# Enantioselective Intramolecular Cyclopropanation of *cis*-Alkenes by Chiral Ruthenium(II) Schiff Base Catalysts and Crystal Structures of (Schiff base)ruthenium Complexes Containing Carbene, $PPh_3$, and CO Ligands

Gong-Yong Li,[†] Jing Zhang,[‡] Philip Wai Hong Chan,[‡] Zhen-Jiang Xu,[†] Nianyong Zhu,[‡] and Chi-Ming Che*[,†,‡]

*Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, 354 Feng Lin Road, Shanghai 200032, People's Republic of China, and Department of Chemistry and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China*

*Received November 22, 2005*

The enantioselective intramolecular cyclopropanation of cis-substituted allylic diazoacetates catalyzed by the chiral ruthenium Schiff base complexes [Ru(Schiff base)$(PPh_3)_2$] (**1**) is described. Among this class of complexes examined, [Ru(2-Br-salen)$(PPh_3)_2$] (**1a**) is the most effective, catalyzing intramolecular cyclopropanation of *cis*-allylic diazoacetates *cis*-$(CRH{=}CH)CH_2OC(O)CHN_2$ (R = alkyl, aryl) in $CHCl_3$ solution to give [3.1.0]-bicyclic lactones with yields and ee values up to 71 and 90%, respectively. The analogous reactions of *cis*-alkenyl diazoacetates using [Ru(Schiff base)(CO)] (**2**) as catalyst gave comparable enantioselectivities (up to 91% ee) but lower product yields of 20−38%. Treatment of [Ru(2,4-X-salen)$(PPh_3)_2$] (**1d**, X = Br; **1e**, X = Cl; **1f**, X = I) with $N_2C(p\text{-}YC_6H_4)_2$ (Y = H, MeO) and *N*-methylimidazole (MeIm) or pyridine (py) gave the monocarbene complexes [Ru(2,4-X-salen)$(C(p\text{-}YC_6H_4)_2)$(MeIm)] (**3a**, X = Br, Y = H; **3b**, X = Cl, Y = H; **3c**, X = I, Y = H; **3d**, X = Br, Y = OMe) and [Ru(2,4-Br-salen)$(CPh_2)$(py)] (**4**, $H_2$(2,4-Br-salen) = bis(3,5-dibromosalicylidene)-(1*R*,2*R*)-cyclohexanediamine), respectively. X-ray crystal structure determinations revealed Ru=C(carbene) distances of 1.921(12) Å for **3a**, 1.913(5) Å for **3b**, 1.919(14) Å for **3c**, 1.910(2) Å for **3d**, and 1.917(4) Å for **4**. A comparison of the structures and electrochemistry of **1**, [Ru(Schiff base)(CO)(MeIm)], **3**, and **4** with those of the porphyrin analogues is presented.

## Introduction

Cyclopropanes are useful $C_3$ building blocks for organic synthesis; they are also important structural moieties found in many biologically active natural and therapeutic drug compounds.[1] Among the myriad of stoichiometric and catalytic processes known for the construction of cyclopropanes, those using transition-metal catalysts have been receiving growing attention in recent years.[1,2] Indeed, high enantioselectivities have been achieved for intramolecular cyclopropanation of unsaturated diazocarbonyl compounds in the presence of either chiral Cu(I)[2,3] or $Rh_2$(II,II)[2,4] catalysts. Doyle and co-workers showed that intramolecular C−C bond formation reactions could be used for the construction of macrocyclic compounds with excellent enantioselectivity and modest diastereoselectivity (Scheme 1).[5]

* To whom correspondence should be addressed at The University of Hong Kong. E-mail: cmche@hku.hk.

† Shanghai Institute of Organic Chemistry.

‡ The University of Hong Kong.

(1) (a) Donaldson, W. A. *Tetrahedron* **2001**, *57*, 8589. (b) Doyle, M. P.; Ren, T. *Prog. Inorg. Chem.* **2001**, *49*, 113. (c) Doyle, M. P.; Protopopova, M. N. *Tetrahedron* **1998**, *54*, 7919. (d) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (e) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. (f) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385. (g) Salaün, J. *Chem. Rev.* **1989**, *89*, 1247.

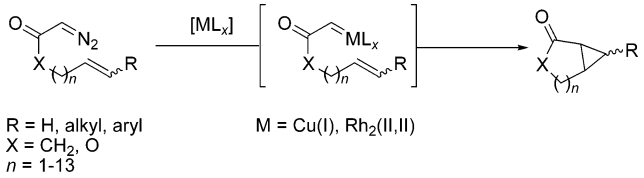
(2) (a) Katsuki, T. *Compr. Coord. Chem. II* **2004**, *9*, 207. (b) Maas, G. *Chem. Soc. Rev.* **2004**, *33*, 183. (c) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977. (d) Davies, H. M. L.; Antoulinakis, E. G. *Org. React.* **2001**, *57*, 1. (e) Che, C.-M.; Huang, J.-S. *Coord. Chem. Rev.* **2002**, *231*, 151. (f) Simonneaux, G.; Le Maux, P. *Coord. Chem. Rev.* **2002**, *228*, 43. (g) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*; Wiley: New York, 1998.

(3) For examples using copper(I) catalysts, see: (a) Sawada, T.; Nakada, M. *Adv. Synth. Catal.* **2005**, *347*, 1527. (b) Doyle, M. P.; Hu, W. *Tetrahedron Lett.* **2000**, *41*, 6265. (c) Doyle, M. P.; Hu, W. H.; Chapman, B.; Marnett, A. B.; Peterson, C. S.; Vitale, J. P.; Stanley, S. A. *J. Am. Chem. Soc.* **2000**, *122*, 5718. (d) Doyle, M. P.; Hu, W.; Phillips, I. M.; Wee, A. G. H. *Org. Lett.* **2000**, *2*, 1777. (e) Doyle, M. P.; Chapman, B. J.; Hu, W.; Peterson, C. S.; McKervey, M. A.; Garcia, C. F. *Org. Lett.* **1999**, *1*, 1327. (f) Sato, H.; Kim, Y. S.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 2973. (g) Tokunoh, R.; Tomiyama, H.; Sodeoka, M.; Shibasaki, M. *Tetrahedron Lett.* **1996**, *37*, 2449. (h) Gant, T. G.; Noe, M. C.; Corey, E. J. *Tetrahedron Lett.* **1995**, *36*, 8745. (i) Piqué, C.; Fähndrich, B.; Pfaltz, A. *Synlett* **1995**, 491.

(4) For examples using dirhodium(II,II) catalysts, see: (a) Lin, W.; Charette, A. B. *Adv. Synth. Catal.* **2005**, *347*, 1547. (b) Barberis, M.; Pérez-Prieto, J.; Herbst, K.; Lahuerta, P. *Organometallics* **2002**, *21*, 1667. (c) Barberis, M.; Pérez-Prieto, J.; Stiriba, S.-E.; Lahuerta, P. *Org. Lett.* **2001**, *21*, 3317. (d) Barberis, M.; Lahuerta, P.; Pérez-Prieto, J.; Sanaú, M. *Chem. Commun.* **2001**, 439. (e) Doyle, M. P.; Hu, W. *Adv. Synth. Catal.* **2001**, *343*, 299. (f) Davies, H. M. L.; Calvo, R. L.; Townsend, R. J.; Ren, P.; Churchill, R. M. *J. Org. Chem.* **2000**, *65*, 4261. (g) Davies, H. M. L.; Doan, B. D. *J. Org. Chem.* **1999**, *64*, 8501. (h) Doyle, M. P.; Kalinin, A. V. *J. Org. Chem.* **1996**, *61*, 2179. (i) Doyle, M. P.; Zhou, Q.-L.; Dyatkin, A. B.; Ruppar, D. A. *Tetrahedron Lett.* **1995**, *36*, 7579. (j) Rogers, D. H.; Yi, E. C.; Poulter, C. D. *J. Org. Chem.* **1995**, *60*, 941. (k) Doyle, M. P.; Austin, R. E.; Bailey, A. S.; Dwyer, M. P.; Dyatkin, A. B.; Kalinin, A. V.; Kwan, M. M. Y.; Liras, S.; Oalmann, C. J.; Pieters, R. J.; Protopopova, M. N.; Raab, C. E.; Roos, G. H. P.; Zhou, Q. L.; Martin, S. F. *J. Am. Chem. Soc.* **1995**, *117*, 5763. (l) Martin, S. F.; Spaller, M. R.; Liras, S.; Hartmann, B. *J. Am. Chem. Soc.* **1994**, *116*, 4493. (m) Doyle, M. P.; Pieters, R. J.; Martin, S. F.; Austin, R. E.; Oalmann, C. J.; Mueller, P. *J. Am. Chem. Soc.* **1991**, *113*, 1423.

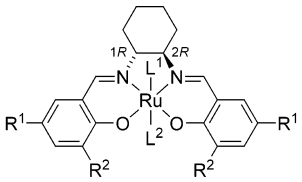
10.1021/om051009i CCC: $33.50 
Publication on Web 02/22/2006

**Scheme 1**




In contrast to the extensive investigations of $Rh_2$(II,II)- and Cu(I)-catalyzed enantioselective intramolecular alkene cyclopropanations, examples of analogous reactions using other chiral metal catalysts are sparse. Recently, ruthenium catalysts have demonstrated useful applications in alkene cyclopropanations.[2,6−9] Nishiyama and co-workers showed that high product yields and ee values could be achieved in asymmetric intramolecular cyclopropanation of *trans*-allylic diazoacetates by employing chiral Ru(II)-pybox (pybox = bis(oxazolinyl)-pyridine) catalysts.[6] We,[7] Katsuki,[8a,b] and Scott[9] subsequently reported the highly enantioselective intramolecular cyclopropanation of *trans*-allylic diazoacetates using Ru(II) catalysts containing chiral porphyrin or sterically encumbered Schiff base ligands. Despite these advances, there have been no reports on ruthenium catalysts for highly enantioselective intramolecular cyclopropanation of *cis*-allylic diazoacetates, which are useful reactions for the construction of chiral bicyclic compounds.

As part of our program to develop chiral ruthenium catalysts for C−C bond formation reactions, we envision that chiral ruthenium Schiff base catalysts have potential practical applications in enantioselective carbenoid transfer reactions (Figure 1). Our previous studies showed that amidation of silyl enol ethers and aziridination of alkenes using PhI═NTs as the nitrogen source and chiral [Ru(Schiff base)($PPh_3$)$_2$] catalyst proceeded with high product ee values.[11] Zheng and co-workers reported that similar chiral ruthenium catalysts generated in situ exhibited moderate to good product ee values in the intermolecular cyclopropanation of alkenes with ethyl diazoacetate (EDA).[12] Herein, we describe enantioselective intramolecular cyclopropanation of *cis*-alkenyl diazoacetates using chiral [Ru(Schiff base)($PPh_3$)$_2$] catalysts. The highest product ee value of 90% accomplished in this work is comparable to that achieved for enantioselective intramolecular cyclopropanation of *cis*-alkenyl diazoacetates using chiral $Rh_2$(II,II) catalyst.[4h,j] We also describe the isolation and structural characterization of five ruthenium monocarbene complexes containing Schiff base ligands having long M···C(carbene) distances as defined by X-ray crystal analysis.




**1a**: $R^1$ = H, $R^2$ = Br, $L^1$ = $L^2$ = $PPh_3$, [Ru(2-Br-salen)($PPh_3$)$_2$];
**1b**: $R^1$ = Br, $R^2$ = H, $L^1$ = $L^2$ = $PPh_3$, [Ru(4-Br-salen)($PPh_3$)$_2$];
**1c**: $R^1$ = Cl, $R^2$ = H, $L^1$ = $L^2$ = $PPh_3$, [Ru(4-Cl-salen)($PPh_3$)$_2$];
**1d**: $R^1$ = $R^2$ = Br, $L^1$ = $L^2$ = $PPh_3$, [Ru(2,4-Br-salen)($PPh_3$)$_2$];
**1e**: $R^1$ = $R^2$ = Cl, $L^1$ = $L^2$ = $PPh_3$, [Ru(2,4-Cl-salen)($PPh_3$)$_2$];
**1f**: $R^1$ = $R^2$ = I, $L^1$ = $L^2$ = $PPh_3$, [Ru(2,4-I-salen)($PPh_3$)$_2$];
**1g**: $R^1$ = $R^2$ = H, $L^1$ = $L^2$ = $PPh_3$, [Ru(salen)($PPh_3$)$_2$];
**2a**: $R^1$ = H, $R^2$ = Br, $L^1$ = CO, [Ru(2-Br-salen)(CO)];
**2b**: $R^1$ = Br, $R^2$ = H, $L^1$ = CO, [Ru(4-Br-salen)(CO)];
**2c**: $R^1$ = $R^2$ = Cl, $L^1$ = CO, [Ru(2,4-Cl-salen)(CO)];
**2d**: $R^1$ = $R^2$ = Br, $L^1$ = CO, [Ru(2,4-Br-salen)(CO)];
**2e**: $R^1$ = $R^2$ = I, $L^1$ = CO, [Ru(2,4-I-salen)(CO)];
**3a**: $R^1$ = $R^2$ = Br, $L^1$ = $CPh_2$, $L^2$ = MeIm, [Ru(2,4-Br-salen)($CPh_2$)(MeIm)];
**3b**: $R^1$ = $R^2$ = Cl, $L^1$ = $CPh_2$, $L^2$ = MeIm, [Ru(2,4-Cl-salen)($CPh_2$)(MeIm)];
**3c**: $R^1$ = $R^2$ = I, $L^1$ = $CPh_2$, $L^2$ = MeIm, [Ru(2,4-I-salen)($CPh_2$)(MeIm)];
**3d**: $R^1$ = $R^2$ = Br, $L^1$ = C(*p*-$MeOC_6H_4$)$_2$, $L^2$ = MeIm, [Ru(2,4-Br-salen)(C(*p*-$MeOC_6H_4$)$_2$)(MeIm)];
**4**: $R^1$ = $R^2$ = Br, $L^1$ = $CPh_2$, $L^2$ = py, [Ru(2,4-Br-salen)($CPh_2$)(py)].

