbene oxide (9) <i>trans</i> -stilbene oxide (2.4)
norbornene	<i>exo</i> -norbornene oxide (13)
norbornene <sup>d</sup>	<i>exo</i> -norbornene oxide (12)
norbornene <sup>e</sup>	<i>exo</i> -norbornene oxide (5)
norbornene <sup>f</sup>	<i>exo</i> -norbornene oxide (<1)
cyclohexane	cyclohexanone (<1)

<sup>a</sup> Reaction conditions: Ru catalyst, [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(py)]<sup>+</sup> (1.5 mg); solvent, CH<sub>2</sub>Cl<sub>2</sub> (1 mL); substrate (1 mL); PhIO (100 mg); stirred at room temperature for 5 h. <sup>b</sup> Percent yield based on PhI generated. <sup>c</sup> Small amounts of cyclohexenone and cyclohexenol were also detected (less than 3% yield). <sup>d</sup> Catalyst: [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(N<sub>3</sub>)]. <sup>e</sup> Catalyst: [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(TsO)]. <sup>f</sup> Catalyst: [NBu<sub>4</sub>][Ru<sup>III</sup>(salen)(CN)<sub>2</sub>].

**Table III.** Solvent Effect on the Catalytic Oxidation of Norbornene<sup>a</sup>

solvent	reacn time, h	% yield of epoxide <sup>b</sup>
CH <sub>2</sub> Cl <sub>2</sub>	4	13
C <sub>6</sub> H <sub>6</sub>	11	9
CH <sub>3</sub> CN	>24	<i>c</i>

<sup>a</sup> Reaction condition: Ru catalyst, [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(py)]<sup>+</sup> (1.6 mg); solvent (2 mL); norbornene (150 mg); PhIO (100 mg); stirred at room temperature. <sup>b</sup> Percent yield based on PhI generated. <sup>c</sup> Reaction incomplete after 24 h.



**Figure 2.** Plot of amount of organic products vs time in the catalytic epoxidation of norbornene: (O) epoxy norbornene; (●) iodobenzene.

cyclohexane. Only a trace amount of cyclohexanone (<1%) was detected after 1 day.

The catalytic reactions usually took 2–4 h for completion, as indicated by the disappearance of the solid PhIO. A typical plot of time dependence of amount of organic products in the oxidation of norbornene was shown in Figure 2. No induction period has been observed, and the yield of epoxide leveled off after 2 h. The yield of *exo*-norbornene oxide from norbornene was low (5–13%) irrespective of the identity of the ruthenium catalyst (Table III). No catalytic oxidation was found when [NBu<sub>4</sub>][Ru<sup>III</sup>(salen)(CN)<sub>2</sub>] was used as the catalyst. The effect of solvent on the catalytic epoxidation has also been studied, and the results are set in Table III. The catalytic reaction in dichloromethane was faster than that in benzene, which was faster than that in acetonitrile.

## Discussion

The ruthenium(III)–salen complexes constitute another class of metal–salen complexes that are catalysts for the oxidation of

