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Synthesis, Structural Characterization and Catalysis of Ruthenium(II) Complexes Based on 2,5-bis(2'-pyridyl)pyrrole Ligand

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Abstract

Treatment of 2,5-bis(2'-pyridyl)pyrrolato (PDP') anion with $\{Ru(COD)Cl_2\}_n$ in THF readily yielded [Ru(PDP)(COD)Cl] (1) in almost quantitative yield. Anion metathesis of 1 in organic solvent by NO₃⁻ and OTf' (OTf = triflato) gave $[Ru(PDP)(COD)(NO_3)]$ (2) and [Ru(PDP)(COD)(OTf)] (3), and in aqueous solution by BF₄⁻ and PF₆⁻ afforded aqueous complexes $[Ru(PDP)(COD)(H_2O)](BF_4)$ (4⁺·BF₄⁻) and $[Ru(PDP)(COD)(H_2O)](PF_6)$ (4⁺·PF₆⁻), respectively. Treatment of 1 with PhICl₂ in CH₂Cl₂ afforded 5 with halogenated pyrrole. These complexes exhibits similar structure, including one Ru(II) atom, one 2,5-bis(2'-pyridyl)pyrrole and one monodentate anion or aqua ligand. Each Ru(II) tightly binds to three adjacent coplanar sites of PDP⁻ ligand to form a meridional configuration. Complex 1 with NaIO₄ as the oxidant in EtOAc-CH₃CN-H₂O (ratio = 3:1:2) is proved to be highly effective in the catalytic oxidation of olefins to carbonyl products.

Introduction

The oxidative cleavage of olefins to carbonyl products is a synthetically important reaction to introduce oxygen into organic molecules.^{1, 2} Transition-metal complexes as catalysts combined with a variety of co-oxidants such as oxone, H₂O₂, ^tBuOOH, PhI(OAc)₂, NaIO₄ and etc are used. The ruthenium complexes are one of the most popular catalysts for olefins oxidation due to being readily available to form ruthenium intermediates in high oxidation state.^{3,4} Recently, Bera and co-workers reported [Ru(COD)(L)Br₂] (L = imidazo[1,2-a][1,8]naphthyridine) as excellent catalyst toward oxidation of C=C bond to aldehydes for a wide range of substrates.⁵ The catalytic reaction starts from oxidation of COD ligand. The formed ruthenium-cis-dioxo intermediate is stabilized by aromatic naphthyridine ligand. Compared with the ruthenium salt and oxide without application of ligands, 6 [Ru(COD)(L)Br₂] has less loading, better selectivity, higher efficiency for olefin oxidation reactions. The rational design of ligand to stabilize the intermediate can enable the generation of superior catalysts. We have a long-standing interest in the metal complexes based on 2,5-bis(2'-pyridyl)pyrrolide (HPDP).⁷ HPDP ligand contains a large conjugated backbone, and its central pyrrolato N atom can behave as σ -donor and π -donor/acceptor corresponding to the metal electron properties. Thus, PDP⁻ anion is also capable of stabilizing metal center in low and high oxidation states.^{8,9} In some sense, aromatic properties of HPDP are similar to that of naphthyridine ligand in [Ru(COD)(L)Br₂], which forms favorable to make its ruthenium complex as a potential oxygen transfer catalyst. The ruthenium complexes containing bispyridylpyrrolide ligand,^{10, 11} such as [Ru(PDP)(bipy)]⁺, [Ru(PDP)(tpy)]⁺ and [Ru(PDP)₂], have been reported previously, however, these works were focused on the study of their syntheses and structures. Inspired by Bera's work, we herein will describe the preparation, structures of a set of ruthenium COD complexes based on HPDP ligand, and we also report their catalytic properties for olefin oxidation reactions.