**Figure 1.** Ruthenium Schiff base complexes prepared in this work. For **2a**−**c**, the complexes could be five-coordinate or $L^2$ = solvent molecule.[10]

## Results

**Synthesis.** The chiral (Schiff base)ruthenium catalysts **1** (Figure 1) were prepared by following literature methods;[11] treatment of [Ru($PPh_3$)$_3$$Cl_2$] with chiral $H_2$(Schiff base) ligand in refluxing MeOH solution containing $Et_3N$ gave [Ru(Schiff base)($PPh_3$)$_2$] (**1**) as brown crystals. Reaction of **1** with CO at room temperature gave [Ru(Schiff base)(CO)] (**2**) (Figure 1). The [Ru(Schiff base)(CO)] (**2**) complexes have a low solubility in organic solvents but could be readily dissolved in pyridine or upon treatment with MeIm in $CH_2Cl_2$ (1/3 v/v) to give [Ru(Schiff base)(CO)(MeIm)]. In this work, we have also prepared the chiral carbene complexes [Ru(2,4-X-salen)(C(*p*-$YC_6H_4$)$_2$)(MeIm)] (**3a**, X = Br, Y = H; **3b**, X = Cl, Y = H; **3c**, X = I, Y = H; **3d**, X = Br, Y = OMe) (Figure 1). The five-coordinate complexes [Ru(2,4-X-salen)(C(*p*-$YC_6H_4$)$_2$)] were obtained as green solids in quantitative yields by reacting [Ru(2,4-X-salen)($PPh_3$)$_2$] (**1d**, X = Br; **1e**, X = Cl; **1f**, X = I) with the respective diazo compounds $N_2C$(*p*-$YC_6H_4$)$_2$ (Y = H, MeO) in $CH_2Cl_2$ solutions at room temperature under argon. Slow addition of $N_2C$(*p*-$YC_6H_4$)$_2$ was needed to minimize catalytic decomposition of the diazo compounds. The [Ru(2,4-X-salen)(C(*p*-$YC_6H_4$)$_2$)] solid has a low solubility in MeOH, $CHCl_3$, and $CH_2Cl_2$ and is only sparsely soluble in DMSO and DMF but can be recrystallized by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution in the presence of MeIm to give **3** as yellow-brown crystals. The fact that both **2** and [Ru(2,4-X-salen)(C(*p*-$YC_6H_4$)$_2$)] are soluble in $CH_2Cl_2$ solutions containing an excess amount of MeIm could be due to the coordination of an axial MeIm ligand to ruthenium, resulting in the formation of [Ru(Schiff base)(CO)(MeIm)] and **3**, the structures of which have been characterized by X-ray crystallographic analysis (see below).

**Reactivity.** In the literature, Nishiyama,[13] Woo,[14] and Bianchini[15] demonstrated that a number of monocarbene complexes of ruthenium and osmium can undergo stoichiometric cyclopropanation reactions. In light of these works, we were intrigued about the possibility of developing similar stoichiometric alkene cyclopropanation chemistry with the [Ru(2,4-X-salen)(C(*p*-$YC_6H_4$)$_2$)] complexes and **3**. However, treatment of [Ru(2,4-Br-salen)($CPh_2$)(MeIm)] (**3a**) with either excess styrene or

(5) Doyle, M. P.; Hu, W. *Synlett* **2001**, 1364.
(6) Park, S.-B.; Murata, K.; Matsumoto, H.; Nishiyama, H. *Tetrahedron: Asymmetry* **1995**, *6*, 2487.
(7) Che, C.-M.; Huang, J.-S.; Lee, F.-W.; Li, Y.; Lai, T.-S.; Kwong, H.-L.; Teng, P.-F.; Lee, W.-S.; Lo, W.-C.; Peng, S.-M.; Zhou, Z.-Y. *J. Am. Chem. Soc.* **2001**, *123*, 4119.
(8) (a) Saha, B.; Uchida, T.; Katsuki, T. *Tetrahedron: Asymmetry* **2003**, *14*, 823. (b) Saha, B.; Uchida, T.; Katsuki, T. *Chem. Lett.* **2002**, 846. (c) Saha, B.; Uchida, T.; Katsuki, T. *Synlett* **2001**, 114. (d) Uchida, T.; Saha, B.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 2521.
(9) Munslow, I. J.; Gillespie, K. M.; Deeth, R. J.; Scott, P. *Chem. Commun.* **2001**, 1638.
(10) Abbreviations: $H_2$(2-Br-salen) = bis(3-bromosalicylidene)-(1*R*,2*R*)-cyclohexanediamine, $H_2$(4-Br-salen) = bis(5-bromosalicylidene)-(1*R*,2*R*)-cyclohexanediamine, $H_2$(4-Cl-salen) = bis(5-chlorosalicylidene)-(1*R*,2*R*)-cyclohexanediamine, $H_2$(2,4-Br-salen) = bis(3,5-dibromosalicylidene)-(1*R*,2*R*)-cyclohexanediamine, $H_2$(2,4-Cl-salen) = bis(3,5-dichlorosalicylidene)-(1*R*,2*R*)-cyclohexanediamine, $H_2$(2,4-I-salen) = bis(3,5-diiodosalicylidene)-(1*R*,2*R*)-cyclohexanediamine, $H_2$(salen) = bis(salicylidene)-(1*R*,2*R*)-cyclohexanediamine.
(11) Liang, J.-L.; Yu, X.-Q.; Che, C.-M. *Chem. Commun.* **2002**, 124.
(12) Yao, X.; Qiu, M.; Lü, W.; Chen, H.; Zheng, Z. *Tetrahedron: Asymmetry* **2001**, *12*, 197.

*p*-methoxystyrene (20 equiv) in toluene under reflux conditions for 24 h gave no reaction, as determined by $^1$H NMR and GC analysis of the reaction mixtures. Similarly, [Ru(2,4-Br-salen)(CPh$_2$)] was found to be inert toward stoichiometric cyclopropanation of either styrene or *p*-methoxystyrene, but it could act as a catalyst for intramolecular cyclopropanation of *cis*-3-phenylallyl diazoacetate (see below). This reaction is comparable to that reported for the analogous stoichiometric and catalytic cyclopropanations using [Ru($D_4$-Por*)(CPh$_2$)] ($H_2$($D_4$-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).[7] The reaction of [Ru(2,4-Br-salen)(C(*p*-MeOC$_6$H$_4$)$_2$)] with excess PPh$_3$ (10 equiv) in CH$_2$Cl$_2$ solution under reflux conditions for 16 h did not lead to any reaction, on the basis of $^1$H NMR spectroscopy and FAB spectrometry. In contrast, treating a CH$_2$Cl$_2$ suspension of [Ru(2,4-Br-salen)(CPh$_2$)] with pyridine at room temperature followed by recrystallization by diffusion of Et$_2$O gave [Ru(2,4-Br-salen)(CPh$_2$)(py)] (**4**) (Figure 1) as dark red-brown crystals.

**Characterization.** The complexes [Ru(Schiff base)(PPh$_3$)$_2$] (**1**) are stable in solid state and can be stored under ambient conditions for several weeks. They are insoluble in EtOH and MeOH but could be dissolved in either CHCl$_3$ or CH$_2$Cl$_2$. Exposure of a CHCl$_3$ solution containing [Ru(2-Br-salen)(PPh$_3$)$_2$] (**1a**) to air at room temperature for 5 min led to an immediate color change from crimson red to dark brown. Analysis of the resultant dark brown solution by FAB mass spectrometry revealed the presence of cluster peaks at *m*/*z* 733, 996, and 998 that could be assigned to [M − 2PPh$_3$]$^+$, [M − PPh$_3$]$^+$, and [M + H − C$_6$H$_2$Br$_2$O]$^+$, respectively. The sensitivity of **1** toward air in various deuteriochlorinated solvents rendered characterization by NMR spectroscopy difficult. The instability of **1** in solution could be attributed to PPh$_3$ dissociation to give the complexes [Ru(Schiff base)(PPh$_3$)(L)] (L = solvent molecule, vacant), which are susceptible to attack by dioxygen. Recall that the reaction of **1** with CO gas readily gave [Ru(Schiff base)(CO)] (**2**).

Unlike **1**, complexes **2**, [Ru(2,4-X-salen)(C(*p*-YC$_6$H$_4$)$_2$)], **3**, and **4** are all stable in solid state and in solution. The [Ru(2,4-X-salen)(C(*p*-YC$_6$H$_4$)$_2$)] complexes are also thermally stable, as demonstrated by the following experiment. Heating a suspension of [Ru(2,4-Br-salen)(CPh$_2$)] in toluene solution under reflux conditions for 24 h did not cause any observable change, and no product resulting from coupling of the carbene ligands was detected by either $^1$H NMR spectroscopy or mass spectrometry.

The $^1$H NMR spectra of **2** and [Ru(2,4-X-salen)(C(*p*-YC$_6$H$_4$)$_2$)] in deuterated pyridine reveal well-resolved signals at normal fields, consistent with the diamagnetic nature of mononuclear ruthenium(II) complexes.[7,13,17] For **2**, the azomethine and ArC*H* protons are slightly shifted upfield by 0.03−0.22 ppm relative to the respective signals in the free Schiff base ligand (6.60−8.60 ppm), which is assignable to a shielding effect by the axial CO ligand. A similar upfield shift for the bridging methylene (3.11−3.46 ppm vs 3.65−3.60 ppm for the free ligand) and cyclohexane protons (0.98−1.74 ppm vs 1.40−1.85 ppm for the free ligand) has also been observed. The cyclohexane ring protons syn to the CO ligand and vicinal to the bridging methylene C atoms are the only signals found to slightly shift downfield (2.41−2.69 ppm vs 1.90−2.00 ppm for the free ligand), presumably due to through-space deshielding effect by the axial CO ligand. Replacing the axial CO ligand in **2** with a CAr$_2$ ligand to form [Ru(2,4-X-salen)(C(*p*-YC$_6$H$_4$)$_2$)] has a minimal effect on the proton chemical shifts of the coordinated Schiff base ligand. For example, a comparison of **2d** and [Ru(2,4-Br-salen)(CPh$_2$)], both containing the same chiral Schiff base ligand, reveals that the azomethine proton signals in these complexes are located at $\delta_{N=CH}$ 8.26 and 8.36 ppm for **2d** and at 8.26 and 8.41 ppm for [Ru(2,4-Br-salen)(CPh$_2$)]. One possible reason for this observation could be the long Ru=C distance in **3** (see below) minimizing the increase in the inductive effect of the axial carbene ligand.

For [Ru(2,4-X-salen)(C(*p*-YC$_6$H$_4$)$_2$)], a low-field $^{13}$C NMR signal that can be attributed to the resonance of the coordinated carbene C atom is found in the region $\delta_{Ru=C}$ 316.3−317.3 ppm. These resonances are comparable to those reported for [Ru(TPP)(CPh$_2$)] ($\delta_{M=C}$ 317.5 ppm, $H_2$(TPP) = 5,10,15,20-tetraphenylporphyrin), [Ru(TTP)(CPh$_2$)] ($\delta_{M=C}$ 316.4 ppm, $H_2$(TTP) = 5,10,15,20-tetra-*p*-tolylporphyrin),[17d] and [Ru($D_4$-Por*)(CPh$_2$)] ($\delta_{M=C}$ 315 ppm).[7] This suggests that the electronic properties of the Ru=C moieties in [Ru(2,4-X-salen)(C(*p*-YC$_6$H$_4$)$_2$)] could be similar to those reported for ruthenium porphyrin carbene complexes.[7] As a matter of fact, [Ru(2,4-X-salen)(C(*p*-YC$_6$H$_4$)$_2$)], **3**, and [Ru($D_4$-Por*)(CPh$_2$)] are unreactive toward stoichiometric cyclopropanation of styrenes. The almost identical $\delta_{Ru=C}$ values for [Ru(2,4-Br-salen)(CPh$_2$)] ($\delta_{Ru=C}$ 317.0 ppm) and [Ru(2,4-Br-salen)(C(*p*-MeOC$_6$H$_4$)$_2$)] ($\delta_{Ru=C}$ 317.3 ppm), which contain the same chiral Schiff base ligand, reflect that the two carbene ligands affect the electronic properties of the Ru=C bond to comparable extents.

In contrast, the $^1$H NMR spectra of **3** in CDCl$_3$ reveal poorly resolved broad signals at normal fields. Presumably, the trans MeIm ligands of these complexes undergo dissociation in CDCl$_3$ solution. Indeed, precipitation of [Ru(2,4-X-salen)(C(*p*-YC$_6$H$_4$)$_2$)] was observed when CDCl$_3$ solutions of **3** stood at room temperature for 10 min; the precipitate could be redissolved into solution upon addition of excess MeIm (10 mg).

The UV−vis spectra of [Ru(Schiff base)(CO)(MeIm)] (see Table S1 for spectral data and Figures S1−S4 in the Supporting Information) show one absorption band at ca. 330 nm with a shoulder at ca. 360 nm and a second absorption band at ca. 435 nm. The high-energy bands at ca. 330 and 360 nm with respective log $\epsilon$ values in the ranges 4−4.03 and 4.07−4.13 dm$^3$ mol$^{-1}$ cm$^{-1}$ are dominated by intraligand charge-transfer transitions of the coordinated Schiff base ligands. As depicted in Figure 2, the UV−vis spectra of **3a** and **4**, as representative

(13) (a) Nishiyama, H.; Aoki, K.; Itoh, H.; Iwamura, T.; Sakata, N.; Kurihara, O.; Motoyama, Y. *Chem. Lett.* **1996**, 1071. (b) Park, S.-B.; Sakata, N.; Nishiyama, H. *Chem. Eur. J.* **1996**, *2*, 303.

(14) Smith, D. A.; Reynolds, D. N.; Woo, L. K. *J. Am. Chem. Soc.* **1993**, *115*, 2511.

(15) Lee, H. M.; Bianchini, C.; Jia, G.; Barbaro, P. *Organometallics* **1999**, *18*, 1961.

(16) Ariel, S.; Dolphin, D.; Domazetis, G.; James, B. R.; Leung, T. W.; Rettig, S. J.; Trotter, J.; Williams, G. M. *Can. J. Chem.* **1984**, *62*, 755.

