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Photochemical Reactivity of Group 9 Metal Pinacolate Complexes

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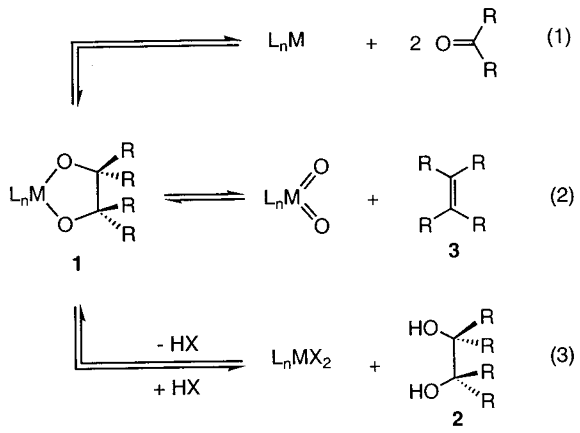
Coordinatively unsaturated pentamethylcyclopentadienyl pinacolate complexes of the group 9 transition metals (**4**−**6**) have been prepared and characterized. Photolysis of either the cobalt complex **4** or the rhodium complex **5** results in cleavage of the central carbon−carbon bond in the diolate, generating acetone. Various trapping studies demonstrate that an intact [Cp*M] fragment is produced in these reactions, and in the absence of added traps this fragment reacts either with aromatic solvents or with an intact molecule of the starting pinacolate complex. The oxidation of the resulting rhodium(II) product **11** by air (or O_2) in the presence of pinacol regenerates the rhodium(III) pinacolate complex **5**. Photolysis of rhodium complex **5** in the presence of pinacol and oxidant (either O_2 or N_2O) results in the catalytic conversion of pinacol to acetone.

Introduction

Because of their relevance to both biological and synthetic catalytic systems,[1−5] organometallic compounds containing late-metal−oxygen bonds have been studied increasingly in recent years. Advances in their syntheses have allowed for thorough investigations of many metal−alkoxo and −aryloxo species,[1,6] but this realm of study has only very rarely been extended to include chelating bis(alkoxo) complexes (**1**). This omission is surprising, given the diverse reactivity and synthetic relevance of those metal glycolate complexes that have been prepared. Early-metal glycolates can be formed by the coupling of organic carbonyl compounds at low-valent metal centers[7] (Scheme 1, eq 1 reverse reaction), and this reaction constitutes the key step in the metal-mediated preparation of unsymmetrical diols[7] (**2**) and alkenes[8] (**3**) by reductive coupling. Diolate complexes with sufficiently oxophilic metal centers have been observed to undergo a cycloreversion reaction in which the carbon chain of the diolate is extruded as an olefin, leaving behind a metal dioxo species (Scheme 1, eq 2).[9−12] This transformation plays a central role in both reductive couplings by early metals and the catalytic reduction of glycols and epoxides to olefins by metals as late as group 7.[13,14] The reverse reaction, the dihydroxylation of alkenes, is well established to involve osmium glycolate intermediates formed by a cycloaddition reaction.[15]

Scheme 1



In the only report to date of the chemistry of glycolates that bear metals beyond group 8 of the transition series, Andrews and co-workers reported that dppePt(glycolate) complexes undergo a photochemical transformation of the type shown in eq 1 of Scheme 1.[16] The diolate is cleaved to produce the corresponding organic carbonyl compounds, generating an unsaturated [dppePt] fragment that can be trapped convincingly by several added reagents. This reaction (postulated to take place in a [2 + 2 + 2] cycloreversion) also echoes the mechanism of oxidative diol cleavage by HIO_4.[17]

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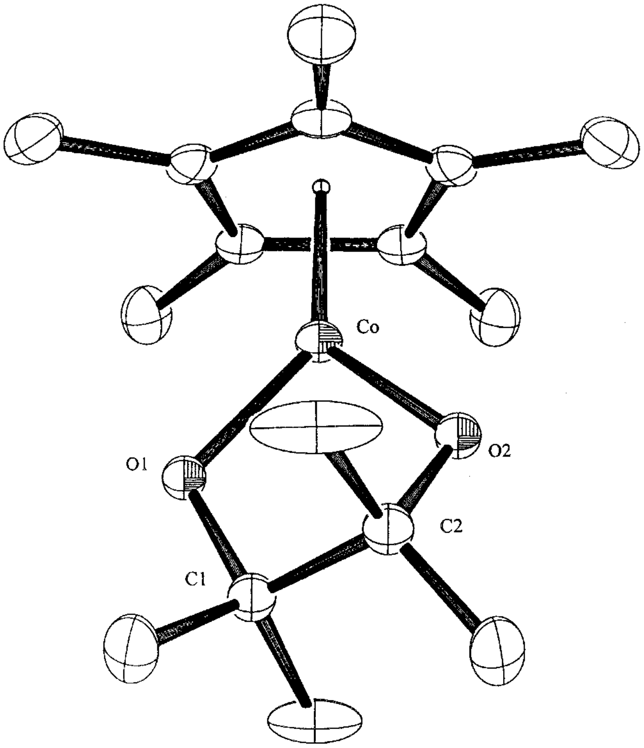


Figure 1. ORTEP diagram of **4** (displacement ellipsoids at 50% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Co−O(1), 1.806(3); Co−O(2), 1.823(3); C(2)−O(2), 1.438(6); C(1)−O(1), 1.452(5); C(1)−C(2), 1.533(6); O(1)−Co−O(2), 88.64(11); Co−O(1)−C(1), 112.5(3); Co−O(2)−C(2), 110.6(3); O(1)−C(1)−C(2)−O(2), 41.9(4).

This chemistry is instructive, given its place in the pattern of reactivity known for other metal glycolates. Additionally, though, it offers the real prospects of both effecting a useful synthetic transformation via late metal glycolates and generating coordinatively unsaturated late-metal centers via this cycloreversion. An alternative to the relatively harsh periodate and lead tetraacetate methodologies for oxidative cleavage of diols would be welcome, and coordinatively unsaturated late-metal centers have consistently proven to exhibit remarkable reactivity. For these reasons, we have expanded the family of late-metal glycolates to group 9 of the transition series and explored the reactivity of these complexes on both of the fronts mentioned above. Herein, we report the syntheses of pinacolate complexes of cobalt, rhodium, and iridium, their photochemistry, and their role in the catalysis of oxidative glycol cleavage.