Experimental Section

General Considerations. ¹H NMR spectrum was recorded on a Bruker AVANCE 500M spectrometer operating at 500 MHz, and chemical shifts (δ , ppm) were reported with reference to SiMe₄. Infrared spectra (KBr) were recorded on Nicolet 6700 spectrometer FT-IR spectrophotometer. Elemental analyses for C, H and N were performed on a Perkin Elmer 240C elemental analyzer. GC experiment was performed on a Kejie 5890F GC system with a FID detector. ESI-MS was performed in a Bruker Daltonik GmbH, Bremen mass spectrometer equipped with an electrospray ionization (ESI) source, and the experimental parameters were as follows: capillary temperature, 200 °C; capillary voltage, 4500 V; flow rate, 4 L/min; hexapole, 127 V. Potential measured in CH₃CN with 0.1 M [n-Bu₄N]PF₆ as supporting electrolyte; scan rate = 100 mVs⁻¹; $E_{1/2} = 1/2(E_{pa} + E_{pc})$; Glassy carbon working electrode, Pt counter electrode, reference electrode: AgNO₃/Ag (0.1 M acetonitrile); potentials reported in V vs $Cp_2Fe^{+/0}$. GC conditions: Chromatogram column: SE-30; Injection temperature: 200 °C; Detection temperature: 280 °C. The starting 2,5-bis(2'-pyridyl)pyrrole was prepared according to literature methods.^{12, 13} All of other chemicals were obtained from J&K Scientific.

Preparation of [Ru(PDP)(COD)CI] (1): A mixture of HPDP (718 mg, 3.25 mmol) and 60% NaH (130 mg, 3.25 mmol) in THF (30 mL) was stirred for about five minutes. To the resulting yellow solution was added {Ru(COD)Cl₂}_n (910 mg, 3.25 mmol). The reaction suspension mixture was stirred and kept refluxing overnight. The solvent was removed by vacuum, and the brown residual was re-dissolved in CHCl₃. The precipitate was filtered off. The darkish brown filtrate was layered with ether and hexane mixture to give brown crystals of **1**, which were suitable for X-ray diffraction study. Isolated yield: 1435 mg (95 %). ¹H NMR (CDCl₃): δ 8.62 (d, J = 4.36 Hz, 2H), 7.65 (t, J = 6.36, 5.86 Hz, 2H), 7.48(d, J = 6.42 Hz, 2H), 7.01(td, J = 5.30, 5.26 Hz, 2H), 6.73(s, 2H), 4.69(m, 2H), 2.95(m, 2H), 2.69(m, 2H), 2.49(m, 2H), 2.09(m, 2H),

1.92(m, 2H). ¹³C NMR (CDCl₃): δ 158.87, 153.27, 139.45, 137.29, 119.76, 118.59, 109.92, 95.38, 89.01, 30.77, 28.98. IR (KBr, cm⁻¹): 2908(w), 2846(w), 1599(s), 1499(s), 1429(w), 1396(s), 1298(m), 1272(w), 1231(w), 1146(m), 1051(w), 999(w), 873(w), 758(s), 509(w), 454(w). Anal. Calc. for RuClN₃C₂₂H₂₂: C, 56.83; H, 4.77; N, 9.04%. Found: C, 56.01; H, 4.90; N, 8.95%.

Preparation of [Ru(PDP)(COD)(NO₃)] (2): The mixture of **1** (763 mg, 1.64 mmol) and AgNO₃ (288 mg, 1.69 mmol) in THF (20mL) was stirred for 8 h. The resultant solution was filtered, and the filtrate was layered by ether to give brown crystals of **2**, which were suitable for X-ray diffraction study. Isolated yield: 739 mg (92 %). ¹H NMR (CDCl₃): δ 8.67 (d, J = 5.40 Hz, 2H), 7.70 (t, J = 7.32, 8.00 Hz, 2H), 7.49 (d, J = 8.00 Hz, 2H), 7.02 (t, J = 6.62, 6.62 Hz, 2H), 6.72 (s, 2H), 5.00 (m,2H), 2.93 (m, 2H), 2.67 (m, 2H), 2.58(m, 2H), 2.10 (m, 2H), 1.93 (m, 2H). ¹³C NMR (CDCl₃): δ 159.52, 153.35, 140.03, 138.06, 119.87, 118.85, 110.36, 96.04, 86.81, 30.92, 30.77, 28.11. IR (KBr, cm⁻¹): 2946(w), 2848(w), 1600(s), 1498(s), 1468(s), 1396(s), 1273(s), 1143(w), 1042(w), 982(m), 881(w), 755(m), 510(w), 453(w). Anal. Calc. for RuO₃C₂₂H₂₂N₄·H₂O: C, 51.86; H, 4.75; N, 11.00% . Found: C, 51.69; H, 4.53; N, 10.85%.

