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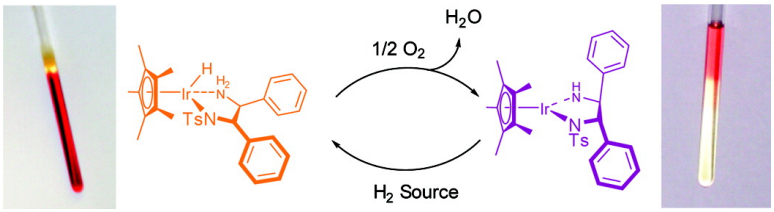

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Homogeneous Catalytic Reduction of Dioxygen Using Transfer Hydrogenation Catalysts

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Abstract: Solutions of Cp*IrH(*rac*-TsDPEN) (TsDPEN = $H_2NCHPhCHPhN(SO_2C_6H_4CH_3)^-$) (**1**H(H)) with O_2 generate Cp*Ir(TsDPEN-H) (**1**) and 1 equiv of H_2O. Kinetic analysis indicates a third-order rate law (second order in [**1**H(H)] and first order in [O_2]), resulting in an overall rate constant of 0.024 ± 0.013 M^{-2} s^{-1}. Isotopic labeling revealed that the rate of the reaction of **1**H(H) + O_2 was strongly affected by deuteration at the hydride position ($k_{HH_2}/k_{DH_2} = 6.0 \pm 1.3$) but insensitive to deuteration of the amine ($k_{HH_2}/k_{HD_2} = 1.2 \pm 0.2$); these values are more disparate than for conventional transfer hydrogenation (Casey, C. P.; Johnson, J. B. *J. Org. Chem.* **2003**, *68*, 1998−2001). The temperature dependence of the reaction rate indicated $\Delta H^{\ddagger} = 82.2$ kJ/mol, $\Delta S^{\ddagger} = 13.2$ J/mol·K, and a reaction barrier of 85.0 kJ/mol. A CH_2Cl_2 solution under 0.30 atm of H_2 and 0.13 atm of O_2 converted to H_2O in the presence of **1** and 10 mol % of $H(OEt_2)_2BAr^F{}_4$ ($BAr^F{}_4^- = B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4^-$). The formation of water from H_2 was verified by ^2H NMR for the reaction of $D_2 + O_2$. Solutions of **1** slowly catalyze the oxidation of amyl alcohol to pentanal; using 1,4-benzoquinone as a cocatalyst, the conversion was faster. Complex **1** also catalyzes the reaction of O_2 with RNH_2BH_3 (R = H, *t*-Bu), resulting in the formation of water and H_2. The deactivation of the catalyst **1** in its reactions with O_2 was traced to degradation of the Cp* ligand to a fulvene derivative. This pathway is not observed in the presence of amine-boranes, which were shown to reduce fulvenes back to Cp*. This work suggests the potential of transfer hydrogenation catalysts in reactions involving O_2.

Introduction

The Knall gas reaction, $2H_2 + O_2 \rightarrow 2H_2O$, supplies energy in fuel cells and some bacteria.[2] Although platinum metal has been known since Dobereiner's time to catalyze this reaction,[3] homogeneous catalysts are rare. The realization that the "difficult side" of the H_2-O_2 fuel cell is the oxygen reduction reaction (ORR),[4,5] not hydrogen oxidation, motivates the development of alternative approaches to oxygen reduction. We propose that the development of new homogeneous catalysts for the hydrogenation of oxygen could lead to new mechanistic insights relevant to the design of new heterogeneous catalysts.

The hydrogenation of dioxygen by conventional homogeneous catalysts is challenging. Many complexes that are reactive toward H_2 are rapidly and irreversibly oxidized upon treatment with O_2.[6] Complementarily, complexes that are reactive toward O_2 are, after oxidation, generally inert toward H_2.[7] Promising is the fact that metal hydrides do react with O_2 to produce hydroxides and hydroperoxides.[8−10] For example, Goldberg and Stahl have recently described the reaction of 16e palladium hydrides with O_2 to give hydroperoxides.[9,11−13] The resulting M−O_2H and M−OH complexes are not readily catalytic since they resist hydrogenolysis, which is required to regenerate the starting hydride (Scheme 1, reaction A).[10,11,14] A possible exception to this pattern is the hydroperoxide derived from $[HCo(CN)_5]^{3-}$, which hydrolyzes to an aqua complex in the presence of protons.[15] This unusual case highlights the

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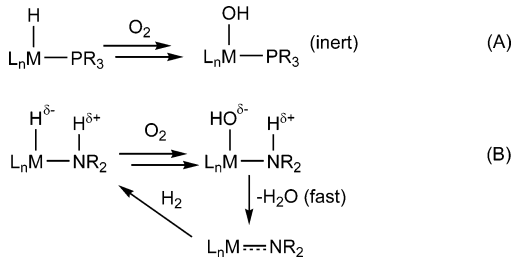
Scheme 1. Differing Reactivity Patterns Anticipated for Oxygen toward Classical Metal and Amino-Hydrides

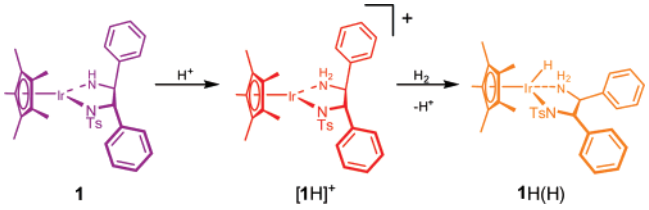


potential benefits of catalysis in water, which facilitates scission of M−O_xH bonds (where $x = 1$ or 2).

A relatively new generation of transfer hydrogenation catalysts, which operate via heterolytic mechanisms, presents new options for the regeneration of the metal hydride after formation of hydroxides or hydroperoxides. In fact, these transfer hydrogenation catalysts operate by the elimination of alcohols (and likely water) from alkoxy amine intermediates, thus avoiding catalyst deactivation.[16−21,22,23] Given the fact that transfer hydrogenation catalysts will not deactivate through formation of stable M−OR species (Scheme 1, reaction B), we investigated them as possible catalysts for the hydrogenation of O_2.