alkenes by iodosylbenzene. The  $E^\circ$  values for the Ru(IV)/Ru(III) couples lie between 0.37 and 0.76 V vs Ag/AgNO<sub>3</sub>, suggesting that Ru(IV)-salen complexes should be accessible through chemical oxidation with common oxidants. As an oxo group should be a much better  $\sigma$ - and  $\pi$ -donor than a cyano group, we believe that [Ru<sup>IV</sup>(salen)O(L)] (L = neutral monodentate ligand) should not be particularly oxidizing in view of the measured  $E^\circ$  of 0.37 V for the Ru(IV)/Ru(III) couple of [Ru<sup>III</sup>(salen)(CN)<sub>2</sub>]<sup>-</sup>. The Ru(III)/Ru(II) couple of [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(py)]<sup>+</sup> is considerably less anodic (more than 400 mV) than that of *trans*-[Ru<sup>III</sup>(NH<sub>3</sub>)<sub>4</sub>(py)<sub>2</sub>]<sup>3+</sup> and [Ru<sup>III</sup>(TPP)(py)<sub>2</sub>]<sup>+</sup> (H<sub>2</sub>TPP = tetraphenylporphyrin).<sup>11</sup> Furthermore, the Ru(III)/Ru(II) couple of [Ru<sup>III</sup>(salen)(CN)<sub>2</sub>]<sup>-</sup> is about 170 mV more cathodic than that of K[Ru<sup>III</sup>(TPP)(CN)<sub>2</sub>] ( $E^\circ = -0.61$  V).<sup>12</sup> These results suggest that the dianionic salen ligand is a better donor than (NH<sub>3</sub>)<sub>4</sub> and TPP. As high-valent [Ru<sup>VI</sup>(TPP)(O)<sub>2</sub>]<sup>13</sup> and *trans*-[Ru<sup>VI</sup>(NH<sub>3</sub>)<sub>4</sub>(O)<sub>2</sub>]<sup>2+</sup><sup>14</sup> complexes are known, it would not be surprising to find that the analogous oxoruthenium-salen complexes exist and are stable enough for isolation under appropriate conditions.

A high-valent oxometal complex is usually suggested to be the reactive intermediate in the metalloporphyrin-catalyzed PhIO oxidation. On the other hand, both Hill and Valentine and others<sup>15,16</sup> indicated that, under certain conditions, the metal-catalyzed PhIO oxidation may proceed with a M-O-I-Ph reactive intermediate. Such species has been isolated by Hill and co-workers in their previous works on the manganese porphyrin system.<sup>15</sup> In this work, we cannot unambiguously assign whether it is an oxo species or an iodosylbenzene adduct that is responsible for the observed epoxidation. It may also be possible that both are reactive intermediates. The ruthenium reactive intermediate(s) would probably be in oxidation state of IV or V. Our electrochemical results indicate that ruthenium-salen complexes with oxidation states higher than III from the oxidation with PhIO are not beyond expectation. *cis*-Stilbene has been used as a mechanistic probe for metalloporphyrin-catalyzed oxidation.<sup>17</sup> In this study, oxidative cleavage of the C=C bond is the major reaction pathway in the oxidation of arenes. This suggests that if the intermediate is an oxoruthenium species, it reacts with alkenes via a noncon-

certed pathway.<sup>17</sup> However, attempts to characterize or identify the reactive intermediate(s) by spectroscopic methods were unsuccessful. Addition of PhIO to a dichloromethane solution of Ru(III)-salen complexes did not show any apparent spectral change; the reaction of the ruthenium catalyst with PhIO has been found to be slow (100 mg of PhIO was used up in 2-4 h). The yield of oxidation is low in most cases; presumably, the intermediate ruthenium species is used in other side reactions.

Acetonitrile is known to be a  $\pi$ -donor ligand for ruthenium. Accordingly, reaction in acetonitrile has been found to be very slow (incomplete even after 24 h) indicating that binding of PhIO to ruthenium is an important step for the activation of the oxidant. In accordance to this, the substitutionally inert [Ru<sup>III</sup>(salen)(CN)<sub>2</sub>]<sup>-</sup> species has been found to be ineffective in bringing about catalytic oxidation.

The yields of epoxidation by Ru(III)-salen complexes are comparable to that of the "Ru(III)-OEP + PhIO" system, in which [Ru<sup>IV</sup>(OEP)O]<sup>+</sup> (OEP = octaethylporphyrin cation radical) was suggested to be the reactive intermediate.<sup>18</sup> For example, the yield of norbornene oxide with [Ru<sup>III</sup>(OEP)(PBU<sub>3</sub>)Br] is 8%, which is similar to that found in this work. In contrast to the iron(III)-<sup>4b</sup> and manganese(III)-porphyrin<sup>19</sup> and manganese(III)-salen<sup>2</sup> systems, both Ru(III)-salen and -porphyrin complexes are poor catalysts for alkane hydroxylation. The reason(s) underlying is not certain. However, if oxoruthenium complexes are the reactive intermediates in both the ruthenium-salen and -porphyrin systems, these species undergo some unknown but facile deactivation pathway(s).