Preparation of [Ru(PDP)(COD)(OTf)] (3): Complex **3** was synthesized by the similar procedure with that of **2**, only using AgOTf in place of AgNO₃. Isolated yield: 571 mg (60 %). ¹H NMR (CDCl₃): δ 8.73 (t, J = 5.20, 5.24 Hz, 2H), 7.74 (m, 2H), 7.50 (t, J = 7.58, 7.96 Hz, 2H), 7.16 (t, J = 6.62, 6.64 Hz, 1H), 7.08 (td, J = 6.60, 6.66 Hz, 1H), 6.73 (d, J = 4.96 Hz, 2H), 5.08 (m, 2H), 3.01 (m, 1H), 2.93 (m, 1H), 2.68 (m, 2H), 2.45 (m, 2H), 2.04 (m, 2H), 1.94 (m, 2H). ¹³C NMR (CDCl₃): δ 159.57, 158.93, 154.04, 153.55, 138.93, 138.50, 121.10, 120.11, 119.05, 118.95, 110.77, 110.58, 95.90, 95.48, 85.93, 84.23, 30.92, 30.89, 30.69, 27.90, 27.79. IR (KBr, cm⁻¹): 2960(w), 2857(w), 1602(s), 1500(s), 1434(m), 1403(s), 1298(m), 1284(m), 1249(s), 1224(s),

1169(m), 1150(m), 1029(s), 930(w), 781(m), 752(m), 635(m), 512(m), 454(w). Anal. Calc. for RuSO₃F₃C₂₃H₂₂N₃.1.5(H₂O): C, 45.62; H, 4.16; N, 6.94%. Found: C, 45.52; H, 4.29; N, 6.92% .

Preparation of $[Ru(PDP)(COD)(H_2O)](X) X = BF_4^- (4^+ \cdot BF_4^-); X = PF_6^- (4^+ \cdot PF_6^-):$ The mixture of 1 (188 mg, 0.40 mmol) and $AgBF_4$ (82 mg, 0.42 mmol) in acetone/water (15mL, v:v=1:1) was stirred for 6 h and filtered under nitrogen. The filtrate was layered with hexane to give brown single crystals, which was identified as 4^+ BF₄ by X-ray diffraction analysis. The yield of 4^+ BF₄ is low (ca. 6 %). Alternatively, the filtrate was added excess NH_4PF_6 (98 mg, 0.60mmol) and stirring for 4 h. The acetone was slowly removed by vacuum to give an orange suspension. After filtered, residual solid was washed with water, redissolved in dichloromethane and dried with anhydrous sodium sulfate. Recrystallization from CH₂Cl₂/ether, hexane solvent system obtained crystalline $4^+ \cdot PF_6^-$. Isolated yield: 197 mg (83 %). ¹H NMR $(acetone-d^{6})$: $\delta 8.97$ (t, J = 3.64, 3.68 Hz, 2H), 8.02 (m, 2H), 7.84 (d, J = 6.40 Hz, 1H), 7.78 (d, J = 6.42 Hz, 1H), 7.35 (m, 2H), 6.93 (s, 1H), 6.86 (s, 1H), 5.10 (m, 1H), 5.04 (m, 1H), 3.01 (m, 2H), 2.87 (m, 2H), 2.57 (m, 2H), 2.20 (m, 2H), 2.09 (s, 2H), 2.00 (m, 2H). ¹³C NMR (CDCl₃): δ 158.56, 154.08, 139.49, 138.87, 121.39, 119.14, 110.61, 93.45, 92.98, 29.90, 29.09. IR (KBr, cm⁻¹): 3645(w), 3564(w), 2951(w), 2843(w), 1680(w), 1603(m), 1500(m), 1435(w), 1399(m), 1298(w), 1269(w), 1154(w), 1603(w), 11048(w), 1002(w), 840(s), 752(m), 555(m), 456(w). Anal. Calc. for RuPF₆OC₂₂H₂₄N₃: C, 44.60; H, 4.08; N, 7.09%. Found: C, 44.14; H, 4.54; N, 7.17%.

