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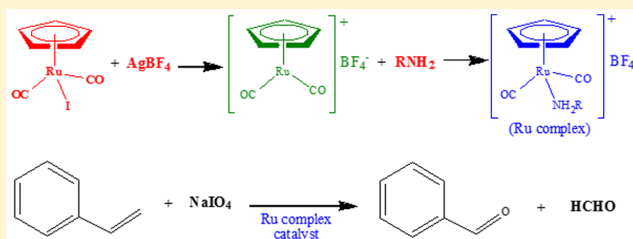
Synthesis and Characterization of New (η^5 -Cyclopentadienyl)dicarbonylruthenium(II) Amine Complexes: Their Application as Homogeneous Catalysts in Styrene Oxidation

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S Supporting Information

ABSTRACT: The water-soluble ruthenium(II) mononuclear complexes $[\text{CpRu}(\text{CO})_2\text{NH}_2\text{R}]\text{BF}_4$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{R} = \text{C}_6\text{H}_{11}$ (1), C_6H_5 (2), $\text{CH}_2\text{C}_6\text{H}_5$ (3), $\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ (4), $\text{CH}_2(\text{C}_6\text{H}_4\text{O})\text{CH}_3$ (5), $\text{CH}_2(\text{C}_6\text{H}_4)\text{CN}$ (6), $\text{C}_6\text{H}_2(\text{CH}_3)_3$ (7), CH_2CHCH_2 (8), $\text{CH}(\text{CH}_3)_2$ (9)) were synthesized from the reaction of the organometallic Lewis acid $[\text{CpRu}(\text{CO})_2]\text{BF}_4$ with amine ligands at room temperature. These complexes are reported for the first time and have been fully characterized by IR, high-resolution mass spectrometry, ^1H and ^{13}C NMR spectroscopy, and elemental analysis. Spectral data show that the amines are σ -bonded to the metal center via the nitrogen atom. The crystal structures of complexes 3 and 8 were determined by single-crystal X-ray crystallography. The 4-methoxybenzylamine, 4-aminomethylbenzonitrile and allylamine groups preferentially bind to the metal center via the amine nitrogen. The ruthenium complexes 1, 3–6, 9, and $[\text{CpRu}(\text{CO})_2\text{NH}_2\text{CH}_3]\text{BF}_4$ (10) and the dinuclear complex $[\text{CpRu}(\text{CO})_2\text{NH}_2(\text{CH}_2)_6\text{NH}_2(\text{CO})_2\text{Ru}(\text{Cp})][\text{BF}_4]_2$ (11) demonstrated excellent catalytic activity in the oxidation of styrene using NaIO_4 as the co-oxidant with over 95% conversion and benzaldehyde yields, respectively, in some cases.



INTRODUCTION

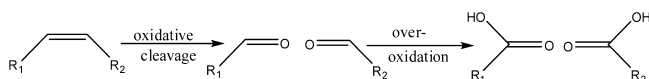
The development of the organometallic chemistry of ruthenium complexes is of great interest due to their multiple applications in many different scientific fields, ranging from biomedicine to catalysis.^{1–4} Ruthenium complexes containing the cyclopentadienyl group have been the subject of investigation by many research groups during the past few decades because of their widespread applications in transition-metal-catalyzed organic syntheses.^{5–11} Extensive studies have been carried out on methods for specific catalytic oxidations of various organic substrates such as alcohols, amines, amides, and hydrocarbons using low-valent ruthenium complexes.^{12,13}

Oxidation catalysis represents the core of a variety of useful chemical processes for producing bulk and fine chemicals. One such process is the oxidation of olefins, which can give a variety of products depending on the conditions of the reaction. Olefin oxidation, for example, can take place by epoxidation, dihydroxylation, vinylic and allylic oxidation, or $\text{C}=\text{C}$ double bond cleavage (Scheme 1). The oxidative cleavage of a $\text{C}=\text{C}$ double bond involves cleaving the double bond with inclusion of oxygen into the two fragments, forming aldehydes and/or ketones, depending on the extent of substitution. Over-

oxidation of the products may result in the formation of carboxylic acids.

Oxidative cleavage of olefinic double bonds to carbonyl compounds can be achieved by ozonolysis and stoichiometric oxidation processes.^{14–16} It can be effected by conversion of olefins into 1,2-diols, followed by cleavage with NaIO_4 or other co-oxidants,¹⁷ or by direct cleavage into a variety of functionalized products, depending on the workup conditions.^{18–20} The direct oxidative cleavage of olefinic double bonds is largely achieved at the industrial level by the use of ozone. The large-scale use of ozone for this application has major drawbacks, because of safety issues and the need to use expensive equipment.²¹ There are relatively few alternative reactions that duplicate the direct cleavage of olefins without formation of 1,2-diols.^{22,23} Stoichiometric amounts of some transition-metal compounds have been successfully used in the oxidative cleavage of olefinic double bonds. KMnO_4 , for instance, oxidizes olefins to aldehydes²⁴ or carboxylic acids^{25–27} in water as the solvent, but the organic substrates formed are often poorly soluble in the aqueous reaction medium. In addition, KMnO_4 cannot be used in catalytic amounts due to the irreversible precipitation of MnO_2 after oxidation of the substrate. On the other hand, chromyl chloride (CrO_2Cl_2)²⁸ oxidizes styrene into benzaldehyde and phenylacetaldehyde²⁹ but its use is discouraged due to the high toxicity of chromium(VI) salts. Osmium tetroxide, OsO_4 , has been

Scheme 1. General Illustration of the Oxidative Cleavage of Substituted Alkenes



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successfully used in stoichiometric amounts and as a catalyst in the oxidation of olefins to diols and carboxylic acids, but the main drawback in its use is its high toxicity.^{30,31}

Simple ruthenium compounds, such as $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, RuO_2 , and RuO_4 , have been successfully used as catalysts for the direct oxidative cleavage of the olefinic double bonds to form aldehydes and carboxylic acids. They form a variety of reactive, high-valent oxo complexes with rich redox chemistry. $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, for instance, has been used as a catalyst for the oxidative cleavage of alkenes to acids.^{22,32,33} To achieve the cleavage, NaIO_4 , NaOCl , and oxone (KHSO_5) were used as co-oxidants in different solvent systems. Most of the oxidative cleavage reactions of the olefinic double bonds gave carboxylic acids, but for the reaction where oxone was the primary oxidant with NaHCO_3 , benzaldehyde was formed.²² In addition, $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ and 2–6 equiv of NaIO_4 in $\text{CCl}_4/\text{H}_2\text{O}$ have been used to cleave electron-poor cyclic enolic olefins ($\text{C}=\text{C}$ bond on the β -position) to aldehydes in 35–95% yield.³⁴

The use of catalytic amounts of ruthenium complexes in the oxidative cleavage of olefinic double bonds improves selectivity toward the cleavage products, while preventing side reactions such as epoxidation, dihydroxylation, and allylic oxidation. The coligand coordinated to the metal plays a major role in improving the catalytic activity as well as the selectivity of the catalyst. A few ruthenium complexes, as oxidation catalysts, have demonstrated good selectivity, leading to the formation of $\text{C}=\text{C}$ double bond cleavage products. For example, the complex $\text{cis}[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}$ was reported to be a good catalyst in the chemoselective degradation of aromatic rings to acids, with NaIO_4 as the co-oxidant, and oxidative cleavage of alkenes to acids, with $\text{IO}(\text{OH})_3$ as the co-oxidant, in a CCl_4 – MeCN – H_2O biphasic solvent system.³⁵ The ruthenium complex $[\text{cis-Ru}^{\text{II}}(\text{dmp})_2(\text{H}_2\text{O})_2]^{2+}$ (dmp = 2,9-dimethylphenanthroline) demonstrated good catalytic activity in the oxidative cleavage of terminal alkenes to aldehydes using H_2O_2 as the oxidant in acetonitrile at 55 °C.³⁶ Even though ruthenium complexes are more efficient and selective catalysts for the oxidative cleavage of alkenes to aldehydes than ruthenium salts and oxides, little attention has been given to their catalytic activity. We have studied (η^5 -cyclopentadienyl)-iron and -ruthenium carbonyl complexes with nitrogen-containing species in order to develop their chemistry and also to study their catalytic and antimicrobial activities. The synthesis and characterization of the (η^5 -cyclopentadienyl)-dicarbonyliron and -ruthenium complexes of *n*-alkanamines,³⁷ α,ω -diaminoalkanes,³⁸ and *N*-heterocyclic ligands (DABCO, HMTA, and methylimidazole) were reported.^{39,40}

