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# Proton-Bridged Dinuclear (salen)Ru Carbene Complexes: Synthesis, Structure, and Reactivity of $\{[(\text{salchda})\text{Ru}{=}\text{C(OR)(CH}{=}\text{CPh}_2)]_2\cdot\text{H}\}^+$

Chun-Yuen Wong,*,† Wai-Lun Man,† Chao Wang,† Hoi-Lun Kwong,† Wai-Yeung Wong,‡
and Tai-Chu Lau*,†

*Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong,*
*Hong Kong, People's Republic of China, and Department of Chemistry, Hong Kong Baptist University,*
*Waterloo Road, Kowloon Tong, Hong Kong, People's Republic of China*

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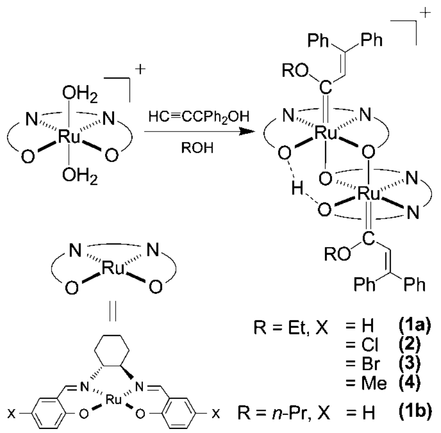
*Summary: Hydrogen-bridged dinuclear ruthenium carbene complexes supported by salen have been prepared and found to be active catalysts for the cyclopropanation of alkenes; electrochemical and theoretical studies suggest the existence of electronic communication between the Ru centers.*

The chemistry of transition-metal carbene complexes is of interest, because they are believed to be active intermediates for carbene insertions into C=C bonds.[1] Although carbene complexes of ruthenium porphyrins have received much attention for their activity toward catalytic cyclopropanation,[2] studies of ruthenium carbene complexes bearing salen-type ligands remain sparse in the literature.[3,4] Herein we report a series of proton-bridged dinuclear ruthenium carbene complexes, $\{[(5,5'\text{-X}_2\text{-salchda})\text{Ru}{=}\text{C(OR)(CH}{=}\text{CPh}_2)]_2\cdot\text{H}\}(\text{PF}_6)$ (**1**−**4**; 5,5′-$\text{X}_2$-salchda = *N,N′*-bis(5-X-salicylidene)-1,2-cyclohexyldiamine dianion; X = H, Cl, Br, Me; R = Et, *n*-Pr).[5]

**Scheme 1**



Complexes **1**−**4** were prepared in ca. 80% yields by reacting the Ru(III) aqua complex $[(\text{salchda})\text{Ru}(\text{OH}_2)_2](\text{PF}_6)$ with 1,1-diphenyl-2-propyn-1-ol in ethanol or propan-1-ol (Scheme 1). $[(\text{salchda})\text{Ru}(\text{OH}_2)_2](\text{PF}_6)$ was prepared by a N···N coupling reaction of $[(\text{salchda})\text{Ru(N)}](\text{PF}_6)$ in water/acetone.[6] The formation of **1**−**4** might be conceived as an addition of ROH to a transient allenylidene species (i.e., $[\text{Ru}{=}\text{C}{=}\text{C}{=}\text{CPh}_2]$).[7−10] The complexes are sufficiently stable to be handled in air under ambient conditions in solution and solid forms. Their $^1$H and $^{13}$C spectra show well-resolved signals at normal fields. For example, **1**−**4** show low-field $^{13}$C NMR signals at 303.7−305.0 ppm, which are characteristic for the carbene carbon atoms.[7−10] As **1**−**4** are diamagnetic, the ruthenium centers should have a Ru(II) formulation, and the *H* in $\{[(\text{salchda})\text{Ru}{=}\text{C(OR)}\text{(CH}{=}\text{CPh}_2)]_2\cdot H\}(\text{PF}_6)$ can be rationalized as a $\text{H}^+$ ion, presumably coming from the alcohol solvents. The reduction of the Ru centers from III to II upon the formation of carbene complexes is a combined effect of the $\text{HC}{\equiv}\text{CC(OH)Ph}_2$ ligand and the solvent (EtOH or *n*-PrOH) because (1) no reaction was observed between $[(\text{salchda})\text{Ru}(\text{OH}_2)_2]^+$ and $\text{HC}{\equiv}\text{CC(OH)Ph}_2$ in refluxing $\text{CH}_2\text{Cl}_2$, 1,2-dichloroethane, acetone, THF, or MeOH and (2) refluxing $[(\text{salchda})\text{Ru}(\text{OH}_2)_2]^+$ in EtOH or *n*-PrOH in the absence of $\text{HC}{\equiv}\text{CC(OH)Ph}_2$ showed no observable change. A reasonable mechanism would be that the EtOH