Preparation of [Ru(PDP_{Cl})(COD)Cl] (5): A mixture of **1** (110.5 mg, 0.24 mmol) and PhICl₂ (73.3 mg, 0.26 mmol) in CH₂Cl₂ (12 mL) was stirred overnight. The precipitate was filtered off. The filtrate was layered with ether and hexane mixture to give yellow crystals of **5**, which were suitable for X-ray diffraction study. Isolated yield: 117.0 mg (91 %). ¹H NMR (CDCl₃): δ 8.67 (d, J = 4.40 Hz, 2H), 7.93 (d, J =

8.78 Hz, 1H), 7.76 (t, J = 6.16, 6.16 Hz, 2H), 7.13 (t, J = 5.28, 5.30 Hz 2H), 4.71(m, 2H), 2.96(m, 2H), 2.69(m, 2H), 2.48(m, 2H), 2.11(m, 2H), 1.91(m, 2H). ¹³C NMR (CDCl₃): δ 158.45, 157.71, 153.48, 153.41, 153.34, 153.26, 137.62, 120.44, 120.42, 119.30, 118.79, 109.43, 95.75, 95.70, 89.60, 89.51, 30.75, 30.69, 30.67, 30.61, 28.96, 28.93, 28.90. IR (KBr, cm⁻¹): 2943(w), 2845(w), 1600(s), 1497(s), 1433(w), 1400(w), 1337(w), 1295(m), 1150(m), 1011(w), 977(w),878(w), 775(m), 751(m), 507(w), 458(w). Anal. Calc. for RuCl₃C₂₂H₂₀N₃·0.5(Et₂O): C, 50.49; H, 4.41; N, 7.36% .

Oxidation of olefins. Typically, a suspension solution of olefin (0.1 mmol), catalyst of **1** (3 mol%) and NaIO₄ (0.25 mmol) in EtOAc-CH₃CN-H₂O (ratio = 3:1:2) was vigorously stirred at 30 °C. The color of solution was changed from brown-red to olive-green, then to brown during the catalytic reaction proceed. Yield of corresponding product at suitable interval time were determined by GC analysis using internal standard.

X-ray crystallography Diffraction data of **1-5** were recorded on a Bruker CCD diffractometer with monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). The collected frames were processed with the software SAINT. The absorption correction was treated with SADABS.¹⁴ Structures were solved by direct methods and refined by full-matrix least-squares on F² using the SHELXTL software package.¹⁵ Atomic positions of non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were introduced at their geometric positions and refined as riding atoms.

Results and Discussion

Synthesis and characterization of Ru complexes. Treatment of HPDP with NaH followed by one equiv of $\{Ru(COD)Cl_2\}_n$ gave 1 in almost quantitative yield (Scheme 1). Anion metathesis of 1 in organic solvent by NO₃⁻ and OTf (OTf = trifluoromethanesulfonate) gave the complex 2 and 3, respectively, that could be isolated as crystalline solid in high yield. The BF₄⁻ salt of $4^+ \cdot BF_4^-$ was prepared by 1 with AgBF₄, unfortunately, isolated yield was poor. Alternatively, excess of NH₄PF₆ was added into the reaction mixture of 1 and AgBF₄, resulting in formation of PF₆⁻ salt of $4^+ \cdot PF_6^-$ in high yield. Treatment of 1 with PhICl₂ in CH₂Cl₂ afforded 5 with halogenated pyrrole. The analogous bispyidylpyrrolide ligand by dithiocyanate functionalized 3,4-positions of the pyrrole ring was synthesized by treating the bare ligand with (SCN)₂.⁸ Complexes 1-5 are soluble in polar organic solvent, such as acetone, CH₂Cl₂, CH₃CN, DMSO, but insoluble in water, ether and hexane.

These complexes are characterized by ESI-MS, IR, ¹H NMR and single crystal X-ray diffraction analysis. ESI-MS of **1** displayed a signal at m/z 465.07 (z = 1) assigned to $[1 + H^+]$. In the IR spectrum of **1**, C=C, C=N stretching frequencies of PDP⁻ ligand were determined to be 1599 - 1396 cm⁻¹. The ¹H NMR shows multiply peaks at 4.69-1.93 ppm range for COD ligand, doublet peaks at 8.61, 7.65, 7.47 7.00 ppm for pyridine, and a single peak at 6.73 ppm assigned to the proton resonances of pyrrole ring. IR spectra of **2-5** are similar with that of **1**. The distinctive signals at 1273 cm⁻¹ for **2** and 1249-1284 cm⁻¹ for **3** are due to N=O and S=O stretching frequencies of the coordinated nitrate and triflato ligands in **2** and **3**, respectively. Complex **4**⁺ shows weak bands at 3645 and 3564 cm⁻¹ attributed to the O-H bond of the coordinated water. ¹H NMR spectra of **2-5** closely resemble those in **1**, which clearly reveals the formation of Ru-N_{pyrrole} bond owing to the absence of the N_{pyrrole}-H resonance indicates the formation of C-Cl bond, which is consistent with the solid state structure.