Results

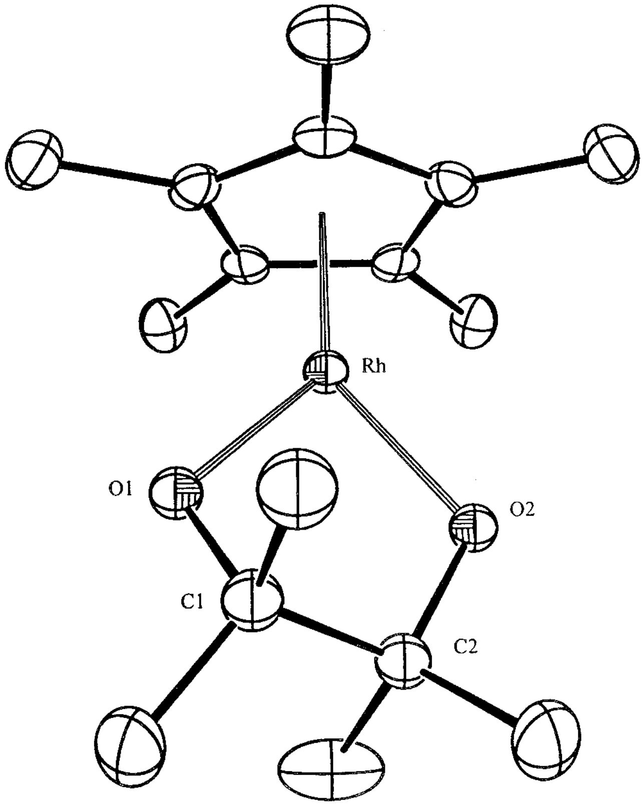
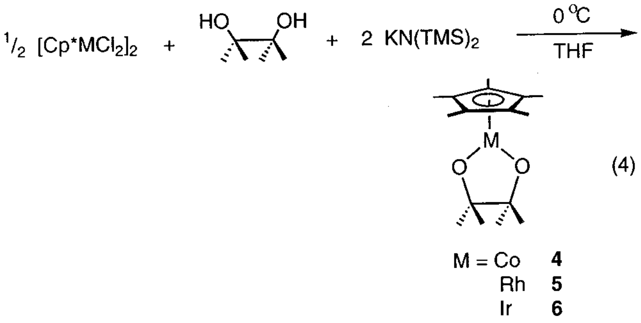


Figure 2. ORTEP diagram of **5** (displacement ellipsoids at 50% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−O(1), 1.9752(28); Rh−O(2), 1.9612(24); C(1)−O(1), 1.4056(46); C(2)−O(2), 1.4324(41); C(1)−C(2), 1.5278(47); O(1)−Rh−O(2), 82.90(8); Rh−O(1)−C(1), 111.33(24); Rh−O(2)−C(2), 113.08(20).

Synthesis and Thermal Stability of Pinacolate Complexes. The group 9 pentamethylcyclopentadienyl pinacolate complexes **4**−**6** were synthesized by treatment of the corresponding dichloro dimers with pinacol and base in THF (eq 4). They were isolated in good yield (ca. 75%) as green, purple, and maroon crystals, respectively, following benzene extraction and recrystallization from diethyl ether. The yields and purities of **4** and **5** were substantially diminished when solutions were exposed to light for significant periods of time, and rigorous protection of the compound from light was required for the isolation of the rhodium complex **5** in high purity. The structures of all three complexes were confirmed by single-crystal X-ray diffractometry, and the structures and selected bond distances and angles are given in Figures 1−3. The complexes were found to be monomers and to exhibit twisted dioxametallocyclopentane rings similar to those reported for other metal glycolate complexes.[18,19] This twisting resulted in disorder in the crystal structures, as both "left-handed" and



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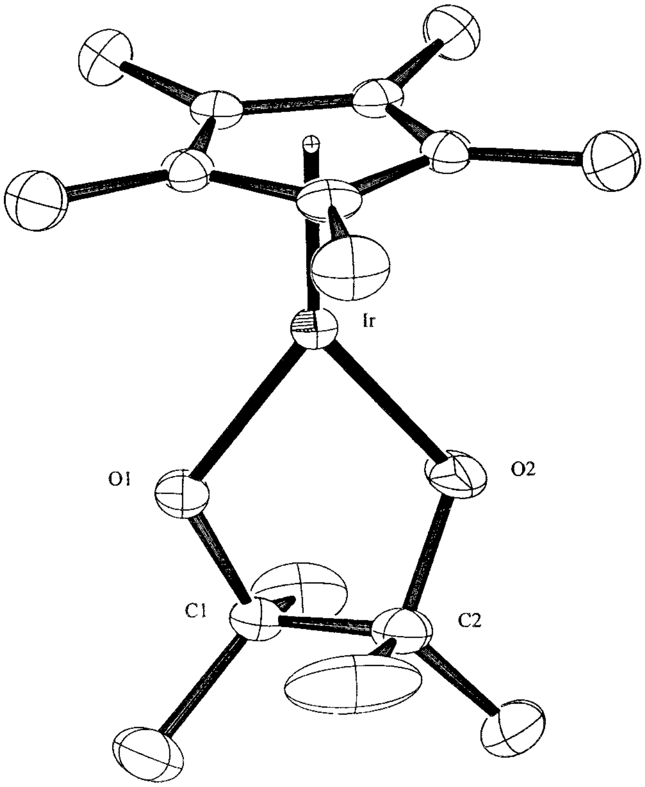


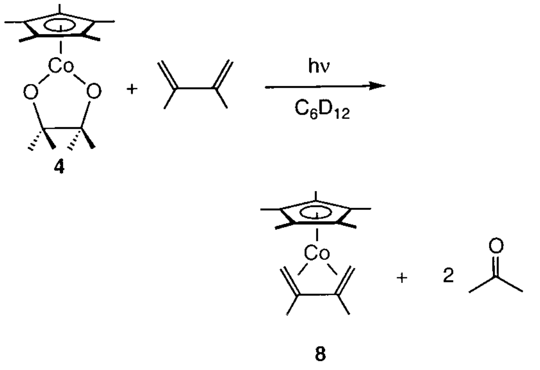
Figure 3. ORTEP diagram of **6** (displacement ellipsoids at 50% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir–O(1), 1.936(3); Ir–O(2), 1.936(3); C(1)–O(1), 1.51(1); C(2)–O(2), 1.50(1); C(1)–C(2), 1.51(1); O(1)–Ir–O(2), 80.2(2); Ir–O(1)–C(1), 112.6(4); Ir–O(2)–C(2), 111.6(5).

“right-handed” conformations cocrystallized owing to the essentially identical positions of the four methyl groups in the two twist isomers. Figures 1–3 show the results of modeling of the central carbon and oxygen atoms of the pinacolate as half-occupancy pairs of atoms with isotropic thermal parameters. The ^{1}H NMR spectra of all three complexes at room temperature each showed only one signal for the four pinacolate methyl groups, indicating a low barrier to interconversion of the two possible ring-twist isomers.

All the complexes were found to be moderately air- and water-sensitive but were thermally stable in solution at room temperature and to varying extents at elevated temperatures. Upon extended heating, all three compounds ultimately decomposed to yield numerous unidentified products. While the complexes are formally 16 e$^-$ species, they show no propensity to form stable 18 e$^-$ adducts. Addition of 1 equiv of trimethylphosphine to iridium pinacolate **6** did yield a new, yellow compound with features in its ^{1}H and ^{31}P NMR spectra consistent with the formulation Cp*Ir(PMe$_3$)(pin) (δ 1.49 (d, 2.0 Hz, 15H) 1.43 (s, 6H) 1.42 (s, 6H) 1.35 (d, 10.4 Hz, 9 H) ppm). However, this complex decomposed at room temperature within several minutes to give multiple products, including the starting pinacolate **6**. Similarly, addition of various trialkylphosphines, triarylphosphines, or isonitriles to these complexes led to decomposition to multiple products, and no adducts were observed at room temperature (as monitored by ^{1}H NMR spectroscopy) with imines, ethers, dienes, amines, or thiophenes. These complexes do not form stable adducts but do undergo clean thermal reactions with CO and various heterocumulenes, and this chemistry will be reported separately.

