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Synthesis and Structures of Dioxoruthenium(VI) Complexes. Oxo Transfer from *trans*-$O_2Ru(py)_2(O_2CR)_2$

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The direct synthesis of a series of dioxoruthenium(VI) complexes $O_2Ru(py)_2(O_2CR)_2$ with R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, and C_6H_5 is carried out in one step from the readily available, but highly insoluble, barium ruthenate. X-ray crystallography of $O_2Ru(py)_2(O_2CCH_3)_2$: space group $P\bar{1}$ (triclinic) with lattice constants a = 8.359 (2) Å, b = 9.599 (4) Å, c = 13.431 (8) Å, α = 89.68 (5)°, β = 74.20 (5)°, γ = 69.52 (3)°, and Z = 2. This establishes the linear *trans*-dioxo functionality with a pair of trans-pyridine and trans-acetato ligands to complete the octahedral coordination. The relatively long O═Ru bond length of 1.726 (1) Å is discussed in terms of the oxidative reactivity of these dioxoruthenium(VI) complexes toward oxygen atom transfer to various substrates including phosphines, olefins, phenols, alkanes, and ethers—especially with regard to the competitive insertion into C═C and saturated C—H bonds of olefins.

Introduction

Ruthenium complexes acting via the high oxidation states Ru(IV, V, VI) are important promoters for the metal catalysis of various organic oxidations.[1,2] Among these reactive intermediates, dioxoruthenium(VI) complexes are of particular interest owing to the central role of the Ru(VI) oxidation state in most redox cycles.[3,4] Unfortunately, only a few examples of dioxoruthenium(VI) complexes are extant.[1,5] Heretofore, the limited preparations of dioxoruthenium(VI) complexes either proceeded from the in situ reduction of ruthenium(VIII) tetraoxide in the presence of added ligands[6] or derived from the oxidations of various ruthenium(II) or ruthenium(III) precursors.[7-9] Several attempts have been made at the synthesis of dioxoruthenium(VI) complexes directly from potassium ruthenate(VI),[10-12] K_2RuO_4, but the products were either ill-defined or dimeric in nature.[6] Recently Griffith and Pawson[6] successfully isolated $Ph_4P^+RuO_2Cl_3^-$ as well as $Ru(bpy)O_2Cl_2$ from strongly alkaline solutions of ruthenate(VI) that were reductively generated from RuO_4.[13] However aqueous alkali is generally deleterious to oxometalates in high oxidation states, particularly those with labile ligands that are sensitive to water and base. Accordingly our goal was to develop general synthetic methods for dioxoruthenium(VI) complexes stemming from barium ruthenate, $BaRuO_4$, since it is a precursor that is stable, nonhygroscopic and readily prepared.[14,15] We report here the synthesis, X-ray crystal structure, and oxidative reactivity of a general class of neutral, non-halogen-containing complexes $O_2RuL_2Y_2$, where L is pyridine and Y is a carboxylato ligand.[16]

Results and Discussion

Synthesis of Dioxoruthenium(VI) Complexes. The brick-red barium ruthenate[14] $BaRuO_3(OH)_2$ can be readily converted to 60–70% yields by a combination of carboxylic acid and pyridine in acetonitrile at 0 °C to a series of orange crystalline dioxoruthenium(VI) derivatives. The separation of the insoluble barium carboxylate led to $O_2Ru(py)_2(O_2CR)_2$ with the stoichiometry

$$BaRuO_3(OH)_2 + 4RCO_2H + 2py \rightarrow Ba(O_2CR)_2 + O_2Ru(py)_2(O_2CR)_2 + 3H_2O \quad (1)$$

when R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$–, and C_6H_5. Such a multiple substitution of oxo and hydroxo ligands at the anionic ruthenium(VI) center by acetate and pyridine proceeded in two stages, since the treatment of $BaRuO_3(OH)_2$ could be initially effected separately with acetic acid alone in acetonitrile. The first-formed green solution consisting of an uncharacterized mixture of oxo(acetato)ruthenium(VI) species was then transformed to a golden yellow solution of $O_2Ru(py)_2(OAc)_2$ upon the subsequent addition of pyridine followed by the filtration of barium acetate. It is noteworthy that the acetoxylation of the highly insoluble barium ruthenate(VI) in this manner was promoted by a small amount of water since the brick-red slurry under anhydrous conditions remained unchanged even upon prolonged stirring. Although the crystalline dioxoruthenium(VI) complexes could be handled in air, they were photolabile and were best stored in the dark at −20 °C. Under these conditions the fatty acid derivatives could be kept intact for weeks and the benzoates for at least a year. The acetato and benzoato derivatives of $O_2Ru(py)_2(O_2CR)_2$ were both readily soluble in dichloromethane as well as acetonitrile, but they were insoluble in carbon tetrachloride, diethyl ether, and hexane. For convenience, the family of these dioxoruthenium(VI) complexes will be hereafter referred to generically as $O_2RuL_2Y_2$ with L = pyridine or γ-picoline and Y = carboxylate.

Structure of the Dioxoruthenium(VI) Complexes. The orange crystals of $O_2RuL_2Y_2$ were all diamagnetic, as expected for ruthenium(VI) complexes with $d_{xy}{}^2$ ground states.[17] The ^1H NMR spectrum of $O_2Ru(py)_2(OAc)_2$ showed the methyl group of the acetato ligand at the unshifted resonance of δ 2.11 (singlet) as well as the three sets of pyridine protons at δ 7.61 (triplet), 8.08 (triplet) and 9.12 (doublet) indicative of the presence of magnetically equivalent pairs of acetates and pyridines. The oxo

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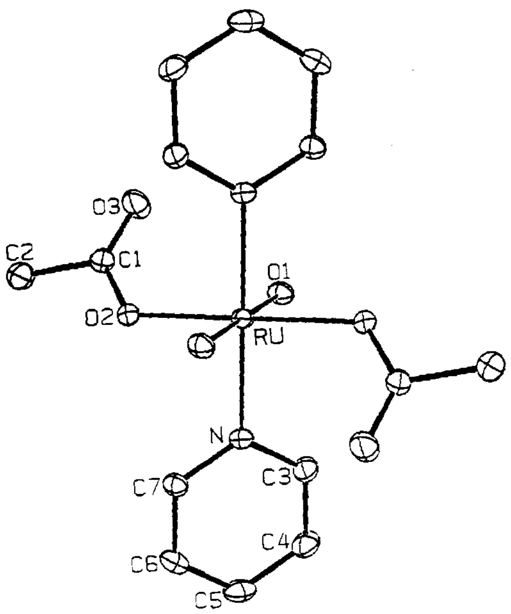

Figure 1. ORTEP diagram of $O_2Ru(py)_2(O_2CCH_3)_2$ showing the linear *trans*-dioxoruthenium(VI) moiety. For clarity hydrogen atoms are not included.