Description of the crystal structures. The crystallographic data and experimental details for **1-5** are shown in table 1. Selected bond distances and bond angles are listed in table 2. ORTEP diagram of Ru complexes are

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displayed in Figure 1-5, respectively. Complexes $1-4^+$ have a similar structure, including one Ru(II) center, one 2,5-bis(2'-pyridyl)pyrrole, one COD and one monodentated ligands. Ru(II) is best described as pseudo-octahedral with COD occupying the two coordination sites in a η^2 , η^2 -fashion, three N atoms of PDP⁻ ligand and X (X = Cl⁻ for 1, NO₃⁻ for 2, OTf for 3, H₂O for 4⁺) occupying the remaining coordination sites. In these complexes, the Ru-C bonds have almost similar bond distances with an average bond length of 2.197 Å, which are well comparable to those of Ru^{II}(COD) complexes.¹⁶ Bond distance of Ru-N_{pvrrole} (av. 1.964(2) Å) is significantly shorter that of Ru-N_{pyridine} (av. 2.169(2) Å), which can be explained by a stronger coordination of the deprotonated pyrrole nitrogen donor to the metal centre versus the neutral pyridyl group. The Ru-Cl bond length in 1 is 2.4243(7) Å. The bond distances of Ru-O in 2-4⁺ are 2.124(2), 2.190(3) and 2.131(4) Å, respectively. The PDP⁻ as pincer-type ligand coordinates to Ru(II), which is almost planar. The dihedral angles between pyrrole and pyridine rings are 5.2° and 8.1° for 1, 11.3° and 12.9° for 2, 8.4° and 8.8° for **3**, 9.4° and 14.1° for **4**⁺, respectively. That is well comparable to that of $[Ru(bipy)(PDP)]^+$, $[Ru(tpy)(PDP)]^+$ $[Ru(PDP)_2]$ -type complexes.¹¹ The bond angles of N_{pvr}-Ru-N_{pv} and N_{pv}-Ru-N_{pv}, are about in the range of 74 ° and 146 °, respectively. Complex 5 shares the same geometry as 1. Only difference is chloride atom substituted at the 3- and 4-position of the pyrrole ring in 5. The dihedral angles between pyrrole and pyridine rings for 5 are 5.4° and 10.6° .

Catalytic olefins oxidation. The formal potentials for the **1-5** in CH₃CN have been determined by cyclic voltammetry and are listed in S1. The cyclic voltammograms for these complexes display reversible oxidation couples assignable to the metal-centered Ru^{III}/Ru^{II} couples at range of 0.55-0.81 V. One additional wave in more positive direct due to oxidation of the bispyridylpyrrolide ligand is observed. The catalytic utility and selectivity of **1-5** was examined by the olefins oxidation. Variations in catalyst loading, reaction times and solvents are summarized in S3. The yield of carbonyl product is dependent on catalyst, solvent and oxidant. The heterogeneous solvent system EtOAc-CH₃CN-H₂O (ratio = 3:1:2) gave the highest yield. All complexes **1-5** have similar catalytic activity. Thus, we chose **1** as a model for catalytic olefin oxidation. Although 1 mol% of **1** performed very well in the oxidative cleavage of styrene (98 % yield of benzaldehyde after 1 h at 30 °C), this low catalyst loading is not recommended for the cleavage of other olefins such as cyclooctene since the conversion was only 48 % after 2 h. Thus, 3 mol % of **1** was used throughout the study.

A variety of olefins were subjected to this optimized condition at 30 °C (Table 3). Styrene and their derivatives were efficiently converted to the corresponding aldehydes (entry 1). Better yield have been achieved with the substrates comprising of electron donating group whereas lower yield is obtained for the substrates containing electron withdrawing group. For the latter, besides the formation of benzaldehyde, benzoic acid (~10%) was obtained as the side product. *cis*-Stilbene and *trans*-stilbene offered quantitative yield to benzaldehyde (entry 2 and 3). In the case of 1,1-disubstitued styrene (entry 4 and 5), ketone products were gave with 82% and 64% yield, respectively, maybe due to the steric reason. The allkylbenzene, aliphatic cyclic substrates such as cyclooctene and cyclohexene employed under identical conditions and afforded medium yield (entry 6-8), however, long-chain olefins offered the corresponding scission products in poor product yield (entry 9). In the case of norbornylene, the formation of dialdehyde was facile (entry 10), probably due to the release of ring strain upon oxidation. To extend to the terminal alkyne such as phenylacetylene, good conversion is achieved to form benzoic acid (entry 11). When the reaction time was extended to 24 h for less-reactive substrates, higher yields were achieved (entry 6-9 and 11), which suggested that active species from 1 remained undiminished for a long time.