(17) (a) Gallo, E.; Caselli, A.; Ragaini, F.; Fantauzzi, S.; Masciocchi, N.; Sironi, A.; Cenini, S. *Inorg. Chem.* **2005**, *44*, 2039. (b) Khalil, M. M. H.; Aboaly, M. M.; Ramadan, R. M. *Spectrochim. Acta, Part A* **2005**, *61*, 157. (c) Li, Y.; Chan, P. W. H.; Zhu, N.; Che, C.-M.; Kwong, H.-L. *Organometallics* **2004**, *23*, 54. (d) Li, Y.; Huang, J.-S.; Xu, G.-B.; Zhu, N.; Zhou, Z.-Y.; Che, C.-M.; Wong, K.-Y. *Chem. Eur. J.* **2004**, *10*, 3486. (e) Thangadurai, T. D.; Anitha, D.; Natarajan, K. *Synth. React. Inorg. Met.-Org. Chem.* **2002**, *32*, 1329. (f) Flower, K. R.; Howard, V. J.; Pritchard, R. G.; Warren, J. E. *Organometallics* **2002**, *21*, 1184. (g) Zhou, X.-G.; Huang, J.-S.; Ko, P.-H.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1999**, 3303. (h) Klose, A.; Solari, E.; Floriani, C.; Geremia, S.; Randaccio, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 148. (i) Galardon, E.; Le Maux, P.; Toupet, L.; Simonneaux, G. *Organometallics* **1998**, *17*, 565. (j) Slebodnick, C.; Seok, W. K.; Kim, K.; Ibers, J. A. *Inorg. Chim. Acta* **1996**, *243*, 57. (k) Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141.

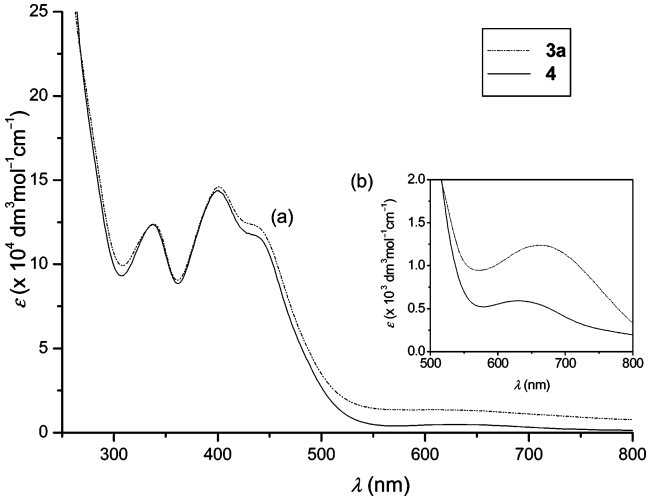



**Figure 2.** UV/vis spectra of **3a** and **4** in $CH_2Cl_2$ solutions at (a) $1 \times 10^{-5}$ mol dm$^{-3}$ and (b) $1 \times 10^{-3}$ mol dm$^{-3}$ (shown in the inset).

**Table 1. Electrochemical Data for the Ruthenium Schiff Base Complexes 1d−f, [Ru(2,4-Br-salen)(CO)(MeIm)], 3, and 4 in $CH_2Cl_2$**

| complex | oxidn (V)[a] |
|---|---|
| **1d** | −0.36,[b] 0.91[b] |
| **1e** | −0.38,[b] 0.91[b] |
| **1f** | −0.36,[b] 0.89[b] |
| [Ru(2,4-Br-salen)(CO)(MeIm)] | 0.20,[b] 1.34[b] |
| **3a** | 0.04,[c] 0.25,[c] 0.36,[c] 0.86,[d] 1.05,[d] 1.25[d] |
| **3b** | 0.08,[c] 0.24,[c] 0.36,[c] 0.77,[c] 0.86,[d] 1.02[d] |
| **3c** | 0.06,[c] 0.25,[c] 0.34,[c] 0.77,[c] 0.98,[d] 1.28[d] |
| **3d** | −0.04,[c] 0.11,[c] 0.23,[c] 0.71,[c] 0.88,[d] 1.14[d] |
| **4**[c] | 0.15,[c] 0.40,[c] 0.63,[c] 0.89[d] |

[a] Versus the $Cp_2Fe^{+/0}$ couple. [b] Reversible, $E_{1/2}$. [c] Irreversible, $E_{p,a}$. [d] Quasi-reversible, $E_{1/2}$.

examples, reveal a weak low-energy absorption at ca. 630−660 nm (log $\epsilon$ = 2.80−3.12 dm$^3$ mol$^{-1}$ cm$^{-1}$). We attribute this low-energy absorption to d−d transitions. Such transitions have previously been reported at 520 nm (log $\epsilon$ = 2.56 dm$^3$ mol$^{-1}$ cm$^{-1}$) for [$RuCl_2$(=CHPh)($PCy_3$)$_2$] (Cy = cyclohexyl).[18]

The electrochemical properties of **1d−f**, [Ru(2,4-Br-salen)(CO)(MeIm)], **3**, and **4** in $CH_2Cl_2$ solutions have been examined. The electrochemical data are tabulated in Table 1. Figure 3 shows the cyclic voltammograms of **1d**, [Ru(2,4-Br-salen)(CO)(MeIm)], and **3a**.

The cyclic voltammograms of **1d−f** show two reversible couples. We attribute the first couple at $E_{1/2}$ values ranging from −0.36 to −0.38 V as the Ru(II)/Ru(III) couple and the second couple at $E_{1/2}$ values ranging from 0.89 to 0.91 V to ligand-centered oxidation. We note that the cyclic voltammogram of [Ru(2,4-Br-salen)(CO)(MeIm)] also reveals two reversible couples at 0.20 and 1.34 V assigned to the Ru(II)/Ru(III) couple and ligand-centered oxidation, respectively. In contrast, electrochemical oxidation of **3** exhibits a series of irreversible oxidation waves. The first oxidation wave of **3** with $E_{p,a}$ values ranging from −0.04 to 0.08 V are more anodic than the $E_{1/2}$-[Ru(II)/Ru(III)] values of **1d−f** but less anodic than those of [Ru(2,4-Br-salen)(CO)(MeIm)] and **4**. For **3** and **4**, there are quasi-reversible oxidation waves with $E_{1/2}$ values ranging from 0.88 to 1.02 V, which could be due to ligand-centered oxidations.

For **1d−f** and **3a−c**, the halogen substituent on the Schiff base ligand has little effect on the $E_{1/2}$[Ru(II)/Ru(III)] values

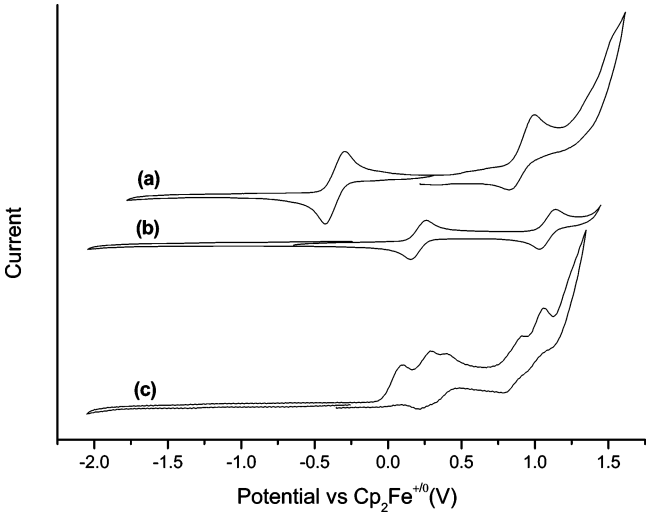



**Figure 3.** Cyclic voltammograms of (a) **1d**, (b) [Ru(2,4-Br-salen)(CO)(MeIm)], and (c) **3a** in $CH_2Cl_2$ solutions at 298 K with 0.1 M $(Bu_4N)PF_6$ as supporting electrolyte (scan rate, 50 mV s$^{-1}$; working electrode, pyrolytic graphite).

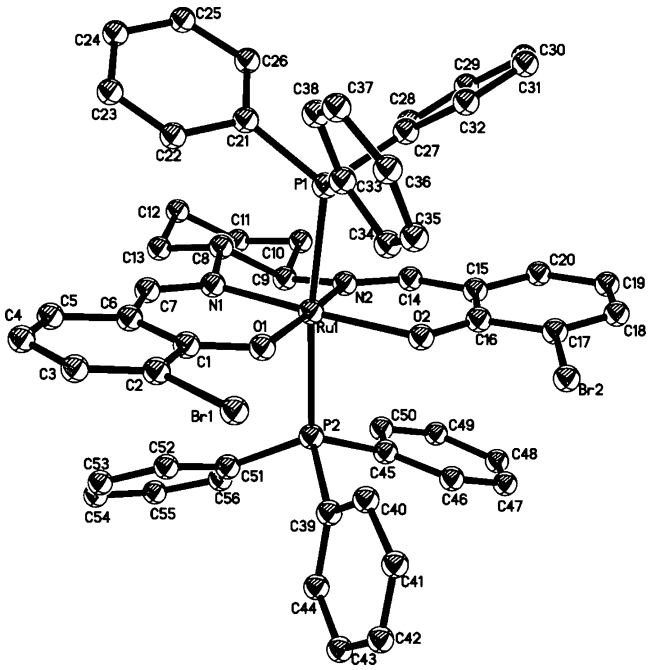



**Figure 4.** Perspective view of **1a**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−N(1) = 1.997(7), Ru(1)−N(2) = 1.975(6), Ru(1)−O(1) = 2.092(5), Ru(1)−O(2) = 2.094(6), Ru(1)−P(1) = 2.413(2), Ru(1)−P(2) = 2.393(2); N(1)−Ru(1)−N(2) = 83.3(3), O(1)−Ru(1)−O(2) = 92.0(2), N(1)−Ru(1)−P(2) = 97.0(2), O(1)−Ru(1)−P(2) = 89.71(16), P(1)−Ru(1)−P(2) = 171.92(8).[22]

of **1d−f** and $E_{p,a}$[Ru(II)/Ru(III)] values of **3a−c**. Moreover, the [Ru(II)/Ru(III)] couples of **1d−f**, [Ru(2,4-Br-salen)(CO)(MeIm)], **3**, and **4** occur at $E_{1/2}$ values significantly less anodic than that for the ligand-centered oxidation of [Ru(TPP)(CO)] ($E_{1/2}$ = 0.87 V).[19]

IR spectroscopic measurements of **1** reveal the absence of $\nu$(OH) stretches at ca. 3410 cm$^{-1}$, suggesting that the phenolic OH groups of the coordinated Schiff base ligand are deprotonated. For **2**, the $\nu$(C≡O) stretching frequencies occur at 1917−1939 cm$^{-1}$. These stretching frequencies are comparable to the

(18) Wong, C.-Y.; Che, C.-M.; Chan, M. C. W.; Leung, K.-H.; Phillips, D. L.; Zhu, N. *J. Am. Chem. Soc.* **2004**, *126*, 2501.

(19) Mu, X. H.; Kadish, K. M. *Langmuir* **1990**, *6*, 51.

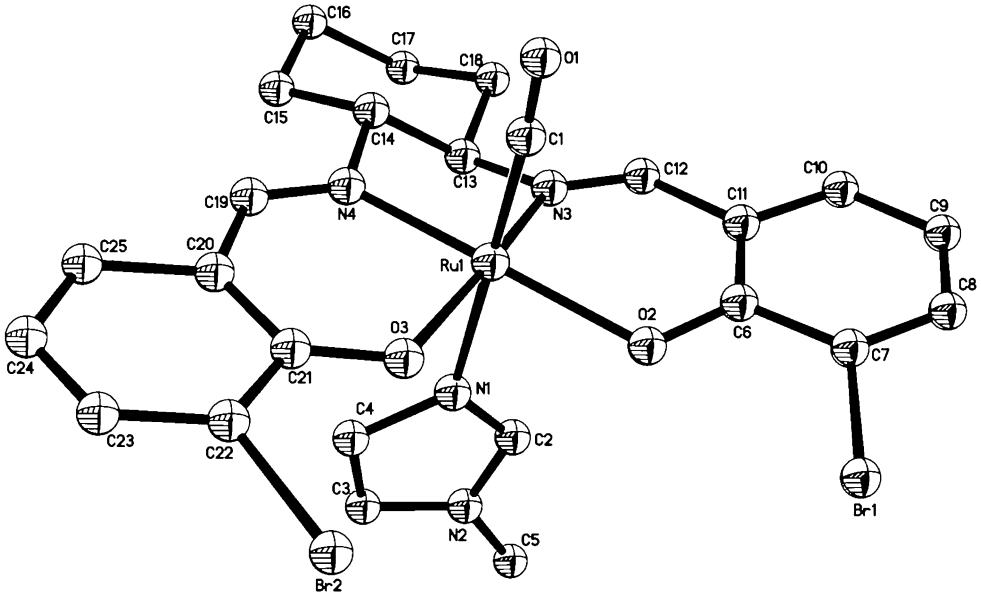



**Figure 5.** Perspective view of [Ru(2-Br-salen)(CO)(MeIm)]. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−N(1) = 2.114(11), Ru(1)−N(3) = 2.006(12), Ru(1)−N(4) = 2.033(11), Ru(1)−O(2) = 2.098(9), Ru(1)−O(3) = 2.100(9), Ru(1)−C(1) = 1.846(13); N(3)−Ru(1)−N(4) = 83.0(5), O(2)−Ru(1)−O(3) = 93.1(3), C(1)−Ru(1)−N(3) = 93.2(5), C(1)−Ru(1)−O(2) = 94.4(5), C(1)−Ru(1)−N(1) = 179.1(5).[22]