Table I. Selected Bond Distances (Å) and Bond Angles (deg) in $O_2Ru(py)_2(O_2CCH_3)_2$

Ru–O1	1.726 (1)	N–C7	1.347 (2)
Ru–O2	2.052 (1)	C1–C2	1.511 (3)
Ru–N	2.100 (2)	C3–C4	1.375 (3)
O2–C1	1.296 (2)	C4–C5	1.363 (3)
O3–C1	1.203 (2)	C5–C6	1.370 (3)
N–C3	1.337 (3)	C6–C7	1.377 (3)
O1–Ru–O1	180.00	N–Ru–N	180.00
O1–Ru–O2	92.51 (6)	Ru–O2–C1	124.8 (1)
O1–Ru–O2	87.49 (6)	Ru–N–C3	121.0 (1)
O1–Ru–N	89.40 (6)	Ru–N–C7	120.3 (1)
O1–Ru–N	90.60 (6)	C3–N–C7	118.7 (2)
O1–Ru–O2	87.49 (6)	O2–C1–O3	125.9 (2)
O1–Ru–O2	92.51 (6)	O2–C1–C2	113.0 (2)
O1–Ru–N	90.60 (6)	O3–C1–C2	121.0 (2)
O1–Ru–N	89.40 (6)	N–C3–C4	122.1 (2)
O2–Ru–O2	180.00	C3–C4–C5	119.0 (2)
O2–Ru–N	85.70 (6)	C4–C5–C6	119.6 (2)
O2–Ru–N	94.30 (6)	C5–C6–C7	119.0 (2)
O2–Ru–N	94.30 (6)	N–C7–C6	121.6 (2)
O2–Ru–N	85.70 (6)		

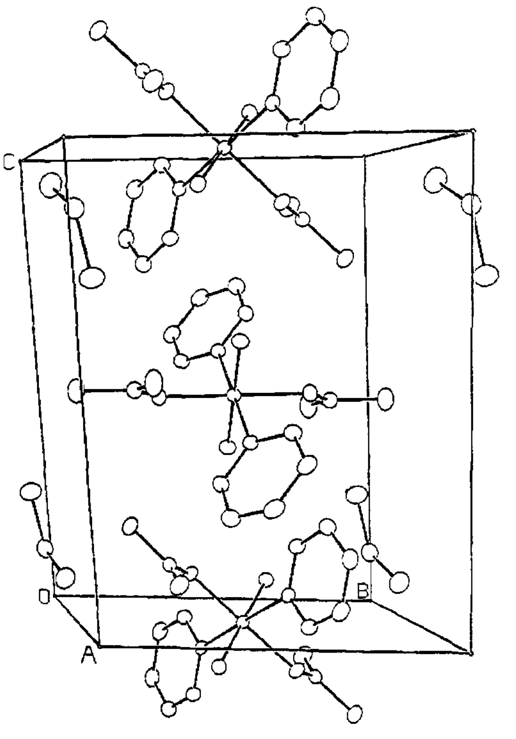

Figure 2. Packing of the two independent molecules in the unit cell of $O_2Ru(py)_2(O_2CCH_3)_2$.

functionality was characterized in the infrared spectrum of $O_2Ru(py)_2(OAc)_2$ by a single strong band at ~840 cm^{-1}, in line with that for the trans configuration reported in other dioxoruthenium(VI) complexes.[7,9,14] Indeed, the electronic spectrum of $O_2Ru(py)_2(OAc)_2$ showed a characteristic weak vibronically structured band at λ_{max} = 400 nm that is also present in the cationic analogues *trans*-$O_2Ru(NH_3)_4^{2+}$, *trans*-$O_2Ru(bpy)_2^{2+}$, and $O_2Ru(TMC)^{2+}$.[8,18,19] These structural assignments were confirmed by the X-ray crystallography of a single crystal of $O_2Ru(py)_2(OAc)_2$ obtained from the slow vapor diffusion of *n*-pentane into a dichloromethane solution at −20 °C. The ORTEP diagram in Figure 1 shows the ruthenium(VI) to be coordinated to a pair of trans-pyridine ligands and a pair of η^1-acetato ligands. The linear *trans*-dioxoruthenium moiety completes the regular octahedral coordination about the ruthenium center. Indeed the presence of a crystallographic center of inversion defines the anticoplanar acetato ligands as well as the coplanar pyridines. Slight differences in the dihedral angles of the pyridines relative to the *trans*-dioxoruthenium(VI) axis leads to a pair of independent molecules of $O_2Ru(py)_2(OAc)_2$ in the unit cell shown in Figure 2. Most importantly, the oxo-ruthenium bond distance of 1.726 (1) Å in Table I is longer than those of 1.705 (7) and 1.718 (5) Å that were recently reported for the cationic analogues $O_2Ru(16\text{-}TMC)^{2+}$ and $O_2Ru(15\text{-}TMC)^{2+}$, respectively.[8,18,19]

Oxygen Atom Transfer from the Dioxoruthenium(VI) Complexes. In order to determine whether the increased $O{=}Ru^{VI}$ bond distance resulted in an enhanced reactivity of $O_2RuL_2Y_2$ in oxygen-atom transfer, we focused our attention on its behavior toward four distinctive types of receptors as follows.