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* To whom correspondence should be addressed. E-mail: acywong@cityu.edu.hk (C.-Y.W.); bhtclau@cityu.edu.hk (T.-C.L.).

† City University of Hong Kong.

‡ Hong Kong Baptist University.

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[5] Each salen dimer complex reported in this work contains only *one* $\text{O}_{\text{salen}}\cdots\text{H}^+\cdots\text{O}_{\text{salen}}$ bond, although there are reports on salen dimer complexes formed by *two* $\text{O}_{\text{salen}}\cdots\text{H}^+\cdots\text{O}_{\text{salen}}$ bonds: see: (a) You, Z.-L.; Zhu, H.-L.; Liu, W.-S. *Acta Crystallogr.* **2004**, *E60*, m805. (b) Mukherjee, P.; Biswas, C.; Drew, M. G. B.; Ghosh, A. *Polyhedron* **2007**, *26*, 3121.

[6] $[(\text{salchda})\text{Ru}(\text{OH}_2)_2](\text{PF}_6)\cdot\text{H}_2\text{O}$: an orange solution of $[(\text{salchda})\text{Ru(N)}](\text{PF}_6)$ (200 mg, 0.33 mmol) in acetone/$\text{H}_2\text{O}$ (50 mL) (4:1 v/v) was refluxed overnight. The resulting green solution was filtered and concentrated to ca. 5 mL. The green solid was filtered, washed with ice-cold $\text{H}_2\text{O}$ and diethyl ether, and then air-dried. Yield: 88%. IR (KBr, cm$^{-1}$): $\nu_{\text{P-F}}$ 835. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4\text{PF}_6\text{Ru}\cdot\text{H}_2\text{O}$: C, 38.72; H, 4.22; N, 4.51. Found: C, 38.35; H, 4.44; N, 4.75. ESI-MS: *m/z* = 458 ($\text{M}^+$). Also see: Man, W.-L.; Tang, T.-M.; Wong, T.-W.; Lau, T.-C.; Peng, S.-M.; Wong, W.-T. *J. Am. Chem. Soc.* **2004**, *126*, 478.

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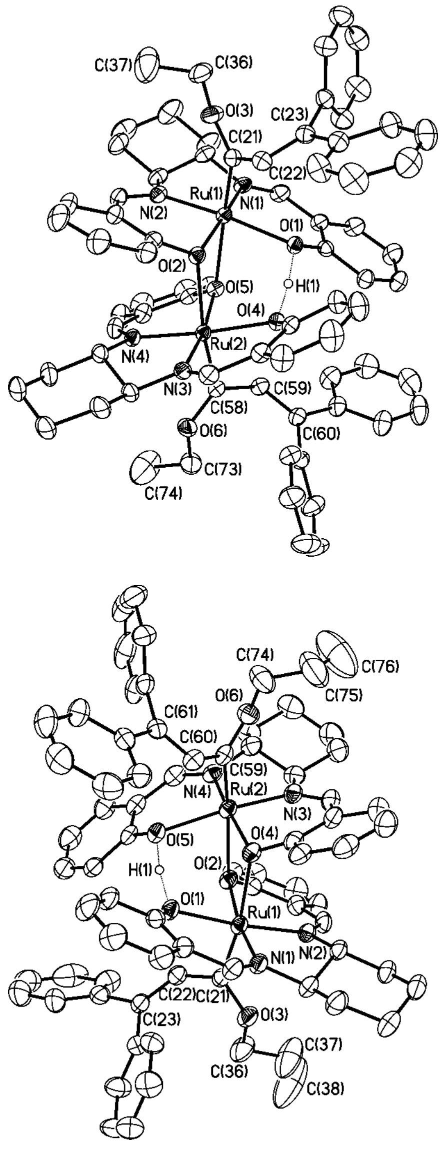