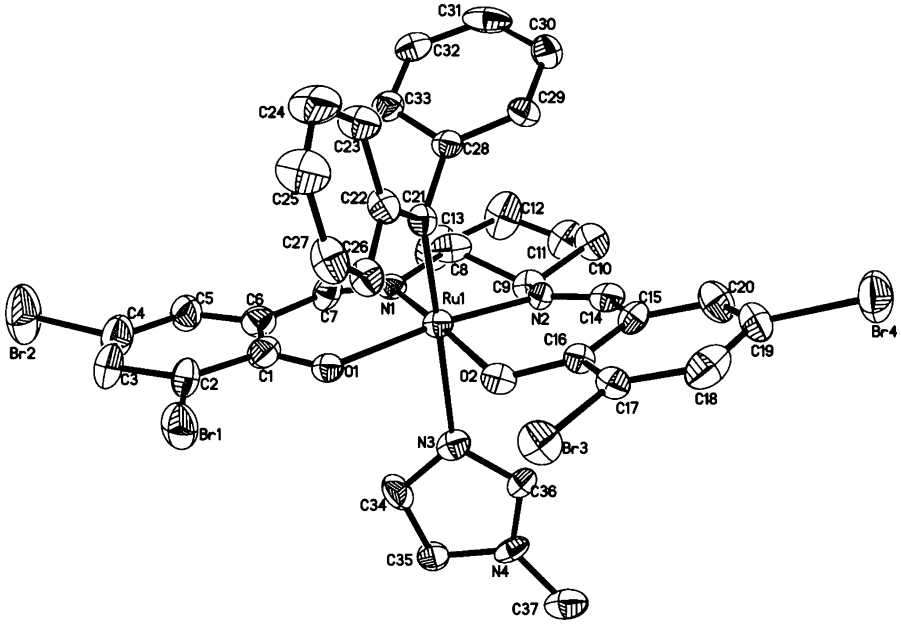



**Figure 6.** Perspective view of **3a**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−O(1) = 2.049(9), Ru(1)−O(2) = 2.061(9), Ru(1)−N(1) = 2.018(12), Ru(1)−N(2) = 1.988(11), Ru(1)−N(3) = 2.289(11), Ru(1)−C(21) = 1.921(12); N(2)−Ru(1)−N(3) = 86.0(4), C(21)−Ru(1)−N(1) = 94.7(5), C(21)−Ru(1)−O(1) = 94.4(5), C(21)−Ru(1)−N(3) = 176.2-(5).[22]

$\nu$(C≡O) values of 1941, 1939, and 1930 $cm^{-1}$ observed for [Ru(TPP)(CO)],[19] [Ru(TPP)(CO)(MeIm)],[17j] and [Ru(TMP)-(CO)] ($H_2$(TMP) = 5,10,15,20-tetramesitylporphyrin),[20] respectively, but are slightly lower than that reported for [Ru(*rac*-salen)(CO)(py)] (1955 $cm^{-1}$; $H_2$(*rac*-salen) = bis(salicylidene)-(±)-cyclohexanediamine).[21] The FAB mass spectra of **1b**−**g**, **3c**,**d**, and **4** exhibit a signal that can be attributed to the parent ion $[M]^+$ for **1b**−**g**, the $[M - MeIm]^+$ fragment for **3c**,**d**, and the $[M - py]^+$ fragment for **4**. Similarly, the positive ion high-resolution ESI and MALDI mass spectra of **1a**, **2** and **3a**,**b** revealed ion clusters consistent with the parent ion $[M]^+$ formulation.

**Structures.** Complex **1a** was recrystallized from 1,2-dichloroethane/*i*-PrOH, while [Ru(2-Br-salen)(CO)(MeIm)] and **3a**−**d** were recrystallized from $Et_2O/CH_2Cl_2$/MeIm at room temperature. Perspective views of **1a**, [Ru(2-Br-salen)(CO)(MeIm)], and **3a** are depicted in Figures 4−6, respectively (see Figures S13−S16 in the Supporting Information for perspective views of **3b**−**d** and **4**), and stick drawings showing the orientation of the axial ligands in these complexes are given in Figure 7. The crystal data and structural refinement details are given in Table 2.[22]

(20) Scharbert, B.; Zeisberger, E.; Paulus, E. *J. Organomet. Chem.* **1995**, *493*, 143.

(21) Karvembu, R.; Hemalatha, S.; Prabhakaran, R.; Natarajan, K. *Inorg. Chem. Commun.* **2003**, *6*, 486.

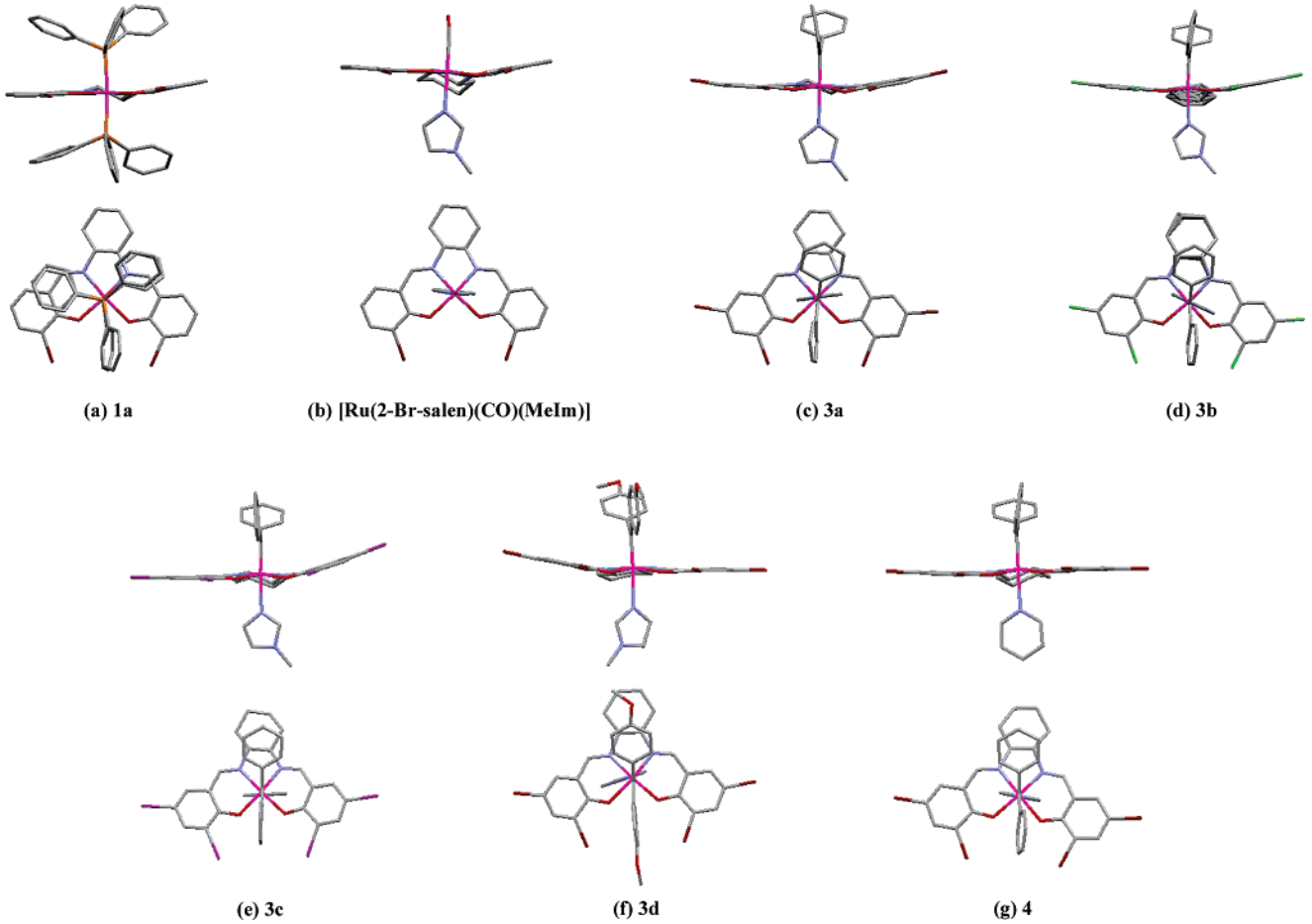



**Figure 7.** Stick drawings showing orientations of the axial ligands in (a) **1a**, (b) [Ru(2-Br-salen)(CO)(MeIm)], (c) **3a**, (d) **3b**, (e) **3c**, (f) **3d**, and (g) **4**.[22]

As shown in Figure 4, the axial $PPh_3$ ligands of **1a** adopt a configuration where the aryl rings are slightly tilted by ca. 4° away from the cyclohexane ring and are in the eclipsed form, presumably to minimize unfavorable steric interactions with the cyclohexane backbone of the Schiff base ligand. The eclipsed conformation adopted by the axial $PPh_3$ ligands of **1a** viewed along the *c* axis is also depicted in Figure 7a. The structures of [Ru(2-Br-salen)(CO)(MeIm)] and **3a** depicted in Figures 5 and 6 and of **3b**−**d** and **4** in Figures S13−S16 of the Supporting Information reveal that the respective CO, $CPh_2$, MeIm, and py ligands in these complexes are also situated in planes which are at near right angles to the plane of the Schiff base ligand. As shown in Figure 7b, the coordinated MeIm ligand in [Ru(2-Br-salen)(CO)(MeIm)] is situated in a plane that transverses the aryl C═C bonds of the Schiff base ligand so as to minimize unfavorable steric interactions between the cyclohexane ring and axial ligand. By a similar reasoning, the phenyl rings of the carbene ligands in **3** and **4** sit in planes that are at near right angles with respect to each other, with a dihedral angle between these planes ranging from 82.4 to 89.1°. The carbene and MeIm or py ligands in these carbene complexes are also located in planes that transverse the cyclohexyl bridging C−C bond and N−Ru−O angles of the Schiff base ligand, respectively, as depicted in Figure 7c−f; the dihedral angle between the planes occupied by the carbene and MeIm or py ligands are equal to 74.5° for **3a**, 65.7° for **3b**, 86.5° for **3c**, 77.6° for **3d**, and 82.7° for **4**. The cyclohexane ring of the chiral Schiff base ligand in **3b** is disordered.

The Ru−P distances in **1a** are 2.413(2) and 2.393(2) Å. These distances are comparable to those in [Ru(OEP)($PPh_3$)$_2$] (2.419(1) and 2.438(1) Å; $H_2$(OEP) = 2,3,7,8,12,13,17,18-octaethylporphyrin)[16] and [Ru($F_6$-acen)($PPh_3$)$_2$] (2.383(7) and 2.393(7) Å; $H_2$($F_6$-acen) = 1,1,1-trifluoro-4-[2-(4,4,4-trifluoro-3-hydroxy-1-methyl-but-2-enylideneamino)ethylimino]pent-2-en-2-ol).[23] Similarly, the Ru−C(CO) distance of 1.846(13) Å in [Ru(2-Br-salen)(CO)(MeIm)] is in good agreement with that of 1.849 Å found in [Ru(*R*-binaphsalen)(CO)] ($H_2$(*R*-binaphsalen) = (a*R*)-2′-phenyl-3-formyl-2-hydroxy-1,1′-binaphthyl)[24] but slightly longer than those found in [Ru(TPP)(CO)(MeIm)] (1.828(2) Å)[17j] and [Ru(TMP)(CO)] (1.805(1) Å).[20] The Ru═C(carbene) distances are 1.921(12) Å for **3a**, 1913(5) Å for **3b**, 1.919(14) Å for **3c**, 1910(2) Å for **3d**, and 1.917(4) Å for **4**, which are significantly longer than that of 1.845(3) Å in [Ru(TTP)($CPh_2$)(MeOH)],[25] 1.860(6) Å in [Ru($D_4$-Por*)($CPh_2$)],[7] 1.876(3) Å in [Ru($F_{20}$-TPP)($CPh_2$)(MeIm)] ($H_2$($F_{20}$-TPP) = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin),[17d] 1.874(8) Å in [Ru(tmtaa)($CPh_2$)] (tmtaa = 7,16-dihydro-6,8,15,17-tetramethyldi-

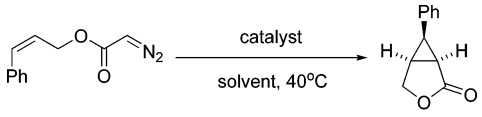
(22) CCDC 252437−252439, 270753, 277479, 281163, and 281164 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

(23) Serron, S. A.; Haar, C. M.; Nolan, S. P.; Brammer, L. *Organometallics* **1997**, *16*, 5120.
(24) Omura, K.; Uchida, T.; Irie, R.; Katsuki, T. *Chem. Commun.* **2004**, 2060.
(25) Kawai, M.; Yuge, H.; Miyamoto, T. K. *Acta Crystallogr., Sect. C* **2002**, *58*, M581.