Phosphine donors are known to be highly susceptible to oxygen atom transfer from even the least active oxometals[1-4] and thus represented our benchmark test for dioxoruthenium(VI) reactivity. Indeed, the treatment of an acetonitrile solution of $O_2Ru(py)_2(OAc)_2$ with an equimolar amount of triphenylphosphine resulted in the immediate discharge of the orange color, and a quantitative yield of triphenylphosphine oxide was formed. Moreover, the same amounts of triphenylphosphine oxide were obtained in the presence of 2, 3, 5 or 10 molar equiv of added triphenylphosphine. The quantitative recovery of the unreacted triphenylphosphine (0, 1, 2, 4 and 9 equiv, respectively) from the green mother liquor was consistent with the simple stoichiometry

$$O_2Ru(py)_2(OAc)_2 + Ph_3P \rightarrow Ph_3PO + ORu(py)_2(OAc)_2 \quad (2)$$

A similar facile oxidation of trimethyl phosphite occurred when it was exposed to an orange solution of the benzoato analogue $O_2Ru(py)_2(O_2CC_6H_5)_2$ in acetonitrile. The reduced ruthenium product could be isolated as a water-soluble, dark green solid showing two distinct absorption bands at λ_{max} = 458 nm ($\epsilon = 4 \times 10^3$ cm^{-1}) and 626 nm ($\epsilon = 2 \times 10^3$ M^{-1} cm^{-1}) in the visible spectrum. The absence of notable IR bands in the region (800–900 cm^{-1}) characteristic of the O=Ru stretching frequency,[3,9,20] coupled with the highly broadened carbonyl absorptions[21] (1500–1700 cm^{-1}), suggested that the coordinatively unsaturated oxoruthenium(IV) species presented in eq 2 may actually exist as a mixture of μ-oxo oligomers.[22] Our repeated and varied

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(21) Compare the IR spectra of the reduced ruthenium products described in the Experimental Section.

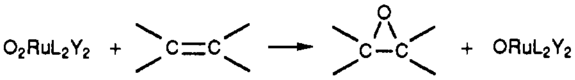
Table II. Olefin Epoxidation with O_2 $Ru(py)_2(O_2CC_6H_5)_2$[a]

olefin (amt, mmol)	additive[b] (amt, equiv)	amt of epoxide 10^3 mmol	byproducts[c] (amt, 10^3 mmol)
norbornene (1.0)	none	5	$C_7H_{10}O_2$ (~5)
	py (2.5)	5	$C_7H_{10}O_2$ (~5)
styrene (0.87)	none	4	PhCHO (4)
	pyO (5)		PhCHO (5)
	Et_3PO (5)	2	PhCHO (4)
α-methylstyrene (0.77)	none	12	$PhC(CH_3)O$ (4.5) $Ph(CH(CH_3)CHO$ (2.5)
E-β-methylstyrene (0.75)	none	3[d]	PhCHO (3) PhCH=CHCHO (3.4)
Z-β-methylstyrene (0.75)	none	10[e]	PhCHO (11) PhCH=CHCHO (1.1)
cyclohexene (1.0)	none	<0.1[f]	C_6H_8O[g] (11)
	py (2.5)	<0.1[f]	C_6H_8O (11)
	PPN^+OAc^- (1)		C_6H_8O (9)
octene-1 (0.69)	none	trace	*h*
z-hexene-2 (0.80)	none	trace	*i*

[a] In dichloromethane (2 mL) containing 0.025 mmol of $O_2Ru(py)_2(O_2CC_6H_5)_2$ as described in the text. Trace is <0.01 mmol. [b] Molar equivalents relative to oxoruthenium(VI): py = pyridine, pyO = pyridine *N*-oxide, and Et_3PO = triethylphosphine oxide. [c] Includes only those identified by GC-MS, others present but unidentified. [d] *E* isomer predominently. [e] Approximately equimolar mixture of *Z* and *E* isomers. [f] Mixture of cyclohexene oxide and 2-cyclohexenol. [g] 2-Cyclohexen-1-one. [h] *n*-Heptaldehyde. [i] None identified.

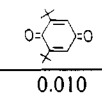
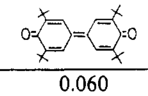
attempts to crystallize the green solid were unsuccessful.

Olefins. Epoxidation represents a critical test of oxometal reactivity in catalytic oxidations,[3,4] e.g.


(3)

Accordingly, three separate classes of olefins were exposed to the dioxoruthenium(VI) complex under a standard set of mild reaction conditions. Typically, a solution of $O_2Ru(py)_2(O_2CC_6H_5)_2$ in dichloromethane was prepared at −20 °C to allow olefin admixture without complications from any spontaneous reaction during the mixing. After the oxidation was complete (typically <30 min), the reduced dark green ruthenium product was separated from solution by the addition of diethyl ether prior to quantitative analysis of the organic products by gas chromatography. The epoxide yields in Table II related directly to the limited efficacy of the dioxoruthenium(VI) complex in a direct oxygen atom transfer to norbornene and styrene, despite their generally favorable oxophilic properties. Moreover, the absence of stereospecificity in oxygen-atom transfer, as shown by the formation of a mixture of cis and trans epoxides from β-methylstyrene, accorded with the stepwise transfer of oxygen. Among the reactive intermediates must be those contributing to the oxidative scission of the C=C bonds as indicated by the formation of benzaldehyde as a relevant byproduct from styrene and β-methylstyrene, as well as acetophenone from α-methylstyrene. Most important was the competition from oxidative processes resulting from oxygen atom insertion into carbon–hydrogen bonds, as judged by the presence of sizable amounts of cinnamaldehyde from both *cis*- and *trans*-β-methylstyrene. Such an allylic oxidation was the dominant process in the formation of cyclohexenone from cyclohexene—especially since the control experiment established that the presumed intermediate cyclohexenol was quantitatively converted to cyclohexenone under the conditions extant during cyclohexene oxidation. If the dioxoruthenium(VI) complex is considered to be a 2-equiv oxidant (as in eq 3), the overall conversion to cyclohexenone proceeded in 88% yield. Similar high conversions of dioxoruthenium(VI) were indicated by accounting for the organic products derived from β-methylstyrene. Thus it is reasonable to attribute the poor material balance with some of the other olefins (e.g., norbornene, styrene, and especially octene-1 or hexene-2) to the further oxidation of labile intermediates to carboxylic acids and related byproducts that were not readily subject to gas chromatographic analysis. It is important to note that the infrared spectrum (KBr disk) of the ruthenium product isolated as dark green solids from the olefin oxidations showed the characteristic broad carbonyl absorption (~1600 cm^{-1}) but no oxometal absorption in the region 800–900 cm^{-1}. The visible spectrum in dichloromethane consisted of an intense pair of bands at λ_{max} = 420 nm ($\epsilon = 6 \times 10^3$ M^{-1} cm^{-1}) and 577 nm ($\epsilon = 3 \times 10^3$ M^{-1} cm^{-1}).

Table III. Oxidation of 2,6-Di-*tert*-butylphenol by Oxometal Complexes[a]

	amt of product, mmol	
oxometal (amt, mmol)		
$O_2Ru(py)_2(OAc)_2$ (0.10)	0.010	0.060
$O_2RuCl_3^-PPh_4^+$ (0.10)	0.050	0.040
$OCr(salen)^+OTf^-$ (0.10)	0.040	0.020

[a] Under standard conditions in 3 mL of dichloromethane containing 0.20 mmol of 2,6-di-*tert*-butylphenol at 25 °C.

