Highly Cooperative Tetrametallic Ruthenium-*μ*-Oxo-*μ*-Hydroxo Catalyst for the Alcohol Oxidation Reaction

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The tetrametallic ruthenium-oxo-hydroxo-hydride complex $\{[(PCy_3)(CO)RuH]_4(\mu_4\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)\}$ (**1**) was synthesized in two steps from the monomeric complex $(PCy_3)(CO)RuHCl$ (**2**). The tetrameric complex **1** was found to be a highly effective catalyst for the transfer dehydrogenation of alcohols. Complex **1** showed a different catalytic activity pattern toward primary and secondary benzyl alcohols, as indicated by the Hammett correlation for the oxidation reaction of $p\text{-X-}C_6H_4CH_2OH$ ($\rho = -0.45$) and $p\text{-X-}C_6H_4\text{-}CH(OH)CH_3$ ($\rho = +0.22$) (X = OMe, CH_3, H, Cl, CF_3). Both a sigmoidal curve from the plot of initial rate vs $[PhCH(OH)CH_3]$ ($K_{0.5} = 0.34$ M; Hill coefficient, $n = 4.2 \pm 0.1$) and the phosphine inhibition kinetics revealed the highly cooperative nature of the complex for the oxidation of secondary alcohols.

Introduction

Considerable efforts have been devoted to the design of cooperative metal catalysts, for such catalysts may lead to increase in activity and serve as functional models for natural metalloenzymes.[1] For example, Jacobsen showed cooperative effects of chiral metal−salen complexes in catalytic asymmetric epoxide ring-opening and conjugate addition reactions.[2] Shibasaki also discovered cooperative effects of heterobimetallic catalysts for asymmetric conjugate addition and related reactions.[3] By employing a supramolecular approach, Mirkin and co-workers recently synthesized dimeric analogues of Jacobsen's epoxidation catalyst and demonstrated the allosteric nature in asymmetric epoxide ring-opening reactions.[4] Bimetallic Cu- and Zn-polypyridine[5] and tetrametallic Mn-oxo complexes[6] were found to exhibit cooperative catalytic activity for the hydrolysis of phosphate esters and the disproportionation of H_2O_2, respectively. Bimetallic cooperativity of cationic Rh complexes for cyclopropanation and hydroformylation reactions[7] and of Ru complexes for alkyne coupling reactions[8] has also been well-documented. A number of different bimetallic supramolecular hosts have been found to bind guests allosterically.[9]

Despite such recent progress, however, only a few well-defined polymetallic catalysts have been shown to exhibit cooperative catalytic activity. Moreover, most synthetic metal catalysts contain only one or two substrate-binding sites; multiple substrate-binding sites are necessary for achieving high degrees of cooperativity. Inspired by recent reports on unusual reactivity of low-valent late metal complexes with "hard" oxygen and nitrogen ligands,[10] we have begun to utilize the ruthenium-hydroxo and -amido complexes for selective bond activation reactions.[11] Here we report the synthesis of a novel tetrametallic ruthenium-oxo-hydroxo complex $\{[(PCy_3)(CO)\text{-}RuH]_4(\mu_4\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)\}$ (**1**) and its cooperative catalytic activity for the alcohol oxidation reaction.

Results and Discussion

The tetrametallic complex **1** was synthesized in two steps from the ruthenium-hydride complex $(PCy_3)_2(CO)RuHCl$ (**2**) (Scheme 1). Thus, the reaction of **2** with KOH in 2-propanol produced the bimetallic complex **3**, which was isolated in 85% yield after recrystallization in hexanes.[12] The subsequent treatment of **3** with acetone at 95 °C yielded complex **1** in 84% yield as a brown-red solid. The ^1H NMR spectrum of **1** in CD_2-

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(12) See the Supporting Information for X-ray crystallographic data of **3**.