We now report the synthesis of nine new water-soluble ruthenium(II) complex salts, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{NH}_2\text{R}]\text{Y}$ ($\text{Y} = \text{BF}_4, \text{CF}_3\text{SO}_3$; $\text{R} = \text{C}_6\text{H}_{11}$ (1), C_6H_5 (2), $\text{CH}_2\text{C}_6\text{H}_5$ (3), $\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ (4), $\text{CH}_2(\text{C}_6\text{H}_4\text{O})\text{CH}_3$ (5), $\text{CH}_2(\text{C}_6\text{H}_4)\text{CN}$ (6), $\text{C}_6\text{H}_2(\text{CH}_3)_3$ (7), CH_2CHCH_2 (8), $\text{CH}(\text{CH}_3)_2$ (9)) (Figure 1), their catalytic activity, and also the catalytic activity of $\text{CpRu}(\text{CO})_2\text{NH}_2\text{CH}_3\text{BF}_4$ (10) and $[\text{CpRu}(\text{CO})_2\text{NH}_2(\text{CH}_2)_6\text{NH}_2(\text{CO})_2\text{Ru}(\text{Cp})][\text{BF}_4]_2$ (11) in the oxidation of styrene with NaIO_4 . To the best of our knowledge, these ruthenium complexes and their catalytic activity in the oxidation of alkenes have not been reported previously.

RESULTS AND DISCUSSION

Synthesis and Characterization. The mononuclear complexes $[\text{CpRu}(\text{CO})_2\text{NH}_2\text{R}]\text{BF}_4$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{R} = \text{C}_6\text{H}_{11}$ (1), C_6H_5 (2), $\text{CH}_2\text{C}_6\text{H}_5$ (3), $\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ (4),

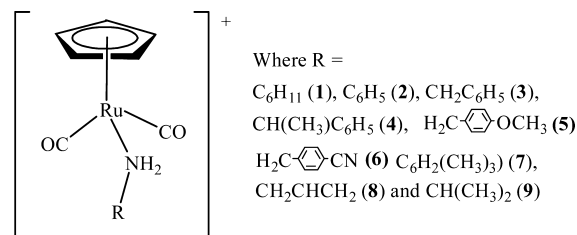


Figure 1. Ruthenium(II) complexes synthesized and catalytic activity tested in the homogeneous oxidation of styrene.

$\text{CH}_2(\text{C}_6\text{H}_4\text{O})\text{CH}_3$ (5), $\text{CH}_2(\text{C}_6\text{H}_4)\text{CN}$ (6), $\text{C}_6\text{H}_2(\text{CH}_3)_3$ (7), CH_2CHCH_2 (8), $\text{CH}(\text{CH}_3)_2$ (9)) (Figure 1) were formed in good yields from the reaction of the organometallic Lewis acid $[\text{CpRu}(\text{CO})_2]\text{BF}_4$ with the respective amines at room temperature. The complexes form white, air-stable crystals which are generally soluble in polar solvents such as water, methanol, acetone, acetonitrile, and dimethyl sulfoxide and in the chlorinated solvents chloroform and methylene chloride in some cases but are insoluble in nonpolar solvents such as hexane and diethyl ether. The elemental analysis and high-resolution mass spectrometry results for the complexes correlate with the calculated values; this is an indication that the complexes were formed as predicted.

The ^1H NMR data for the complexes were obtained and peaks were assigned using 2D NMR, as well as D_2O tests for the amine protons. The ^1H NMR spectra for the complexes in CDCl_3 , CD_3CN , and D_2O showed a sharp singlet peak in the region ca. 5.60–5.75 ppm, assignable to the five equivalent Cp protons. This is an indication that the ligands in complexes 5, 6, and 8, which have two possible coordination sites, bonded to the metal center via only one of the sites. Coordination to both sites would have shown either a single peak or two peaks in the same region, ca. 5.60–5.75 ppm, but with peaks assignable to 10 protons for the Cp peaks in the ^1H NMR spectrum. Regioselective coordination of the metal to the NH_2 is clearly indicated by the downfield shift in the amine proton peaks, in the ^1H NMR spectra of compounds 5, 6, and 8, relative to those of the uncoordinated ligands. For complexes 1, 8 and 9, a singlet peak in the ^1H NMR spectra obtained in CDCl_3 was observed at ca. 3.70, 3.79, and 3.78 ppm, respectively, and assigned to the two amine protons. The amine proton signals in the complexes were observed more downfield in comparison to those of the free ligand peaks (approximately 2 ppm), probably due to the deshielding by the metal center; this is an indication of coordination of the amines to the metal center through the N atom.³⁷ Hydrogen bonding between the amine group protons and the fluoride atoms of the tetrafluoroborate counteranion can also contribute to the downfield shift of the amine protons in the ^1H NMR spectra. The amine proton peaks for complexes 2, 3, and 5–7 were observed more downfield than those for 1, 8, and 9 due to the electron-withdrawing effect of the aromatic ring. It is worth noting that, whereas the amine group proton peak for the free ligand in complex 4 was observed as a singlet peak at ca. 1.59 ppm, two singlet peaks were observed at ca. 4.28 and 4.01 ppm for the complex in the ^1H NMR spectrum in CD_3CN . This is an indication that the two NH_2 protons are diastereotopic. The reason only one NMR signal is observed for the NH_2 protons in the free amine is rapid inversion on the N center, which cannot happen when the amine is coordinated to Ru. The ^1H NMR spectrum of complex 8 shows well-resolved characteristic

olefinic peaks; a multiplet peak assignable to the single proton attached to the β -carbon atom was observed at ca. 5.88 ppm, and two doublets were observed at ca. 5.42 and 5.27 ppm, each integrating for one proton, assignable to the two nonequivalent protons H_a and H_b , respectively, on the γ -carbon atom (Figure 2). These values are within the range reported for the

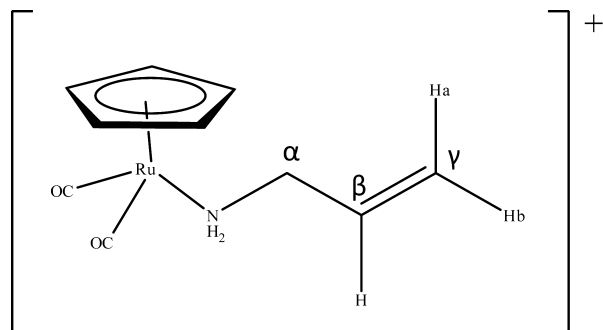


Figure 2. Structure of the 3-aminopropyl-1-ene (allylamine) ruthenium complex 8.

analogous iron complexes.³⁹ The protons on the α -carbon atom exhibited a quartet at ca. 3.30 ppm, a 0.35 ppm shift downfield from that reported for the iron complex analogue.³⁹

The ^{13}C NMR spectra of the complexes show two peaks at ca. 87.8 and 195.7 ppm, corresponding to the five equivalent Cp carbons and two identical carbonyls, respectively. Unlike the rest of the complexes, the ^{13}C spectrum of complex 4 shows two Cp peaks at 87.97 and 87.95 ppm and two CO peaks at 195.99 and 195.59 ppm. This is a further indication that the Cp and CO ligands are diastereotopic. The ^{13}C NMR spectrum of 8 clearly shows peaks corresponding to the allylic carbon atoms at ca. 135.17 and 118.57 ppm for the β - and γ -carbon atoms, respectively.

The IR spectra of complexes 1–9 showed $\nu(\text{CO})$ absorption bands in the expected region for terminal carbonyl groups for amine-coordinated metal complexes.^{37,39–41} The $\nu(\text{CO})$ absorption bands were observed as two strong peaks, one in the region ca. 2061–2049 cm^{-1} for the asymmetric CO stretching vibrations and one at ca. 2016–1987 cm^{-1} for symmetric CO stretching vibrations. It is worth noting that the symmetric CO stretching frequency for the cyclohexylamine complex 1 is lower than those observed for complexes 2–7, which have the phenyl ring as a substituent of the amine group. This can be attributed to the fact that the cyclohexyl group, a strong electron donor, increases electron density at the ruthenium center from the amine σ donation. The electrons are thus passed to the CO π^* orbital, and this is reflected in a decreased $\nu(\text{CO})$ stretching frequency, which corresponds to weaker CO bonds. The symmetric $\nu(\text{CO})$ stretching frequency for complex 6 is greater than that for complex 5, probably because the nitrile group substituent in the para position of the phenyl ring in 6 is electron withdrawing, while the methoxy group, a para substituent in the phenyl ring in complex 5, is electron donating.