**Table 2. Crystal Data and Structure Refinement Details for Complexes 1a, [Ru(2-Br-salen)(CO)(MeIm)], 3, and 4[22]**

| | **1a** | [Ru(2-Br-salen)(CO)-(MeIm)]·2.5$CH_2Cl_2$ | **3a**·$H_2O$ | **3b**·0.5$C_4H_{10}O$·$CH_3CN$ | **3c** | **3d** | **4** |
|---|---|---|---|---|---|---|---|
| formula | $C_{56}H_{48}Br_2N_2O_2P_2Ru$ | $C_{27.5}H_{29}Br_2Cl_2N_4O_3Ru$ | $C_{37}H_{34}Br_4N_4O_3Ru$ | $C_{41}H_{40}Cl_4N_5O_{2.50}Ru$ | $C_{76}H_{66}Cl_6I_8N_8O_4Ru_2$ | $C_{78.5}H_{73.5}Br_8N_8O_{8.50}Ru_2$ | $C_{42}H_{41}Br_4N_3O_3Ru$ |
| $M_r$ | 1103.79 | 901.69 | 1003.39 | 885.65 | 2585.41 | 2106.37 | 1056.49 |
| $\lambda$, Å | 0.71073 | 0.71073 | 0.71073 | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| $T$, K | 301 | 294 | 301 | 293 | 294 | 294 | 253 |
| cryst syst | monoclinic | monoclinic | monoclinic | triclinic | monoclinic | triclinic | monoclinic |
| space group | $P2_1$ | $P2_1$ | $P2_1$ | $P\bar{1}$ | $P2_1$ | $P\bar{1}$ | $C2/c$ |
| $a$, Å | 10.867(2) | 8.447(2) | 14.154(3) | 12.581(9) | 16.799(7) | 12.508(2) | 37.444(8) |
| $b$, Å | 24.938(5) | 16.420(3) | 20.696(4) | 19.094(14) | 14.783(6) | 17.364(3) | 13.021(3) |
| $c$, Å | 17.882(4) | 27.958(6) | 16.472(3) | 19.308(14) | 17.330(7) | 20.387(4) | 19.997(4) |
| α, deg | 90 | 90 | 90 | 66.238(2) | 90 | 106.689(4) | 90 |
| $\beta$, deg | 91.81(3) | 93.96(3) | 107.22(3) | 74.952(1) | 102.725(9) | 99.487(4) | 121.11(3) |
| $\gamma$, deg | 90 | 90 | 90 | 76.860(2) | 90 | 91.450(4) | 90 |
| $V$, Å$^3$ | 4843.6(17) | 3868.5(13) | 4608.9(16) | 4059.7(5) | 4198(3) | 4170.9(12) | 8347(3) |
| $Z$ | 4 | 4 | 4 | 4 | 2 | 2 | 8 |
| $\rho_{cacld}$, Mg m$^{-3}$ | 1.514 | 1.548 | 1.446 | 1.449 | 2.045 | 1.677 | 1.681 |
| $\mu$(Mo Kα), mm$^{-1}$ | 2.084 | 2.848 | 3.842 | 0.692 | 3.544 | 4.251 | 4.246 |
| $F$(000) | 2232 | 1780 | 1968 | 1812 | 2448 | 2073 | 4176 |
| index ranges | $-12 \le h \le 12$, $-29 \le k \le 29$, $-20 \le l \le 21$ | $-9 \le h \le 9$, $-19 \le k \le 19$, $-33 \le l \le 33$ | $-17 \le h \le 17$, $-24 \le k \le 25$, $-18 \le l \le 18$ | $-14 \le h \le 14$, $-22 \le k \le 18$, $-22 \le l \le 22$ | $-22 \le h \le 12$, $-19 \le k \le 19$, $-22 \le l \le 22$ | $-14 \le h \le 12$, $-20 \le k \le 20$, $-24 \le l \le 24$ | $-45 \le h \le 45$, $-15 \le k \le 15$, $-24 \le l \le 24$ |
| no. of rflns collected | 15 770 | 19 092 | 23 803 | 20 524 | 28 948 | 23 644 | 29 346 |
| no. of indep rflns | 15 770 | 10 571 | 12 502 | 14 055 | 18 888 | 14 655 | 7623 |
| refinement method | full-matrix least squares on $F^2$ | | | | | | |
| no. of data/restraints/ params | 15 770/1/1171 | 10 571/38/719 | 12 502/1/853 | 14 055/6/911 | 18 888/1/955 | 3948/0/946 | 7623/0/474 |
| goodness of fit | 0.92 | 1.07 | 1.00 | 0.76 | 0.96 | 1.13 | 0.689 |
| final $R$ indices, $I > 2\sigma(I)$ | R1 = 0.034, wR2 = 0.078 | R1 = 0.068, wR2 = 0.19 | R1 = 0.07, wR2 = 0.20 | R1 = 0.056, wR2 = 0.098 | R1 = 0.056, wR2 = 0.123 | R1 = 0.098, wR2 = 0.212 | R1 = 0.030, wR2 = 0.066 |
| largest diff peak/hole, e Å$^{-3}$ | 0.50/−0.73 | 1.42/−1.09 | 1.76/−1.21 | 0.48/−0.62 | 1.55/−0.84 | 1.78/−1.14 | 0.45/−0.83 |

**Table 3. Enantioselective Intramolecular Cyclopropanation of 5a Catalyzed by Chiral Ruthenium Schiff Base Complexes[a]**




**5a** **6a**

| entry | catalyst | solvent | yield (%)[b] | ee (%)[c] |
|---|---|---|---|---|
| 1 | **1a** | $CHCl_3$ | 61 | 90 |
| 2 | **1a** | $CH_2Cl_2$ | 45 | 73 |
| 3 | **1a** | $C_6H_6$ | 50 | 73 |
| 4 | **1a** | toluene | 44 | 80 |
| 5 | **1a** | 1,2-dichloroethane | 53 | 66 |
| 6 | **1b** | 1,2-dichloroethane | 42 | 25 |
| 7 | **1c** | 1,2-dichloroethane | 61 | 32 |
| 8 | **1d** | 1,2-dichloroethane | 47 | 51 |
| 9 | **1e** | 1,2-dichloroethane | 53 | 64 |
| 10 | **1g** | 1,2-dichloroethane | 61 | 34 |
| 11 | **2a** | $CHCl_3$ | 38 | 91 |
| 12 | **2b** | $CHCl_3$ | 22 | 28 |
| 13 | **2c** | $CHCl_3$ | 20 | 57 |
| 14 | [Ru(2-Br-salen)(CO)(MeIm)] | $CHCl_3$ | *d* | |
| 15 | **3a** | $CHCl_3$ | *d* | |
| 16 | [Ru(2,4-Br-salen)($CPh_2$)] | $CHCl_3$ | 43 | 27 |
| 17 | [Ru(2,4-$^t$Bu-salen)$py_2$] | $CH_2Cl_2$ | 76 | 16 |
| 18 | [Ru(2,4-$^t$Bu-phensalen)$py_2$] | $CH_2Cl_2$ | 70 | 20 |

[a] Reaction conditions: catalyst/**5a** = 1/100, solvent, 40 °C, addition of **5a** for 10 h followed by stirring for 2 h. [b] Isolated product yield. [c] Determined by HPLC analysis (Chiralcel OA column). [d] Starting alkene **5a** was recovered in 90−94% yield.

benzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato dianion),[17h] and 1.88(7) Å in [Ru(pybox)($C(CO_2Me)_2$)$Cl_2$].[13a]

**Enantioselective Intramolecular Cyclopropanation of *cis*-Alkenyl Diazoacetates (5) Catalyzed by 1 and 2.** At the outset, we examined the enantioselective intramolecular cyclopropanation of *cis*-3-phenylallyl diazoacetate (**5a**) using [Ru(2-Br-salen)($PPh_3$)$_2$] (**1a**) as catalyst. This revealed that slow addition of **5a** to a $CHCl_3$ solution containing 1 mol % of **1a** at 40 °C gave the best result, affording *cis*,*cis*-6-phenyl-3-oxabicyclo-[3.1.0]hexan-2-one (**6a**) with an ee value of 90% and in 61% yield, which, to our knowledge, represents the highest enantiocontrol so far achieved for intramolecular cyclopropanation of *cis*-allylic diazoacetates using a ruthenium catalyst (Table 3, entry 1).[2,6−9] These product yield and ee values are also comparable to those achieved for the analogous reaction reported by Doyle and co-workers with [$Rh_2$(5*S*-MEPY)$_4$] (H(5*S*-MEPY) = methyl-2-pyrrolidone-(5*S*)-carboxylic acid) as catalyst (70% yield, ≥94% ee).[4h,j] Examination of the solvent effect showed a slight decrease in product yield on changing the solvent from $CHCl_3$ to $CH_2Cl_2$, $C_6H_6$, toluene, or 1,2-dichloroethane. The effect of solvent on enantioselectivity was more dramatic. Lower product ee values of 66−80% were obtained when the reaction was conducted in $CH_2Cl_2$, $C_6H_6$, toluene, or 1,2-dichloroethane (entries 2−5).

The effect of ligand structure on the ruthenium Schiff base catalyzed intramolecular cyclopropanation reaction of **5a** was examined (Table 3, entries 6−18). Among the other [Ru(Schiff base)($PPh_3$)$_2$] catalysts **1b**−**e**,**g**, the performance of **1e** was similar to that of **1a** (entry 9). Reactions catalyzed by either **1b**−**d** or **1g** were also found to proceed with product yields similar to those found with either **1a** or **1e** (42−61%) as catalyst but were less enantioselective and gave **6a** with lower product ee values of 25−51% (entries 6−8 and 10). The chiral Ru(II) catalysts **2** containing an axial CO are significantly less reactive (entries 11−13). In the presence of 1 mol % of **2a** as catalyst in $CHCl_3$ solution at 40 °C, **6a** was afforded in 38% yield and with an ee value of 91% ee (entry 11). Under similar conditions, reactions with either **2b** or **2c** as catalyst were found to proceed in product yields of 22 and 20% but with markedly lower ee values of 28 and 57%, respectively (entries 12 and 13). No product formation could be detected by $^1$H NMR analysis for the reaction of **5a** using either [Ru(2-Br-salen)(CO)(MeIm)] or **3a** as catalyst; in both instances, the starting alkene substrate was recovered in 90−94% yield (entries 14 and 15). As mentioned in an earlier section, while [Ru(2,4-Br-salen)($CPh_2$)] was found to be inactive toward the stoichiometric cyclopropanation of either styrene or *p*-methoxystyrene, it could catalyze the intramolecular cyclopropanation of **5a** to give **6a** in 43% yield and with an ee value of 27% (entry 16).

In this work, we have also examined the cyclopropanation of **5a** with the chiral ruthenium Schiff base complexes [Ru(2,4-$^t$Bu-salen)$py_2$] ($H_2$(2,4-$^t$Bu-salen) = bis(3,5-di-*tert*-butylsalicylidene)-(1*R*,2*R*)-cyclohexanediamine) and [Ru(2,4-$^t$Bu-phensalen)$py_2$] ($H_2$(2,4-$^t$Bu-phensalen) = bis(3,5-di-*tert*-butylsalicylidene)-(1*R*,2*R*)-diphenylethanediamine) as catalysts, which were reported by Nguyen and co-workers to exhibit high enantioselectivities (up to 99% ee) and trans selectivities (trans:cis ratio up to 100:1) in the intermolecular cyclopropanation of alkenes with EDA.[26] Slow addition of a $CH_2Cl_2$ solution containing **5a** via a syringe pump over 3 h to a $CH_2Cl_2$ solution containing either [Ru(2,4-$^t$Bu-salen)$py_2$] or [Ru(2,4-$^t$Bu-phensalen)$py_2$] as catalyst at room temperature afforded **6a** in 70−76% yield but with markedly lower ee values of 16−20% (entries 17 and 18).

To explore the scope of the intramolecular cyclopropanation reaction, we examined the reactions of other *cis*-allylic diazoacetates (**5b**−**g**) with **1a** as catalyst. The results are summarized in Table 4. The [3.1.0] bicyclic cyclopropanes (**6b**−**g**) were afforded in 46−71% yields and with ee values up to 75% (entries 2−7). Notably, higher product yields (67−71%) and ee values (70−75%) were obtained for *cis*-allylic diazoacetates (**5d**,**e**) bearing electron-donating substituents (cis substituent = *p*-$MeC_6H_4$, *m*-$MeC_6H_4$) than for those with halogen functional groups (cis substituent = *p*-$ClC_6H_4$, *p*-$BrC_6H_4$; 52−53% yield, 44−55% ee) (cf. entries 2 and 3 and entries 4 and 5). A comparison of isolated product yields revealed that the position of the substituent on the substrate can also affect the efficiency and enantioselectivity. On going from *p*-Me-$C_6H_4$(CH=CH)$CH_2$-OC(O)$CHN_2$ (**5d**) to *m*-Me-$C_6H_4$(CH=CH)$CH_2$OC(O)$CHN_2$ (**5e**) to *o*-Me-$C_6H_4$(CH=CH)$CH_2$OC(O)$CHN_2$ (**5f**), the product yields and enantioselectivities of the resulting [3.1.0] bicyclic cyclopropanes (**6d**−**f**) decrease from 71 to 46% and from 75 to 66% ee, respectively (entries 4−6).

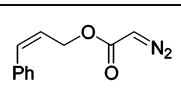
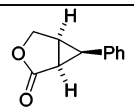
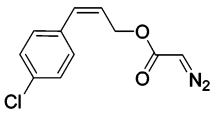
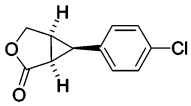
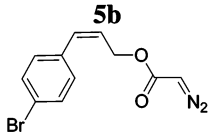
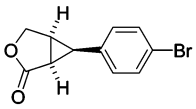
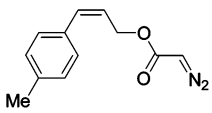
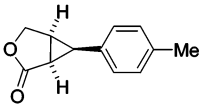
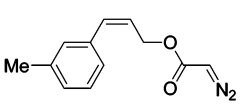
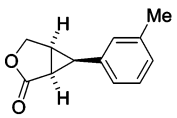
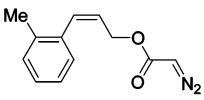
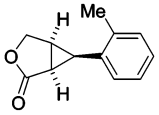
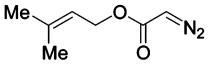
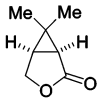
## Discussion

**Development of Metal Schiff Base Cyclopropanation Catalysts.** The utilization of metal catalysts in intramolecular cyclopropanation of alkenes can be traced back to 1961, when Stork and Ficini reported that an alkenyl diazoketone cyclized in the presence of a catalytic amount of copper-bronze powder.[27] Despite the advantage that such intramolecular reactions usually

(26) (a) Miller, J. A.; Jin, W.; Nguyen, S. B. T. *Angew. Chem., Int. Ed.* **2002**, *41*, 2953. (b) Miller, J. A.; Hennessy, E. J.; Marshall, W. J.; Scialdone, M. A.; Nguyen, S. B. T. *J. Org. Chem.* **2003**, *68*, 7884.

(27) Stork, G.; Ficini, J. *J. Am. Chem. Soc.* **1961**, *83*, 4678.