**Figure 1.** Perspective views of the cation in **1a** (top) and **1b**$\cdot 2CH_2Cl_2$ (bottom). Hydrogen atoms, except for those involved in hydrogen bonding, are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. **1a**: Ru(1)−C(21) = 1.866(2), Ru(2)−C(58) = 1.870(2), Ru(1)−O(5) = 2.267(2), Ru(2)−O(2) = 2.272(2), O(1)$\cdots$H$\cdots$O(4) = 2.423; C(21)−Ru(1)−O(5) = 170.59(9), C(58)−Ru(2)−O(2) = 169.61(8). **1b**$\cdot 2CH_2Cl_2$: Ru(1)−C(21) = 1.865(5), Ru(2)−C(59) = 1.873(5), Ru(1)−O(4) = 2.266(3), Ru(2)−O(2) = 2.270(3), O(1)$\cdots$H$\cdots$O(5) = 2.448; C(21)−Ru(1)−O(4) = 170.53(17), C(59)−Ru(2)−O(2) = 168.45(18).

or *n*-PrOH is able to reduce the $\{[(salchda)Ru(OH_2)_2]^+ + HC{\equiv}CC(OH)Ph_2\}$ intermediate.

The formulation $\{[(salchda)Ru{=}C(OR)(CH{=}CPh_2)]_2\cdot H\}(PF_6)$ for complexes **1**−**4** is supported by crystallographic and spectroscopic evidence. The crystal structures for **1a** and **1b**$\cdot 2CH_2Cl_2$ (Figure 1) revealed the presence of one $\{[(salchda)Ru{=}C(OR)(CH{=}CPh_2)]_2\cdot H\}$ dimeric unit and one $PF_6$ group per asymmetric unit. The two monomer units within the dimer are structurally similar. In the monomer units, the short Ru−$C_\alpha$ distances (1.865(5)−1.873(5) Å), together with the angles around the $C_\alpha$ (which are consistent with $sp^2$ hybridization), indicate the presence of ruthenium−carbon multiple bonds. These Ru−$C_\alpha$ distances are notably shorter than those for arene/phosphine-supported derivatives bearing a $[Ru{=}C(OR)(CH{=}CPh_2)]$ moiety (1.92−1.98 Å).[10a,d,f,h] The bonding interactions of heteroatom-stabilized carbenes are generally represented by the mesomeric structures $[M{=}C{-}OR] \leftrightarrow [M^-{-}C^+{-}OR] \leftrightarrow [M^-{-}C{=}O^+R]$; the shorter Ru−C distances in **1a**,**b** are in accordance with the stronger electron-donating effect of salen compared with that of arene/phosphine, which destabilizes the last two mesomeric forms to a greater extent and gives a stronger Ru−C $\pi$-interaction. Interestingly, the Ru−C distances in **1a**,**b** are comparable to those in some salen/porphyrin ruthenium non-heteroatom-stabilized carbene complexes: $[(salen)(N\text{-}methylimidazole)Ru{=}CPh_2]$ (1.910(2)−1.921(12) Å);[3] $[Ru(D_4\text{-}Por^*)(CPh_2)]$ (1.860(6) Å; $H_2D_4$-Por* = 5,10,15,20-tetrakis-{(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl}porphyrin);[11] $[Ru(F_{20}\text{-}TPP)(CPh_2)(N\text{-}methylimidazole)]$ (1.876(3) Å; $H_2(F_{20}\text{-}TPP)$ = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin).[12]

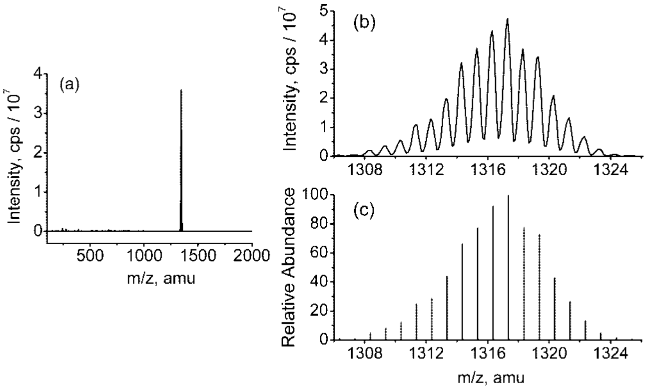

**Figure 2.** (a, b) ESI mass spectrum (positive mode) and experimental isotopic distribution pattern of **1a** in acetone. (c) Simulated isotopic distribution pattern of $\{[(5,5'\text{-}H_2\text{-}salchda)Ru{=}C(OEt)(CH{=}CPh_2)]_2] + H\}^+$.