The IR spectra also show two characteristic absorption bands in the regions ca. 3325–3270 and 3293–3264 cm^{-1} , which correspond to the NH_2 asymmetric and symmetric peaks, respectively. These bands are found at wavenumbers lower than those for the uncoordinated ligands, due to coordination of the amine functionality to the metal center and likely due to the participation of the NH_2 protons in hydrogen bonding.

Molecular structure of complexes 3 and 8. Crystals for complexes 3 and 8 suitable for single-crystal X-ray analysis were obtained by layering with diethyl ether an acetonitrile solution of each. Their molecular structures were determined by X-ray diffraction, giving the molecular structures shown in Figures 3

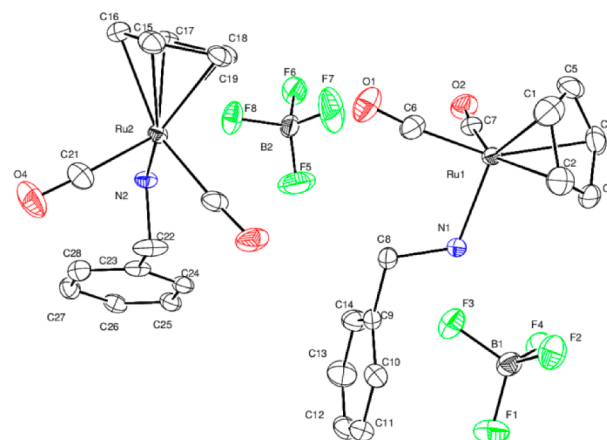


Figure 3. Molecular structure of complex 3 showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are not shown for clarity.

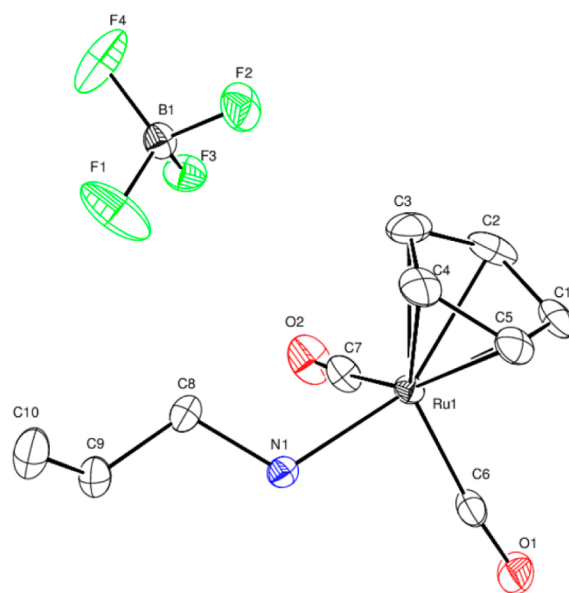


Figure 4. Molecular structure of complex 8 showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are not shown for clarity.

and 4. Important bond distances and angles for both complexes are given in Table 1. Complex 3 crystallizes with four nonsymmetrically related molecules in its asymmetric unit: two cationic molecules, $[\text{CpRu}(\text{CO})_2\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2]^+$, and two counteranions, BF_4^- . However, complex 8 crystallizes with two molecules in its asymmetric unit: one cationic molecule, $[\text{CpRu}(\text{CO})_2\text{CH}_2\text{CHCH}_2\text{NH}_2]^+$, and one counteranion.

Coordination around the ruthenium center is the same in both complexes. The amine ligands coordinate to the ruthenium centers of the $\text{CpRu}(\text{CO})_2$ moieties via the nitrogen atoms by σ bonds. The Cp ligand and the two carbonyl ligands

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for Complexes 3 and 8

bond param ^a	3		8
	molecule 1	molecule 2	
Cg–Ru	1.866	1.867	1.870
Ru–N	2.146(1)	2.138(2)	2.140(1)
N–C	1.488(2)	1.479(3)	1.486(2)
NC–C	1.506(3)	1.505(3)	1.492(3)
C=C			1.316(3)
Cg–Ru–N	122.68	122.84	124.11
Ru–N–C	118.9(1)	119.4(1)	115.60(2)
N–C–C	112.3(2)	113.0(2)	113.1(1)
Cg–Ru–N–C	150.10	162.57	71.40
Ru–N–C–C	173.4(1)	176.1(1)	179.3(1)

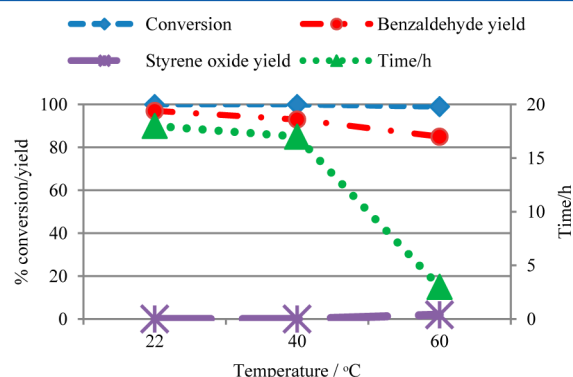
^aCg is the centroid of the Cp ring.

occupy the remaining coordination sites resulting in distorted-octahedral coordination geometries around the ruthenium centers. Within these geometries the Cp ligands occupy three coordination sites and the remaining three sites are occupied by the two carbonyl ligands and the amine in what is normally referred to as a “pseudo-octahedral three-legged piano stool”. In the stool the Cp ligands occupy the apical position with the carbonyl and amine ligands serving as the legs. Bond parameters in the two complex salts in 3 and in 4 are similar. The Ru–N bond lengths are comparable to similar Ru–N bond lengths of previously reported (η^5 -cyclopentadienyl)-dicarbonylruthenium(II) *n*-alkylamine complexes: 2.139(1) Å for [CpRu(CO)₂NH₂CH₂CH₃](BF₄), 2.1406(12) Å for [CpRu(CO)₂NH₂(CH₂)₂CH₃](BF₄), and 2.139(1) Å for [CpRu(CO)₂NH₂(CH₂)₃CH₃](BF₄).³⁷ The coordinated allylamine bond lengths (N–C, 1.484(8) Å; C–C_{allyl}, 1.498(8) Å; C=C, 1.300(9) Å) in the iron complex CpFe(CO)₂NH₂CH₂CHCH₂](BF₄) are comparable to those found for complex 8. This implies that the metal center does not affect the bond lengths within the allylamine ligand. As previously observed for CpFe(CO)₂NH₂CH₂CHCH₂](BF₄),³⁹ the C=C bond distance in the allylamine coordinated to the ruthenium center is slightly shorter than the formal C=C double bond (1.34 Å)^{40,42} but is comparable with the calculated distances for a terminal C=C bond: 1.315 Å for ethylene, 1.316 Å for propene, and 1.321 Å for 2-methylpropene.⁴³ The bond angles of complex 3 and 8 are comparable to those of (η^5 -cyclopentadienyl)dicarbonylruthenium(II) amine complexes: Cg–Ru–N, 122.92–124.08 Å; Ru–N–C, 113.2–118.53 Å.³⁷ In the crystal structures of complexes 3 and 8, the cations are linked to the anions through a series of weak N–H⋯F and C–H⋯O intermolecular interactions that stabilize the crystal lattices.

Catalytic Oxidation of Styrene. Oxidative cleavage of the olefinic carbon–carbon bond in styrene has been achieved in very good conversions and benzaldehyde yields using sodium periodate (NaIO₄) as the co-oxidant and the (η^5 -cyclopentadienyl)dicarbonylruthenium(II) complexes as catalysts. Acetonitrile/water (1/1 v/v; 6 mL) was selected as the solvent system, because of the need to have all the reagents and catalysts in the same phase. Complex 1 was used as the model catalyst for optimization studies. The solubility of the substrate and oxidant and, hence, homogeneity of the system depends on temperatures higher than ambient.