**Table 4. Enantioselective Intramolecular Cyclopropanation of *cis*-Allylic Diazoacetates (5a−h) Catalyzed by 1a[a]**

| Entry | Substrate | Product | Yield (%)[b] | Ee (%)[c] |
|---|---|---|---|---|
| 1 |  **5a** |  **6a** | 61 | 90 |
| 2 |  **5b** |  **6b** | 53 | 55 |
| 3 |  **5c** |  **6c** | 52 | 44 |
| 4 |  **5d** |  **6d** | 71 | 75 |
| 5 |  **5e** |  **6e** | 67 | 70 |
| 6 |  **5f** |  **6f** | 46 | 66 |
| 7 |  **5g** |  **6g** | 69 | 70 |

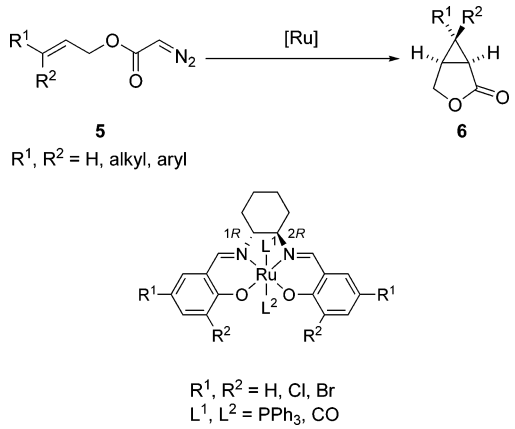
[a] Reaction conditions: catalyst/substrate = 1/100, $CHCl_3$, 40 °C, addition of substrate over 10 h and stirring for 2 h. [b] Isolated product yield. [c] Determined by HPLC analysis (Chiralcel OA column).

afford only one diastereomer because of geometric constraints (unlike intermolecular alkene cyclopropanation, in which diastereocontrol is an important issue), it was not until 1995 that the first enantioselective version of these reactions was developed. Pfaltz and co-workers showed that the cyclization of alkenyl diazoketones using a chiral copper semi-corrin catalyst could be accomplished with ee values up to 85%, albeit in moderate product yields.[3i] Lahuerta and co-workers subsequently disclosed the use of dirhodium(II,II) catalysts containing chiral ortho-metalated arylphosphine ligands, which gave the desired cyclopropane products in very high yields (>90%) and with enantioselectivities comparable to those reported by Pfaltz.[4b] The development of a myriad of homogeneous chiral copper and dirhodium(II,II) catalysts for asymmetric intramolecular cyclopropanation of alkene-containing diazocarbonyl compounds has followed these seminal discoveries.[3,4]

There are a wide variety of chiral metal Schiff base catalysts known in the literature, whose catalytic behavior toward asymmetric alkene epoxidation has been examined.[2a,28] However, few of them have been utilized as catalysts for asymmetric intramolecular alkene cyclopropanation reactions; recent examples are the applications of [M(Schiff base)L] (M = Ru, Co; L = axial ligand) in the asymmetric intramolecular cyclopropanation reactions depicted in Scheme 2, as already described in the Introduction.[8,9] Currently, the most effective catalyst for such enantioselective intramolecular C−C bond formation reactions is the dirhodium(II,II) carboxamidate catalyst developed by Doyle and co-workers.[4h,j] Although the enantioselectivity for such intramolecular cyclizations obtained using **1a** is

(28) (a) Xia, Q.-H.; Ge, H.-Q.; Ye, C.-P.; Liu, Z.-M.; Su, K.-X. *Chem. Rev.* **2005**, *105*, 1603. (b) McGarrigle, E. M.; Gilheany, D. G. *Chem. Rev.* **2005**, *105*, 1563.

**Scheme 2**




not superior to that for the foregoing dirhodium(II,II) carboxamidate catalyst, the present work first demonstrates the efficiency of a chiral metal Schiff base catalyst in catalyzing such asymmetric intramolecular cyclopropanations.

The results shown in Table 3 (entry 1; 90% ee, 61% yield) represent the highest enantioselectivity yet obtained for the cyclization of *cis*-alkenyl diazoacetates using a ruthenium catalyst, which to our knowledge also represents the highest enantiocontrol attained for ruthenium Schiff base catalyzed intramolecular cyclopropanation of *cis*-3-phenylallyl diazoacetate (**5a**), whose trans product **6a** is an important precursor for the synthesis of renin analogues (aspartic proteinase inhibitors).[29] Prior to this work, the best ee values obtained for ruthenium-catalyzed intramolecular cyclization of *cis*-alkenyl diazoacetates have been those with [Ru(*D*$_4$-Por*)(CO)(EtOH)] as catalyst. For the intramolecular cyclopropanation of **5a**,**f** using [Ru(*D*$_4$-Por*)(CO)(EtOH)] catalyst, the corresponding cyclopropane adducts **6a**,**f** were obtained in yields of 24 and 65% with ee values of 53 and 36%, respectively.[7] These values are lower than that of 61% product yield with an ee value of 90% for **6a** and 69% product yield with an ee value of 70% for **6f** obtained in this work when **1a** was used as catalyst.

**Structures of Ruthenium Schiff Base Monocarbene Complexes.** In the literature, it is widely believed that the active intermediates in metal-catalyzed inter- and intramolecular cyclopropanations of alkenes are electrophilic metal carbene complexes. In the case of intermolecular cyclopropanations, a few metallocarbenoid complexes have been isolated by treating the catalysts with the respective diazoacetates in the absence of alkenes.[13−15,17,26,30,31] Concerning metal Schiff base complexes, we are not aware of such intermediates bearing an axial carbene ligand isolated and structurally characterized. This is surprising in view of previous studies on ruthenium(II), cobalt(II) and cobalt(III) Schiff base complex catalyzed intramolecular cyclopropanations, all of which invoked the intermediacy of the respective metallocarbenoid complexes.[8,9] Recent works from our laboratory have shown that the isolation of chiral ruthenium porphyrin carbene complexes could provide useful information for rationalizing the observed enantioselectivities in chiral ruthenium porphyrin catalyzed cyclopropanantions.[7] In addition, the isolation and characterization of metal−oxo and −imido reactive intermediates containing Schiff base ligands[2a,32] have proven to be useful in understanding the mechanism of the respective C−O and C−N bond formation reactions.

Although the mechanism is currently unclear, it would not be unreasonable to speculate that **1a**-catalyzed intramolecular alkene cyclopropanation occurs via initial formation of an active electrophilic metallocarbenoid intermediate. In this work, the reactions of **1d**−**f** with either $N_2CPh_2$ or $N_2C(p\text{-}MeOC_6H_4)_2$ to form the respective six-coordinate carbene complexes **3** and **4** reveal the possible formation of a chiral ruthenium carbene Schiff base, [Ru(Schiff base)(CHX)] or [Ru(Schiff base)(CHX)(L)], where X = R(CH=CH)$CH_2CO_2$ and L is an axial ligand that exhibits a strong trans effect or is CHX. In this context, the structures of **3** and **4**, to our knowledge, represent some of the few examples of isolated ruthenium carbene Schiff base complexes derived from a diazo compound, whose structural characterization signifies the intermediacy of such species in intramolecular cyclopropanation of alkenyl diazoacetates mediated by a metal Schiff base catalyst.

While X-ray crystal analysis revealed that the structures of **3** and **4** feature long Ru=C distances, which generally suggest that such complexes would be reactive, these carbene complexes are very stable toward stoichiometric alkene cyclopropanation. As mentioned earlier, **3a** was found to be inert toward cyclopropanation of either styrene or *p*-methoxystyrene, similar to the case reported for [Ru(*D*$_4$-Por*)($CPh_2$)];[7] the latter contains a shorter Ru=C bond.

**Rationalization of the Enantioselectivity in 1a-Catalyzed Intramolecular Cyclopropanations.** The understanding of enantiocontrol in **1a**-catalyzed cyclizations of allylic diazoacetates (**5**) is of fundamental importance for future development of these types of catalysts. In this context, we rationalize the high ee values of up to 91% ee by considering the two possible transition states $TS_d$ and $TS_f$ of the proposed ruthenium carbene intermediate depicted in Figure 8. Presumably to avoid unfavorable steric interactions between the substrate and the Schiff base ligand, the alkenyl moiety preferentially approaches the ruthenium carbenoid along the Ru−N(2) bond through the pseudoboat conformation $TS_f$ in the transition state. This results in enantiocontrol being dictated by the chiral ligand conformation of the ruthenium Schiff base catalyst, which is determined by the chirality of the diamine unit (route II in Figure 8). Such a transition state would also explain the low product ee values obtained for reactions catalyzed by **1b**,**c**,**g**, containing sterically less bulky substituents ortho to the phenolic oxygen atom on the Schiff base ligand (see entries 6, 7, and 10 in Table 3), and decrease in product ee values as the steric bulk of the cis substituent on the C=C bond of the substrate increases on going from **5b** to **5c** and **5d** to **5e** to **5f** in Table 4. The marked difference in product yields for reactions of **5a** catalyzed by **1**

(29) Martin, S. F.; Austin, R. E.; Oalmann, C. J.; Baker, W. R.; Condon, S. L.; deLara, E.; Rosenberg, S. H.; Spina, K. P.; Stein, H. H.; Cohen, J.; Kleinert, H. D. *J. Med. Chem.* **1992**, *35*, 1710.

(30) (a) Zhang, J.; Liang, J.-L.; Sun, X.-R.; Zhou, H.-B.; Zhu, N.-Y.; Zhou, Z.-Y.; Chan, P. W. H.; Che, C.-M. *Inorg. Chem.* **2005**, *44*, 3942. (b) Zhou, C.-Y.; Yu, W.-Y.; Chan, P. W. H.; Che, C.-M. *J. Org. Chem.* **2004**, *69*, 7072. (c) Zhou, C.-Y.; Chan, P. W. H.; Yu, W.-Y.; Che, C.-M. *Synthesis* **2003**, *9*, 1403. (d) Zhang, J.-L.; Chan, P. W. H.; Che, C.-M. *Tetrahedron Lett.* **2003**, *44*, 8733. (e) Li, Y.; Huang, J.-S.; Zhou, Z.-Y.; Che, C.-M. *Chem. Commun.* **2003**, 1362, 3052. (f) Lai, T.-S.; Kwong, H.-L.; Che, C.-M. *Tetrahedron: Asymmetry* **2003**, *14*, 837. (g) Li, Y.; Huang, J.-S.; Zhou, Z.-Y.; Che, C.-M.; You, X.-Z. *J. Am. Chem. Soc.* **2002**, *124*, 13185. (h) Li, Y.; Huang, J.-S.; Zhou, Z.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2001**, *123*, 4843. (i) Lo, W.-C.; Che, C.-M.; Cheng, K.-F.; Mak, T. C. W. *Chem. Commun.* **1997**, 1205.

(31) Woo, L. K.; Smith, D. A. *Organometallics* **1992**, *11*, 2344.

(32) (a) Katsuki, T. *Synlett* **2003**, 281. (b) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905. (c) Katsuki, T. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000; p 287. (d) Jacobsen, E. N.; Wu, M. H. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; p 607. (e) Müller, P. In *Advances in Catalytic Processes*; Doyle, M. P., Ed.; JAI Press: Greenwich, CT, 1997; Vol. 2, p 113.

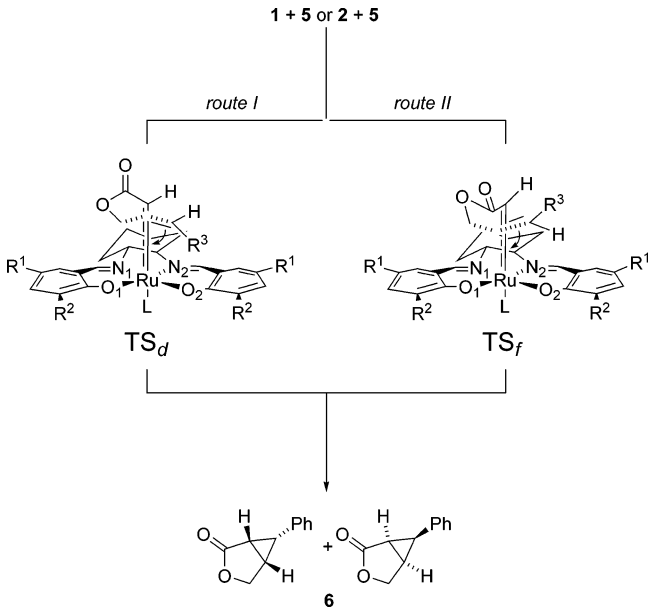



**Figure 8.** Proposed transition states for asymmetric intramolecular cyclopropanation of **5** catalyzed by **1** or **2**.

and **2** could be due to the poor solubility of the latter catalyst in various organic solvents.

## Conclusion

The present work describes the enantioselective intramolecular cyclopropanation of cis-substituted diazoacetates catalyzed by chiral ruthenium Schiff base complexes containing either a $PPh_3$ or CO ligand. Our studies revealed that **1a** represents an effective ruthenium Schiff base catalyst for an asymmetric intramolecular cyclopropanation process, catalyzing the cyclopropanation of several *cis*-alkenyl diazoacetates (**5**) in up to 90% ee and product yields up to 71%. The active intermediates in the **1a**-catalyzed intramolecular cyclopropanations of **5** could be the respective chiral ruthenium carbene complexes [Ru(2-Br-salen)(CHX)] (X = R(CH═CH)$CH_2CO_2$) or [Ru(2-Br-salen)(CHX)(L)], where L is a labile axial ligand that exhibits a strong trans effect. The reactions of **1d**−**f** with $N_2CAr_2$ gave the corresponding stable six-coordinate chiral ruthenium Schiff base monocarbene complexes **3** and **4**. The isolation of these chiral metal Schiff base carbene complexes provides indirect evidence for the involvement of such intermediates in ruthenium Schiff base catalyzed intramolecular cyclopropanations. Although X-ray analysis showed that **3** and **4** have unusually long Ru═C(carbene) bonds, suggesting that these ruthenium carbene complexes may exhibit interesting reactivities, neither [Ru(2,4-Br-salen)($CPh_2$)] nor **3a** was found to be active toward stoichiometric alkene cyclopropanation.

## Experimental Section

**General Considerations.** Unless otherwise stated, all reactions were carried out in anhydrous solvents under a positive pressure of argon gas. All solvents were distilled under an argon atmosphere prior to use: $Et_3N$ was distilled from sodium; $Et_2O$, THF, $C_6H_6$, and toluene were distilled from sodium and benzophenone; MeOH, $CH_2Cl_2$, and 1,2-dichloroethane were distilled from $CaH_2$; $CHCl_3$ was dried over anhydrous $CaSO_4$ and distilled prior to use. Commercially available reagents were used as received unless otherwise specified. Chiral Schiff base ligands were prepared from reaction of the respective substituted 2-hydroxybenzaldehyde with (1*R*,2*R*)-cyclohexanediamine in ethanol (2/1 v/v).