The mechanism of olefins oxidation catalyzed by ruthenium complexes has been studied extensively so far. Generally, ruthenium-oxo, -peroxo, and/or -hydroperoxo have been proposed to be active species or intermediates in oxidation reactions.^{3, 17} As

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mentioned in the introduction section, Ru^{VI}-cis-dioxo is the most active species in catalytic oxidation olefins by $[Ru(COD)(L)Br_2]$ complex. Complex 1 has similar coordination environment around ruthenium with that in [Ru(COD)(L)Br₂], except of bispyridylpyrrolide instead of naphthyridine ligand in [Ru(COD)(L)Br₂]. There is a similar plausible mechanism in our work, as shown in Scheme 2. It is likely that **1** is oxidized by NaIO₄ to give a Ru^{VI}-cis-dioxo intermediate, subsequently to form a Ru^{IV} cycloadduct by [3+2] cycloaddition reaction. The following two-electron reduction and cleavage of C-C bond leads to the corresponding carbonyl products. The key proposed Ru^{VI}-cis-dioxo species from 1 was identified by ESI-MS analysis (Fig. S4). ESI-MS of 1 in EtOAc-CH₃CN-H₂O (ratio = 3:1:2) exhibits the parent peak $[1]^+$ at m/z 465.1. Upon addition of 80 equiv of NaIO₄ for 10 min, additional peak m/z 389.0 for $[Ru(PDP)Cl + 2O]^+$ together with m/z 354.0 for $[Ru(PDP) + 2O]^+$ appeared. The signals in the range of m/z 340-470 changed with time. When the mixture above was stirred for 1 h, the parent peak disappeared, and a minor peak at m/z 436.1 appeared, which may be assigned to $[Ru(PDP) + 2O + 2CH_3CN]^+$. The observation of peaks with two additional O atoms may be assigned as two oxo species, indicating of formation of Ru^{VI}-cis-dioxo intermediate, namely [Ru(PDP)(O)₂Cl]. The ESI-MS of the resulting solution of olefins oxidation catalyzed by 1 was measured. The parent ion peak changed to m/z 451.07 corresponding to $[Ru(PDP) + CH_3CN + EtOAc]^+$. It was indicated that oxygen atom was probably transferred from Ru^{VI}-cis-dioxo species to organic substrate, and PDP⁻ anion is tightly bound to Ru in the throughout catalytic cycle.

Conclusions

In summary, a set of ruthenium complexes based on bispyridylpyrrole ligand have been successfully synthesized. Structural analysis displays the PDP⁻ ligand binds to ruthenium center with meridional geometry. The 3,4-positions of the pyrrole ring was readily halogenated by treating the complex **1** but not the bare ligand with PhICl₂. **1** is highly effective in the oxidative cleavage of olefins to carbonyl products by NaIO₄ in an aqueous/organic solvent mixture. The Ru^{VI} -cis-dioxo intermediate is probably involved.

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Notes and references

† Electronic Supplementary Information (ESI) available. CCDC reference numbers 1480593, 1483072-1483075 for complex 1-5, respectively. see DOI: 10.1039/b000000x/.

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Table 1 X-ray Crystallographic Data for 1-5.

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	1	2	3	$4^+ \cdot BF_4^-$	5
Formula	C ₂₂ H ₂₂ ClN ₃ Ru	$C_{22}H_{22}N_4O_3Ru$	$C_{23}H_{22}F_3N_3O_3RuS$	C ₂₂ H ₂₄ BF ₄ N ₃ ORu	$C_{22}H_{20}Cl_3N_3Ru$
fw	464.95	491.50	1157.13	534.32	533.83
crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	P21/c	P21/c	P21/c	P1	-P2ac2ab
a, Å	13.7766(4)	16.181(2)	11.2980(6)	7.9945(2)	16.7129(5)
b, Å	8.1417(3)	9.1454(15)	27.7584(14)	11.5727(2)	7.7974(2)
c, Å	16.7532(6)	13.653(2)	15.1162(7)	12.2086(2)	31.1102(8)
α, deg	90	90.00	90.00	98.6740(10)	90
β, deg	104.071(2)	102.043(6)	108.956(3)	105.5400(10)	90
γ, deg	90	90.00	90.00	90.7500(10)	90
V, Å ³	1822.74(11)	1975.9(5)	4483.6(4)	1074.08(4)	4054.19(19)
Z	4	4	4	2	8
ρ_{calc} , g cm ⁻³	1.694	1.652	1.714	1.652	1.749
Т, К	120(2)	293(2)	296(2)	296(2)	296(2)
μ, mm ⁻¹	1.019	0.826	0.850	0.784	1.184
F(000)	944	1000	2336	540	2144
No. of reflection	16332	10716	29573	37556	25005
No. of independent reflection	4020	4476	10072	4947	4643