Photochemistry of Cp*Co(pin) (4). Irradiation of the cobalt complex **4** in C$_6$D$_6$ (500 W mercury lamp, through Pyrex) yielded 2 equiv of acetone (Scheme 2). Immediately upon irradiation, this was the only resonance evident in the ^{1}H NMR spectrum. Over time in the dark at room temperature, the initially purple product solution turned brown, and all the resonances in the ^{1}H NMR spectrum of the sample became extremely broad. The secondary products of this reaction have not been explored at length. Efforts to isolate the purple intermediate were also unsuccessful, as the complex does not precipitate from solution as clean material and is unstable at higher concentrations. The exposure of C$_6$D$_6$ solutions of **4** to ambient light, as well as mercury-lamp irradiation of **4** in C$_6$D$_{12}$, yielded similarly complex results, although in these cases a dinuclear Co(II) pinacolate complex, **7**, was also generated in modest and variable yield (<50%). This complex could be produced in 80% spectroscopic yield by adding a second equivalent of **4** to a freshly irradiated solution of **4** in C$_6$D$_6$ and allowing the mixture to stand in the dark for 1 day. The identity of the dinuclear cobalt pinacolate **7** was confirmed by independent synthesis from pinacol, base, and [Cp*CoCl]$_2$ (Scheme 2).

We sought to simplify this reaction by trapping the [Cp*Co] fragment to form a single product. Various phosphines, isonitriles, silanes, and hydrogen reacted thermally with the starting material, and bipyridine and several dienes reacted upon irradiation with cobalt pinacolate **4** to give multiple products. In the presence of excess 2,3-dimethylbutadiene, irradiation of **4** in C$_6$D$_6$ still initially yielded 2 equiv of acetone and purple, NMR-silent material. Over a matter of hours, however, the known diene adduct **8**[20] was formed in >90% yield as determined by ^{1}H NMR spectroscopy. In C$_6$D$_{12}$, **8** was produced in >95% yield immediately upon irradiation (as determined by ^{1}H NMR spectroscopy) and isolated in 70% yield by recrystallization from ether (eq 5).



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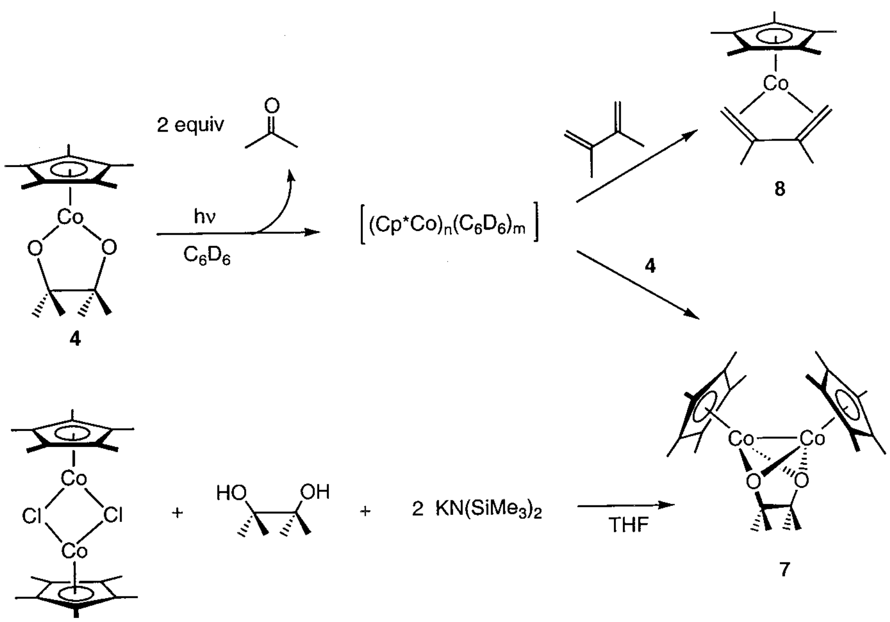
Photochemistry of Cp*Rh(pin) (5). Irradiation of **5** in C$_6$D$_6$ for 30–40 min yielded 2 equiv of acetone along with the di- and trinuclear, solvent-incorporated products **9** and **10** (Scheme 3; Table 1, entry 2). These products typically accounted for >90% of the total cyclopentadienyl resonances in the ^{1}H NMR spectra of the products, and their characterization is described below. The ratio of species **9** and **10** remained unchanged when the product mixture was subjected to the photolysis conditions for an additional 24 h or more.

Scheme 2



Scheme 3

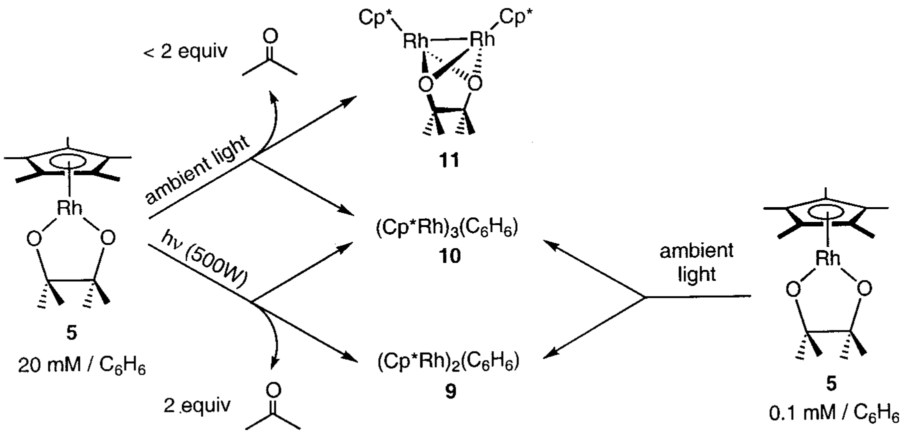


Table 1. Photolysis of 5

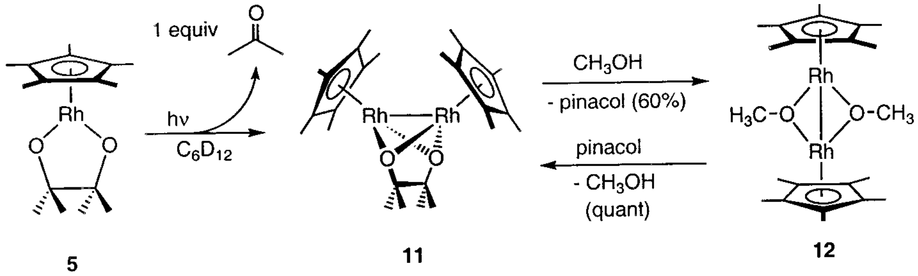
entry	[**5**] (C_6D_6) (±0.5 mM)	light source	filter	filter cutoff (nm)	time required	amt of acetone, equiv (±0.1)	% **11** (±5)	% **10** (±5)	% **9** (±5)
1	20	Hg lamp	quartz	<150	<20 min	2	0	30	65
2	20	Hg lamp	Pyrex	300	30–40 min	2	<5	35	55
3	20	Hg lamp	U-glass	334	40–50 min	1.9	10	40	45
4	20	Hg lamp	amber	402	70–80 min	1.8	15	40	40
5	20	ambient	Pyrex	300	36–48 h	1.5	50	45	5
6	0.1	ambient	Pyrex	300	1–2 h	na	<5	30	50
7	20 (C_6D_{12})	Hg lamp	Pyrex	300	30–60 min	1.0	>95	0	0