Given that alkoxy (hydroxyl) intermediates will spontaneously eliminate alcohol (water), one other reaction that is critical to the development of catalysts for the hydrogenation of oxygen is the hydrogenation step. The direct addition of H_2 to transfer hydrogenation catalysts has recently been examined.[24] The Mashima−Ikariya system Cp*Ir(TsDPEN-H) (**1**, TsDPEN = *rac*-$H_2NCHPhCHPhN(SO_2C_6H_4CH_3)^-$) slowly adds H_2 to give the amine hydride Cp*IrH(TsDPEN) (**1**H(H)).[16,18] We recently reported that this reaction is accelerated by Brønsted acids such as $H(OEt_2)_2BAr^F{}_4$ ($BAr^F{}_4^- = B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4^-$), which converts **1** into the unsaturated iridium(III) amine cation $[Cp^*Ir(TsDPEN)]^+$ ([**1**H]$^+$, see Scheme 2).[23]

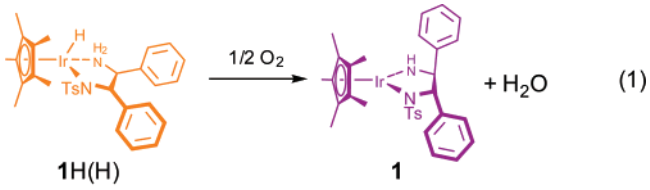
Scheme 2



Assuming the eventual development of new classes of oxygen reduction catalysts, it will still be necessary in the future to conduct O_2 reduction and H_2 (or other substrates) oxidation in separate compartments connected by a load-bearing circuit.[4] For the present report, however, we focus exclusively on the oxidative reactivity of iridium-based transfer hydrogenation catalysts in a homogeneous solution.

Results

We found that the 18e amino-hydride Cp*IrH(TsDPEN) reacts with molecular oxygen to give Cp*Ir(TsDPEN-H) (**1**) and 1 equiv of water (eq 1). The conversion is signaled by a color change from pale orange to purple, associated with **1**H(H) and **1**, respectively.[16] UV−vis experiments indicated that intermediates do not accumulate (Figure 1).



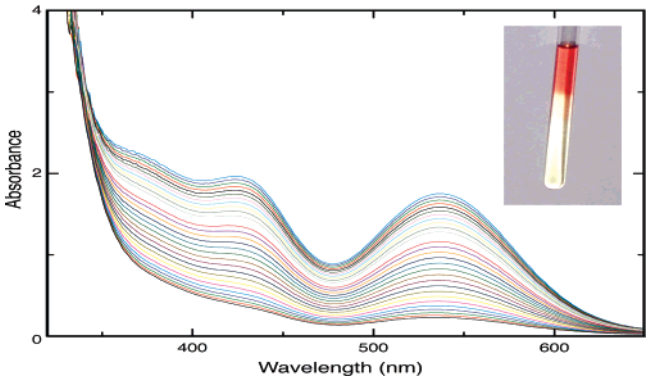


Figure 1. UV−vis spectrum of an unstirred acetonitrile solution of Cp*IrH(TsDPEN) in air, recorded at 10-min intervals. The absorption bands arise from formation of Cp*Ir(TsDPEN-H). Inset: the effects of diffusion of air (O_2) into a CD_3CN solution of Cp*IrH(TsDPEN). The red color is due to Cp*Ir(TsDPEN-H).

The catalytic nature of the $H_2 + O_2$ reaction was formally established stepwise, in a batch process. Thus, after conversion of **1**H(H) into **1** with oxygen, the apparatus was purged with argon and then treated with 10 mol % of $H(OEt_2)_2BAr^F{}_4$ to generate some [**1**H]$^+$. After 1 atm of H_2 was introduced, the solution color changed from purple to light orange over the course of 15 h, indicative of **1**H(H). The apparatus was then purged with argon, and the addition of O_2 induced a quantitative change to purple **1** over the course of 30 min. Rehydrogenation of the resulting **1** proceeded without any further addition of acid, followed by dehydrogenation to **1** to demonstrate 2.5 turnovers. Each transformation was verified by ^{1}H NMR spectroscopy. The progress of the catalytic hydrogenation of O_2 is visually obvious (Figure 2).

The rate of dehydrogenation of **1**H(H) by O_2 was found to be highly solvent-dependent. Under typical conditions using 1 atm of O_2, reactions were complete within the time of mixing in benzene. Reactions required ∼1 h in acetonitrile and several minutes in dichloromethane. The dehydrogenation of solutions of **1**H(H) was also found to proceed in air but slowly (solid samples of **1**H(H) were dehydrogenated by air over a period of months). We conducted most experiments in MeCN or CH_2Cl_2 solutions, wherein reactions proceeded at rates convenient for mechanistic analysis.

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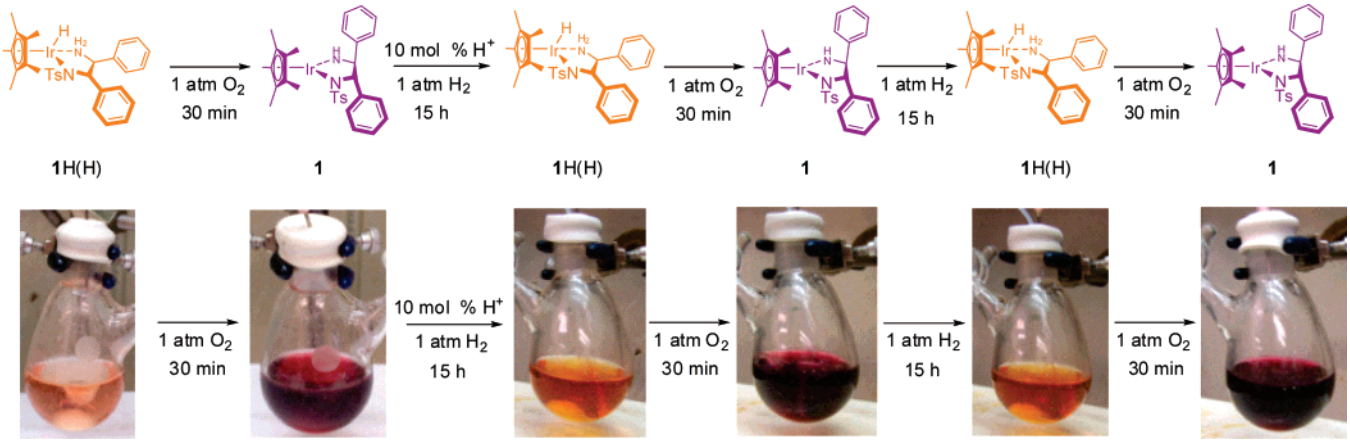

Figure 2. Sequential exposure of a methylene chloride solution of Cp*IrH(TsDPEN) and 10 mol % of $H(OEt_2)_2BAr^F{}_4$ ($BAr^F{}_4^- = B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4^-$) to O_2 and H_2. Racemic mixtures of TsDPEN were used; Cp*IrH(*S*,*S*-TsDPEN) and Cp*Ir(*S*,*S*-TsDPEN-H) are shown only as an example.