**Instrumentation.** The progress of reactions was monitored by thin-layer chromatography (TLC) and visualized with a UV lamp (254 nm), iodine absorbed on silica, and/or permanganate solution (1% $KMnO_4$ and 2% $Na_2CO_3$ in $H_2O$) activated with heat. $^1H$ NMR spectra were recorded at 300 MHz on either a Bruker AM300 or a Varian Mercury 300 spectrometer. $^{13}C$ NMR spectra were recorded on a Varian Mercury 300 (75 MHz) spectrometer and are proton-decoupled. IR measurements were performed as KBr disks on a Bio-Rad FTS-185 instrument. Optical rotations were performed on a Perkin-Elmer 341MC polarimeter at 589 nm and 20 °C. Mass spectra were measured on either an HP HP5989A or Agilent HP5873 spectrometer at an ionization voltage of 70 eV. High-resolution mass spectra were obtained with a Kratos Concept 1H spectrometer. Elemental analyses were run on an Elemantar Vario EL instrument at the Analytical and Testing Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Enantioselectivities were determined on a Waters 5151 HPLC equipped with a Chiralpak OA column.

**General Procedure for Synthesis of [Ru(Schiff base)($PPh_3$)$_2$] (1).** To a degassed solution of MeOH (8 mL) containing chiral $H_2$R-salen (0.55 mmol) and $Et_3N$ (1.5 mL) was added [Ru($PPh_3$)$_3Cl_2$] (0.5 mmol). The reaction mixture was refluxed for 18 h, and after it was cooled to room temperature, it was subsequently filtered and washed with *i*-PrOH (3 × 10 mL). The red-brown solid obtained was recrystallized from 1,2-dichloroethane/*i*-PrOH to give brown crystals of the title compound.

**[Ru(2-Br-salen)($PPh_3$)$_2$] (1a).**[22] Yield: 73%. Anal. Calcd for $C_{56}H_{48}Br_2N_2O_2P_2Ru$: C, 60.93; H, 4.38; N, 2.54. Found: C, 60.94; H, 4.17; N, 2.35. IR (KBr pellet, $cm^{-1}$): 3049, 1584, 1449, 1435, 1123, 694, 516. HRMS (ESI): *m*/*z* calcd for $C_{38}H_{34}Br_2N_2O_2PRu$, 840.9762; found, 840.9743.

**[Ru(4-Br-salen)($PPh_3$)$_2$] (1b).** Yield: 71%. Anal. Calcd for $C_{56}H_{48}Br_2N_2O_2P_2Ru$: C, 60.93; H, 4.38; N, 2.54. Found: C, 60.44; H, 4.20; N, 2.34. IR (KBr pellet, $cm^{-1}$): 3051, 2937, 1587, 1459, 1434, 694, 514. MS (FAB): *m*/*z* 1102 $[M]^+$.

**[Ru(4-Cl-salen)($PPh_3$)$_2$] (1c).** Yield: 68%. Anal. Calcd for $C_{56}H_{48}Cl_2N_2O_2P_2Ru$: C, 66.27; H, 4.77; N, 2.76. Found: C, 66.06; H, 4.93; N, 2.61. IR (KBr pellet, $cm^{-1}$): 3050, 2929, 1586, 1439, 1133, 694, 516. MS (FAB): *m*/*z* 1014 $[M]^+$.

**[Ru(2,4-Br-salen)($PPh_3$)$_2$] (1d).**[33] Yield: 83%. Anal. Calcd for $C_{56}H_{46}Br_4N_2O_2P_2Ru$: C, 53.31; H, 3.68; N, 2.22. Found: C, 53.02; H, 3.42; N, 2.11. IR (KBr pellet, $cm^{-1}$): 3050, 2929, 1440, 1142, 695, 516. MS (FAB): *m*/*z* 1258 $[M]^+$.

**[Ru(2,4-Cl-salen)($PPh_3$)$_2$] (1e).**[33] Yield: 81%. Anal. Calcd for $C_{56}H_{46}Cl_4N_2O_2P_2Ru$: C, 62.06; H, 4.28; N, 2.58. Found: C, 61.98; H, 4.13, N, 2.39. IR (KBr pellet, $cm^{-1}$): 3049, 2935, 1583, 1448, 1156, 694, 516. MS (FAB): *m*/*z* 1082 $[M]^+$.

**[Ru(2,4-I-salen)($PPh_3$)$_2$] (1f).**[33] Yield: 70%. IR (KBr pellet, $cm^{-1}$): 3051, 2927, 1438, 1140, 690, 517. MS (FAB): *m*/*z* 1450 $[M]^+$, 1188 $[M - PPh_3]^+$.

**[Ru(salen)($PPh_3$)$_2$] (1g).**[33] Yield: 61%. Anal. Calcd for $C_{56}H_{50}N_2O_2P_2Ru$: C, 71.10; H, 5.33; N, 2.96. Found: C, 70.83; H, 5.19; N, 2.76. IR (KBr pellet, $cm^{-1}$): 3049, 2935, 1598, 1446, 694, 514. MS (FAB): *m*/*z* 946 $[M^+]$.

**General Procedure for the Synthesis of [Ru(Schiff base)(CO)] (2).** To a Schlenk tube charged with 1 atm of CO gas was sequentially added **1** (0.5 mmol) and $CH_2Cl_2$ (5 mL) at room temperature. The reaction mixture was stirred overnight and filtered, and the residue was washed with diethyl ether (3 × 2 mL). The residue was dried under reduced pressure to give the title compound as a yellow solid. For **2a**, the crude product was recrystallized from a solution containing $Et_2O/CH_2Cl_2$/MeIm (10/3/1) to give [Ru(2-Br-salen)(CO)(MeIm)].[22]

(33) For full characterization data of [Ru(Schiff base)($PPh_3$)$_2$], see refs 11 and 12 and: (a) Sun, W.; Kühn, F. E. *Appl. Catal., A: Gen.* **2005**, *285*, 163. (b) Bhowon, M. G.; Wah, H. L. K.; Narain, R. *Polyhedron* **1999**, *18*, 341.

**[Ru(2-Br-salen)(CO)] (2a).** Yield: 80%. Anal. Calcd for $C_{21}H_{18}Br_2N_2O_3Ru\cdot0.5CH_2Cl_2$: C, 39.74; H, 2.95; N, 4.31. Found: C, 40.05; H, 3.33; N, 4.24. $^1$H NMR ($C_5D_4N$, 500 MHz): $\delta$ 8.40 (d, 1H, $J$ = 1.2 Hz), 8.30 (d, 1H, $J$ = 1.4 Hz), 7.70 (dd, 1H, $J$ = 7.4, 1.6 Hz), 7.35 (dd, 1H, $J$ = 7.8, 1.5 Hz), 7.32 (dd, 1H, $J$ = 7.9, 1.5 Hz), 6.43 (t, 1H, $J$ = 7.6 Hz), 6.34 (t, 1H, $J$ = 7.6 Hz), 3.20−3.28 (m, 1H), 3.10−3.18 (1H, m), 2.52 (br d, 1H, $J$ = 9.6 Hz), 2.41 (br d, 1H, $J$ = 9.8 Hz), 1.63 (br t, 2H, $J$ = 13.4 Hz), 1.02−1.30 (m, 4H). IR (KBr pellet, cm$^{-1}$): 1931, 1629, 1590, 1436, 1315. HRMS (MALDI): *m*/*z* calcd for $C_{21}H_{19}Br_2N_2O_3Ru$, 606.8800; found, 606.8814.

**[Ru(4-Br-salen)(CO)] (2b).** Yield: 83%. Anal. Calcd for $C_{21}H_{18}Br_2N_2O_3Ru\cdot0.5CH_2Cl_2$: C, 39.74; H, 2.95; N, 4.31. Found: C, 39.91; H, 3.36; N, 4.25. $^1$H NMR ($C_5D_4N$, 500 MHz): $\delta$ 8.40 (s, 1H), 8.30 (s, 1H), 7.80 (d, 1H, $J$ = 6.1 Hz), 7.70 (d, 1H, $J$ = 6.1 Hz), 7.35 (d, 1H, $J$ = 6.7 Hz), 7.32 (d, 1H, $J$ = 6.7 Hz), 6.43 (t, 1H, $J$ = 7.6 Hz), 6.35 (t, 1H, $J$ = 7.6 Hz), 3.20−3.29 (m, 1H), 3.11−3.19 (m, 1H), 2.52 (br d, 1H, $J$ = 10.5 Hz), 2.41 (br d, 1H, $J$ = 9.9 Hz), 1.63 (br t, 2H, $J$ = 13.5 Hz), 0.97−1.31 (m, 4H). IR (KBr pellet, cm$^{-1}$): 1939, 1627, 1445, 1312, 1163. HRMS (ESI): *m*/*z* calcd for $C_{21}H_{18}Br_2N_2O_3Ru$, 606.8805; found, 606.8824.

**[Ru(2,4-Cl-salen)(CO)] (2c).** Yield: 82%. Anal. Calcd for $C_{21}H_{16}Cl_4N_2O_3Ru\cdot0.5CH_2Cl_2$: C, 41.01; H, 2.72; N, 4.45. Found: C, 40.61; H, 3.20; N, 4.23. $^1$H NMR ($C_5D_4N$, 500 MHz): $\delta$ 8.40 (d, 1H, $J$ = 1.0 Hz), 8.28 (d, 1H, $J$ = 1.2 Hz), 7.58 (d, 1H, $J$ = 2.7 Hz), 7.51 (s, 1H), 7.33 (d, 1H, $J$ = 2.7 Hz), 7.31 (d, 1H, $J$ = 2.7 Hz), 3.27−3.34 (m, 1H), 3.11−3.20 (m, 1H), 2.64 (br d, 1H, $J$ = 10.0 Hz), 2.49 (br d, 1H, $J$ = 9.3 Hz), 1.67 (br t, 2H, $J$ = 15.5 Hz), 1.35 (br d, 1H, $J$ = 10.3 Hz), 1.30 (br d, 1H, $J$ = 10.3 Hz), 1.11−1.24 (m, 1H), 0.98−1.10 (m, 1H). IR (KBr pellet, cm$^{-1}$): 3068, 1917, 1625, 1462, 1309, 1169. HRMS (MALDI): *m*/*z* calcd for $C_{21}H_{17}Cl_4N_2O_3Ru$, 586.9031; found, 586.9054.

**[Ru(2,4-Br-salen)(CO)] (2d).** Yield: 60%. Anal. Calcd for $C_{21}H_{16}Br_4N_2O_3Ru\cdot C_4H_6N_2$: C, 35.56; H, 2.63; N, 6.64. Found: C, 35.08; H, 2.58, N, 6.50. $^1$H NMR ($C_5D_4N$, 500 MHz): $\delta$ 8.36 (s, 1H), 8.26 (s, 1H), 7.90 (d, 1H, $J$ = 2.5 Hz), 7.81 (d, 1H, $J$ = 2.5 Hz), 7.47 (d, 1H, $J$ = 2.5 Hz), 7.45 (d, 1H, $J$ = 2.5 Hz), 3.29−3.37 (m, 1H), 3.21−3.29 (m, 1H), 2.65 (br d, 1H, $J$ = 9.9 Hz), 2.52 (br d, 1H, $J$ = 10.0 Hz), 1.68 (br t, 2H, $J$ = 14.5 Hz), 1.24−1.43 (m, 2H), 1.13−1.24 (m, 1H), 1.02−1.13 (m, 1H). IR (KBr pellet, cm$^{-1}$): 1933. MS (FAB): *m*/*z* 738 [M − CO]$^+$.

**[Ru(2,4-I-salen)(CO)] (2e).** Yield: 50%. Anal. Calcd for $C_{21}H_{16}I_4N_2O_3Ru\cdot C_4H_6N_2$: C, 28.97; H, 2.14; N, 5.41. Found: C, 29.43; H, 2.52, N, 5.66. $^1$H NMR ($C_5D_4N$, 500 MHz): $\delta$ 8.26−8.33 (m, 2H), 8.16−8.20 (m, 2H), 7.59 (dd, 2H, $J$ = 7.3, 2.2 Hz), 3.32−3.46 (m, 2H), 2.59−2.69 (m, 1H), 2.52−2.59 (m, 1H), 1.65−1.74 (m, 2H), 1.42−1.51 (m, 1H), 1.10−1.39 (m, 3H). IR (KBr pellet, cm$^{-1}$): 1954. MS (FAB): *m*/*z* 926 [M − CO]$^+$.

**General Procedure for the Synthesis of [Ru(Schiff base)(C(*p*-$YC_6H_4)_2$)(MeIm)] (3).** To a $CH_2Cl_2$ (5 mL) solution containing [Ru(Schiff base)($PPh_3)_2$] (**1**; 0.3 mmol) was added slowly a solution of $N_2C(p\text{-}YC_6H_4)_2$ (Y = H, OMe) (1.3 mmol) in $CH_2Cl_2$ (5 mL) via a syringe pump over a 10 h period. This resulted in the formation of a green precipitate, which was filtered and sequentially washed with copious amounts of $CH_2Cl_2$ and MeOH. The crude green precipitate obtained was dried under reduced pressure and recrystallized from a solution containing $Et_2O/CH_2Cl_2$/MeIm (10/3/1) to give the title compound.

**[Ru(2,4-Br-salen)($CPh_2$)(MeIm)] (3a).**[22] Yield: 85%. Anal. Calcd for $C_{37}H_{32}Br_4N_4O_2Ru$: C, 45.10; H, 3.27. Found: C, 44.79; H, 3.45. $^1$H NMR ($C_5D_4N$, 300 MHz): $\delta$ 8.41 (s, 1H), 8.26 (s, 1H), 7.73 (d, 1H, $J$ = 2.4 Hz), 7.66 (d, 1H, $J$ = 2.4 Hz), 7.50−7.59 (m, 5H), 7.31−7.44 (m, 5H), 3.30−3.40 (m, 1H), 2.56−2.69 (m, 2H), 2.25−2.40 (m, 1H), 1.57−1.75 (m, 2H), 1.25−1.41 (m, 1H), 1.10−1.25 (m, 1H), 0.85−1.02 (m, 2H). $^{13}$C NMR ($C_5D_4N$, 100 MHz): $\delta$ 317.0 (Ru═C). IR (KBr pellet, cm$^{-1}$): 2932, 1577, 1438, 1145. HRMS (ESI): *m*/*z* calcd for $C_{33}H_{26}Br_4N_2NaO_2Ru$, 922.7664; found, 922.7658.