10.1021/om0510674 CCC: $33.50

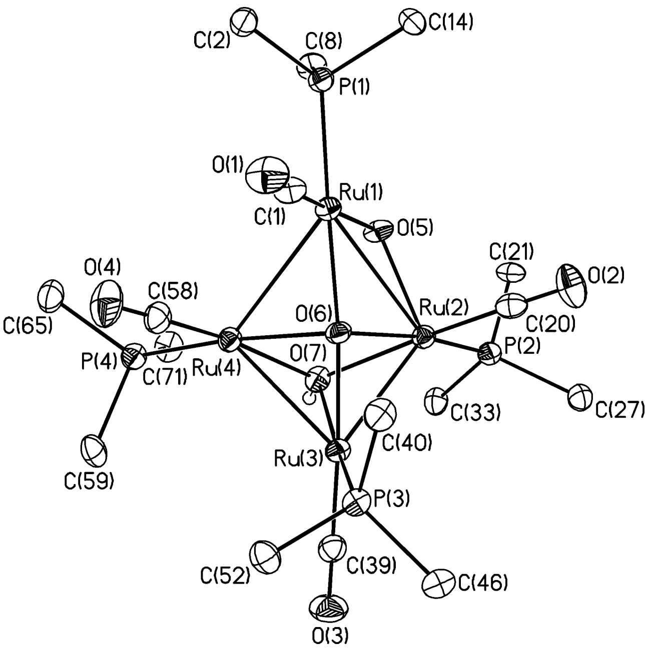


Figure 1. Molecular structure of **1** drawn with 50% thermal ellipsoids. Cyclohexyl groups are omitted for clarity.

Scheme 1

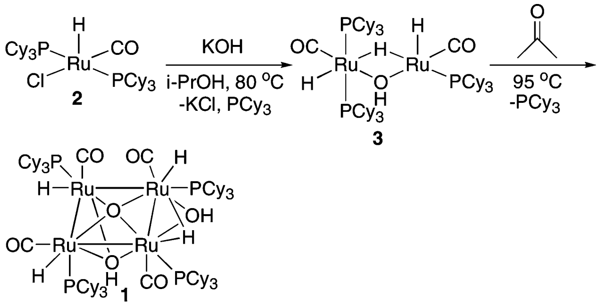
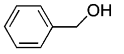
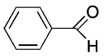
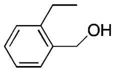
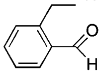
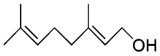
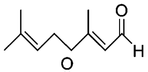
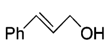
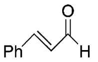
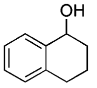
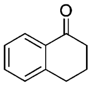
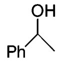
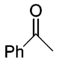
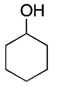
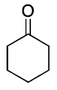
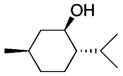
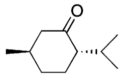
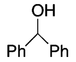
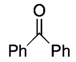
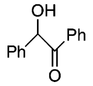
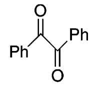


Table 1. Catalytic Oxidation of Alcohols Mediated by 1[a]

entry	alcohol	product	time (h)	convn (%)[b]	yield (%)[c]
1			22	87	84
2			18	100	62
3			3.5	95	85
4			19	100	85
5			18	100	94
6			20	100	97
7			4	100	86
8			6	100	98
9			6	100	97
10			16	83	79

[a] Reaction conditions: alcohol (1.0 mmol), **1** (2.5 mol % Ru), acetone (3 mL), 80 °C. [b] The conversion was determined by GC. [c] Isolated yield.

Cl_2 exhibited four metal-hydride peaks at δ −18.64 (dt, J_{HP} = 13.2, 4.8 Hz), −15.28 (d, J_{HP} = 34.5 Hz), −15.01 (d, J_{HP} = 16.8 Hz), and −14.55 (d, J_{HP} = 20.1 Hz), of which the resonance at δ −18.64 was assigned to the bridging hydride on the basis of its coupling pattern. Two μ-hydroxo proton signals at δ −2.50 and −2.60 were found to readily undergo H/D exchange upon treatment with D_2O.