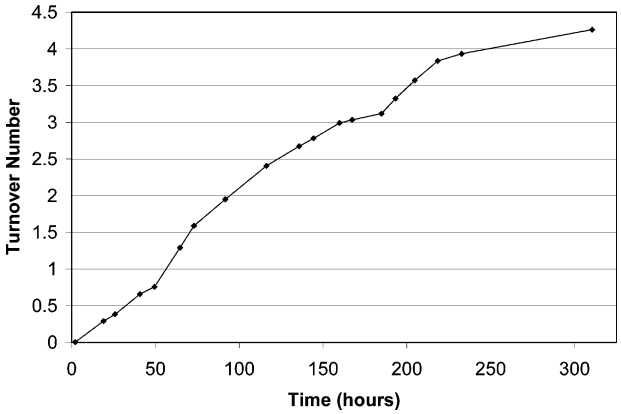

Figure 3. Turnover plot for the reaction of Cp*Ir(TsDPEN-H) with 17.5 mol % of [Cp*Ir(TsDPEN)]$BAr^F{}_4$, 0.30 atm of H_2, and 0.18 atm of O_2 in CD_2Cl_2. TON is defined as moles of H_2O per mole of Cp*Ir(TsDPEN-H).

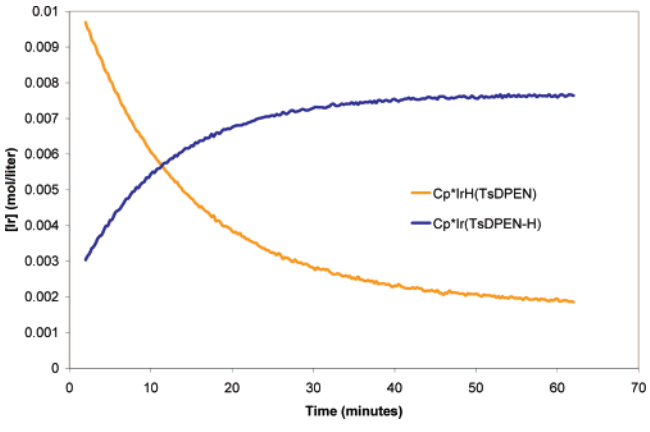

Figure 4. Time course for the reaction of Cp*IrH(TsDPEN) with O_2 in CD_3CN solution. Two minutes were required to set up the data collection.

In the presence of 10 mol % of [Cp*Ir(TsDPEN)]$BAr^F{}_4$ ([**1**H]$BAr^F{}_4$), a CD_2Cl_2 solution of **1** under 0.30 atm of H_2 and 0.13 atm of O_2 produced 4.26 equiv of water over the course of ca. 300 h (Figure 3).[25] The formation of water (D_2O) was verified by ^2H NMR spectroscopy for the reaction of **1** with 15 mol % of [Cp*Ir(TsDPEN)]$BAr^F{}_4$ ([**1**H]$BAr^F{}_4$) in CD_2Cl_2 in the presence of 0.56 atm of D_2 and 0.35 atm of O_2. The turnover number for these reactions was limited by mass transfer, i.e., mixing, which is important in processes involving gaseous and dissolved reagents (see below).

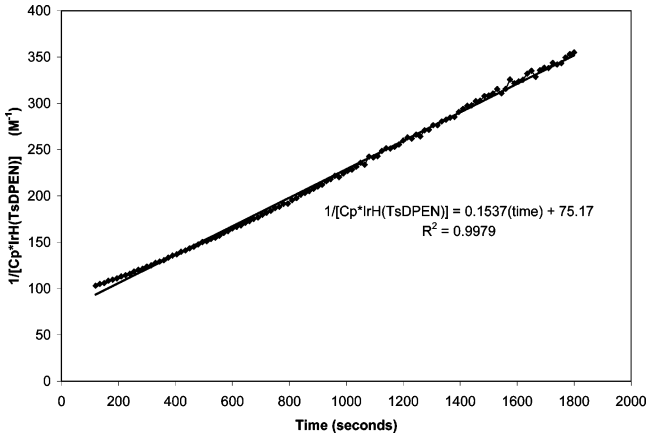

Figure 5. Plot indicating second-order dependence of the reaction of Cp*IrH(TsDPEN) with O_2 in CD_3CN solution. The deviation at early reaction times is attributed to incomplete temperature equilibration following rapid thawing of the sample (77−293 K, ∼3 min).

Kinetics and Isotope Effects. Studies of the reaction rate for **1**H(H) + O_2 were conducted under conditions of excess, constant P_{O_2} ([O_2]:[**1**H(H)] > 10). The solvent CD_3CN was selected to intentionally slow the reaction to allow for kinetic analysis (only 8−10 data points could be obtained using CD_2Cl_2). An 85−95% conversion of **1**H(H) to **1** was observed (Figure 4). The rate of the dehydrogenation, $-d[\mathbf{1}H(H)]/dt$, followed a second-order dependence on [**1**H(H)], as indicated by the linearity of a plot of 1/[**1**H(H)] vs time (Figure 5). A first-order dependence on [O_2] was indicated by the observation of a doubling of the second-order rate constant when [O_2] was doubled. With a first-order dependence on [O_2], an overall rate constant of 0.024 ± 0.013 M^{-2} s^{-1} (20.0 °C) was determined over three half-lives. The presence of 2 equiv of the radical traps BHT and TEMPO did not affect the yield of **1** by the reaction of O_2 with **1**H(H).[26,27] The rates of reduction of O_2

(25) Although the dehydrogenation of **1**H(H) by O_2 in benzene-d_6 was rapid, catalytic hydrogenation was problematic because [**1**H]$BAr^F{}_4$ is insoluble in benzene-d_6, slowing the hydrogenation of **1** to 40% conversion over 30 vs 16 h, for complete conversion in CD_2Cl_2.

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were slower only by factors of 2× and 4× for BHT and TEMPO, respectively, which we attribute to medium effects since the reduction of O_2 is sensitive to solvent polarity. The rate of the reaction was evaluated over the temperature range −15 to 20 °C. The temperature dependence of the rate constants indicated $\Delta H^{\ddagger} = 82.8$ kJ/mol and $\Delta S^{\ddagger} = 13.2$ J/mol·K, for a net $\Delta G^{\ddagger} = 78.9$ kJ/mol at 298 K (see Experimental Section).