Table IV. Hydrocarbon and Ether Oxidation with the Dioxoruthenium(VI) Complex[a]

substrate (amt, mmol)	oxidation product (amt, 10^3 mmol)[b]
tetrahydrofuran (1.23)	γ-butyrolactone (8)
toluene (0.94)	benzaldehyde (3)
cyclohexane (0.92)	cyclohexanone (3)
diphenylacetylene (0.56)	benzil (c)

[a] In 2 mL of dichloromethane containing 0.025 mmol of $O_2Ru(py)_2(O_2CC_6H_5)_2$. [b] By quantitative gas chromatographic analysis. [c] Identified by GC-MS but not quantified.

Phenols. The oxidative activation of allylic C–H bonds in cyclohexene and β-methylstyrene by $O_2RuL_2Y_2$ extends to the aromatic C–H bonds in phenols.[2] Among these substrates, we selected 2,6-di-*tert*-butylphenol owing to the ready identification and analysis of its oxidation products.[23] Indeed, the comparison of $O_2Ru(py)_2(O_2CCH_3)_2$ with the behavior of two other oxometals,[13,24] the anionic $O_2RuCl_3^-$ and the cationic $OCr(salen)^+$, in Table III shows the consistently high oxidative conversion of 2,6-di-*tert*-butylphenol selectively at the para position to afford

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the *tert*-butylated quinone and diphenylquinone. Previous studies indicated that these products of phenolic oxidation arise via the phenoxy radical $t\text{-}Bu_2C_6H_3O^\bullet$ as the common precursor that is either further oxidized directly to the quinone or undergoes prior dimerization followed by rapid oxidation to diphenoquinone.[25] If so, the relatively low selectivity to quinone suggests that $O_2Ru(py)_2(OAc)_2$ is less active than either $O_2RuCl_3^-$ or $OCr(salen)^+$ in their competition for phenoxy radicals via oxo transfer relative to dimerization.

Hydrocarbons and Ethers. In order to determine the reactivity of dioxoruthenium(VI) in the activation of saturated C–H bonds,[26] a standard amount of $O_2Ru(py)_2(O_2CC_6H_5)_2$ was exposed to the series of substrates in Table IV under the same set of reaction conditions (see Experimental Section). Although tetrahydrofuran reacted upon mixing at −20 °C, toluene and cyclohexane were noticeably less reactive as qualitatively judged by the rate of color change from orange to green. Nonetheless, the gas chromatographic analysis of the reaction mixture (subsequent to the separation of the reduced ruthenium product) showed the presence of only one component, viz. benzaldehyde and cyclohexenone, respectively. Control experiments established that both benzyl alcohol and cyclohexanol, as possible intermediates, were quantitatively converted to benzaldehyde and cyclohexanone under the reaction conditions described above. It is also noteworthy that tetrahydrofuran yielded only γ-butyrolactone on gas chromatographic analysis. Conversion to the carbonyl products formally represented the 4-electron oxidation of the hydrocarbons and ether. Since the molar amounts of these oxidation products were less than the equivalents of $O_2Ru(py)_2(O_2CC_6H_5)_2$ added (the ambiguity regarding the ruthenium stoichiometry notwithstanding), the analysis of the other byproducts that were not detectable by the GC method requires further study.

Comments on the Oxidative Reactivity of the Dioxoruthenium(IV) Complexes. The formation patterns of the organic products in Tables II–IV clearly point to a series of dioxoruthenium(VI) complexes $O_2RuX_2Y_2$ that are active but unselective oxo transfer agents. Furthermore the addition of the ligating bases: pyridine, pyridine *N*-oxide, and triethylphosphine oxide, which we previously found to be effective in mediating oxo transfer from the oxochromium(V) reagent,[27] had no noticeable effect on the alteration of product selectivity with the dioxoruthenium(VI) complex in Table II. The reduced ruthenium products were consistently isolated as dark green amorphous solids, irrespective of the donor employed, be it from phosphine, olefin, phenol, or hydrocarbon. This fact, coupled with the severely broadened ^1H and ^{13}C NMR spectrum of these green solids, leads us tentatively to suggest that structurally related ruthenium(IV) products are common to all the organic substrates. Further, the presence of severely broadened carbonyl absorptions (~1650 cm^{-1}, in contrast to the well-defined pair of bands in $O_2RuL_2Y_2$) and the singular absence of any prominent bands in the spectral region 800–900 cm^{-1}, diagnostic for terminal O=Ru absorption, accord with μ-oxo linkages extant in oligomeric structure(s) of the reduced ruthenium product. If so, the polymerization of the coordinatively unsaturated units of $ORuL_2Y_2$ can be deduced from the clean and unambiguous conversion of triphenylphosphine in eq 2.

Despite the absence of kinetic data and the incomplete ruthenium stoichiometry, the complexion of organic products is sufficient to provide a qualitative picture of dioxoruthenium(VI) reactivity. For example, the oxygen atom insertion into C=C and C—H bonds are more or less competitive processes, as shown in Table II by the simultaneous formation of both epoxides and carbonyl compounds. The latter also derive from saturated C–H centers (Table IV), most likely via secondary alcohols that suffer further oxidation to the carbonyl products by dioxoruthenium(VI) established by control experiments. As such, a common pathway that involves an initial hydrogen atom transfer in eq 4 readily accommodates the uniform oxidation of diverse substrates with R_2CH_2 = alkane, arene, alkene, ether, etc. of different polar properties, i.e., as seen in Scheme I.[28,29]

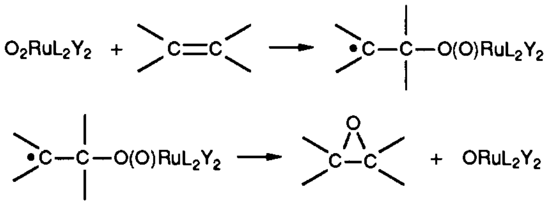
Scheme I

$$O_2RuL_2Y_2 + R_2CH_2 \rightarrow HO(O)\,RuL_2Y_2 + R_2CH^\bullet \quad (4)$$

$$R_2CH^\bullet + HO(O)RuL_2Y_2 \xrightarrow{\text{fast}} ORuL_2Y_2 + R_2CHOH,\ \text{etc.} \quad (5)$$

A related homolytic process leading to epoxide involves the stepwise addition to the unsaturated center,[30] i.e., as seen in Scheme II.