Identically prepared samples of **5** exposed to ambient fluorescent light for 1–2 days also reacted to completion but produced somewhat less than 2 equiv of acetone and yielded a dramatically different product ratio (Table 1, entry 5). Dinuclear benzene adduct **9** was almost entirely absent, and the new dinuclear pinacolate **11** was observed in addition to trinuclear complex **10**. This product mixture was stable to irradiation for at least 24 h. Early in the course of both ambient and mercury-lamp photolyses (<5% conversion), only products **9** and **11** were observed. The concentration of dinuclear benzene adduct **9** was actually observed by ^{1}H NMR to decrease when a briefly irradiated sample containing ~50% starting material was exposed to ambient light for 1 day.

The use of filters with the mercury lamp (Table 1, entries 3 and 4) could not reproduce the ambient-light product ratio. When filters were used, dinuclear pinacolate **11** was produced in significant quantities, the production of benzene adduct **9** was noticeably diminished, and the time required for complete disappearance of starting material increased. Irradiation through quartz (entry 1) produced the opposite result; a product mixture unusually rich in **9** and poor in **11** was observed.

When a very dilute (0.1 mM) benzene solution of **5** was exposed to ambient light (Table 1, entry 6), complete conversion to a product mixture similar to that obtained through mercury-lamp irradiation was observed within 2 h.

Scheme 4



The irradiation of **5** in cyclohexane-d_{12} generated only 1 equiv of acetone and a nearly quantitative yield of the dinuclear Rh(II) pinacolate **11** (Scheme 4; Table 1, entry 7). This species was thus obtained on a larger scale in 54% isolated yield by irradiation of **5** in pentane and subsequent recrystallization from ether. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the compound suggest a single pinacolate ligand and two equivalent Cp* groups, and both mass spectrometry and elemental analysis confirmed the formulation $(Cp^*Rh)_2(pin)$. This species was found to undergo no exchange with acetone-d_6 upon either irradiation or mild heating. Stirring **11** in methanol for 3 days yielded the known compound $(Cp^*Rh)_2(OMe)_2$ (**12**)[21] and pinacol (both in 60% yield as measured by ^1H NMR spectroscopy). Treatment of the dimethoxo species **12** with pinacol produced **11** in quantitative NMR yield after 1 h at 45 °C, and the product was isolated in 39% yield. These results suggest a structure in which a single, intact pinacolate ligand bridges two [Cp*Rh] fragments, as illustrated in Scheme 4.

Products **9** and **10** were prepared on a larger scale by mercury-lamp irradiation of **5** in C_6H_6 through Pyrex. Recrystallization of the photoproducts from diethyl ether provided compound **10** as a black solid (26% yield) which exhibited ^1H NMR singlets at δ 2.06 and 1.78 ppm in a 15:30 ratio, and three additional multiplets downfield integrated to two protons each. Products from various photolyses in C_6D_6 were also recrystallized from ether (<10% yield) to give similar black material that lacked any downfield ^1H NMR resonances. A mass spectrum of this partially deuterated **10** included an M^+ peak at m/z 798, which corresponds to $(Cp^*Rh)_3(C_6D_6)$. Although efforts to cleanly isolate the dinuclear species **9** have been unsuccessful, spectra of **9** and **10** together include a singlet at δ 1.75 ppm (30H) and 3 multiplets downfield (6H) that are not associated with trinuclear adduct **10**. While we lack sufficient evidence to unambiguously assign structures to **9** or **10**, the NMR data suggest that the benzene unit is intact (no typical rhodium–hydride signals are observed) and that in both cases the benzene most likely is bound to each rhodium center in an η^2 or η^4 manner. The NMR spectra of such bridging arene complexes[22–26] sometimes exhibit large shifts in the bound arene resonances, as do those reported here. Unfortunately, it appears that no known complexes exhibit spectroscopic features sufficiently similar to those observed here to offer particularly useful comparisons. Possible structures for complexes **9** and **10** are illustrated in Figure 4.

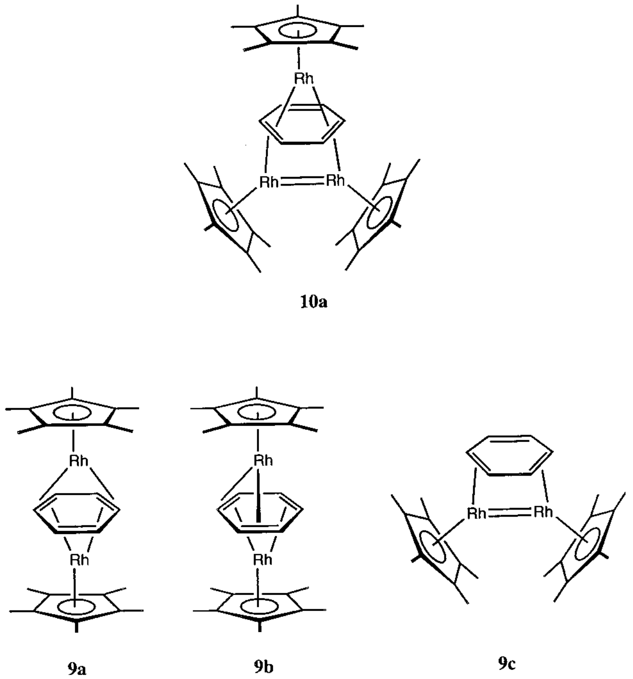
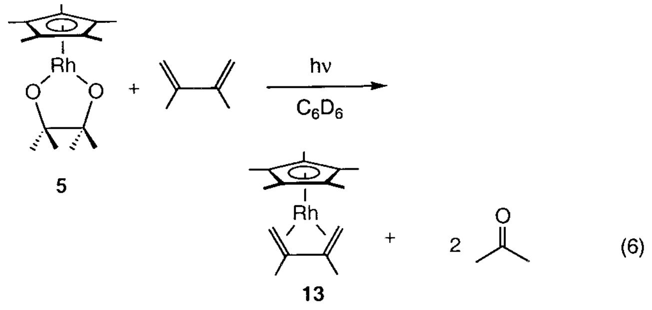


Figure 4. Possible structures for complexes **9** and **10**.

Again we sought to simplify the system by the use of an appropriate trap and found that irradiation of **5** in the presence of excess 2,3-dimethylbutadiene produced 2 equiv of acetone and the diene adduct Cp*Rh(diene) (**13**) in >95% yield by NMR spectroscopy (eq 6) and 66% isolated yield. The products of reaction showed no dependence on solvent or light source.