Isotope effects were examined to probe the relative roles of N−H and Ir−H in the reactions. In their study on the reduction of acetophenone by [2,5-Ph_2-3,4-$Tol_2(C_4COH)$]$RuH(CO)_2$ in CD_2Cl_2 solution, Casey and co-workers measured isotope effects of 1.2 for deuteration at the OH and 2.2 for deuteration at the hydride.[28] Casey and co-workers also estimated the isotope effects for the reduction of acetone using equilibrium measurements from the dehydrogenation of isopropanol with (*p*-cymene)Ru(TsDPEN-H), resulting in isotope effects of 1.6 for deuteration at the amine and 2.4 for deuteration at the hydride.[1] We found a more dramatic isotope effect for the reduction of O_2: deuteration of the hydride gave $k_{HH_2}/k_{DH_2} = 6.0 \pm 1.3$. An isotope effect of similar magnitude was observed by Goldberg and coworkers ($k_H/k_D = 5.8$) for the oxygenation of an organopalladium hydride with dioxygen.[9] Deuteration of the amine of **1**H(H) was found to have a relatively minor effect ($k_{HH_2}/k_{HD_2} = 1.2 \pm 0.2$).

Alternative Hydrogen Donors. 1. Amine-Boranes. We sought to test the ability of **1** to catalyze the oxidation of amine-boranes, which have attracted recent attention as hydrogen sources for possible applications in fuel cells.[29] Several metal complexes have been shown to catalyze the dehydrogenation of NH_3BH_3.[30] We first investigated the dehydrogenation of NH_3BH_3 by **1**. We confirmed that NH_3BH_3 rapidly converted *2 equiv* of **1** into **1**H(H) in a matter of seconds (eq 2). Excess NH_3BH_3 converted **1**H(H) into $[(Cp^*Ir)_2(\mu\text{-}H)_3]^+$, arising from protonolysis of the TsDPEN ligand. We have previously reported that this hydrogenolysis is accelerated by protic reagents.[23]

$$2Cp^*Ir(TsDPEN\text{-}H) + NH_3BH_3 \rightarrow 2Cp^*IrH(TsDPEN) + {}^1/_n(NHBH)_n \quad (2)$$

The efficient conversion of **1** into **1**H(H) by NH_3BH_3 led us to couple this dehydrogenation with the reduction of O_2. Due to the low solubility of NH_3BH_3 in organic solvents,[31,32] we used *t*-$BuNH_2BH$ in O_2-coupled reactions.[33,34] Using 4 mol % of **1** in the presence of 11 atm of O_2 and *t*-$BuNH_2BH_3$ in CD_2Cl_2 gave H_2 and H_2O, which was confirmed by ^{1}H NMR spectroscopy. No *t*-$BuNH_2BH_3$ was found to remain in the solution after 6 h, and the presence of **1** was verified by ^{1}H NMR spectroscopy. Quantification of turnover from H_2 and H_2O was precluded by the reaction of the cogenerated water with *t*-$BuNH_{2-x}BH_{3-x}$. Hydrolysis of *N*-alkylborazoles to amines and boric acid has been reported.[35]

Alternative Hydrogen Donors. 2. Alcohols. Alcohols have been recently employed as hydrogen donors in fuel cells[36] and are well known to convert **1** into **1**H(H), concomitant with formation of ketones and aldehydes.[16] In conjunction with the reactivity of **1**H(H) toward O_2, this dehydrogenation step defines a catalytic cycle (eqs 3 and 4).

$$Cp^*Ir(TsDPEN\text{-}H) + RCH_2OH \rightarrow Cp^*IrH(TsDPEN) + RCHO \quad (3)$$

$$Cp^*IrH(TsDPEN) + 0.5O_2 \rightarrow Cp^*Ir(TsDPEN\text{-}H) + H_2O \quad (4)$$

To establish proof of concept, we examined the oxidation of amyl alcohol in the presence of 5 mol % of **1**. Under 3.5 atm of O_2, pentanal was produced, albeit with only 4−5 turnovers. Oxygen pressures greater than 2.5 atm ($[O_2]$:[**1**] > 2:1) were found to have little effect on turnover number (TON) or turnover frequency. TON was defined as moles of aldehyde per mole of **1**. The presence of 25 mol % of triethylamine also had no effect. Doubling the catalyst loading from 5 to 10 mol % was found to reduce the TON by a factor of 2.[37]

We surveyed other hydrogen-transfer catalysts. Ir-based catalysts were found to be slightly more active in the case of alcohol oxidation than the Ru derivatives, and the Rh derivative was the least active. Shvo's catalyst, $\{[(\eta^5\text{-}Ph_4C_4CO)]_2(\mu\text{-}H)\}\text{-}Ru_2(\mu\text{-}H)(CO)_4$,[38] was also found to catalyze the oxidation of pentanol and proved more robust than the Mashima−Ikariya catalyst (Table 1, see also Supporting Information).

The efficiency of the alcohol dehydrogenation reaction was significantly enhanced by the presence of *p*-benzoquinone (BQ) in addition to O_2. Thus, using 50 mol % of BQ, 2 atm of O_2, and still 5 mol % of **1**, we observed oxidation of 10 equiv of alcohol over the course of 12 h.[39] BQ functions as a hydrogen acceptor that augments the action of O_2. Alcohol oxidation experiments involving BQ and air were only half as effective as those with BQ and pure O_2. Separate experiments (see below) demonstrated that BQ rapidly dehydrogenates **1**H(H).

Dehydrogenation of 1H(H) by Other Oxidants. Experiments were conducted to test the viability of H_2O_2 as an

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(39) The ability of BQ to oxidize alcohols prompted an examination of its hydrogenation by **1**H(H). In the presence of 10% $H(OEt_2)_2BAr^F{}_4$, **1**H(H) indeed catalyzes the hydrogenation of BQ to *p*-$C_6H_4(OH)_2$ (HQ). At ∼1 atm of H_2, in a methylene chloride solution, 5 equiv of BQ was converted to HQ over the course of 12 h.