Scheme II


(6)
(7)

Indeed, the reactive intermediate in Scheme II accounts for the lack of stereospecificity in epoxide formation as well as the prevalence of C=C bond cleavage during the oxidation of olefins by dioxoruthenium(VI).[31] The stepwise processes in Schemes I and II for the oxygen atom transfer from dioxoruthenium(VI) complexes, though somewhat speculative, were mostly chosen to emphasize the pronounced contrast in oxidative behavior relative to the behavior of the oxochromium(V) complexes examined previously.[27] Thus oxygen atom transfer from the cationic $OCr(salen)^+$ to olefins is highly stereospecific and selectively occurs with little or no competition from either allylic oxidation or C=C scission—in a manner strongly suggestive of a concerted electrophilic process.[32] Although the minor variation in the carboxylate ligand in $O_2RuL_2Y_2$ from Y = acetato to benzoato had no effect in moderating the competition in C=C versus C—H insertion, we hope that more profound changes in the ligands will lead to dioxoruthenium(VI) complexes that exhibit greater oxidative selectivity without an offsetting sacrifice in reactivity.

Experimental Section

Materials. Ruthenium(III) chloride $RuCl_3{\cdot}xH_2O$ (Platina Laboratories, 41.6% Ru content) was converted to barium *trans*-dihydroxotrioxoruthenate(VI), $BaRuO_3(OH)_2$, as described in the literature.[14] Pyridine (Fisher) and 4-methylpyridine (Aldrich) were refluxed over KOH and distilled under an argon atmosphere. Acetic (Mallinckrodt, glacial), propionic (Matheson), *n*-butyric (Fisher) and isobutyric (Fisher) acids were used as received. Benzoic acid (Fisher, sublimed) was recrystallized from *n*-heptane. Dichloromethane (Mallinckrodt, reagent) was repeatedly stirred with fresh concentrated H_2SO_4 until the acid layer remained colorless. It was then washed with water and aqueous $NaHCO_3$, dried with anhydrous $CaCl_2$, initially distilled from P_2O_5, and finally redistilled from CaH_2 under an argon atmosphere. *n*-Hexane (Mallinckrodt, reagent) and carbon tetrachloride (Fisher, reagent) were treated similarly, but the final distillations were from sodium and P_2O_5, respectively, under an argon atmosphere. Acetonitrile (Mallinckrodt, reagent) was stirred over $KMnO_4$ for 24 h, filtered, an distilled. The

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(25) Kharasch, M. S.; Joshi, B. S. *J. Org. Chem.* **1957**, *22*, 1439. See also: Seok, W. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7358.

(26) Compare Hill, C. L. In *Advances in Oxygenated Process*; Baumstark, A. L., Ed.; Jai Press: Greenwich, CT, 1989, Chapter 1.

(27) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606.

(28) Compare: Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, 108, 2309.

(29) For the facile oxidation of alkyl radicals in eq 5, see: Kochi, J. K. In *Free Radicals*; Wiley: New York 1973; Vol. 1, p 591 f.

(30) Compare: (a) Srinivasan, K.; Perrier, S.; Kochi, J. K. *J. Mol Catal.* **1986**, *36*, 297. (b) Koola, J. D.; Kochi, J. K. *J. Org. Chem.* **1987**, *52*, 4545.

(31) For the homolytic processes, see: Lloyd, W. G. In *Methods in Free-Radical Chemistry*; Huyser, E. S. Ed.; Dekker: New York, 1973; Vol. 4. See also: Marmion, M. E.; Leising, R. A.; Takeuchi, K. J. *J. Coord. Chem.* **1988**, *19*, 1.

(32) See: Berti, G. In *Topics in Stereochemistry*; Allinger, N. L.; Eliel, E. L., Eds.; Wiley: New York, 1973; Vol. 5.

distillate was refluxed over P_2O_5, distilled, and then redistilled from CaH_2 under an argon atmosphere. Diethyl ether (Baker, anhydrous) was stirred with aqueous $KMnO_4$ for 24 h and then washed serially with water, H_2SO_4, and water. After being dried over $CaCl_2$, it was distilled from sodium under an argon atmosphere. The olefin and olefin oxides were obtained from previous studies.[27,30] 2,6-Di-*tert*-butylphenol (Aldrich) was distilled in vacuo, and converted to 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone as described in the literature.[25] Triphenylphosphine (Matheson) was recrystallized from *n*-hexane and triphenylphosphine oxide (Aldrich) was recrystallized from diethyl ether.

Instrumentation. Infrared spectra were obtained on a Nicolet 10DX FT-IR spectrometer with 2-cm^{-1} resolution by using either KBr disks or Nujol mulls. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 chromatograph with a 12.5-m cross-linked dimethylsilicone capillary column. GC-MS measurements were carried out on a Hewlett-Packard 5890A chromatograph interfaced to a HP 5970 mass spectrometer (EI) operating at 70 eV. ^1H NMR spectra were measured in chloroform-*d* on either a JEOL FX90Q or a General Electric QE 300 FT spectrometer with TMS used as an internal standard. Electronic absorption spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer with 2-nm resolution. Magnetic susceptibilities of the ruthenium complexes were measured at 25 °C by the Evans method.[33] Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA 30091.