The structure of **1** was further established by X-ray crystallography (Figure 1). The molecular structure of **1** showed a puckered butterfly geometry of the ruthenium core, which is supported by both μ_4-oxo and μ_3- and μ_2-hydroxo ligands. Two of the PCy_3 ligands on Ru(1) and Ru(4) occupy pseudoaxial positions, while the PCy_3 ligands on Ru(2) and Ru(3) can be viewed as pseudoequatorial ones relative to the metal core geometry. The *anti* geometry between two axial PCy_3 ligands (P(2) and P(3)) was also indicated by a relatively large coupling constant ($^3J_{PP}$ = 14.0 Hz) in the solution ^{31}P NMR.

Complex **1** was found to be a highly effective catalyst for the oxidation of both primary and secondary alcohols under transfer dehydrogenation conditions (Table 1). A considerably different reactivity pattern was noted between primary and secondary alcohol substrates. For example, the treatment of the primary alcohol $PhCH_2OH$ (1.0 mmol) in acetone (3 mL) in the presence of **1** (2.5 mol %) at 80 °C produced predominantly benzaldehyde (87% conversion after 22 h). For these *primary* alcohols, the red-brown color of the reaction mixture (due to catalyst **1**) turned bright yellow after 15 min of heating at 80 °C, and the ruthenium catalyst could not be recovered from the reaction mixture because it was completely soluble in the solution (entry 1−4). In sharp contrast, the red-brown color of the reaction mixture remained unchanged throughout the catalytic reaction for the *secondary* alcohols (entries 5−9) (Figure S1, Supporting Information). Furthermore, the catalyst **1** was readily recovered at the end of the catalysis by a simple filtration, as it became insoluble at room temperature. The ^1H NMR spectrum of the recovered catalyst was found to be identical to that of **1**, and its activity was found to be same after five repeated cycles. In general, the catalytic activity of **1** was found to be substantially higher than both mono- and bimetallic complexes **2** and **3**.[13]

Encouraged by these initial results, the Hammett study was performed for both primary and secondary benzyl alcohols, p-X-$C_6H_4CH_2OH$ and p-X-$C_6H_4CH(OH)CH_3$ (X = OMe, CH_3, H, Cl, CF_3), to compare the electronic effects of alcohol substrates on the oxidation reaction. As shown in Figure 2, an opposite trend was observed from the plots of $\log(k_X/k_H)$ vs σ_p between these primary and secondary alcohols ($\rho = -0.45$ for p-X-C_6H_4-CH_2OH; $\rho = +0.22$ for p-X-$C_6H_4CH(OH)CH_3$). A negative Hammett ρ value, which is indicative of a developing positive charge on the α-carbon, has commonly been observed for the alcohol oxidation reactions. On the other hand, a positive ρ value has been much less commonly observed for alcohol oxidation reactions mediated by synthetic metal catalysts. Relatively large positive ρ values have been reported for enzymatic oxidation reactions of benzyl alcohols and amines, wherein carbanion character of the carbonyl and imine carbon on the transition state has been implicated.[14] Very recently, Sigman observed a

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[13] See the Supporting Information for a representative example.

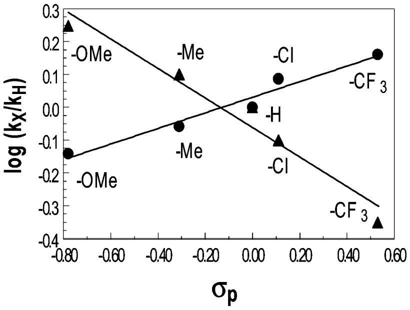

Figure 2. Hammett plots of p-X-$C_6H_4CH_2OH$ (▲) and p-X-C_6H_4-$CH(OH)CH_3$ (●) (X = OMe, CH_3, H, Cl, CF_3).

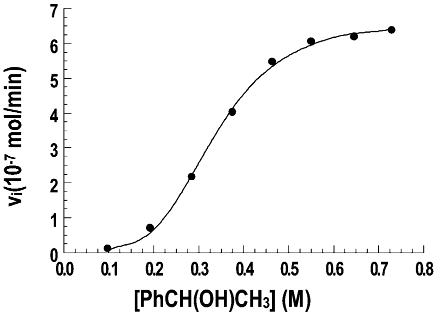

Figure 3. Plot of initial rate (v_i) vs [$PhCH(OH)CH_3$].

small, but positive ρ value of 0.03 from the palladium-catalyzed aerobic oxidation of benzyl alcohols.[15]