0.0446

1.024

0.0508, 0.1048

0.1111, 0.1325

0.0226

1.026

0.0538, 0.1776

0.0667, 0.2031

R_{int}	0.0503	0.0370
	1.017	1.018
R1, σ wR2 σ [I > 2 σ (I)]	0.0295, 0.0583	0.0367, 0.0884
R1, wR2 (all data)	0.0578, 0.0680	0.0669, 0.1044
^a GoF = $[\Sigma w(F_{o} - F_{c})^{2}/(N_{obs} -$	(N_{param})] ^{1/2} . ${}^{b}R_{1} = \Sigma F_{0} - F_{c} /\Sigma$	$E F_{\rm o} .$ ^c wR ₂ [($\Sigma w F_{\rm o} $ –

1.019		1
0.0489, 0.1071		Ì
0.0400, 0.1010		
	_	
		l
		1

0.0283

Bond distances (Å)				Bond angles (°)		
Complex	Ru-N _{pyr}	Ru-N _{py}	Ru-C _{COD}	Ru-X	N _{pyr} -Ru-N _{py}	N _{py} -Ru-N _{py}
1 1.9	1.0(4(2))	2.169(2)	2.189(3)	Ru-Cl	74.27(9)	146.38(9)
	1.904(2)	2.185(2)	2.218(3)	2.4243(7)	74.25(9)	
2 1.963(3)	1 063(3)	2.184(3)	2.171(4)	Ru-O _(NO3)	74.81(11)	145 06(11)
	1.905(3)	2.185(3)	2.208(3)	2.124(2)	74.02(11)	143.90(11)
2 10	1.960(4)	2.186(4)	2.158(5)	Ru-O _(OTf)	74.32(17)	146 09(16)
5	3 1.900(4)	2.187(4)	2.234(5)	2.190(3)	74.42(17)	140.09(10)
$4^+ \cdot BF_4^-$	1.960(5)	2.189(5)	2.162(6)	Ru-O _(H2O)	73.9(2)	146.0(2)
		2.192(5)	2.204(6)	2.131(4)	74.8(2)	140.0(2)
5	1.971(3)	2.189(5)	2.201(3)	Ru-Cl	74.20(11)	146 74(10)
		2.188(3)	2.212(3)	2.4139(9)	74.44(11)	140.74(10)

Table 2 Selected bond distances (Å) and bond angles (°) of 1-5.

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Table 3. Oxidative cleavage of olefins by $\mathbf{1}$ with NaIO₄^a

Entry	Substrate	Product	Time (h)	Yield (%)
1			1	95, 95, 85, 90
2	(R=H, OM	e, F, Br)	1	97
3	Ph Ph	0	1	99
4			2	82
5			2	64
6			2	32
б	\bigcirc	0	24	56
7		°,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	2	38
		~(~) _n _0	24	69
8	(n=1)	, 3,5) , 040	2	80
-			24	90
9		ОН	2	3, 22, 10
			24	13, 21, 27
10			1	100
			2	63
11 ^b			24	86

^a Reaction conditions: 0.1 mmol of substrate, 3 mol% catalyst 1, 0.25 mmol of NaIO₄, EtOAc-CH₃CN-H₂O (ratio = 3:1:2) solvent system, 30 °C, yield determined by GC.

^b two drops of con. H_2SO_4 was added.

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Figure 1 ORTEP diagram of **1** with ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity.



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Figure 3 ORTEP diagram of **3** with ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity.



Figure 4 ORTEP diagram of $4^+ \cdot BF_4^-$ with ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity.



Figure 5 ORTEP diagram of **5** with ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity.



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