Table 1. Effect of Precatalyst on Oxidation of Amyl Alcohol Using Molecular Oxygen

precatalyst	substrate	base[a]	solvent	O_2 pressure (atm)	TON[b]
Cp*Ir(TsDPEN-H)	amyl alcohol	NEt_3	CD_2Cl_2	5	4.26
Cp*Ir(*S,S*-TsDPEN-H)	amyl alcohol	NEt_3	CD_2Cl_2	5	4.23
Cp*IrCl(TsDPEN)	amyl alcohol	NEt_3	CD_2Cl_2	5	3.00
Cp*RhCl(TsDPEN)	amyl alcohol	KOH[c]	CD_2Cl_2	5	0.54
(*p*-cymene)RuCl(TsDPEN)	amyl alcohol	NEt_3	CD_2Cl_2	5	2.4
Shvo's catalyst	amyl alcohol		CD_2Cl_2	5	5.53[d]

[a] 25 mol % (60 μmol) of base relative to alcohol was used; 72 μmol of base was used in the case of amino-chloride precatalysts. [b] 5 mol % of precatalyst (12 μmol) and alcohol (240 μmol) under an O_2 atmosphere in 0.8 mL of CD_2Cl_2 was monitored via ^{1}H NMR for 36 h. [c] KOH (72 μmol) was used in the Rh case due to the fact that NEt_3 was not significantly strong enough to dehydrohalogenate the amino-chloride. [d] 2.5 mol % of Shvo's dimer, $\{[(Ph_4(\eta^5\text{-}C_4CO)]_2(\mu\text{-}H)\}Ru_2(\mu\text{-}H)(CO)_4$, was used; TON is reported after 29 h, where 53% of Shvo's dimer remained.[38]

intermediate in the reduction of O_2. No formation of H_2O_2 was observed via ^{1}H NMR spectroscopy (δ 8.84 in CD_3CN) upon treating a CD_3CN solution of **1**H(H) with excess O_2 in an NMR tube. A CD_3CN solution of **1**H(H) was found to rapidly react with substoichiometric amounts of H_2O_2 (0.3 equiv) to give **1** as the main product. Larger amounts (2 equiv) of H_2O_2 were found to destroy the organoiridium complexes, as indicated by the loss of the Cp* and TsDPEN signals in the ^{1}H NMR spectrum. Treatment of **1**H(H) with 1 equiv of *t*-BuOOH resulted in the formation of **1**, *t*-BuOH, and H_2O (eq 5); further equivalents of *t*-BuOOH resulted in destruction of the organoiridium complexes, as seen with excess H_2O_2.

$$\text{Cp*IrH(TsDPEN)} + \text{ROOH} \rightarrow \text{Cp*Ir(TsDPEN-H)} + \text{H}_2\text{O} + \text{ROH} \quad (\text{R} = t\text{-Bu, H}) \quad (5)$$

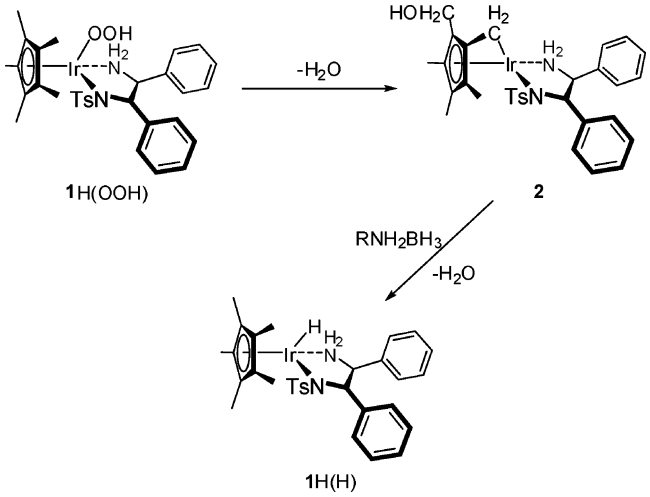
In addition to H_2O_2 and *t*-BuOOH, nitrosobenzene dehydrogenated **1**H(H) to give *N*-phenylhydroxylamine.[41,42] **1**H(H) was found to be dehydrogenated by diethyl azodicarboxylate and nitric oxide. Azobenzene and nitrous oxide were inert with respect to **1**H(H). Surprisingly, the transfer hydrogenation of quinones has been lightly studied.[39,40] 1,4-Benzoquinone rapidly and cleanly dehydrogenated **1**H(H) to give **1** and 1,4-dihydroxybenzene (eq 6).

$$\text{Cp*IrH(TsDPEN)} + \text{X} \rightarrow \text{Cp*Ir(TsDPEN-H)} + \text{H}_2\text{X} \quad (\text{X} = p\text{-}C_6H_4O_2, \text{PhNO}, N_2(CO_2Et)_2) \quad (6)$$

Catalyst Deactivation. For both the catalytic hydrogenation of O_2 and the oxidations of pentanol, the **1**H(H) turned over ca. 4−10×. We note again that reactions were optimized for product analysis (e.g., NMR tubes), not turnovers. Nonetheless, we sought insights into the weaknesses in this catalytic system. We confirmed that **1**, [**1**H]BAr^F_4, and the hydrogenolysis product of **1**H(H) ($[Cp^*_2Ir_2H_3]^+$) are stable toward O_2.[43] Careful scrutiny showed, however, that the stoichiometric dehydrogenation of **1**H(H) by O_2 to give **1** proceeded in only 85−95% conversion (Figure 4). This reaction produces a minor product (**2**) in 5−15% yield that could be observed by NMR spectroscopy. Compound **2** was also detected in the reaction of H_2O_2 and *t*-BuOOH with both **1** and **1**H(H). The yield of **2** was found to depend on the initial concentration of **1**H(H), but was largely insensitive to [O_2]. This finding suggests that the degradation is competitive with reduction of an intermediate (**1**H(OOH), see Conclusions and Mechanistic Considerations) with **1**H(H).