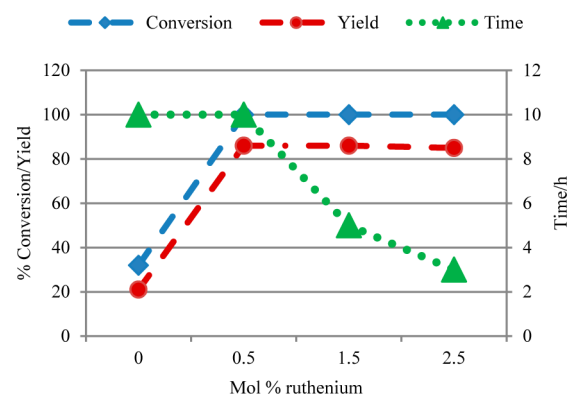
At 22 and 40 °C, more than 99% conversion and 90% benzaldehyde yield is achieved in 18 and 17 h, respectively

(Figure 5). At 60 °C, a homogeneous mixture is obtained and more than 99% conversion and 85% benzaldehyde and 2%

**Figure 5.** Effect of temperature on the conversion and yield for the ruthenium complex catalyzed oxidation of styrene. Reaction conditions: 0.478 mmol of styrene, 3 equiv of NaIO₄, 2.5 mol % of complex 1, CH₃CN/H₂O (3 mL/3 mL). The time to achieve the highest conversion is given in hours.

styrene oxide yields are achieved in 3 h. The temperature of 60 °C was chosen for all catalytic reactions, since it gave a homogeneous mixture and high conversion in a shorter time.

The oxidative cleavage of styrene with 3 equiv of NaIO₄ in the absence of the ruthenium complexes affords 32% conversion and 21% benzaldehyde yield in 10 h, while in the presence of 2.5 mol % of the ruthenium complexes, the conversion and benzaldehyde yield rise to 99% and 85%, respectively, in 3 h (Figure 6).

**Figure 6.** Effect of catalyst concentration on the oxidative cleavage of the olefinic double bond in styrene. Reaction conditions: 0.478 mmol of styrene, 3 equiv of NaIO₄, *x* mol % of complex 1, CH₃CN/H₂O (1/1; 6 mL) at 60 °C. The time taken to achieve the highest conversion is given in hours.

This is a clear indication that the ruthenium complexes reported herein are effective catalysts for the oxidative cleavage of the olefinic carbon–carbon bond in styrene (Scheme 2).

It was noted that the conversion, yield, and time needed for the reaction to go to completion are proportional to the amount of the co-oxidant used. Studies done on the effect of co-oxidant concentration on the reaction progress indicate that an excess of the co-oxidant is necessary for the reaction to give 100% conversion (Figure 7).

This observation augments the step in the proposed mechanism where the intermediate product, the metal diether,

Scheme 2. General Equation for the Oxidative Cleavage of Styrene to Benzaldehyde

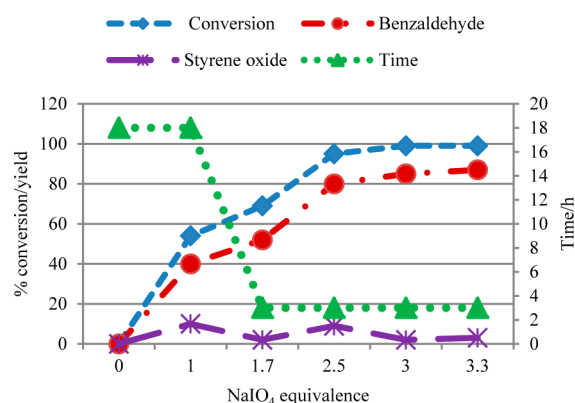
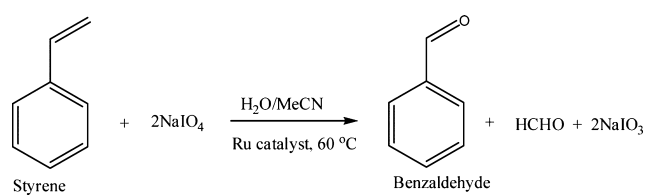
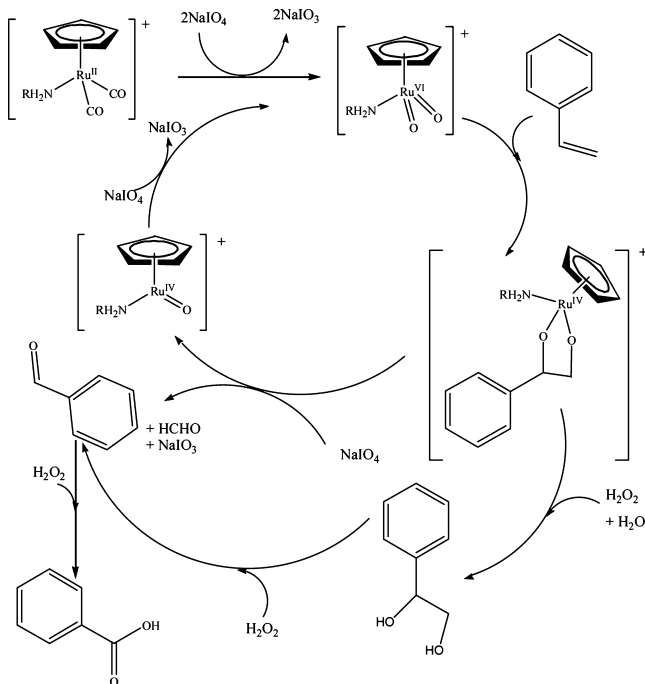


Figure 7. Effect of NaIO₄ concentration on the percent conversion and percent benzaldehyde yield for the ruthenium complex catalyzed oxidation of styrene. Reaction conditions: 0.478 mmol of styrene, x equiv of NaIO₄, 2.5 mol % of complex 1, CH₃CN/H₂O (3 mL/3 mL) at 60 °C. The time taken to achieve the highest conversion is given in hours.

requires “oxygen” to form the benzaldehyde (Scheme 3). Hence, 3 equiv of NaIO₄ was selected as the optimum amount of oxidant suitable for the process.

The use of hydrogen peroxide and K₂S₂O₈ as co-oxidants in the oxidation of styrene in the presence of the ruthenium

Scheme 3. Proposed Mechanism for the Ruthenium(II) Complex Based Catalyzed Oxidation of Styrene⁴⁴



complex catalysts was compared with that of NaIO₄. It was observed that NaIO₄ gave excellent conversion and yield under the reaction conditions to afford benzaldehyde. Hydrogen peroxide as an oxidant gave good conversion (86%) but low yields of benzaldehyde (23%) and styrene glycol (9%) in 18 h (Figure 8). The rest of the product was confirmed to be

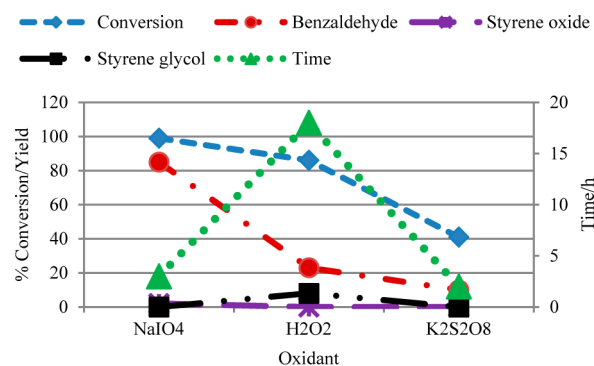


Figure 8. Oxidation products from different oxidants for the ruthenium complex catalyzed oxidation of styrene. Reaction conditions: 0.478 mmol of styrene, 3 equiv of oxidant, 2.5 mol % of complex 1, CH₃CN/H₂O (3 mL/3 mL) at 60 °C. The time taken to achieve the highest conversion is given in hours.

benzoic acid, an indication that overoxidation of benzaldehyde had taken place. The styrene glycol is probably formed as an intermediate product which is eventually oxidized to benzaldehyde.⁴⁴ The reaction with K₂S₂O₈ as an oxidant, for the oxidation of styrene, was noted to have stopped at 2 h, giving a maximum of 40% conversion. NaIO₄ was thus retained as the best primary oxidant for the oxidative cleavage of the olefinic C–C bond.