We next examined the kinetics of the catalytic reaction to gain further insights on the reaction mechanism. The kinetic analysis for the oxidation reaction of secondary alcohols revealed the cooperative nature of complex **1**. Thus, the initial rate of the oxidation of 1-phenylethanol (0.05−0.4 mmol) in acetone-d_6 (0.5 mL) was monitored by NMR at 80 °C at different alcohol concentrations. The plot of initial rate (v_i) vs [$PhCH(OH)CH_3$] showed a sigmoidal curve with saturation behavior typically seen for natural allosteric enzymes (Figure 3). The data were successfully fitted to the Hill equation, $v_i/V_{max} = [PhCH(OH)CH_3]^4/(K_{0.5}{}^4 + [PhCH(OH)CH_3]^4)$, from which $K_{0.5} = 0.34 \pm 0.01$ M and the Hill coefficient, $n = 4.2 \pm 0.1$, were obtained. The similar value of $n_{app} = 4.1$ was also calculated from an Eadie−Scatchard plot (Figure S5, Supporting Information).

The phosphine inhibition kinetics was conducted to further establish the cooperative nature of complex **1** (Figure 4). The Hill coefficient from the plot of initial rate vs [$PhCH(OH)CH_3$] was found to decrease to 2.4 upon addition of 1.0 equiv of PCy_3, and the cooperativity was effectively lost with the addition of 2.0 equiv of PCy_3, giving a Hill coefficient of 1.1. In contrast, the analogous inhibition kinetic plots for a primary benzyl alcohol, $PhCH_2OH$, gave hyperbolic curves that are commonly observed in Michaelis−Menton-type kinetics (Figure S6, Supporting Information).

In an effort to detect possible intermediate species, the reaction of **1** with both primary and secondary benzyl alcohols (8 equiv) in benzene-d_6/acetone-d_6 (1:1) was monitored by VT NMR. For the $PhCH(OH)CH_3$ case, the presence of complex **1** was clearly evident after 3 h at 40−60 °C, as seen by ^1H NMR, along with small amounts of secondary products, whose hydride signals are similar to that of **1** (Figure S7, Supporting Information). In contrast, a set of new peaks rapidly appeared at the expense of **1** upon warming to 40 °C for the reaction with $PhCH_2OH$. In this case, the new Ru−H peak at δ −14.79 (d, J_{PH} = 32.1 Hz) exhibited characteristic features of a monomeric ruthenium species similar to previously observed ruthenium-hydride complexes $(PCy_3)(CO)(X)Ru(H)L_2$ (X = OR; L = solvent).[11a] Both **1** and the new complex rapidly decomposed into a complex mixture of products within 10 min upon warming to 50 °C. These results further indicate the different reactivity pattern of **1** toward primary and secondary alcohols.

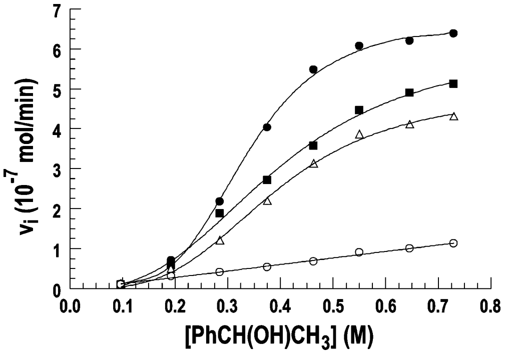

Figure 4. Plots of initial rate vs [$PhCH(OH)CH_3$] at various concentrations of added PCy_3. Without added PCy_3 (●); 1.0 equiv of PCy_3 (■); 1.5 equiv of PCy_3 (△); 2.0 equiv of PCy_3 (○).