In the dimeric structures of **1a** and **1b**$\cdot 2CH_2Cl_2$, the Ru atoms adopt a distorted-octahedral geometry: each Ru atom coordinates not only to a salchda and a carbene ligand but also to a phenolate oxygen atom on the neighboring monomer unit, forming two long Ru−O bonds (2.266(3)−2.272(2) Å). It is interesting to note that in each dimer the two non-neighboring phenolate oxygen atoms have a short distance of 2.423−2.448 Å. A hydrogen atom was also located between the oxygen atoms from the Fourier difference map. These findings support the existence of a hydrogen bond in the form of $O_{salen}\cdots H^+\cdots O_{salen}$. The presence of this $H^+$ not only explains the association of a $PF_6^-$ ion with each dimer in these diamagnetic samples but is also consistent with the finding that the positive ESI mass spectra show peaks corresponding to $\{2 \times [(salchda)Ru{=}C(OR)(CH{=}CPh_2)] + H\}^+$ (see Figure 2 for **1a**). To our knowledge, this is the first example of salen-supported dinuclear complexes bridged by a hydrogen bond in the form of $O_{salen}\cdots H^+\cdots O_{salen}$.[5]

The NMR, UV/vis, IR, mass spectral and electrochemical data of **1**−**4** are compiled in the Supporting Information. Complexes **1**−**4** exhibit two intense high-energy bands at ca. 310 and 400 nm ($\epsilon_{max} \approx (2{-}3) \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$), which are attributed to the intraligand transition of the coordinated Schiff base ligands. Their cyclic voltammograms (vs $Cp_2Fe^{+/0}$) show a reversible one-electron oxidation couple at $E_{1/2}$ = 0.04−0.25 V and an irreversible oxidation wave at $E_{p,a}$ =

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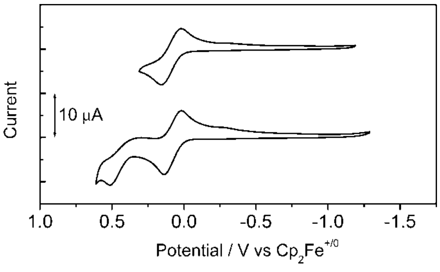

**Figure 3.** Cyclic voltammograms of **1a** (scan rate 100 mV $s^{-1}$, 0.1 M $[Bu_4N]PF_6$ in $CH_2Cl_2$ as supporting electrolyte).

0.53−0.61 V (scan rate 100 mV $s^{-1}$, 0.1 M $[Bu_4N]PF_6$ in $CH_2Cl_2$ as supporting electrolyte; the latter wave is irreversible even at scan rates of up to 1000 mV $s^{-1}$) (Figure 3). The $E_{1/2}$ value for each first oxidation couple increases with the electron-withdrawing capacity of the 5,5′-$X_2$-salchda ligand [(0.04 V for **4** (X = Me); 0.09 V for **1a** (X = H); 0.24 V for **2** (X = Cl); 0.25 V for **3** (X = Br)), and this couple is assigned to Ru(II/II)/Ru(II/III) oxidation. Changing the R group in $\{[(salchda)Ru{=}C(OR)(CH{=}CPh_2)]_2 \cdot H\}^+$ from Et (**1a**) to *n*-Pr (**1b**) has no effect on the $E_{1/2}$ value of the couple. As the two ruthenium centers are not oxidized at the same potential, the existence of electronic communication between the two monomeric units is demonstrated.[13]