The effect of basic, acidic, and neutral conditions on the catalytic oxidation of styrene was investigated and revealed that the conversion of styrene is highest under neutral and acidic conditions (Figure 9). This implies that a base is not suitable, while an acid is not essential for the reaction to proceed to completion. Thus, the environmentally more friendly neutral conditions were selected for all other tests.

Once 100% styrene conversion is achieved, the reaction mixture turns from colorless to orange. The catalyst present in

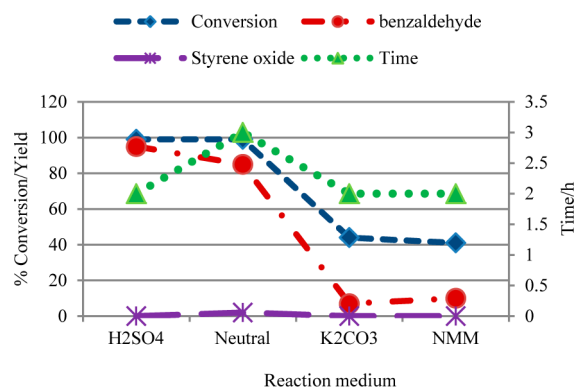


Figure 9. Effect of acidic, basic, and neutral conditions on the ruthenium complex catalyzed oxidation of styrene. Reaction conditions: 0.478 mmol of styrene, 3 equiv of NaIO₄, 2.5 mol % of complex 1, CH₃CN/H₂O (1/1; 6 mL) at 60 °C. The time taken to achieve the highest conversion is given in hours.

the mixture at the end of the reaction was shown to have the ability to catalyze the oxidation of fresh styrene to give 100% conversion and more than 99% benzaldehyde yield. Furthermore, complete conversion was achieved within a shorter time with the “reused” catalyst in comparison to that when fresh catalyst was used. This may imply that the (η^5 -cyclopentadienyl)dicarbonylruthenium(II) complex is converted to a catalytically active intermediate which is not deactivated at the end of the reaction. It is worth noting that, when further catalytic tests were consecutively done on the resulting mixture, the catalytic activity gradually decreased. This may be an indication that the catalytic species present in the mixture gradually deactivates/decomposes.

The catalytic activity of the dark orange oil obtained from the reaction mixture, in this study, was tested. Gas chromatographic analysis done on the mixture immediately after mixing showed that the reaction was very fast, since the conversion of styrene already was greater than 98%, with an 84% yield to benzaldehyde determined after 1 h (Figure 10). This is a clear indication that the dark orange compound is catalytic in nature.

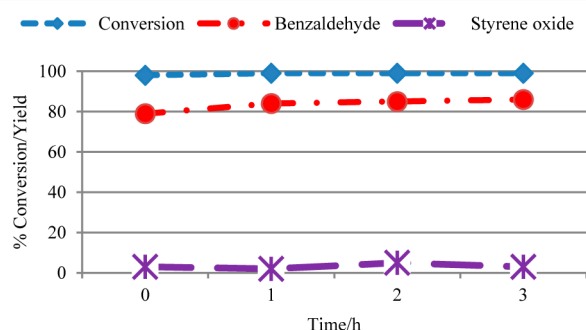


Figure 10. Catalytic activity of the orange compound obtained from the reaction mixture.

The UV–vis spectrum obtained for the dark orange compound recovered at the end of the reaction, with model catalyst, showed a peak at ca. 360 nm (Figure 11). A similar

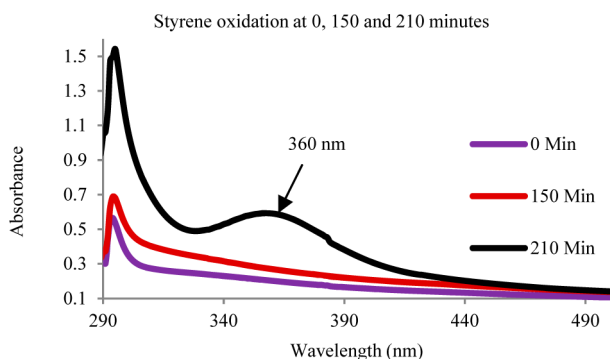


Figure 11. Electronic spectra of samples obtained at different times in the catalyzed reaction using 2.5 mol % of complex 1.

peak was observed by Goldstein and Drago, at 365 nm, and was assigned to the $\text{Ru}^{\text{VI}}=\text{O}$ species.⁴⁵ Their study was based on the hydroxylation of methane by hydrogen peroxide as the co-oxidant and $\text{cis-}[\text{Ru}(\text{dmp})_2\text{S}_2](\text{PF}_6)$ (dmp = 2,9-dimethyl-1,10-phenanthroline, S = Me_3CN , H_2O) as the catalyst.

The difference in peak positions may be attributed to the different coordination environments of the complexes reported

herein and those used by Goldstein and Drago. This peak may, therefore, be assigned to a dioxoruthenium(VI) complex species formed as an intermediate in the catalytic oxidation of styrene. It is worth noting that the peak at 360 nm in the UV–vis spectrum was absent in the spectra of the fresh catalyst and the reaction mixtures sampled at 30 min intervals (Figure 11). This implies that the dioxoruthenium species is highly active and hence is only seen in solution once styrene is depleted (Scheme 3). It is worth noting that the peaks observed by Goldstein and Drago at 395 and 425 nm assignable to Ru^{III} and $\text{Ru}^{\text{IV}}=\text{O}$, respectively, were absent in the UV–vis spectra of the recovered catalyst and the reaction mixtures examined (Figure 11). This could imply that, if the catalytic oxidation of styrene involves the formation of Ru^{III} and the postulated $\text{Ru}^{\text{IV}}=\text{O}$ species, these are very rapidly oxidized to $\text{Ru}^{\text{VI}}=\text{O}$ and hence are not detected.

The solid-state IR spectrum obtained for the recovered catalyst, from complex 1, showed new peaks at 793, 769, and 728 cm^{-1} possibly assignable to the symmetric and asymmetric stretches of $\text{Ru}=\text{O}$ bonds of $\text{Ru}(\text{VI})$ dioxo species.⁴⁶ No peaks were observed in the carbonyl region (between 2056 and 1998 cm^{-1}), an indication that the recovered catalyst does not contain coordinated CO ligand. A ^1H NMR spectrum obtained for the recovered catalyst showed a signal at ca. δ 5.67 ppm assignable to the five Cp protons and a peak at ca. δ 4.00 ppm assignable to the amine nitrogen protons. Since the proposed $\text{Ru}(\text{VI})$ dioxo species (d^2) would be paramagnetic in nature, the observed Cp and amine nitrogen proton signals in the ^1H NMR spectrum suggest that there is a diamagnetic species present.

Table 2 shows the results for the catalytic oxidation by 0.5 mol % of catalyst of the various ruthenium complexes under the optimized conditions.

Table 2. Ruthenium Complex (0.5 mol %) Catalyzed Oxidative Cleavage of the Styrene Olefinic Bond^a

complex	time (h) ^b	yield (%)	conversion (%) ^c	TON	TOF (h^{-1})
1	10	86	100	172	17
3	14	81	91	162	11
4	12	87	100	174	14
5	3	99	99	198	66
6	3	94	100	200	65
9	16	98	100	188	12
10	9	87	98	174	19
11	2	99	99	198	99
No	10	21	32	—	—

^aReaction conditions: 0.478 mmol of styrene, 3 equiv of NaO_4 , $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1/1; 6 mL) at 60°C . ^bThe time taken to achieve the highest conversion is given in hours. ^cConversion.