^{1}H NMR spectra confirm that **2** contains intact TsDPEN: the position and multiplicities of the NC*H* resonances indicate equatorial phenyl groups in pseudo-octahedral complexes of the type Cp*IrX(TsDPEN) or $[Cp^*IrL(TsDPEN)]^+$.[23,44] The Cp* group has, however, clearly suffered attack, as indicated by an AB-quartet (2H, δ 2.7−3.4), which is characteristic of a fulvene derivative.[45] Three Cp* methyl groups can be observed (3H each, see Supporting Information).[46] Maitlis, Kirchner, and Sharp have previously demonstrated the ability of O_2 to convert Cp*M centers into related tetramethylfulvene complexes,[42,47,48] which in turn can undergo further activation of the methyl groups.[48] The degradation product **2** is therefore assigned the formula [η^6-($C_5Me_3(CH_2OH)CH_2$)Ir(TsDPEN)] (Scheme 3). Compound **2** is proposed to arise via intramolecular H-atom abstraction from the Cp* methyl by an intermediate hydroperoxide. Degradation is competitive with the second-order reaction of the hydroperoxide with **1**H(H). Consistent with this scenario, the relative yield of **2** was found to increase at high dilutions (Supporting Information). Further characterization of **2** was precluded by its limited stability. Similar C−H bond hydroxylation has been observed in studies of copper hydroperoxo complexes.[49]

Scheme 3



Consistent with the proposed assignment, the degradation product completely converted into **1**H(H) in the presence of

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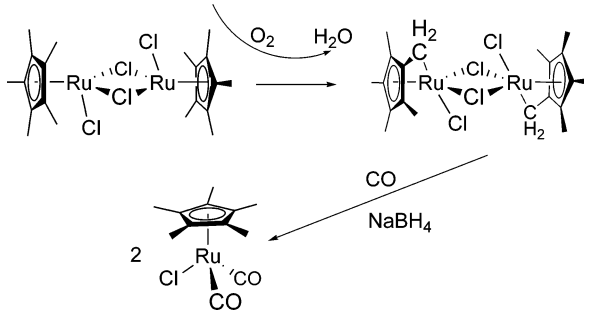
(46) ^{1}H NMR (500 MHz, CD_3CN): δ 0.75 (s, 3H), 1.48 (s, 3H), 2.02 (s, 3H), 2.36 (s, 3H), 2.77 (d, 1H, J = 2.7 Hz), 3.40 (d, 1H, J = 2.7 Hz), 3.87 (ddd, 1H, J = 3.7, 11.1, 14 Hz, $H_2NCHPhCHPhNTs$), 4.5 (br d, 1H, $HHNCHPhCHPhNTs$), 4.80 (d, 1H, J = 11.1 Hz, $HHNCHPhCHPhNTs$), 4.91 (br t, 1H, $HHNCHPhCHPhNTs$), 5.41 (s, 1H), 5.54 (s, 1H), 6.83−7.38 (m, 14H).

t-$BuNH_2$·BH_3, which explains the high TONs observed with amine-boranes as substrates (Scheme 3). Maitlis has described the conversion of an (η^6-fulvene)Ru complex to its Cp* derivatives using $NaBH_4$ (Scheme 4).[50]

Scheme 4



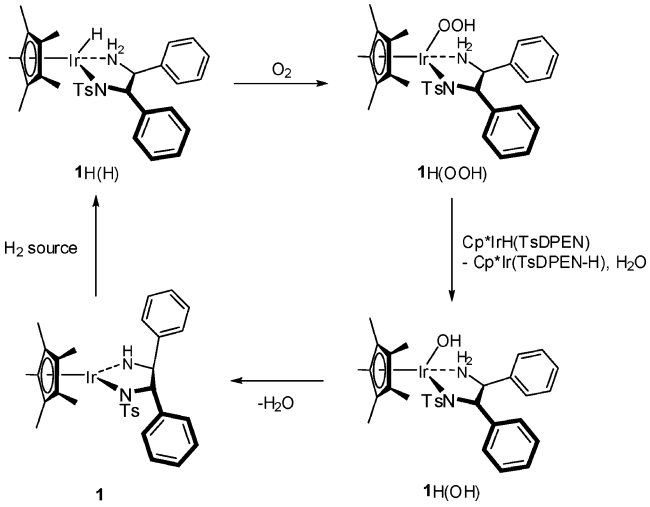
Conclusions and Mechanistic Considerations

The transfer hydrogenation catalysts developed by Mashima and Ikariya et al.[16−18] exhibit unusual reactivity toward oxygen, resulting in its catalytic hydrogenation to give water. Very few complexes are reactive toward both O_2 and H_2. The required unusual combination of mutually compatible reductive and oxidative properties is, however, characteristic of the transfer hydrogenation catalysts.

The second-order dependence on [**1**H(H)] is consistent with the rate-determining reduction of a hydroperoxo complex **1**H(OOH) by **1**H(H). The resulting hydroxy amine Cp*Ir(OH)(TsDPEN) would spontaneously eliminate water, affording **1**, which is poised for reduction by H_2 (Scheme 5). The formation of **1**H(OOH) is consistent with the large difference in the rate of oxidation of Cp*IrD(TsDPEN) vs Cp*IrH(TsDPEN). The disparate magnitudes of the isotope effects for deuteration at the amine and the hydride argue against a concerted mechanism (cyclic transition state), which is accepted to occur in the transfer hydrogenation of ketones.[1,20] Instead, the reactivity is localized at the Ir−H center, analogous to the reaction of O_2 with palladium hydrides.[11,13,51] The efficiency of the O_2 + **1**H(H) reaction was unaffected by radical traps,[26] which argues against the involvement of homolytic pathways. We propose that **1**H(OOH) and **1**H(H) combine to produce **1**, H_2O, and **1**H(OH). An analogous result was observed in the treatment of **1**H(H) with *t*-BuOOH, which was found to produce **1**, H_2O, and *t*-BuOH. A key aspect of the mechanism is the elimination of water from **1**H(OH), a reaction akin to the elimination of alcohol in transfer hydrogenation.

The solvent effects observed in the reduction of O_2 by **1**H(H) are believed to be indicative of ion pairing and possible aggregation in solution.[52] Singlet oxygen ($^1O_2$) was excluded from consideration, although it is known to be highly reactive toward organometallics.[53,54] Previous work on the oxygenation of metal hydrides also assumed $^3O_2(^3\Sigma_g^-)$, not $^1O_2(^1\Delta_g)$.[11,13,51]

Scheme 5. Proposed Catalytic Cycle for Hydrogenation of O_2 by **1**H(H)



Considerable prior work on **1**H(H) and related catalysts has emphasized reductions, although transfer dehydrogenations have recently been coupled to oxidations. Bäckvall et al. have demonstrated aerobic oxidation of amines and alcohols using Shvo's catalyst.[55,56] The Bäckvall system uses a quinone as a hydrogen acceptor and a Co−salen complex to aerobically regenerate the quinone.[56] In our case, the iridium complex affects *both* the oxidation (dehydrogenation) of the alcohol and the reduction (hydrogenation) of the oxygen. Recently, Xiao and co-workers have described Ru and Ir amido-amine catalysts that are effective transfer hydrogenation catalysts in air.[21,57] The chemistry described here shows that O_2 would not be expected to inhibit the transfer hydrogenation of organic substrates, instead serving as a mildly competing hydrogen acceptor.