The iridium analogue **6** proved stable to 8 h mercury-lamp irradiation through quartz both with and without added 2,3-dimethylbutadiene. Extended irradiation (>24

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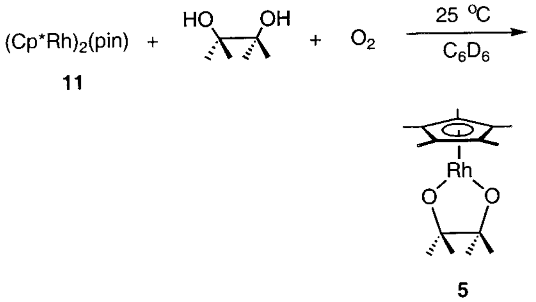
h) under the same conditions produced very slight (<5%) decomposition to numerous products but did not produce acetone.

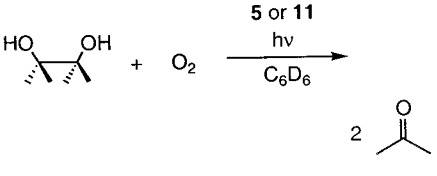
Oxidation of $(Cp^*Rh)_2(pin)$ (7). In the course of exploring the stability of dinuclear rhodium species **11**, it was observed that traces of the mononuclear pinacolate **5** were sometimes generated in impure solutions containing pinacol. Neither the heating of **11** in neat pinacol at 75 °C nor the irradiation of **11** in the presence of >200 equiv of pinacol resulted in any reaction. The exposure of **11** to air yielded only slow decomposition. The reaction of **11** with both the atmosphere and an excess of pinacol, however, yielded **5** in 75% spectroscopic yield (based on rhodium) after 48 h in the dark at room temperature (eq 7). The use of pure O_2 instead of air gave similar results, although the yield could not be improved from 75% by either increasing or decreasing the O_2 pressure. Complex **5** decomposed extremely slowly when exposed to O_2 and H_2O *in the presence of pinacol*; therefore, decomposition of the products under the reaction conditions is likely not the cause of the limited yield.



(7)

Other oxidizing agents have proven ineffective in achieving this transformation. Nitrous oxide, pyridine *N*-oxide, trimethylamine *N*-oxide, diphenyl hydrazine, and 2-methyl-2-nitrosopropane all either failed to react or decomposed upon extended heating or irradiation with **11** and pinacol. The simultaneous use of a ferrocenium salt and base yielded only decomposition of **11**, as did an excess of nitrosobenzene. While oxidation by *tert*-butyl peroxide eventually produced traces of **5**, it did so only after extended heating. The addition of *tert*-butyl hydroperoxide to a mixture of **11** and pinacol did afford a reasonable amount of **5** and *tert*-butyl alcohol within 5 min of mixing. The yield of **5** in this reaction was typically about 70%, as determined by ^1H NMR spectroscopy. With or without pinacol present, the cobalt analogue **7** reacted with oxidizing agents to give **4** in no greater than 50% yield and also produced dark, highly insoluble material.

Catalysis. Irradiation of rhodium pinacolate **5** in the presence of excess pinacol and O_2 resulted in the weakly catalytic conversion of pinacol to acetone (eq 8). When the reaction was carried out in an NMR tube with 0.01 M **11**, 2.0 M pinacol, and bubbling O_2 in C_6D_6 or C_6D_{12}, approximately 40 turnovers (20 TO/Rh) were observed over the course of 18 h (Table 2). The pale yellow solution and red precipitate remaining at the end of this time showed no catalytic activity. When the reaction was repeated under otherwise identical conditions using 0.02 M **5**, 28 turnovers (28 TO/Rh) were observed in the same time period, and the organometallic products were similarly unreactive. The ^1H NMR spectrum of the catalysis reaction mixture after 40 min of irradiation revealed that **5** and a small amount of **9** were the dominant species present. Complex **5** was found to be a better catalyst than a mixture of its photoproducts.



(8)

Table 2. Catalysis Runs, using O_2

entry	catalyst	solvent	[Rh] (mM ±1)	pinacol (equiv ±10%)	O_2 press (±1 Torr)	turnovers per Rh (±0.2)
1	5	C_6D_6	17	200	750	9.8
2	11	C_6D_6	13	20	746	2.8
3	5	C_6D_{12}	17	20	375	3.2
4	5	C_6D_6	14	20	389	3.4
5	11	C_6D_6	14	20	380	2.4
6	photolyzed **5**	C_6D_6	14	20	392	2.7

While catalysis using oxygen as the oxidant required high concentrations of pinacol and did not achieve better than 25% conversion, catalysis using N_2O proved less demanding and more efficient. When an NMR tube was loaded with 0.04 M **5**, 0.80 M pinacol, and 1 atm N_2O, several hours of irradiation with periodic shaking produced acetone in 85% yield and consumed all the starting pinacol.

Related Diolate Complexes. As is the case with other metal glycolates, the pinacolate ligand in this system was observed by ^1H NMR spectroscopy to undergo facile exchange with free diol (the chemical shifts of the pinacolate ligand and free pinacol converge as their concentrations increase).[18] In addition, treatment of rhodium pinacolate **5** with catechol in THF generated the known catecholate species **14**[27] and pinacol quantitatively upon mixing (Scheme 5). Neither **14** nor its phosphine adduct **15** undergo any observable reaction upon irradiation in the presence of excess dimethylbutadiene. Treatment of **4**, **5**, or **6** with secondary and primary diols (butanediol, 1-phenyl-1,2-ethanediol, or ethylene glycol) invariably led to rapid decomposition, and complexes with such diolates also proved inaccessible by direct synthesis from $[Cp^*RhCl_2]_2$ or $Cp^*Rh(PMe_3)Cl_2$.

Discussion

The thermal stability of the pinacolate complexes **4**–**6**, even though they are formally 16 e^- monomeric species, suggests that they are stabilized by significant π donation from oxygen to the metal center. Although there is little useful basis for comparison of the metal–oxygen bond lengths, this notion is further supported by the instability of these complexes toward good Lewis bases. The pinacolate could not be prepared in good yield from the corresponding $Cp^*M(PMe_3)Cl_2$ complexes, and attempts to prepare 18 e^- adducts by treatment of the isolated pinacolates with phosphines were similarly unsuccessful. All such efforts led to decomposition, but

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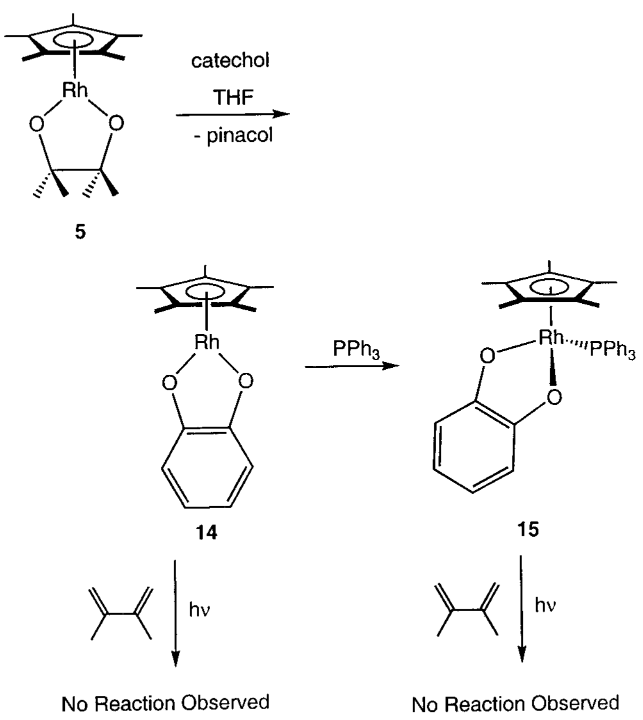
Scheme 5



in the case of iridium complex **6,** NMR evidence indicated that this decay took place via an intermediate Cp*Ir(PMe$_3$)(pin) species. The instability of such a species is consistent with favorable π donation in the parent pinacolate, which would be replaced by destabilizing dπ−pπ repulsion in the adduct.[28]