All the complexes tested afforded more than 90% styrene conversion and over 80% benzaldehyde yield. It is noteworthy that the oxidation process in the presence of the ruthenium dinuclear complex 11 has the highest turnover frequency (TOF) of 99 h^{-1} . This implies that the ruthenium center is directly involved in the oxidation process, since the mole percent in terms of ruthenium is twice as high as those for the mononuclear complexes; probably the oxo species are formed at both metal centers, thus doubling the catalysis rate. It is interesting to note that the mononuclear complexes containing 4-methoxybenzylamine (5) and 4-aminomethylbenzonitrile (6), with the ligand in 5 being more basic than that in 6, demonstrated very good activities with almost equal TOFs of

66 and 65 h⁻¹, respectively. In contrast, the TOF for the benzylamine complex (**3**) was noted to be 11 h⁻¹; the phenyl ring increases the basicity of the amine, thus increasing the π -back-bonding effect on the CO ligand and eventually strengthening the M–CO bond. This would decrease the rate at which the CO ligand is lost in the Ru(II) to Ru(VI) oxidation step, hence decreasing the reaction rate. This observation implies that the loss of CO, which is dependent on the electronic effect of the ligand, and the oxidation of Ru(II) to Ru(VI) steps may be rate determining in forming the working catalyst in the oxidative cleavage of the styrene olefinic double bond. It is worth noting that low TOFs, 12 and 14 h⁻¹, were observed for the complexes containing isopropylamine (**9**) and α -methylbenzylamine (**4**), respectively, in comparison to 19 h⁻¹ observed for the methylamine-containing complex (**10**). This may be due to, in addition to the aforementioned factors, steric hindrance on the metal center caused by the isopropylamine and α -methylbenzylamine groups, thus blocking the accessibility of the metal center by the co-oxidant and the substrate.

The turnover frequencies observed in this study are comparable to those reported by Kogan and co-workers,³⁶ who reported 1 mol % of the complex [*cis*-Ru^{II}(dmp)₂(H₂O)₂](PF₆)₂ as catalyst, but 10 equiv of hydrogen peroxide as oxidant, in a MeCN/H₂O solvent mixture at 60 °C, in the oxidation of styrene to benzaldehyde. They noted a TON of 92 and TOF of 15 h⁻¹. Catalytic oxidation studies of styrene and stilbene performed by Yang and co-workers using 3.5 mol % of RuCl₃ as a catalyst and oxone as oxidant in a basic medium at 60 °C revealed a TON of 21 and TOF of 42 h⁻¹.²²

The oxidation process catalyzed by 2.5 mol % of catalyst **1**, with the cyclohexylamine ligand, formed styrene oxide in addition to benzaldehyde. The complexes **3**–**6**, which contain a phenyl ring in the amine ligand, form benzaldehyde in high yield but styrene oxide is not observed. The expected byproduct, HCHO, was found in all reactions.

Tests performed on the catalytic oxidation of stilbene, a derivative of styrene, and 1-octene using NaIO₄ as the co-oxidant and 2.5 mol % complex **1** as a model catalyst resulted in oxidative cleavage of the olefinic bond and formation of the respective aldehydes in more than 99% yields (Table 3). This

clearly implies that the complexes synthesized in this study are likely excellent and versatile catalysts for the oxidative cleavage of olefinic carbon bonds to form aldehydes.

CONCLUSION


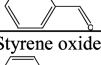
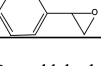
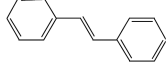
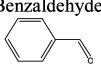

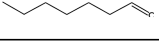
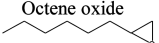
The (η^5 -cyclopentadienyl)dicarbonylruthenium(II) amine complexes [CpRu(CO)₂NH₂R]BF₄ have been successfully synthesized. The amine ligands are linked to the ruthenium center by a σ bond through the nitrogen atom. The 4-methoxybenzylamine, 4-aminomethylbenzonitrile, and allylamine groups preferentially bind to the metal center via the amine nitrogen. Some of the complexes have exhibited excellent catalytic activity in the oxidation of styrene with NaIO₄ to give up to 99% benzaldehyde yield, an increase from 21% achieved in the absence of catalyst. The “pseudo-octahedral three-legged piano stool” structure exhibited by the complexes seems to favor the formation of the *cis*-dioxoruthenium species required for the formation of the important intermediate 2 + 3 metal diether ring.²³ The configuration displayed by the ruthenium complexes favors the oxidative cleavage of the olefinic C–C bond of styrene and thus the formation of benzaldehyde in high yield. Bulky amine ligands seem to reduce the catalytic activity of the complexes. The recovered catalyst is very active in the oxidative cleavage of the olefin double bond of styrene.

EXPERIMENTAL SECTION

General Methods and Materials. Standard Schlenk techniques were employed for all reactions. Chemical reagents and solvents were obtained from the suppliers shown in parentheses. Reagent grade Et₂O (Merck) was distilled from sodium/benzophenone and stored over molecular sieves; dichloromethane was distilled from phosphorus(V) oxide. Silver tetrafluoroborate (Alfa Aesar), ruthenium trichloride hydrate (DLD-Aldrich), dicyclopentadiene, cyclohexylamine, aniline, benzylamine, α -methylbenzylamine, 4-methoxybenzylamine, trimethylamine, allylamine, carbon monoxide, and iodine were used as supplied. 4-Aminomethylbenzonitrile was obtained from 4-aminomethylbenzonitrile hydrochloride by neutralization using a stoichiometric amount of aqueous sodium hydroxide. Nitrogen gas was dried over phosphorus(V) oxide. Melting points were recorded on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. Elemental analyses were performed on a Thermo-Scientific Flash 2000 CHNS/O analyzer. Solid-state infrared spectra were recorded using an ATR PerkinElmer Spectrum 100 spectrophotometer between 4000 and 400 cm⁻¹. NMR spectra were recorded on Bruker Topspin 400 and 600 MHz spectrometers. The deuterated solvents CDCl₃ (Aldrich, 99.8%), C₂D₆SO and CD₃CN (Merck), and D₂O (Aldrich) were used as purchased. Solutions for NMR spectroscopy were prepared under nitrogen using nitrogen-saturated solvents. The high-resolution mass spectra for compounds **3**, **5**, and **6** were recorded on a Waters Synapt G2 instrument by injecting via the ESI probe into a stream of methanol. The precursors Ru₃(CO)₁₂,⁴⁷ [CpRu(CO)₂]₂ (Cp = η^5 -C₅H₅),⁴⁸ CpRu(CO)₂I,⁴⁹ [Cp(CO)₂Ru]BF₄,⁵⁰ and [Cp(CO)₂RuNCCH₃]₂BF₄⁵¹ were prepared by literature methods. The complexes in this work were synthesized by a modification of the method reported for the synthesis of the (η^5 -cyclopentadienyl)dicarbonylruthenium(II) *n*-alkanamine complex salts.³⁷ The ruthenium complexes **10** and **11** used for the catalytic study in this work were synthesized by previously reported methods.^{37,51}

Synthesis of the Complex Salts [CpRu(CO)₂NH₂R]BF₄. *Cyclohexylamine Complex Salt* [CpRu(CO)₂NH₂C₆H₁₁]BF₄ (**1**). CpRu(CO)₂I (0.1638 g; 0.4692 mmol), silver tetrafluoroborate (0.1261 g; 0.6478 mmol), and a magnetic stirrer bar were placed in a Schlenk tube wrapped in aluminum foil. The mixture was evacuated under reduced pressure for 3 h. Dichloromethane (DCM; 20 mL) was added and the mixture stirred for 1½ h. A white precipitate and orange mother liquor formed. The mother liquor was transferred into a clean Schlenk tube by cannula filtration and a slight excess of cyclohexyl-

Table 3. Catalytic Oxidation of Different Substrates^a

Substrate	Time (h) ^b	% conversion	Products	% yield
 Styrene	3	99	Benzaldehyde 	85
			Styrene oxide 	2
 Stilbene	1	100	Benzaldehyde 	100
 1-Octene	3	100	Heptanal 	98
			Octene oxide 	2

^aReaction conditions: 0.478 mmol of substrate, 3 equiv of NaIO₄, 2.5 mol % of complex **1**, CH₃CN/H₂O (1/1; 6 mL) at 60 °C. ^bThe time taken to achieve the highest conversion is given in hours.

amine (0.0820 g; 0.8268 mmol) added while stirring. The mother liquor immediately turned pale yellow. The mixture was stirred for 4 h at room temperature, left to stand for $\frac{1}{2}$ h, and then cannula-filtered under reduced pressure into a Schlenk tube. The solvent was completely removed by evaporation under reduced pressure, leaving a grayish white solid. Acetonitrile (2 mL) was added to the solid to extract the complex salt. The solution was left to stand for $\frac{1}{2}$ h and then filtered into a preweighed Schlenk tube. Diethyl ether (10 mL) was added, and the mixture was shaken and left to stand for 2 h. A white flaky precipitate formed, the mother liquor was filtered, and the precipitate was dried under reduced pressure. Yield: 0.1428 g, 74%. Mp: 188.8–189.2 °C. Anal. Found (calcd) for $C_{13}H_{18}BF_4NO_2Ru$: C, 38.15 (38.25); H, 4.52 (4.45); N, 3.39 (3.43). IR (solid state): $\nu_{\max}/\text{cm}^{-1}$ 2056 and 1999 (CO); 2953 and 2917 (CH₃); 3295 and 3264 (NH₂). ¹H NMR (400 MHz, CDCl₃): δ 5.60 (s, 5H, Cp), 3.70 (s, 2H, NH₂), 2.00 (m, 1H, C-1), 1.76 (m, 2H, C-2,6), 1.59 (m, 2H, C-2,6; 2H C-4), 1.23 (m, 4H, C-3,5). ¹³C NMR (400 MHz, CDCl₃): δ 195.94 (CO), 87.94 (Cp), 59.90 (C-1), 33.71 (C-2,6), 24.59 (C-4), 24.23 (C-3,5).