In summary, Ir-based transfer hydrogenation catalysts have been found to catalyze the hydrogenation of dioxygen using H_2 as well as other hydrogen donors. An intermediate iridium hydroperoxo complex is indicated. Modifications of the co-ligands could be expected to confer greater oxidative stability to these catalysts.[58] Furthermore, we have found that counter-anions (of [**1**H]$^+$) significantly affect the hydrogenation of O_2.[59]

The significance of this work lies in the use of unconventional metal hydrides for oxygen reduction. In future work, we will

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more explicitly investigate the role of a proton donor (the coordinated amine) adjacent to the site of oxygen reduction.

Experimental Section

The preparations of **1**H(H) and **1** are optimized procedures of previously described procedures and are presented in the Supporting Information.[16,18,24] Hydrogen (research grade purity, 99.9999%) and oxygen (99.95%) were used as received from S. J. Smith Co. Seven-inch J. Young tubes were each fitted with a Wilmad-LabGlass 535-PP-7 Precision thin-walled NMR tube (o.d. = 5 mm, i.d. = 4.24 mm, and wall thickness = 0.38 mm) and were used for all NMR-tube-based reactions. Thin-walled tubes can withstand pressures of ~20 atm before fracture. For pressures >15 atm, medium- and thick-walled tubes are recommended for elevated pressure analysis. All ^{11}B NMR chemical shifts were referenced to an external $BF_3{\cdot}Et_2O$ standard.

Caution and Warnings: Reactions involving H_2 and O_2 are dangerous! Gas bulbs were filled, with caution, behind blast shields. Pressures were carefully monitored, especially in experiments involving condensation of O_2! No flames were used in sealing NMR tubes. All NMR tubes were carefully thawed over the course of several minutes, from the top down, before insertion into the spectrometer and transferred while frozen at liquid nitrogen temperatures.

Sequential Addition of H_2 and O_2. A 25-mL CH_2Cl_2 solution of 70 mg (101 μmol) of **1**H(H) was exposed to an atmosphere of O_2 for 30 min. A color change from pale orange to reddish-purple was observed after 10 min. A 10-mL CH_2Cl_2 solution of 9.8 mg (9.7 μmol) of $H(OEt_2)_2BAr^F{}_4$ was added to the **1** solution. An atmosphere of H_2 was then introduced for 15 h, resulting in a color change from reddish-purple to orange-pink. Oxygen was then introduced for 30 min, resulting in a reddish-purple solution. Sequential exposure to H_2 and O_2 was again implemented to demonstrate 2.5 turnovers (Figure 2). The apparatus was purged with argon for 30 min after each gas addition. Samples of 0.5 mL volume were removed before addition of Ar and every 2 h in the presence of H_2 for analysis by ^{1}H NMR spectroscopy. *Note:* Argon was used to purge the apparatus between additions of H_2 or O_2 to avoid the presence of explosive concentrations of H_2 and O_2.

Water Production. A 0.8-mL CD_2Cl_2 solution of 7.5 mg (10.8 μmol) of **1**, 3.0 mg (1.9 μmol) of Cp*Ir(TsDPEN)$BAr^F{}_4$ ([**1**H]$BAr^F{}_4$), and 3.5 mg (21.6 mmol) of C_6Me_6 (internal standard) was prepared under vacuum in a 7-in. J. Young tube, resulting in a reddish-purple solution. After an initial ^{1}H NMR spectrum was acquired, an atmosphere of 0.30 atm of H_2 and 0.18 atm of O_2 was introduced under vacuum using a premixed bulb containing both H_2 and O_2 in a 5:2 ratio by pressure. No immediate changes were observed upon thawing. The sample was monitored for 310 h by ^{1}H NMR spectroscopy (Figure 3).

Production of D_2O. A 0.8-mL CH_2Cl_2 solution of 11.7 mg (16.9 μmol) of **1**, 3.9 mg (2.5 μmol) of Cp*Ir(TsDPEN)$BAr^F{}_4$ ([**1**H]$BAr^F{}_4$), and 15 μL (169.3 μmol) of benzene-d_6 (internal standard) was prepared under vacuum in a 7-in. J. Young tube, resulting in a reddish-purple solution. After an initial ^{2}H NMR spectrum was acquired, an atmosphere of 0.56 atm of D_2 and 0.35 atm of O_2 was introduced. No immediate changes were observed upon thawing. The sample was monitored for 310 h by ^{2}H NMR spectroscopy.

Dehydrogenation of 1H(H) with Dilute H_2O_2. A 1.0-mL CD_3CN solution of 3.0 mg (4.3 μmol) of **1**H(H) and 5.9 mg (36.4 μmol) of C_6Me_6 (internal standard) was treated with a 5-μL aliquot of a 0.244 M (1.2 μmol) solution of H_2O_2 in water/CD_3CN, after an initial ^{1}H NMR spectrum was obtained. An immediate color change from pale orange to reddish-purple was observed. Addition of 5 μL of the H_2O_2 solution was repeated five times, resulting in a darker purple color with each subsequent addition. A ^{1}H NMR spectrum was obtained after each H_2O_2 addition, showing the formation of **1** and ~30% of compound **2**.[46]

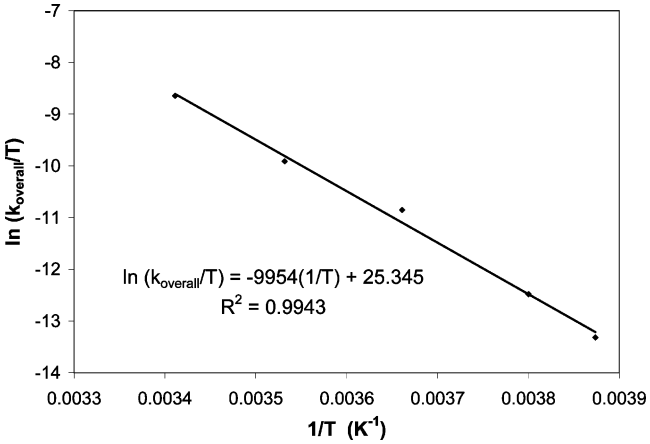

Figure 6. Temperature dependence of the third-order rate constant for the reaction Cp*IrH(TsDPEN) + O_2 in CD_3CN solution.