Trapping experiments with dimethylbutadiene in cyclohexane-d_{12} clearly illustrate that the cobalt and rhodium species **4** and **5** undergo a photochemical transformation analogous to that observed by Andrews for similar types of platinum complexes. In C_6D_6, it appears that the chemistry of the [Cp*Co] fragment generated by photolysis of **4** is complicated by the prompt formation of a long-lived paramagnetic species. Given that this species appears to be formed only in benzene, it seems most likely that it is some sort of $(Cp^*Co)_n(C_6D_6)_m$ arene adduct. However, while such complexes are well-known, they are either diamagnetic[24,25,29] or charged[30,31] species. The exact nature of the kinetic product thus remains unclear. In the presence of a better trap, this species went on to eventually produce the expected thermodynamic products (Scheme 4) and generated either the diene adduct **8** or the dinuclear pinacolate **7** (when mononuclear pinacolate **4** was added as the trap). The reactivity of the $(Cp^*Co)_n$-$(C_6D_6)_m$ species was not further explored because it could not be isolated and tended to produce multiple products, including paramagnetic material.

The fate of the [Cp*Rh] fragment without an added diene was dependent on the reaction conditions (Scheme 6). Irradiation in the absence of aromatic solvents yielded a single product identified as dinuclear Rh(II) complex **11**, in which a single pinacolate ligand bridges two Cp*Rh centers. This species is presumably formed by reaction of the [Cp*Rh] fragment with **5**, and its structure is well precedented by numerous $[Cp^*RhX]_2$ dimers.[32−35] In addition to this dinuclear pinacolate, two new products that incorporate solvent molecules are produced when the photolysis is conducted in benzene. On the basis of the facts that **10** is not produced early in the reaction under any circumstances, **9** is consumed under appropriate circumstances, and **9** is not directly converted to **10** upon irradiation, it seems likely that **9** reacts with the [Cp*Rh] fragment to produce the trinuclear species **10**. Product **9**, then, is likely a dinuclear species that results from the reaction of two [Cp*Rh] fragments with solvent (or, perhaps more likely, two short-lived Cp*Rh−solvent adducts).

The variable ratio of these products can be rationalized based on Scheme 6. The product ratio correlates most directly with the duration of the photolysis (Table 1). During photolysis reactions which are complete after short times, the short-lived [Cp*Rh] fragment should be more abundant relative to other species; therefore, the formation of **9** should be favored. Those reactions in which the starting material persists longer, containing less [Cp*Rh] relative to other species, should favor **11** and **10** relative to **9**. This indeed was observed. This explanation is precedented by the work of Müller and co-workers, who have observed similar reactivity on the part of the unsubstituted [CpRh] fragment, which goes on to form di- and trinuclear arene adducts when generated by photolysis of $CpRh(C_2H_4)_2$ in benzene.[23] It is worth noting, however, that the NMR spectra of complexes **9** and **10** are inconsistent with the basic structural features reported for the analogues bearing unsubstituted Cp ligands.

The preparation of the catecholate analogue **14** demonstrates the viability of synthesizing various glycolate complexes by simple exchange, but unfortunately this approach has yet to yield any species in which C−C cleavage can be observed. A [2 + 2 + 2] cycloreversion in **14** would disrupt aromaticity; therefore, it is unsurprising that this species is stable to irradiation. Equally unsurprising is the rapid decomposition of the less substituted glycolate species presumably formed upon exchange with the pinacolate. They, like the parent compound, would be formally 16 e$^-$ species and have an open site available for decomposition by β-hydride elimination.[36]

Given the results for the cobalt pinacolate **4** and the rhodium analogue **5**, the iridium pinacolate **6** is remarkably stable even to high-energy irradiation. Like the other pinacolates, it has strong absorbances in both the ultraviolet and visible regions; thus, it is unlikely that it simply lacks an accessible chromophore. While third-row-metal complexes are generally less reactive than their first- and second-row counterparts, it is nonetheless surprising that even the high energy available from UV radiation does not effect cycloreversion or other decomposition.

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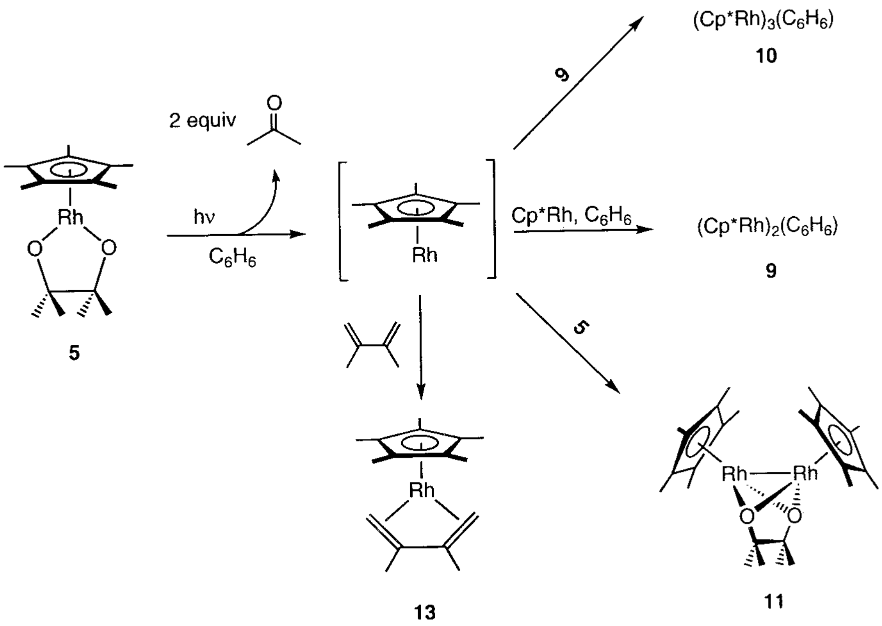
Scheme 6