Phenylamine Complex Salt [CpRu(CO)₂NH₂C₆H₅]BF₄ (2). CpRu(CO)₂I (0.1240 g; 0.3552 mmol) and a slight excess of silver tetrafluoroborate (0.0892 g; 0.4582 mmol) were dried, dissolved in DCM (15 mL), and treated as described for compound 1. Excess phenylamine (0.0621 g; 0.6668 mmol) was added to the filtrate obtained, and the mixture was stirred for 8 h at room temperature. The rest of the procedure was performed as described for compound 1 to give a white solid. Yield: 0.0845 g, 58%. Mp: 116.8–117.6 °C. Anal. Found (calcd) for $C_{13}H_{12}BF_4NO_2Ru$: C, 38.92 (38.83); H, 3.16 (3.01); N, 3.51 (3.48). IR (solid state): $\nu_{\max}/\text{cm}^{-1}$ 2050 and 1992 (CO); 3310 and 3274 (NH₂). ¹H NMR (400 MHz, CD₃CN): δ 7.53–7.37 (m, 5H, C₆H₅), 5.68 (s, 5H, Cp), 4.41 (s, 2H, NH₂). ¹³C NMR (400 MHz, CD₃CN): δ 195.83 (CO), 128.44–128.04 (C-C₆H₅), 87.57 (Cp).

Benzylamine Complex Salt [CpRu(CO)₂NH₂CH₂C₆H₅]BF₄ (3). CpRu(CO)₂I (0.1760 g; 0.5042 mmol) and AgBF₄ (0.1276 g; 0.6555 mmol) were placed in a Schlenk tube wrapped with aluminum foil and treated as described for compound 1. Excess benzylamine (0.0992 g; 0.9265 mmol) was added to the resulting orange filtrate, and the mixture was treated as described for compound 2 to give a white solid. Yield: 0.0928 g, 44%. Mp: 136.7–137.6 °C. Anal. Found (calcd) for $C_{14}H_{14}BF_4NO_2Ru$: C, 40.37 (40.41); H, 3.34 (3.31); N, 3.35 (3.37). HRMS: $[C_{14}H_{14}NO_2Ru]^+$, m/z 330.0070 (330.0068). IR (solid state): $\nu_{\max}/\text{cm}^{-1}$ 2052 and 1986 (CO); 3325 and 3286 (NH₂). ¹H NMR (400 MHz, CD₃CN): δ 7.41–7.33 (m, 5H, C₆H₅), 5.60 (s, 5H, Cp), 4.04 (s, 2H, NH₂), 3.78 (t, 2H, CH₂). ¹³C NMR (400 MHz, CD₃CN): δ 195.57 (CO), 138.27 (C-CH₂), 128.57–128.12 (C₆H₅), 87.73 (Cp), 57.27 (CH₂).

(±)- α -Methylbenzylamine Complex Salt [CpRu(CO)₂NH₂(CH)₂C₆H₅]BF₄ (4). CpRu(CO)₂I (0.0953 g; 0.2730 mmol) and a slight excess of AgBF₄ (0.0701 g; 0.3601 mmol) were placed in a Schlenk tube wrapped with aluminum foil and treated as described for compound 1. Excess (±)- α -methylbenzylamine (0.0658 g; 0.5430 mmol) was added to the resulting orange solution and the mixture treated as described for compound 2 to give a white solid. Yield: 0.0673 g, 57%. Mp: 170.1–170.7 °C. Anal. Found (calcd) for $C_{15}H_{16}BF_4NO_2Ru$: C, 41.79 (41.88); H, 3.78 (3.75); N, 3.25 (3.26)%. IR (solid state): $\nu_{\max}/\text{cm}^{-1}$ 2054 and 1995 (CO); 3301 and 3266 (NH₂). ¹H NMR (400 MHz, CD₃CN): δ 7.45–7.33 (m, 5H, C₆H₅), 5.45 (s, 5H, Cp), 4.28 (s, 1H, NH₂), 4.01 (s, 1H, NH₂), 3.66 (m, 1H, CH), 1.49 (d, 3H, CH₃). ¹³C NMR (400 MHz, CD₃CN): δ 195.66 (CO), 195.59 (CO), 141.99 (C-CH), 128.74 (C-ortho), 127.03 (C-para), 129.14 (C-meta), 87.97 (Cp), 87.95 (Cp), 61.91 (CH₂), 23.99 (CH₃).

4-Methoxybenzylamine Complex Salt [CpRu(CO)₂NH₂CH₂(C₆H₄)OCH₃]BF₄ (5). CpRu(CO)₂I (0.0700 g; 0.2005 mmol) and a slight excess of AgBF₄ (0.04893 g; 0.2513 mmol) were placed in a Schlenk tube wrapped with aluminum foil and treated as described for compound 1. Excess 4-methoxybenzylamine (0.1213 g; 0.8842 mmol) was added to the resulting orange filtrate, and the mixture was stirred for 6 h. The resulting pale yellow solution was treated as described for

compound 2 to give a white solid. Yield: 0.0508 g, 57%. Mp: 174.9–175.6 °C. Anal. Found (calcd) for $C_{15}H_{16}BF_4NO_3Ru$: C, 40.37 (40.38); H, 3.59 (3.61); N, 3.13 (3.14). HRMS: $[C_{15}H_{16}NO_3Ru]^+$, m/z 360.0172 (360.0174). IR (solid state): $\nu_{\max}/\text{cm}^{-1}$ 2053, 2001, and 1974 (CO), 3306 and 3271 (NH₂). ¹H NMR (400 MHz, CDCl₃): δ 5.44 (s, 5H, Cp), 4.22 (s, 2H, NH₂), 7.25 (d, 2H, o-CH), 6.86 (d, 2H, m-CH), 3.64 (t, $J_{\text{HH}} = 7.04$ Hz, 2H, NCH₂), 3.75 (s, 3H, OCH₃). ¹³C NMR (400 MHz, CDCl₃): δ 195.14 (CO), 87.84 (Cp), 130.52 (C-CH₂), 129.45 (o-CH), 114.55 (m-CH), 160.1 (C-p-OCH₃), 56.29 (C-NH₂), 55.24 (OCH₃).

4-Aminomethylbenzonitrile Complex Salt [CpRu(CO)₂NH₂CH₂(C₆H₄)CN]BF₄ (6). CpRu(CO)₂I (0.160 g; 0.4583 mmol), AgBF₄ (0.1181 g; 0.6067 mmol), and a stirrer bar were placed in a Schlenk tube wrapped with aluminum foil and treated as described for compound 1. Excess 4-aminomethylbenzonitrile (0.1175 g; 0.8893 mmol) was dissolved in tetrahydrofuran (10 mL) and added to the filtrate, and the mixture was stirred for 4 h. The mother liquor was filtered into a clean Schlenk tube by use of a cannula. The solvent was completely removed by evaporation under reduced pressure, leaving a pale yellow oil. Acetonitrile (2 mL) was added to the oil, and the solution was left to stand for $\frac{1}{2}$ h and then filtered into a preweighed Schlenk tube. Diethyl ether (10 mL) was added to the filtrate, the mixture was shaken, and a white suspension appeared. The mixture was left undisturbed for 12 h. Shiny white crystals formed. The crystals were separated from the mother liquor and dried under reduced pressure. Yield: 0.1208 g, 59%. Mp: 177.2–178.0 °C. Anal. Found (calcd) for $C_{15}H_{13}BF_4N_2O_2Ru$: C, 40.82 (40.84); H, 3.01 (2.97); N, 6.28 (6.35). HRMS: $[C_{15}H_{13}N_2O_2Ru]^+$, m/z 355.0024 (355.0021). IR (solid state): $\nu_{\max}/\text{cm}^{-1}$ 2061 and 2006 (CO); 2229 (C≡N); 3306 and 3271 (NH₂). ¹H NMR (400 MHz, DMSO): δ 7.90 (d, 2H, m-CH), 7.59 (d, 2H, o-CH), 5.81 (s, 5H, Cp), 5.37 (s, 2H, NH₂), 3.78 (s, 2H, CH₂). ¹³C NMR (400 MHz, DMSO): δ 196.64 (CO), 144.41 (C-CH₂), 132.41 (m-CH), 129.29 (o-CH), 118.64 (CN), 110.61 (C-CN), 88.60 (Cp), 56.28 (C-7).