Synthesis of *trans*-$O_2Ru(py)_2(O_2CR)$ Where R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$, and $(CH_2)_2CH$. In a typical procedure, a suspension of the brick-red $BaRuO_3(OH)_2$ (0.20 g, 0.62 mmol) in 5 mL of acetonitrile was treated with a mixture of acetic acid (1 mL, 17.5 mmol), pyridine (0.7 mL, 8.75 mmol), and a drop of water that was degassed beforehand in a Schlenk flask by three successive freeze–pump–thaw cycles. The slurry (cooled in an ice bath) was stirred magnetically in the dark under an argon atmosphere until a large amount of grayish precipitate formed (ca 1 h). The supernatant solution was carefully removed with the aid of a teflon cannula and combined with the wash (1 mL) of the gray precipitate consisting mostly of barium acetate. The combined dark yellow solution was cooled to −23 °C (using a bath consisting of a CCl_4–dry ice slurry), and precooled diethyl ether was added carefully. The golden yellow crystals were removed by filtration under an argon atmosphere and recrystallized from dichloromethane by the slow addition of hexane. Yield of $O_2Ru(py)_2(O_2CCH_3)_2$: 0.18 g (0.39 mmol). Anal. Calcd for $RuO_6C_{14}H_{16}N_2$: C, 41.08; H, 3.94; N, 6.84. Found: C, 40.59; H, 3.85; N, 6.62. $\mu_{eff} = 0\ \mu_B$. UV–vis (pyridine) λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$): 382 (650), 392 (750), 400 (800), 408 (670), 428 (320). IR (KBr): 3113 (w), 3101 (w), 3074 (w), 3051 (w), 3035 (w), 3012 (w), 2984 (w), 1641 (s), 1609 (s), 1453 (s), 1366 (m), 1281 (s), 1216 (m), 1069 (m), 1012 (m), 928 (m), 841 (s), 766 (s), 691 (s), 653 (s), 534 (w) cm^{-1}. ^1H NMR, 90 MHz ($CDCl_3$): δ 9.12 (d, J = 5.4 Hz, 4 H), 8.08 (t, J = 7.3 Hz, 2 H), 7.61 (t, J = 6.5 Hz, 4 H), 2.11 (s, 6 H). Essentially the same procedure was used to prepare the propionato complex from 17.5 mmol of propionic acid. Yield of orange crystals of $O_2Ru(py)(O_2CC_2H_5)_2$: 0.16 g (55%). Anal. Calcd for $RuO_6C_{16}H_{20}N_2$: C, 43.93; H, 4.61; N, 6.40. Found: C, 43.82; H, 4.63; N, 6.34. IR (KBr): Similar to acetato analogue and 841 cm^{-1} (Ru═O). *n*-Butyric acid (8.75 mmol) was also converted to the *n*-butyrato complex. Yield of $O_2Ru(py)_2(O_2CCH_2CH_2CH_3)_2$: 0.14 g (52%). Anal. Calcd for $RuO_6C_{18}H_{24}N_2$: C, 46.45; H, 5.20; N, 6.02. Found: C, 46.00; H, 5.09; H, 5.93. IR (KBr): vide supra and 841 cm^{-1} (Ru═O). ^1H NMR ($CDCl_3$): δ 9.13 (d, J = 5.6 Hz, 4 H), 8.06 (t, J = 7.8 Hz, 2 H), 7.60 (t, J = 7.0 Hz, 4 H), 2.37 (t, J = 7.2 Hz, 4 H), 1.58 (m, 4 H), 0.83 (t, J = 7.2 Hz, 6 H). Isobutyric acid (17.5 mmol) was converted to the orange isobutyrato complex. Yield of $O_2Ru(py)[O_2CCH(CH_3)_2]_2$: 0.19 g (66%). Ir (KBr): vide supra and 847 cm^{-1} (Ru═O).

Synthesis of *trans*-$O_2Ru(4\text{-}CH_3C_5H_4N)_2(O_2CCH_3)_2$. A mixture of acetic acid (17.5 mmol) and 4-methylpyridine (8.75 mmol) was treated with $BaRuO_3(OH)_2$ (0.62 mmol) in the manner described above to yield orange crystals of $O_2Ru(4\text{-}Mepy)_2(O_2CCH_3)_2$: 0.15 g (52%). Anal. Calcd for $RuO_6C_{16}H_{20}N_2$: C, 43.93; H, 4.61; N, 6.40. Found: C, 43.83; H, 4.60; N, 6.31. IR (KBr): 3128 (w), 3100 (w), 3072 (w), 3051 (w), 3002 (w), 2973 (w), 2931 (w), 1637 (s), 1622 (s), 1437 (m), 1362 (s), 1275 (s), 1209 (m), 1125 (w), 1109 (w), 1072 (s), 1044 (m), 1012 (m), 919 (m), 841 (s), 813 (s), 716 (w), 684 (s), 616 (w), 562 (m), 534 (m), 503 (s) cm^{-1}. ^1H NMR, 90 MHz ($CDCl_3$): δ 8.92 (d, J = 6.1 Hz, 4 H), 7.38 (d, J = 5.9 Hz, 4 H), 2.55 (s, 6 H) 2.10 (s, 6 H).

Synthesis of Benzoato Complexes of Dioxoruthenium(VI). A mixture of benzoic acid (2.13 g, 17.5 mmol), pyridine (0.7 mL, 8.75 mmol) and 2 drops of water in acetonitrile (8 mL) was placed in a Schlenk flask and degassed by three successive freeze–pump–thaw cycles. This solution was added under an argon atmosphere to a suspension of $BaRuO_3(OH)_2$ (0.4 g, 1.24 mmol) in 5 mL of acetonitrile, and the dark red slurry was stirred magnetically at 0 °C in the dark. After 2 h, the thick brown mixture was diluted with acetonitrile (10 mL), and the slurry was stirred for an additional hour. Filtration yielded an orange solution, which was combined with the 3-mL acetonitrile wash of the gray barium benzoate. The combined orange solution was concentrated in vacuo and 200 mL of carbon tetrachloride added, and it yielded, after sitting for 1 h at −20 °C, orange crystals that were recrystallized from dichloromethane with added hexane. Yield of $O_2Ru(py)_2(O_2CC_6H_5)_2$: 0.46 g (70%). Anal. Calcd for $RuO_6C_{24}H_{20}N_2$: C, 54.03; H, 3.78; N, 5.25. Found: 53.00; H, 3.76; N, 5.15. ^1H NMR ($CDCl_3$): δ 9.28 (d, J = 5.4 Hz, 4 H), 8.08 (m, 6 H), 7.37 (m, 10 H). IR (KBr): 3100 (m), 3086 (w), 3051 (w), 3030 (w), 3009 (w), 1634 (s), 1618 (m), 1606 (m), 1578 (w), 1569 (w), 1559 (w), 1484 (s), 1309 (s), 1291 (s), 1212 (w), 1175 (w), 1166 (w), 1153 (w), 1122 (m), 1072 (m), 1025 (w), 850 (s), 766 (m), 713 (s), 700 (s), 678 (w), 653 (w). The 4-picoline compound was similarly prepared from 8.75 mmol of base, and the procedure yielded the better characterized derivative $O_2Ru(4\text{-}Mepy)_2(O_2CC_6H_5)_2$, yield 0.44 g (63%). Anal. Calcd for $RuO_6C_{26}H_{24}N_2$: C, 55.61; H, 4.30, N, 4.99. Found: C, 55.65; H, 4.27; N, 4.98. ^1H NMR ($CDCl_3$): δ 9.07 (d, J = 6.7 Hz, 4 H), 8.05 (m, 4 H), 7.37 (m, 10 H), 2.53 (m, 6 H). Ir (KBr): vide supra and 853 cm^{-1} (Ru═O).