**Acknowledgment.** Financial support from the University of Hong Kong and UPGC is acknowledged. W.-H.L. is grateful for receipt of the Croucher Foundation Studentship and Sir Edward Youde Memorial Fellowship.

**Registry No.** [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(Cl)], 65849-07-2; [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(py)]ClO<sub>4</sub>, 123640-98-2; [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(N<sub>3</sub>)], 123640-99-3; [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(PBU<sub>3</sub>)ClO<sub>4</sub>], 123641-01-0; [Ru<sup>III</sup>(salen)(PPh<sub>3</sub>)(TsO)], 123641-02-1; [NBu<sub>4</sub>][Ru<sup>III</sup>(salen)(CN)<sub>2</sub>], 123674-02-2; [Ru<sup>II</sup>(salen)(PPh<sub>3</sub>)(Cl)]<sup>-</sup>, 123641-03-2; [Ru<sup>II</sup>(salen)(PPh<sub>3</sub>)(py)], 123641-04-3; [Ru<sup>II</sup>(salen)(PPh<sub>3</sub>)(N<sub>3</sub>)]<sup>-</sup>, 123641-05-4; [Ru<sup>II</sup>(salen)(PPh<sub>3</sub>)(PBU<sub>3</sub>)], 123641-06-5; [Ru<sup>II</sup>(salen)(PPh<sub>3</sub>)(TsO)]<sup>-</sup>, 123641-07-6; [Ru<sup>III</sup>(salen)(CN)<sub>2</sub>]<sup>2-</sup>, 123641-08-7; [Ru<sup>IV</sup>(salen)(PPh<sub>3</sub>)(Cl)]<sup>+</sup>, 123641-09-8; [Ru<sup>IV</sup>(salen)(PPh<sub>3</sub>)(py)]<sup>2+</sup>, 123641-10-1; [Ru<sup>IV</sup>(salen)(PPh<sub>3</sub>)(N<sub>3</sub>)]<sup>+</sup>, 123641-11-2; [Ru<sup>IV</sup>(salen)(PPh<sub>3</sub>)(TsO)]<sup>+</sup>, 123641-12-3; [Ru<sup>IV</sup>(salen)(CN)<sub>2</sub>], 123641-13-4; PhIO, 536-80-1; styrene, 100-42-5; cyclohexene, 110-82-7; cyclooctene, 931-88-4; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; norbornene, 498-66-8.

- (10) Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107.  
 (11) Brown, G. M.; Hopf, R. F.; Ferguson, J. A.; Meyer, T. J.; Whitten, G. W. *J. Am. Chem. Soc.* **1973**, *95*, 5939.  
 (12) Kadish, K. M. *Prog. Inorg. Chem.* **1986**, *34*, 553.  
 (13) Che, C. M.; Leung, W. H. Unpublished results.  
 (14) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315.  
 (15) (a) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 2920. (b) Smegal, J. A.; Hill, C. L. *Ibid.* **1983**, *105*, 3515.  
 (16) (a) Tai, F. A.; Magerum, D.; Valentine, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 5006. (b) Franklin, C. C.; Van Atta, R. B.; Tai, F. A.; Valentine, J. S. *Ibid.* **1984**, *106*, 814. (c) Kinneary, J. F.; Albert, J. S.; Burrows, C. J. *Ibid.* **1988**, *110*, 6124.  
 (17) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 158.

- (18) Leung, T.; James, B.; Dolphin, D. *Inorg. Chim. Acta* **1983**, *79*, 26. Leung, T.; James, B.; Dolphin, D. *Ibid.* **1983**, *79*, 180.  
 (19) (a) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375. (b) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *Ibid.* **1980**, *102*, 6377. (c) Mansuy, D.; Fontecane, M.; Bartoli, J.-F. *J. Chem. Soc., Chem. Commun.* **1983**, 253.