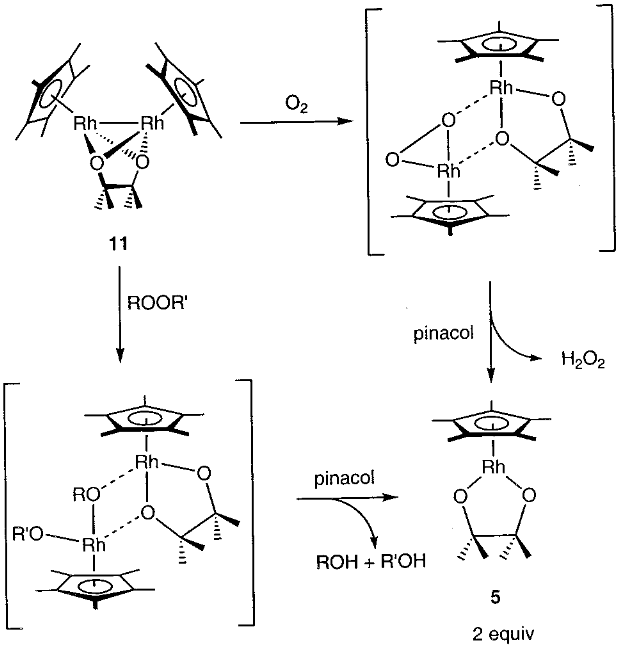


The regeneration of **5** from the dinuclear rhodium pinacolate **11** can be accomplished in reasonable yield even by the very crude method of exposing an appropriately prepared sample to the atmosphere. Unfortunately, while the same reaction takes place under pure O_2, the use of O_2 at various pressures does not offer improved results. Oxidation with other reagents proved fruitless, as oxygen atom donors are totally ineffective, and oxidations through electron transfer or using nitrosobenzene do not yield clean reactions. The specific need for dioxygen suggests a mechanism involving oxygen insertion into the Rh–Rh bond, which has been observed for a similar Rh(II) dimer by Sharp and coworkers.[37,38] As shown in Scheme 7, the peroxo ligand produced by oxygen insertion could be replaced by pinacol via protonolysis to give two molecules of **5** after dimer cleavage. The hydrogen peroxide produced could then react with another 1 equiv of **11** by addition across the Rh–Rh bond, and subsequent alcohol exchange would yield **5** and H_2O. The reaction of **11** with *tert*-butyl hydroperoxide provides support for the viability of the second phase of the mechanism described above. Given that the mononuclear pinacolate **5** decomposes slowly in the presence of either oxygen or peroxide, we suspect that this decomposition pathway (or similar reaction by an intermediate rhodium dihydroxo species) limits the yield of the stoichiometric oxidation reaction.

The fact that one of the photoproducts can incorporate additional pinacol to generate **5** suggested that the catalytic conversion of pinacol to acetone should be possible in this system. This has been found to be true, and several turnovers are consistently observed in NMR tube scale reactions using either **5** or **11** as a catalyst and oxygen as the oxidant. Results are slightly better when **5** is used (Table 2, entries 4 and 5), likely due to the modest yield of the initial oxidation of **11**. Under these conditions, the number of turnovers observed is clearly dependent upon the pinacol concentration (Table 2, entry 1), which is consistent with the notion that rapid conversion of the proposed dihydroxo species is important in preventing decomposition.

Monitoring by ^1H NMR provides evidence that dinuclear pinacolate **11**, while it was the subject of our initial oxidation experiments, is not produced in the course of the catalysis in C_6D_6. Furthermore, when conditions are optimized for the production of **11** (by the use of C_6D_{12} in place of C_6D_6), no improvement in the yield of the catalytic reaction is observed (entries 3 and 4). This suggests that the stoichiometric oxidation mechanism discussed above is not operative in the catalytic system (Scheme 8). One possible alternative is that other photoproducts **9** and **10** are oxidized as well, but efforts to model this step stoichiometrically produced **5** in very low yield, and a mixture of photoproducts showed diminished catalytic activity relative

Scheme 7



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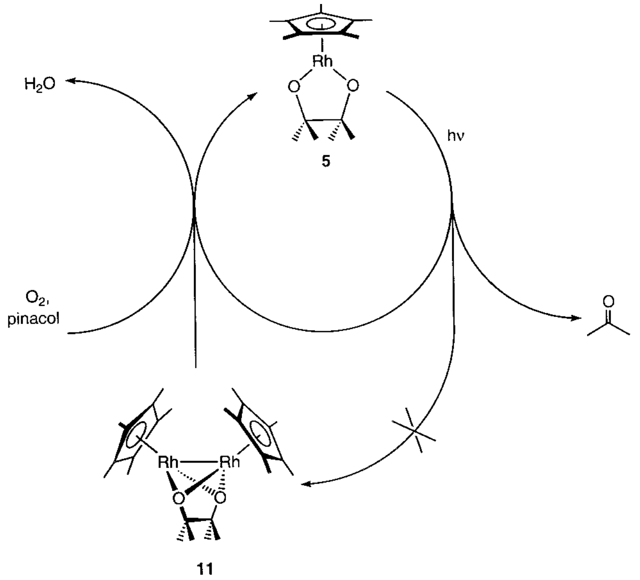
[38] Sharp, P. R.; Hoard, D. W.; Barnes, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 2024.

Scheme 8



to **5** (entries 4 and 6). Rather, we suspect that the [Cp*Rh] fragment is oxidized directly to a peroxo or dihydroxo species by oxygen or hydroperoxide, respectively.

This conjecture is supported by the observation that nitrous oxide, failing to oxidize photoproducts **9**−**11** under either thermal or photochemical conditions, is effective as a replacement for oxygen in the catalytic system. This modification allows for catalysis at much lower concentrations of pinacol (and thus much better conversion), presumably because the side products of the oxidation are only water and nitrogen gas rather than hydrogen peroxide. The mechanism of this oxidation pathway is still under investigation but presumably involves either trapping of [Cp*Rh] by pinacol and subsequent hydrogen atom abstraction by N_2O, or oxygen atom transfer from N_2O to [Cp*Rh] (to form a short-lived rhodium−oxo species) followed by protonolysis.

Conclusions

Both cobalt and rhodium pinacolate complexes have been observed to produce acetone upon irradiation. The [Cp*M] fragments produced by this reaction have been trapped cleanly by 2,3-dimethylbutadiene and have also been observed to react with their respective starting materials to form M(II) dimers. The rhodium dimer **11** reacts with pinacol and oxygen to regenerate the original Cp*Rh(pin) species (**5**), likely by a mechanism involving dioxygen insertion into the Rh−Rh bond and subsequent exchange of diolate for the peroxo ligand. Photolysis of the rhodium complex in the presence of pinacol and either oxygen or nitrous oxide results in catalytic oxidative cleavage of pinacol to acetone. Application of this chemistry to less highly substituted diols will require the use of metal centers less prone to β-hydride elimination.

Experimental Section

General Procedures. The general experimental procedures previously outlined by our group[39] were followed unless otherwise noted. Cp*Co(pin) and solutions containing Cp*Co(pin) or Cp*Rh(pin) were protected from light by aluminum foil except where otherwise noted. Pinacol was distilled under vacuum from 45 to 0 °C, dried over 4 Å sieves in pentane, and recrystallized from pentane at −30 °C. Catechol was dried over 4 Å sieves in pentane and recrystallized from pentane at −30 °C. The complexes $[Cp^*RhCl_2]_2$,[40] $[Cp^*IrCl_2]_2$,[40] $[Cp^*RhOMe]_2$ (**12**),[21] $[Cp^*CoCl_2]_2$,[41] $[Cp^*CoCl]_2$,[42] and $Cp^*Rh(PPh_3)(o\text{-}O_2C_6H_4)$ (**15**)[27] were prepared according to published literature procedures. All other reagents were purchased commercially and used as received.