The exact cooperative mechanism of the catalytic reaction is not clear. We offer a plausible mechanistic model of the sequential cooperative binding of alcohol substrate as shown in Scheme 2 to explain the kinetic data. The Hill coefficient of $n = 4$ obtained from the secondary alcohol oxidation reaction clearly implicates characteristic features for a cooperative mechanism involving all four Ru centers.[16] Since PCy_3 is a much stronger σ-donor than an alcohol substrate, the initial dissociation of PCy_3 should lead to an electron-poor ruthenium center, which might promote the subsequent ligand dissociation by triggering the conformational change of the complex (e.g., by shortening bond lengths). Such strong cooperativity has been rarely observed in nonenzymatic catalysis; an allosteric substrate binding of dicarboxylic acids to a cerium-pyridylporphyrinate complex has been reported to give the Hill coefficient of $n = 4$.[17]

Another important factor for cooperative activity appears to be the reversible nature of the catalytic reaction, and in this regard, both the alcohol dehydrogenation and reverse transfer hydrogenation reactions are well-known to proceed reversibly via a concerted "outer-sphere" mechanism.[18] In a preliminary result, we also demostrated the reversible nature of **1** by running the transfer hydrogenation of acetophenone.[19] Catalyst **1** did not exhibit any cooperative effects for the oxidation of primary alcohols because the sterically less demanding primary alcohols might have led to the rapid breakup of the tetrameric structure (as indicated by the formation of monomeric species). The

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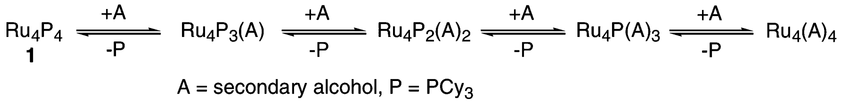
(19) The treatment of $PhCOCH_3$ (120 mg, 1.0 mmol) with **1** (2.5 mol %) in 2-propanol (3 mL) at 85 °C produced $PhCH(OH)CH_3$ in 86% yield. The color of the solution remained red-brown, and complex **1** was recovered at the end of the catalytic reaction.

Scheme 2



resulting monomeric and/or dimeric complexes should favor the stepwise hydrogen transfer via an "inner-sphere" mechanism.[20]

Our kinetic and mechanistic results raise a number of intriguing questions. For instance, why does the Hammett study of secondary benzyl alcohols result in a positive ρ value of $+0.22$? The positive ρ value suggests a developing negative charge on the α-carbon of the alcohol substrate, but normally the alcohol oxidation reactions proceed via a developing positive charge on the α-carbon. One possible explanation for this unusual observation is that sterically more demanding secondary alcohols would favor an "outer-sphere mechanism", which is is promoted by hydrogen-bonding interactions between Ru-OH and alcohol substrates. The hydrogen-bonding interactions between late transition metal-hydride and -hydroxo complexes and protic substrates have been well documented,[21] and in our case, a multiple number of hydrogen-bonding interactions between the catalyst **1** and alcoholic substrates can be envisioned. Under such environments, the developing negative charge on the α-carbon can result either from a concerted hydrogen transfer via a six-membered transition state similar to that of an Oppenhauer-type oxidation reaction or from an *anti*-1,2-hydrogen elimination promoted by an external base, such as free PCy_3 ligand.

Another unresolved issue is the homogeneous vs heterogeneous state of the catalytic reaction. Though the catalytic reaction appears to be "homogeneous", we still cannot rigorously rule out the possibility of the heterogeneous or colloidal nature of active species, especially for the catalytic reaction of secondary alcohols. In an effort to resolve this issue, a Hg test was performed on the catalytic oxidation reaction of a secondary alcohol. Thus, the catalytic reaction of 1-phenylethanol was stirred vigorously in the presence of Hg(0) (2.0 g) in acetone at 80 °C, in which case, the ketone product was obtained in 92% yield after 20 h of reaction time. However, in light of recent reports by Süss−Fink and Finke on Ru_3-oxo complexes,[22] one must be very careful in distinguishing between homogeneous vs heterogeneous catalytic reactions and in establishing the nature of catalytically active species. Clearly, further research is warranted to determine both the nature of the reactive species and the steric and electronic influences on the cooperative activity of complex **1**.

In summary, the tetrametallic ruthenium-oxo-hydroxo complex **1** was found to exhibit strong cooperativity for the catalytic oxidation of secondary alcohols. Efforts are currently underway to establish the origin of cooperative activity as well as the nature of active species for the catalytic oxidation reaction.