Dehydrogenation of 1H(H) with *t*-BuOOH. A 0.75-mL CD_3CN solution of 7.5 mg (10.8 μmol) of **1**H(H) and 1.2 mg (7.4 μmol) of C_6Me_6 (internal standard) was treated with a 1.4 μL (10.2 μmol) of a 70 wt % solution of *t*-BuOOH in water, after an initial ^{1}H NMR spectrum was obtained. A slow color change from pale orange to reddish-purple was observed over 20 min. Appearance of **1**, H_2O, and *t*-BuOH (δ 1.70) was first observed after 60 s, and continued to grow over the 20-min time period (referenced to the internal standard). Additions of further equivalents were found to destroy the organoiridium complexes and result in a black solution. Compound **2** was found to form in about 5% yield.

Kinetic Analysis for the Reaction of Cp*IrH(TsDPEN) + O_2. A 0.8 mL CD_3CN solution of 5 mg (7.2 μmol) of **1**H(H), 4 mg (24.7 μmol) of C_6Me_6 (internal standard), and any other additives (e.g., radical traps, 14.4 μmol) was prepared under vacuum in a 7-in. J. Young NMR tube. An initial NMR spectrum was obtained before the addition of O_2 (delay time of 15 s) (Supporting Information, Table S1). Oxygen was transferred and condensed under vacuum using liquid N_2 and a bulb containing about 1 atm of O_2. The pressure in the J. Young tube was monitored using a manometer and calculated using a mole balance (Supporting Information). An oxygen concentration of 0.10 M was estimated using the Henry's law constant for CH_3CN (203.8 MPa).[60] The affect of solvent deuteration on gas solubility was assumed to be negligible. The sample was carefully thawed, from the top of the solvent down, over the course of 2 min before insertion into the spectrometer from 77 K. Insertion of the sample into the spectrometer was taken as time = 0. The sample was a pale orange color upon insertion. Between 120 and 150 s elapsed during the time of insertion and start of data collection. Data were collected in a pre-acquisition delay array for 60 min, where a spectrum was recorded every 15 s with a pre-acquisition delay time of 5 s, acquisition time of 5 s, and a post-pulse delay time of 5 s at a temperature of 293.0 K. The sample was spun at a rate of 20 rpm for the duration of the experiment. A dark purple solution, characteristic of the presence of **1**, was observed upon ejection from the spectrometer. Rates were determined by following the disappearance of the Cp* signal in accordance with the signal for C_6Me_6 (δ 2.19). The first 110 of the 241 data points were used in the kinetic analysis, accounting for three half-lives. [O_2] dependence was determined to be first-order from the initial kinetic analysis. Tight seals of J. Young tubes can be easily analyzed, where leakage of O_2 pressure from J. Young tubes can be verified by NMR spectrometer lock migration and eventual loss of the lock of the sample and poor data over the course of the experiment.

Dehydrogenation of Ammonia−Borane. A 0.8-mL CD_3CN solution of 15.5 mg (22.4 μmol) of **1** and 1.0 mg (6.2 μmol) of C_6Me_6

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(internal standard) was treated with 350 μL of a 0.0324 M (11.3 μmol) solution of RNH_2BH_3 (where R = H, *t*-Bu). An immediate color change from reddish-purple to yellow-orange was observed upon mixing. The presence of **1**H(H) and ~5% $[(Cp^*Ir)_2(\mu\text{-}H)_3]^+$ was verified by ^{1}H NMR spectroscopy. Exposure of the solution to air for 24 h resulted in quantitative formation of **1** from **1**H(H).

Catalytic Dehydrogenation of Ammonia-Borane. A 0.8-mL CD_2Cl_2 solution of 8.6 mg (12.4 μmol) of **1**, 6.0 mg (24.7 μmol) of C_6Me_6 (internal standard), and 27.8 mg (320 μmol) of *t*-$BuNH_2BH_3$ was prepared under vacuum in a 7-in. J. Young NMR tube. Eleven atmospheres of oxygen was transferred and condensed under vacuum using liquid N_2 as previously described. The pressure in the J. Young tube was monitored using a manometer. The $[O_2]$ was estimated using an Ostwald coefficient of 0.257 for CH_2Cl_2 (Supporting Information, Table S4).[61] The sample was carefully thawed over 2 min, from the top down, resulting in a light yellow solution immediately upon shaking. After 6 h, the solution was a reddish-purple color, and a white solid had precipitated. The disappearance of *t*-$BuNH_2BH_3$ and the presence of **1**, H_2, and H_2O were verified by ^{1}H NMR spectroscopy.

The dehydrogenated "RNBH" product was prepared in a scaled-up preparation containing 2 mol % of **1** and 0.12 g (1.4 mmol) of *t*-$BuNH_2BH_3$ in CH_2Cl_2, achieving 60.0 mg of white solid in 25 h under 1 atm of O_2. The nitrogen−boron-containing coproduct was poorly soluble in CD_2Cl_2 and THF-d_8 but soluble in DMSO-d_6. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.19 (9 H), 3.33 (3 H), 6.42 (4 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 28.41, 50.10. ^{11}B NMR (96 MHz, DMSO-d_6): δ 1.76. Found: C, 47.29; H, 5.35; N, 3.18.

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The values observed do not match with the values reported for *tert*-butyl-borazole (^{1}H, δ 1.36; ^{11}B, δ 31.0), indicating the possibility of hydrolysis (Supporting Information).[31,62]

Oxidation of Pentanol. A 0.75-mL CD_2Cl_2 solution of 5 mol % of catalyst (relative to alcohol) and any other additives (e.g., quinone cocatalyst (50 mol % relative to alcohol) or base (25 mol % relative to alcohol)) in the presence of 4 mg (24.7 μmol) of C_6Me_6 (HMB, internal standard) was prepared in a 7-in. J. Young tube in air and degassed prior to oxygen introduction, resulting in a reddish-purple solution. An initial NMR spectrum was obtained before the addition of O_2. Oxygen was added by condensation at liquid nitrogen temperatures under vacuum as previously described. Upon addition of O_2, reactions were monitored for 36 h. TONs were determined by comparing the intensity of the formyl signal at δ 9.74 vs that of the HMB signal (δ 2.22).

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Supporting Information Available: Experimental methods, O_2 pressure calculations, kinetic analysis, further characterization of the *t*-$BuNH_2BH_3$ dehydrogenation product, alcohol oxidation results, and Arrhenius plot for reduction of O_2 by **1**H(H). This material is available free of charge via the Internet at http://pubs.acs.org.

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