X-ray Crystallography of $O_2Ru(py)_2(OAc)_2$. Single crystals of $O_2Ru(py)_2(OAc)_2$ were grown from dichloromethane solution at −20 °C by the slow vapor diffusion of *n*-pentane. A large apricot-colored plate having approximate dimensions (0.60 × 0.40 × 0.10 mm was mounted on a glass fiber in a random orientation on an Enraf-Nonius CAD-4 automatic diffractometer. The radiation used was Mo Kα monochromatized by a dense graphite crystal assumed for all purposes to be 50% imperfect. Final cell constants, as well as other information pertinent to data collection and refinement were as follows: space group $P\bar{1}$, triclinic, with cell constants a = 8.359 (2) Å, b = 9.599 (4) Å, c = 13.431 (8) Å, α = 89.68 (5)°, β = 74.20 (5)°, γ = 69.52 (3)°, and V = 966 Å^3; molecular formula $RuCl_2O_6N_2C_{15}H_{18}$, formula weight 494.3, $Z = 2$, ρ = 1.70 g cm^{-3}, μ = 11.06 cm^{-1}, radiation Mo Kα, λ = 0.71073 Å, collection range $4° < 2\theta < 45°$; scan width $\Delta\theta = (0.90 + 0.35 \tan \theta)°$, maximum scan time 90 s, scan speed range 0.7–5.0 deg min^{-1}, 2508 total data collected, 2038 independent data with $I > 3\sigma(I)$, 238 total variables, $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.021$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.023$, $w = \sigma(F)^{-2}$. The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be either $P1$ or $P\bar{1}$. Intensities were measured by using the θ–2θ scan technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability. These did not vary significantly despite the fact that the data crystal slowly turned black as the experiment progressed. In the reduction of the data, Lorentz and polarization factors were applied, as well as an empirical absorption correction based on azimuthal ψ scans of five reflections having χ near 90°.[34] The Patterson map exhibited one very large peak apart from the origin, as expected, but it was located at 0, 0, $^1/_2$ which is not characteristic of one heavy atom at a general position. Since the solution for Ru of $^1/_2$, $^1/_2$, $^1/_4$ failed to produce meaningful results, the Patterson map was considered as one involving two independent Ru atoms each constrained to lie on a different inversion center. This proved to be correct, and the asymmetric unit consisted of two half-molecules. An additional methylene chloride of solvation was found. The two independent molecules of $O_2RuL_2Y_2$ showed some significant differences between dihedral angles (up to 7°), which was probably due to packing forces. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions. The methyl protons were located in difference Fourier syntheses and then fixed in the ideal locations closest to those found. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed above. No unusually high correlations were noted between any of the variables in the last cycle of least-squares refinement, and the final difference density map showed no peaks greater than 0.30 e Å^{-3}. The final atomic coordinates and isotropic thermal parameters are included in Table V. All calculations were made by using Molecular Structure Corp.'s TEXRAY 230 modifications of the SDP-PLUS series of programs.

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Table V. Positional Parameters and Their Estimated Standard Deviations for $O_2Ru(py)_2(O_2CCH_3)_2$

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ru	0.500	0.500	0.500	2.309 (8)
O1	0.5539 (3)	0.5138 (2)	0.6139 (2)	3.10 (5)
O2	0.5702 (3)	0.2725 (2)	0.4982 (2)	2.98 (5)
O3	0.8286 (3)	0.2174 (3)	0.5847 (2)	5.16 (7)
N	0.2453 (3)	0.5113 (3)	0.5879 (2)	2.54 (6)
C1	0.7133 (4)	0.1825 (4)	0.5172 (3)	3.26 (9)
C2	0.7246 (5)	0.0220 (4)	0.5162 (3)	4.7 (1)
C3	0.1485 (4)	0.6156 (4)	0.6681 (3)	3.43 (9)
C4	−0.0194 (4)	0.6263 (4)	0.7259 (3)	4.1 (1)
C5	−0.0890 (4)	0.5266 (4)	0.7013 (3)	4.0 (1)
C6	0.0092 (4)	0.4181 (4)	0.6200 (3)	3.57 (9)
C7	0.1761 (4)	0.4130 (4)	0.5640 (3)	2.98 (8)
Ru′	0.500	0.500	0.000	2.122 (8)
O1′	0.2945 (3)	0.6157 (2)	0.0770 (2)	2.78 (5)
O2′	0.4894 (3)	0.3508 (2)	0.1082 (2)	2.72 (5)
O3′	0.7746 (3)	0.2663 (3)	0.1099 (2)	4.10 (6)
N′	0.3779 (3)	0.3940 (3)	−0.0760 (2)	2.38 (6)
C1′	0.6233 (4)	0.2674 (3)	0.1393 (3)	2.86 (8)
C2′	0.5714 (5)	0.1678 (4)	0.2194 (3)	3.8 (1)
C3′	0.4435 (4)	0.3499 (4)	−0.1780 (3)	2.97 (8)
C4′	0.3623 (4)	0.2838 (4)	−0.2287 (3)	3.61 (9)
C5′	0.2094 (4)	0.2628 (4)	−0.1733 (3)	3.85 (9)
C6′	0.1427 (4)	0.3072 (4)	−0.0685 (3)	3.79 (9)
C7′	0.2302 (4)	0.3722 (4)	−0.0220 (3)	3.14 (8)
Cl1	0.0718 (2)	0.9433 (1)	0.25814 (9)	6.23 (3)
Cl2	0.3067 (1)	1.0018 (1)	0.0758 (1)	6.29 (3)
C8	0.1088 (5)	0.9693 (4)	0.1264 (3)	4.3 (1)
H2A	0.8371	−0.0417	0.5312	5*
H2B	0.6196	0.0147	0.5704	5*
H2C	0.7243	−0.0128	0.4462	5*
H3	0.1998	0.6880	0.6865	5*
H4	−0.0895	0.7060	0.7849	5*
H5	−0.2109	0.5326	0.7424	5*
H6	−0.0397	0.3437	0.6015	5*
H7	0.2475	0.3344	0.5042	5*
H8A	0.0072	1.0571	0.1175	5*
H8B	0.1160	0.8777	0.0875	5*
H2A'	0.6782	0.1060	0.2407	5*
H2B'	0.4766	0.2308	0.2814	5*
H2C'	0.5250	0.1006	0.1886	5*
H3'	0.5544	0.3655	−0.2183	5*
H4'	0.4137	0.2513	−0.3048	5*
H5'	0.1474	0.2158	−0.2088	5*
H6'	0.0320	0.2923	−0.0266	5*
H7'	0.1821	0.4039	0.0548	5*

[a] Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Oxidative Behavior of the Dioxoruthenium(VI) Complexes. The oxidation of four types of oxygen atom receptors were examined with various $O_2RuL_2Y_2$ under more or less uniform conditions described as follows.