Experimental Section

General Information. All operations were carried out in a nitrogen-filled glovebox or by using standard high-vacuum and Schlenk techniques unless otherwise noted. Benzene, hexanes, THF, and Et_2O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All organic alcohols were received from commercial sources and used without further purification. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer. Mass spectra were recorded from a Hewlett-Packard HP 5970 GC/MS spectrometer. High-resolution FAB mass spectra were performed at the Center of Mass Spectrometry, Washington University, St. Louis, MO. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

$\{[(PCy_3)_2(CO)RuH]_4(\mu_4\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)\}$ (1). In a glovebox, complex **3** (500 mg, 0.46 mmol) and acetone (5 mL) were added to a 25 mL Schlenk tube equipped with a magnetic stirring bar and Teflon stopcock. The reaction tube was brought out of the glovebox and stirred in an oil bath at 95 °C for 3 h. After the tube was cooled to room temperature, the resulting red solid was filtered, washed with 2-propanol (5 mL, 3 times), and recrystallized in CH_2Cl_2 to obtain product **1** in 84% yield.

Selected spectroscopic data for **1**: ^1H NMR (300 MHz, CD_2Cl_2) δ 2.25−1.15 (m, PCy_3), −2.50 and −2.60 (s, μ-OH), −14.56 (d, J_{PH} = 19.2 Hz, Ru−H), −15.02 (d, J_{PH} = 18.0 Hz, Ru−H), −15.28 (d, J_{PH} = 34.8 Hz, Ru−H), −18.64 (dt, J_{PH} = 13.2, 4.8 Hz, Ru−H−Ru); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.6 MHz) δ 82.13 (s, PCy_3), 79.01 (d, J_{PP} = 14.0 Hz (PCy_3)), 71.96 (s, (PCy_3)), 68.89 (d, J_{PP} = 14.0 Hz, (PCy_3)); IR (CH_2Cl_2) ν_{OH} = 2926, 2849 cm^{-1}, ν_{CO} = 1925, 1912, 1894, 1868 cm^{-1}. Anal. Calcd for $C_{76}H_{138}O_7P_4Ru_4$: C 53.95, H 8.22. Found: C 55.03, H 8.14.

$(PCy_3)_2(CO)RuH(\mu\text{-}OH)(\mu\text{-}H)(PCy_3)(CO)RuH$ (3). In a glovebox, a 25 mL Schlenk tube equipped with a magnetic stirring bar and Teflon stopcock was charged with $(PCy_3)_2(CO)RuHCl$ (**2**) (726 mg, 1.0 mmol), KOH (6.5 mmol), and 2-propanol (5 mL). The reaction tube was brought out of the box and was stirred in an oil bath at 85 °C for 8 h. The solvent was removed under high vacuum, and the residue was washed with 2-propanol and benzene to obtain the product in 85% yield.

Selected spectroscopic data for **3**: ^1H NMR (300 MHz, CD_2Cl_2) δ 2.25−1.22 (m, PCy_3), −1.67 (s, Ru−OH), −8.05 (pseudo q, J_{PH} = 24.3, 18.0 Hz, Ru−H), −9.70 (dt, J_{PH} = 49.8, 5.7 Hz, Ru−H−Ru), −24.34 (dd, J_{PH} = 27.6, 5.7 Hz, Ru−H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 208.7 (t, J_{PC} = 14.6 Hz, CO), 207.0 (d, J_{PC} = 12.8 Hz, CO), 37.3, 36.8, 31.5, 30.7, 30.2, 28.4, and 27.2 (PCy_3 carbons); $^{31}P\{^1H\}$ NMR (121.6 MHz, CD_2Cl_2) δ 80.7 (AB pattern, J_{AB} = 212 Hz, PCy_3), 74.1 (t, J = 37.5 Hz, PCy_3); IR (CH_2Cl_2) ν_{OH} = 3650, ν_{CO} = 1905, 1895 cm^{-1}.