**[Ru(2,4-Cl-salen)($CPh_2$)(MeIm)] (3b).**[22] Yield: 33%. Anal. Calcd for $C_{37}H_{32}N_4O_2Cl_4Ru$: C, 55.08; H, 4.00; N, 6.95. Found: C, 54.77; H, 4.18, N, 6.50. $^1$H NMR ($C_5D_4N$, 500 MHz): $\delta$ 8.43 (s, 1H), 8.27 (s, 1H), 7.69 (br s, 3H), 7.18−7.42 (m, 11H), 3.32−3.40 (m, 1H), 2.43−2.65 (m, 2H), 2.24−2.33 (m, 1H), 1.59−1.70 (m, 2H), 1.25−1.36 (m, 1H), 1.10−1.20 (m, 1H), 0.83−0.95 (m, 2H). $^{13}$C NMR ($C_5D_4N$, 100 MHz): $\delta$ 317.3 (Ru═C). IR (KBr pellet, cm$^{-1}$): 3131, 2933, 2859, 1602, 1585, 1441, 1160, 857, 752. HRMS (MALDI): *m*/*z* calcd for $C_{33}H_{26}N_2O_2Cl_4Ru$, 723.9792; found, 723.9768.

**[Ru(2,4-I-salen)($CPh_2$)(MeIm)] (3c).**[22] Yield: 60%. Anal. Calcd for $C_{37}H_{32}N_4O_2I_4Ru$: C, 37.83; H, 2.75; N, 4.77. Found: C, 37.80; H, 3.01; N, 4.95. $^1$H NMR ($C_5D_4N$, 500 MHz): $\delta$ 8.34 (s, 1H), 8.18 (s, 1H), 8.13 (d, 1H, $J$ = 1.9 Hz), 8.08 (d, 1H, $J$ = 1.9 Hz), 7.70 (d, 1H, $J$ = 1.8 Hz), 7.68 (d, 1H, $J$ = 1.9 Hz), 7.49−7.60 (m, 4H), 7.25−7.40 (m, 6H), 3.34−3.42 (m, 1H), 2.55−2.70 (m, 2H), 2.30−2.37 (m, 1H), 1.58−1.70 (m, 2H), 1.16−1.37 (m, 2H), 0.88−1.20 (m, 1H). $^{13}$C NMR ($C_5D_4N$, 100 MHz): $\delta$ 316.3 (Ru═C). IR (KBr, cm$^{-1}$): 2928, 1561, 1430, 1137. MS (FAB): *m*/*z* 1092 [M − MeIm]$^+$.

**[Ru(2,4-Br-salen)(C(*p*-$MeOC_6H_4)_2$)(MeIm)] (3d).**[22] Yield: 60%. Anal. Calcd for $C_{39}H_{36}N_4O_2Br_4Ru$: C, 44.92; H, 3.48; N, 5.38. Found: C, 44.46; H, 3.63, N, 5.35. $^1$H NMR ($C_5D_4N$, 500 MHz): $\delta$ 8.47 (d, 1H, $J$ = 1.1 Hz), 8.32 (d, 1H, $J$ = 1.1 Hz), 7.80 (d, 1H, $J$ = 2.6 Hz), 7.74 (d, 1H, $J$ = 2.6 Hz), 7.64 (d, 1H, $J$ = 2.6 Hz), 7.60 (d, 1H, $J$ = 2.6 Hz), 7.03 (d, 4H, $J$ = 7.2 Hz), 4.96 (s, 4H), 3.34−3.38 (m, 1H), 2.65 (d, 2H, $J$ = 10.8 Hz), 2.42−2.46 (m, 1H), 1.64−1.71 (m, 2H), 1.36−1.48 (m, 1H), 1.15−1.23 (m, 1H), 0.95−1.03 (m, 2H). $^{13}$C NMR ($C_5D_4N$, 100 MHz): $\delta$ 317.3 (Ru═C). IR (KBr, cm$^{-1}$): 2932, 1589, 1438, 1162. MS (FAB): *m*/*z* 964 [M − MeIm]$^+$.

**[Ru(2,4-Br-salen)($CPh_2$)(py)] (4).**[22] To a $CH_2Cl_2$ (5 mL) solution containing [Ru(2,4-Br-salen)($CPh_2$)] (46 $\mu$mol) was added pyridine (1 mL). The resulting mixture was stirred for 30 min and filtered. Recrystallization by adding $Et_2O$ gave the title compound. Yield: 50%. Anal. Calcd for $C_{38}H_{31}Br_4N_3O_2Ru$: C, 46.46; H, 3.18; N, 4.28. Found: C, 45.77; H, 3.66, N, 3.86. IR (KBr, cm$^{-1}$): 2934, 1578, 1436, 1146. MS (FAB): *m*/*z* 903 [M − py]$^+$.

**General Procedure for Intramolecular Cyclopropanation of (*E*)-Allylic Diazoacetates Catalyzed by 1 or 2.** To a solution of catalyst (0.01 mmol) in solvent (10 mL) was slowly added the (alkenyl)allyl diazoacetate **7** (1 mmol) dissolved in the same solvent (20 mL) over a 10 h period via syringe pump at 40 °C. The solution was stirred for an additional 2 h. After it was cooled to room temperature, the resulting solution was concentrated at reduced pressure and purified by silica gel column chromatography (5/1 petroleum ether/EtOAc as eluent) to give the desired fused [3.1.0] cyclopropane product.

***cis*,*cis*-6-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one (6a).** $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.36−7.32 (m, 5H), 4.83 (ddd, $J$ = 9.9, 2.4 Hz, 1H), 4.06 (d, $J$ = 9.9 Hz, 2H), 2.79 (dd, $J$ = 8.4 Hz, 1H), 2.60 (dd, $J$ = 8.4, 2.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 174.9, 132.3, 129.5, 129.0, 127.8, 65.8, 26.3, 24.0, 23.6. IR (KBr pellet, cm$^{-1}$): 2968, 1742, 1378, 1194, 965, 753, 699, 529. MS (EI): *m*/*z* 174 [M$^+$]. HRMS (ESI): *m*/*z* calcd for $C_{11}H_{10}O_2$: 174.0681; found, 174.0664.

***cis*,*cis*-6-(4-Chlorophenyl)-3-oxabicyclo[3.1.0]hexan-2-one (6b).** $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.28 (d, $J$ = 9.6 Hz, 2H), 7.05 (d, $J$ = 9.6 Hz, 2H), 4.47 (dd, $J$ = 9.3, 4.5 Hz, 1H), 4.42 (d, $J$ = 9.3 Hz, 1H), 2.54−2.48 (m, 1H), 2.33−2.29 (m, 2H). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 174.60, 135.67, 133.04, 128.90, 127.28, 69.61, 28.67, 27.40, 26.13. IR (KBr pellet, cm$^{-1}$): 2969, 2905, 1771, 1748, 1497, 1371, 1039, 529. MS (EI): 208 [M]$^+$. HRMS (EI): *m*/*z* calcd for $C_{11}H_{10}ClO_2$, 231.01833; found, 231.0180.

***cis,cis*-6-(4-Bromophenyl)-3-oxabicyclo[3.1.0]hexan-2-one (6c).** $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.44 (d, $J$ = 8.4 Hz, 2H), 6.95 (d, $J$ = 8.4 Hz, 2H), 4.47 (dd, $J$ = 9.6, 4.8 Hz, 1H), 4.42 (dd, $J$ = 9.3, 0.9 Hz, 1H), 2.53−2.49 (m, 1H), 2.34−2.28 (m, 2H). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 174.6, 136.2, 131.9, 127.7, 121.1, 69.6, 28.8, 27.4, 26.1. IR (KBr pellet, cm$^{-1}$): 1745, 1178, 1039, 813, 527. MS (EI): *m*/*z* 254 $[M]^+$. HRMS (ESI): *m*/*z* calcd for $C_{11}H_9BrO_2$, 251.9790; found, 251.9788.

***cis,cis*-6-(4-Methylphenyl)-3-oxabicyclo[3.1.0]hexan-2-one (6d).** $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.21 (d, $J$ = 8.1 Hz, 2H), 7.15 (d, $J$ = 8.1 Hz, 2H), 4.36 (ddd, $J$ = 9.6, 3.6, 1.8 Hz, 1H), 4.05 (d, $J$ = 9.6 Hz, 1H), 2.77−2.71 (m, 1H), 2.58−2.54 (m, 2H), 2.32 (s, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 175.0, 137.5, 129.7, 129.3, 65.9, 26.0, 24.0, 23.6, 21.2. IR (KBr pellet, cm$^{-1}$): 1770, 1754, 1176, 1039, 980, 835. MS (EI): *m*/*z* 188 $[M]^+$. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{12}O_2$, 188.0837; found, 188.0836.

***cis,cis*-6-(3-Methylphenyl)-3-oxabicyclo[3.1.0]hexan-2-one (6e).** $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.23−7.01 (m, 4H), 4.36 (ddd, $J$ = 9.9, 2.7 Hz, 1H), 4.07 (d, $J$ = 10.2 Hz, 1H), 2.78−2.72 (m, 1H), 2.58−2.55 (m, 2H), 2.33 (s, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 175.0, 138.6, 132.2, 130.1, 128.8, 128.6, 126.5, 65.9, 26.2, 24.0, 23.6, 21.4. IR (KBr pellet, cm$^{-1}$): 1770, 1749, 1196, 1039, 977, 708. MS (EI): *m*/*z* 188 $[M]^+$. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{12}O_2$, 188.0837; found, 188.0842.

***cis,cis*-6-(2-Methylphenyl)-3-oxabicyclo[3.1.0]hexan-2-one (6f).** $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.30−7.15 (m, 4H), 4.36 (dd, $J$ = 9.9, 4.5 Hz, 1H), 3.83 (d, $J$ = 9.9 Hz, 1H), 2.67−2.62 (m, 3H), 2.39 (s, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 138.0, 130.8, 129.2, 128.0, 126.5, 66.0, 25.9, 24.2, 24.1, 19.2. IR (KBr pellet, cm$^{-1}$): 1758, 1173, 970, 738. MS (EI): *m*/*z* 188 $[M]^+$. HRMS (ESI): *m*/*z* calcd for $C_{12}H_{12}O_2$, 188.0837; found, 188.0835.

***cis*-6,6-Dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (6g).** $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 4.37 (dd, $J$ = 9.9, 5.7 Hz, 1H), 4.16 (d, $J$ = 9.9, 2.4 Hz, 1H), 2.06 (t, $J$ = 6.0 Hz, 2H), 1.95 (d, $J$ = 6.0 Hz, 1H), 1.18 (s, 6H). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 174.91, 66.49, 30.55, 30.07, 25.24, 23.03, 14.43. IR (KBr pellet, cm$^{-1}$): 2961, 2910, 1769, 1361, 1180, 1050, 975. MS (EI): *m*/*z* 126 $[M]^+$. HRMS (ESI): *m*/*z* calcd for $C_7H_{10}O_2$, 126.0681; found, 126.0638.

**X-ray Crystallography.** Crystals of **1a** were obtained by slow diffusion of 1,2-dichloroethane into an *i*-PrOH solution of **1a**, whereas those of [Ru(2-Br-salen)(CO)(MeIm)] and **3** were obtained by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution containing MeIm ($CH_2Cl_2$/MeIm, 3/1 v/v) and those of **4** by recrystallization from $Et_2O$. Data collection was carried out on a MAR diffractometer by using crystals of dimensions 0.3 × 0.2 × 0.1 mm (**1a**, at 301(2) K), 0.4 × 0.2 × 0.1 mm ([Ru(2-Br-salen)(CO)(MeIm)]·2.5$CH_2Cl_2$, at 301(2) K), 0.4 × 0.2 × 0.1 mm (**3a**·$H_2O$, at 301(2) K), 0.4 × 0.3 × 0.2 mm (**3b**·0.5$C_4H_{10}O$·$CH_3CN$, at 293(2) K), 0.38 × 0.28 × 0.20 mm (**3c**, at 294(2) K), 0.32 × 0.24 × 0.16 mm (**3d**, at 294(2) K), and 0.5 × 0.25 × 0.2 mm (**4**, at 253(2) K).[22] The structures were refined by full-matrix least squares using the SHELXL-97 program.[34] The images were interpreted and the intensities integrated by using the program DENZO.[35] The structures were solved by direct methods by employing the SHELXS-97 program on a PC.[36] In all cases graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) was used.

**Acknowledgment.** We thank Prof. Zhong-Yuan Zhou (Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong) for assistance in solving the crystal structures of **3c**,**d** reported in this paper. This work has been supported by the Area of Excellence Scheme (Grant No. AoE/P-10-01) established under the University Grants Committee, HKSAR, the Hong Kong Research Grants Council (Grant No. HKU7384/02P), HKSAR, and The University of Hong Kong (University Development Fund). G.-Y.L. and Z.-J.X. thank the Croucher Foundation of Hong Kong for postgraduate studentships. P.W.H.C. thanks The University of Hong Kong (Small Project Funding Program) for funding.

**Supporting Information Available:** Tables and figures giving UV/vis spectral data and spectra of **2**−**4**, cyclic voltammograms of **1d**−**f**, **3b**−**d**, and **4**, and perspective views of **3b**−**d** and **4** and CIF files giving crystallographic data for **1a**, [Ru(2-Br-salen)(CO)(MeIm)], **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051009I

(34) SHELXL97: Sheldrick, G. M. SHELX97: Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen, Göttingen, Germany, 1997.

(35) Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology*; Carter, C. W., Sweet, R. M., Jr., Eds.; Academic Press: New York, 1997; Vol. 276, Macromolecular Crystallography, Part A, p 307.

(36) SHELXS97: Sheldrick, G. M. SHELX97: Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen, Göttingen, Germany, 1997.