2,4,6-Trimethylaniline Complex Salt [CpRu(CO)₂NH₂(CH₃)₃C₆H₂]BF₄ (7). CpRu(CO)₂I (0.0728 g; 0.2085 mmol) and AgBF₄ (0.0598 g; 0.3072 mmol) were placed in a Schlenk tube wrapped with aluminum foil and treated as described for compound 1. Excess 2,4,6-trimethylaniline (0.0246 g; 0.4164 mmol) was added to the resulting orange filtrate, and the mixture was treated as described for compound 2 to give a white solid. Yield: 0.0571 g, 62%. The compound decomposes at temperatures above 188 °C. Anal. Found (calcd) for $C_{16}H_{18}BF_4NO_2Ru$: C, 43.24 (43.26); H, 4.05 (4.08); N, 3.17 (3.15). IR (solid state): $\nu_{\max}/\text{cm}^{-1}$ 2049, 1987, and 1953 (CO); 3270 (NH₂). ¹H NMR (400 MHz, CDCl₃): δ 6.73 (s, 2H, =CH), 5.68 (s, 5H, Cp), 5.42 (s, 2H, NH₂), 2.29 (s, 3H, p-CH₃), 2.19 (s, 6H, o-CH₃). ¹³C NMR (400 MHz, CDCl₃): δ 194.87 (CO), 140.98 (C-NH₂), 135.28 (C-p-CH₃), 130.19 (CH), 126.63 (C-o-CH₃), 88.08 (Cp), 20.56 (p-CH₃), 17.50 (o-CH₃).

Allylamine Complex Salt [CpRu(CO)₂NH₂CH₂CHCH₂]BF₄ (8). To a solution of [CpRu(CO)₂NCCH₃]BF₄ (0.1214 g; 0.3468 mmol) in DCM (20 mL) was added allylamine (0.0349 g; 0.6111 mmol) dropwise at room temperature, and the mixture was stirred for 12 h. The resulting pale yellow solution was evaporated to dryness, and the product was extracted with acetonitrile (5 mL). The mixture was filtered, and the volume of filtrate was reduced to about 2 mL. Diethyl ether (10 mL) was added to the extract, and a white precipitate formed. Filtration followed by drying of the residue under reduced pressure gave a white solid. Yield: 0.0874 g, 72%. The compound decomposes at temperatures >120 °C. Anal. Found (calcd) for $C_{10}H_{12}BF_4NO_2Ru$: C, 32.84 (32.81); H, 3.29 (3.30); N, 3.81 (3.83). IR (solid state): $\nu_{\max}/\text{cm}^{-1}$ 2059, 2016 (CO); 3315, 3280 cm^{-1} (NH₂). ¹H NMR (400 MHz, CDCl₃): δ 5.88 (m, 1H, C- β), 5.60 (s, 5H, Cp); 5.42 (d, 1H_v, C- γ trans); 5.27 (d, 1H_v, C- γ cis); 3.79 (s, 2H, NH₂); 3.30 (q, 2H, C- α). ¹³C NMR (400 MHz, CDCl₃): δ 196.00 (CO), 135.17 (C- β), 118.57 (C- γ), 88.04 (Cp), 55.97 (C- α).

Isopropylamine Complex Salt [CpRu(CO)₂NH₂CH(CH₃)₂]BF₄ (9). CpRu(CO)₂I (0.0982 g; 0.2813 mmol) and AgBF₄ (0.0602 g; 0.3092 mmol) were placed in a Schlenk tube wrapped with aluminum foil and treated as described for compound 1. Excess isopropylamine (0.0325

g; 0.5498 mmol) was added to the resulting orange solution, and the mixture was treated as described for compound 2. A white solid was formed. Yield: 0.0792 g, 77%; Decomposes at temperatures above 188 °C. Anal. Found (calcd) for $C_{10}H_{14}BF_4NO_2Ru$: C, 32.64 (32.63); H, 3.81 (3.83); N, 3.79 (3.81). IR (solid state): ν_{max}/cm^{-1} (CO) 2058, 2018 and 2002; 3331 and 3293 (NH_2). 1H NMR (400 MHz, DMSO): δ 5.80 (s, 5H, Cp), 4.80 (s, 2H, NH_2), 2.58 (m, 1H, CH), 1.08 (d, 6H, CH_3). ^{13}C NMR (400 MHz, DMSO): δ 196.00 (CO); 88.23 (Cp), 51.89 (C-2), 23.11 (CH_3).

X-ray Crystal Structure Determination of Compounds 3 and 8. Crystals of compounds 3 and 8 suitable for single-crystal X-ray diffraction studies were grown by the liquid diffusion method. Solutions of each of the compounds 3 and 8 in acetonitrile were layered with a 4-fold volume of diethyl ether and allowed to stand undisturbed in the dark at room temperature for 24 h to give white crystals. Crystals of compounds 3 and 8 were selected and glued onto the tip of glass fibers separately. The crystals were then mounted under a stream of cold nitrogen at 100(1) K and centered in the X-ray beam using a video camera. The rest of the manipulations were done as per the literature method.⁴¹ Crystal data and structure refinement information for compounds 3 and 8 are summarized in Table S1 in the Supporting Information.

Catalytic Studies. In a typical experiment, a known amount of the co-oxidant was placed in a dry Schlenk tube equipped with a magnetic stirrer bar under an atmosphere of nitrogen. Deionized water (3 mL) was added, and the mixture was stirred at a selected temperature until the co-oxidant dissolved completely (where applicable). The (η^5 -cyclopentadienyl)dicarbonylruthenium(II) amine complex and acetonitrile (3 mL) were added, and the mixture was stirred until all the ruthenium complex had dissolved. Styrene (0.478 mmol) and the internal standard, benzophenone (0.478 mmol), were added to the mixture in the Schlenk tube, and this mixture was stirred for 1 min and then sampled for gas chromatographic (GC) analysis. The stirring was continued and the progress of the reaction monitored hourly by GC. The complex $[CpRu(CO)_2NH_2C_6H_{11}]BF_4$ (1; 2.5 mol %) was used as the model catalyst for optimization of the catalytic conditions. Its catalytic activity was investigated at room temperature (22 °C) and 40 and 60 °C, with different co-oxidants at 60 °C, with different concentrations of $NaIO_4$ at 60 °C, in different solvent systems at 60 °C using the best co-oxidant, and in different reaction media (acidic (H_2SO_4), basic (K_2CO_3 and *N*-methylmorpholine), or neutral). The effect of varying the catalyst concentration on conversion and yield was also investigated under the chosen conditions using 0.5, 1.5, and 2.5 mol % of complex 1. The catalytic activities of the ruthenium complexes 1–6 and 9 were examined and compared under the optimized conditions. The percentage yield of benzaldehyde was calculated on the basis of the GC analysis with benzophenone as the internal standard. The time taken to achieve the highest conversion and benzaldehyde yield is given for each reaction, as presented in Figures 5–10. The best reaction conditions chosen for catalytic testing were 0.478 mmol of styrene, 3 equiv of $NaIO_4$, CH_3CN/H_2O (1/1; 6 mL) at 60 °C; any changed parameter is stated for each reaction. The time taken to achieve the highest conversion is given in hours.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-
met.5b00564.

Crystal data and structure refinement details for compounds 3 and 8 (CCDC 1053455 and 1053456) (PDF)

Crystallographic data for compound 3 (CIF)

Crystallographic data for compound 8 (CIF)

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Notes

The authors declare no competing financial interest.

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