General Procedure of the Catalytic Alcohol Oxidation Reaction. A 25 mL Schlenk tube equipped with a magnetic stirring bar and Teflon stopcock was charged with the alcohol (1.0 mmol) and acetone (3 mL). The reaction tube was cooled in a dry/ice acetone bath, degassed, and brought into a nitrogen-filled glovebox. Complex **1** (44 mg, 2.5 mol %) was added to the reaction tube. The reaction tube was sealed, brought out of the glovebox, and

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(20) Selected recent examples: (a) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000**, *287*, 1636. (b) Mueller, J. A.; Jensen, D. R.; Sigman, M. S. *J. Am. Chem. Soc.* **2002**, *124*, 8202. (c) Jensen, D. R.; Schultz, M. J.; Mueller, J. A.; Sigman, M. S. *Angew. Chem., Int. Ed.* **2003**, *42*, 3810. (d) Steinhoff, B. A.; Guzei, I. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 11268.

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(22) (a) Hagen, C. M.; Vieille-Petit, L.; Laurenczy, G.; Süss-Fink, G.; Finke, R. G. *Organometallics* **2005**, *24*, 1819. (b) Vieille-Petit, L.; Süss-Fink, G.; Therrien, B.; Ward, T. R.; Stoeckli-Evans, H.; Labat, G.; Karmazin-Brelot, L.; Neels, A.; Bürgi, T.; Finke, R. G.; Hagen, C. M. *Organometallics* **2005**, *24*, 6104.

stirred in an oil bath (preset to 80 °C) for 6−24 h. After the reaction was completed, the reaction tube was opened to air and the solution was filtered through a frit. The filtrate solution was analyzed by GC. Analytically pure oxidation product was obtained after column chromatography on silica gel (hexanes/EtOAc).

General Procedure for Kinetic Measurements. To a J-Young NMR tube equipped with a Teflon-coated screw cap, 1-phenylethanol (0.05−0.4 mmol) and aceteone-d_6 (0.5 mL) were added via a syringe. After degassing in a dry ice/acetone bath, the reaction tube was brought into the glovebox, and **1** (4 mg) was added to the tube. The reaction tube was brought out of the glovebox and was stirred in an oil bath that was preset to 80 °C. The tube was removed from the oil bath at 15 min intervals and immediately cooled in a dry ice/acetone bath. The rate of the product formation was determined by ^{1}H NMR by measuring the integration of the appearance of the product peak at δ 2.63 (PhC(O)CH_3) vs the disappearance of the alcohol peak at δ 1.92 (PhCH(OH)CH_3). The initial rate was obtained from a first-order plot of [PhC(O)CH_3] vs time. The data were fit to the Hill equation by using a nonlinear regression method (ProStat version 4.0). An analogous procedure was used to determine the product formation by measuring the disappearance of the benzyl alcohol peak at δ 4.43 ($C_6H_5CH_2OH$) against an internal standard (hexamethylbenzene).

General Procedure for Hammett Study. To each of five separate J-Young NMR tubes equipped with a Teflon-coated screw cap was added p-X-$C_6H_4CH(OH)CH_3$ (X = OMe, Me, H, Cl, CF_3) (0.05−0.40 mmol) via syringe. Acetone-d_6 (400−450 μL) and benzene-d_6 (200−300 μL) were added to bring the total volume to 600 μL in each tube. The tubes were brought into the glovebox. Complex **1** (4 mg, 25 μmol) was added to each tube. The sealed tubes were brought out of the glovebox, and the ^{1}H NMR spectrum of each sample was initially taken at room temperature. The tubes were placed in an oil bath preset to 85 °C. The tube was removed from the oil bath at 15 min intervals and immediately cooled in a dry ice/acetone bath. The ^{1}H NMR spectrum of each sample was recorded at room temperature. The procedure was repeated 4 or 5 times. The initial rate was determined by measuring the integration of the appearance of the product peak (ArC(O)CH_3) vs time. The plot of concentration vs rate was fit to the Hill equation by using a nonlinear regression method (ProStat version 4.0). An analogous procedure was used to determine the initial rates for p-X-C_6H_4-CH_2OH (X = OMe, Me, H, Cl, CF_3).

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Supporting Information Available: Experimental procedures and crystallographic data of **1** and **3**. This material is available free of charge via the Internet at http//:pubs.acs.org.

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