Phosphine. Triphenylphosphine (79 mg, 0.3 mmol) was added to an orange solution of $O_2Ru(py)_2(OAc)_2$ (41 mg, 0.10 mmol) in 5 mL of acetonitrile. The dark green solution was stirred for an additional hour and the solvent removed in vacuo. The dark green solid was repeatedly washed with diethyl ether (4 × 2 mL) on a glass-fritted funnel. The combined ethereal extracts were analyzed by quantitative gas chromatography (using benzophenone as the internal standard) programmed at 150 °C [concentration, mmol, compound (retention time, min)]: 0.050, benzophenone (3.46); 0.097, triphenylphosphine (5.46); 0.20, triphenylphosphine oxide (7.06). IR (KBr) for the green solid: 1560 (v br, s), 1456 (m), 1375 (s), 1319 (s), 1218 (m), 1154 (w), 1070 (m), 1047 (m), 1017 (m), 763 (s), 694 (s), 647 (s) cm^{-1}. Attempts to crystallize the dark green solids from various solvents and mixtures including hexane/dichloromethane, acetonitrile/ether, and benzene failed. Dissolution of the green solid in water followed by the addition of ammonium hexafluorophosphate yielded a dark green precipitate that also could not be successfully crystallized. IR (KBr): 1484 (w), 1471 (w), 1436 (m), 1314 (w), 1187 (w), 1162 (w), 1121 (m), 1096 (m), 1073 (w), 1027 (w), 999 (w), 839 (br, s), 746 (m), 722 (m), 697 (s), 557 (m), 542 (m), 519 (m) cm^{-1}. This and the absence of carboxylato ligands suggested a mixture of (μ-oxo)ruthenium oligomers.

Olefins. In a typical procedure, 13.4 mg (0.025 mmol) of $O_2Ru(py)_2(O_2CC_6H_5)_2$ was added to 2 mL of dichloromethane (precooled to −20 °C) containing *n*-hexane (0.014 mmol) as the internal standard. A measured amount of olefin (see Table I) was added, and the ice bath was removed to allow the orange solution to warm to room temperature. After the mixture was stirred for an hour, diethyl ether (4 mL) was added to ensure the complete precipitation of the green reduced ruthenium product. Gas chromatographic analysis of the colorless supernatant solution was carried out on a 12.5-m cross-linked dimethylsilicone capillary column that was programmed from 60 °C at 20 deg min^{-1} with the following retention times (min) for each compound given in parentheses: cyclohexene (1.05), cyclohexene oxide (1.83), 2-cyclohexen-1-ol (2.03), 2-cyclohexen-1-one (2.27), norbornene (1.10), norbornene oxide (2.49), styrene (1.97), styrene oxide (3.49), benzaldehyde (2.55), phenylacetaldehyde (3.37), α-methylstyrene (3.01), α-methylstyrene oxide (3.44), α-phenylpropionaldehyde (3.75), acetophenone (3.22), *Z*-β-methylstyrene (2.97), *E*-β-methylstyrene (3.25), *Z*-β-methylstyrene oxide (3.85), *E*-β-methylstyrene oxide (3.95), phenylacetone (4.32), cinnamaldehyde (5.13). In each case the identity of the gc components were verified by comparison of their (GC) MS cracking patterns with those of authentic samples.[27,28,30] IR (KBr) for the green ruthenium product: 1580 (v br, s), 1319 (s), 1217 (m), 1157 (w), 1070 (m), 1050 (m), 1017 (m), 766 (s), 722 (m), 694 (s), 677 (w), 649 (w) cm^{-1}. Treatment of 0.2 mmol of cyclohexenol with 20.5 mg (0.050 mmol) of $O_2Ru(py)_2(OAc)_2$ in 3 mL of dichloromethane in a similar procedure afforded 0.048 mmol (96%) of 2-cyclohexen-1-one and 0.145 mmol (96%) of recovered 3-cyclohexen-1-ol. The dark green reduced ruthenium product was isolated by precipitation with diethyl ether (vide supra). IR (KBr): 1580 (v br, s), 1324 (s), 1217 (m), 1157 (m), 1070 (m), 1050 (m), 1017 (m), 766 (s), 722 (w), 697 (s), 677 (w), 649 (w) cm^{-1}.

Phenol. A solution of 0.10 mmol of $O_2Ru(py)_2(O_2CCH_3)_2$ in 3 mL of dichloromethane at −20 °C (vide supra) was treated with 0.20 mmol of 2,6-di-*tert*-butylphenol. After an hour, the solvent was removed in vacuo, and the green residue was taken up with 4 mL of diethyl ether. Gas chromatography of the orange ethereal solution was carried out on a 12.5-m cross-linked dimethylsilicone capillary column that was programmed from 100 °C at 25 deg min^{-1} for retention times (min) of 2,6-di-*tert*-butylphenol (3.79), 2,6-di-*tert*-butylquinone (3.94), 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenylquinone (9.43).

Hydrocarbons. A solution of 0.025 mmol of $O_2Ru(py)_2(O_2CC_6H_5)_2$ in 2 mL of dichloromethane at −20 °C was treated with a 20–40 mol excess of hydrocarbon. Removal of the icebath and additional stirring at room temperature for an hour was followed by a 4-mL aliquot of diethyl ether. The colorless supernatant solution was analyzed by the gas chromatographic procedure used for olefin analysis (vide supra) for the following compounds with retention times (min) given in parentheses: tetrahydrofuran (0.75), γ-butyrolactone (1.98), toluene (1.30), benzaldehyde (2.55), cyclohexanone (2.02). The GC analysis of diphenylacetylene (4.98) and benzil (8.89) was programmed from 100 °C at 25 deg min^{-1}. Cyclohexanol was quantitatively converted to cyclohexanone under the same reaction conditions.

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Supplementary Material Available: Table of the observed and calculated structure factor amplitudes for $O_2Ru(py)_2(O_2CCH_3)_2$ (11 pages). Ordering information is given on any current masthead page.