Density functional theory (DFT) calculations were performed on the cation of **1b**, $\{[(5,5'\text{-}H_2\text{-}salchda)Ru{=}C(OPr)(CH{=}CPh_2)]_2 \cdot H\}^+$ (**1b′**), which was used as a model for complexes **1**−**4**.[14] The fully optimized structure of **1b′** is in good agreement with the X-ray structure of **1b** and is confirmed to be a stationary point via frequency analysis. The highest occupied molecular orbital (HOMO) of **1b′** is composed of both monomeric units (percentages of the two monomers in the HOMO are 74.37% and 25.42%), and the electron density is delocalized over the entire dimeric units (Figure 4). This molecular orbital description suggests the existence of electronic communication between the ruthenium centers, which is in accordance with the electrochemical measurements of **1**−**4**. A counterpoise calculation on the optimized $[(5,5'\text{-}H_2\text{-}salchda)Ru{=}C(OPr)(CH{=}CPh_2)]_2$ backbone (**1b′**–$\mathbf{H^+}$) was performed to obtain insight into the stabilization of $[(5,5'\text{-}H_2\text{-}salchda)Ru{=}C(OPr)(CH{=}CPh_2)]_2$ by $H^+$. The $O_{salen} \cdots H^+ \cdots O_{salen}$ distance in **1b′** (2.389 Å) is notably shorter than the $O_{salen} \cdots H^+_{(ghost)} \cdots O_{salen}$ distance in **1b′**–$\mathbf{H^+}$ (2.976 Å). It is also found that **1b′** is 1231 kJ $mol^{-1}$ more stable than **1b′**–$\mathbf{H^+}$, and this stabilization is not solely electrostatic: (1) the sum of the electrostatic energies for the O···H interactions within the $[O_{salen} \cdots H \cdots O_{salen}]$ moiety (calculated using natural charges[15]) is −906 kJ $mol^{-1}$; (2) the Wiberg bond indices (from natural bond orbital analysis) for the two O···H units are 0.2774 and 0.4041. Thus, these findings signify the presence of hydrogen bonds within the $[O_{salen} \cdots H \cdots O_{salen}]$ moiety.

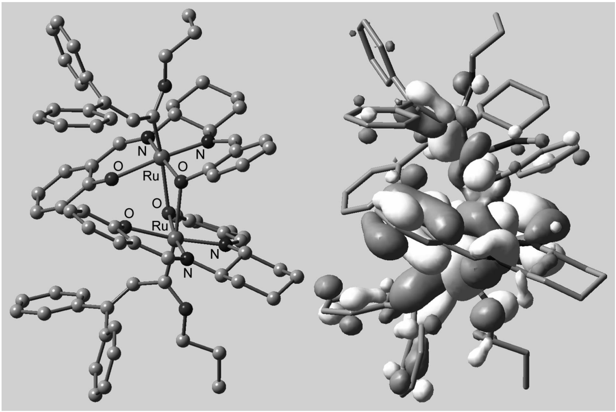

**Figure 4.** (left) Optimized structure of **1b′** using the PBE1PBE functional (hydrogen atoms are omitted for clarity). (right) Plot of the HOMO surface of **1b′** (isovalue 0.02 au).

The catalytic activity of **1a** in cyclopropanation was investigated. Treatment of ethyl diazoacetate (EDA) with excess styrene in the presence of **1a** (2 mol % relative to EDA) results in the formation of the corresponding ethyl 2-phenylcyclopropanecarboxylic acid ester in 77% yield with a trans to cis isomer ratio of 2:1.

In summary, the $\{[(salchda)Ru{=}C(OR)(CH{=}CPh_2)]_2 \cdot H\}(PF_6)$ system represents an unprecedented proton-bridged dimeric structure of ruthenium carbene complexes. Complex **1a** is an active catalyst for the intermolecular cyclopropanation of styrene with EDA. Work is in progress to dissociate these dimers with various donor ligands and bases; this would result in the formation of a variety of novel mononuclear carbenes, [(salen)(L)Ru=C(OR)(CH=CPh)].

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**Supporting Information Available:** Text, tables, and figures giving experimental details and characterization, electrochemical, and UV/vis spectroscopic data of **1**−**4** and theoretical calculation details for **1b′** and **1b′**–$\mathbf{H^+}$ and CIF files giving crystallographic data for **1a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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