Except where otherwise noted, yields of NMR tube reactions were determined by integration against a 1,3,5-trimethoxybenzene internal standard (added with the solvent) using single pulse spectra and an initial delay of at least 30 s. The internal standard (δ 6.25 (s, 3H), 3.30 (s, 9H) ppm in C_6D_6) was first calibrated with respect to starting materials by means of an initial spectrum acquired before irradiation, heating, or the addition of reactive species.

"Mercury-lamp" irradiation was performed using a 500 W medium-pressure Hanovia mercury vapor lamp housed in a water-cooled quartz immersion well. During irradiation, samples were immersed in spectral grade methanol maintained by a Neslab Endocal circulating refrigeration bath at 20 °C. "Ambient light" photolyses were conducted under typical fluorescent room lights in the glovebox or on the laboratory bench.

Cp*Co(pin) (4). A 20 mL vial wrapped with aluminum foil was charged with a stir bar, $[Cp^*CoCl_2]_2$ (507 mg, 0.959 mmol), pinacol (227 mg, 1.92 mmol), and THF (10 mL). To the resulting green slurry was added, dropwise with stirring, a THF slurry (5 mL) of $KN(TMS)_2$ (764 mg, 3.83 mmol). Over the course of the addition the mixture became homogeneous and took on a brownish tint. The vial was capped, and the solution was stirred for 2 h at room temperature in the dark. The solution was then reduced to dryness under vacuum to yield a brownish green solid, which was extracted with benzene (20 mL) to yield a green extract and brown-yellow residue. The extract was reduced to dryness under vacuum, and recrystallization of the resulting green solid from ether (6 mL) at −30 °C yielded **4** as blocky green crystals (442 mg, 75% yield). ^1H NMR (C_6D_6): δ 1.68 (s, 15H), 0.97 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 90.53 (s, C_5Me_5), 80.88 (s, $OCMe_2$), 29.39 (s, $OC\mathit{Me}_2$), 8.43 (s, $C_5\mathit{Me}_5$) ppm. IR (KBr): 2959 (s), 1457 (m), 1348 (m), 1140 (s), 953 (s), 891 (s) cm^{-1}. UV−vis (nm (M^{-1} cm^{-1})): 227 (11 000), 286 (11 000), 365 (3900), 662 (200), 922 (330). Anal. Calcd for $C_{16}H_{27}O_2Co$: C, 61.93; H, 8.77. Found: C, 61.93; H, 8.91.

Crystallographic Study of Cp*Co(pin) (4). A green plate-shaped crystal having approximate dimensions 0.20 × 0.22 × 0.18 mm obtained by recrystallization from ether at −30 °C was mounted on a glass fiber using Paratone N hydrocarbon oil. Data were collected using a SMART CCD area detector with graphite monochromated Mo Kα radiation. Hydrogen atoms were included but not refined. The structure obtained is disordered about the mirror plane at $y = {}^1/_4$, because the pinacolate is coordinated almost perpendicular to the mirror plane and apparently adopts both "left-handed" and "right-handed" conformations in the solid state. Because the two conformations have very similar steric bulk, neither conformation is favored upon crystallization, resulting in the two superimposed five-membered rings. The two conformations also superimpose the pinacolate methyl groups upon each other. Two of these methyl groups, C10 and C11, are located near the mirror plane at $y = {}^1/_4$ and have been refined as full-occupancy carbon atoms lying on the mirror plane. The large "thermal motion" parameters for these two atoms result from

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the assumption that they are imposed on the mirror plane. The clarified structure given in Figure 1 is based on modeling of the central carbon and oxygen atoms of the ligand as half-occupancy pairs of atoms with isotropic thermal parameters. Selected bond lengths are given in Figure 1. Crystallographic data are as follows: space group *Pnma*, $a = 16.3777(5)$ Å, $b = 12.3570(4)$ Å, $c = 7.9567(3)$ Å, $V = 1610.27(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.280$ g/cm^3, μ(Mo Kα) = 10.62 cm^{-1}, 1733 unique reflections, 1317 reflections with $I > 3.00\sigma(I)$, $R = 3.12\%$.

Cp*Rh(pin) (5). A 20 mL vial wrapped with aluminum foil was charged with a stir bar, [Cp*RhCl$_2$]$_2$ (519 mg, 0.840 mmol), pinacol (199 mg, 1.68 mmol), and THF (10 mL). To the resulting brick red slurry was added, dropwise with stirring, a THF slurry (5 mL) of KN(TMS)$_2$ (669 mg, 3.36 mmol). Over the course of the addition, the mixture became homogeneous and turned purple-brown. The vial was capped, and the solution was stirred for 1 h at room temperature in the dark. The solution was then reduced to dryness under vacuum to yield a purple solid, which was extracted with benzene (30 mL) to yield a purple extract and brown-yellow residue. The extract was reduced to dryness under vacuum, and recrystallization of the resulting purple solids from ether (7 mL) at −30 °C yielded **5** as blocky purple crystals (430 mg, 72% yield). ^{1}H NMR (C$_6$D$_6$): δ 1.42 (s, 12H), 1.31 (s, 15H) ppm. In the presence of pinacol, the δ 1.42 ppm resonance is shifted upfield and slightly broadened due to facile exchange with free diol. For all cases where pinacol is present, **5** was identified and quantified only on the basis of the δ 1.31 ppm signal or the sum of the two signals when they overlapped. Removal of pinacol by sublimation returned the pinacolate resonance to δ 1.42 ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 89.35 (d, $J_{Rh-C} = 8.7$ Hz, *C*$_5$Me$_5$), 84.67 (s, O*C*Me$_2$), 28.07 (s, OC*Me*$_2$), 9.40 (s, C$_5$*Me*$_5$) ppm. IR (KBr): 1140 (s), 1028 (s), 951 (s) cm^{-1}. UV−vis (nm (M^{-1} cm^{-1})): 234 (12 000), 335 (3900), 585 (570). EI-MS: *m*/*z* 296 ([Cp*Rh(CMe$_2$O)]$^+$), 238 ([Cp*Rh]$^+$). Anal. Calcd for C$_{16}$H$_{27}$O$_2$Rh: C, 54.23; H, 7.68. Found: C, 54.00; H, 7.98.

Crystallographic Study of Cp*Rh(pin) (5). Small red-brown crystals of the compound were obtained by slow crystallization from ether at −30 °C. A crystal was mounted on a glass fiber using polycyanoacrylate cement. Data were collected at −126 °C using an Enraf CAD-4 diffractometer. The 2438 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. The structure was refined in the space group *Pnam*, and removal of systematically absent data and averaging of Friedel planes gave 1137 unique data. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The structure showed disorder similar to that observed for **4** (see above), and the structure given in Figure 2 is based on modeling of the central carbon and oxygen atoms of the ligand as half-occupancy pairs of atoms with isotropic thermal parameters. Selected bond lengths are given in Figure 2. Crystallographic data are as follows: space group *Pnma*, $a = 16.9561(4)$ Å, $b = 7.8747(5)$ Å, $c = 12.2873(4)$ Å, $V = 1640.6(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.434$ g/cm^3, 1137 unique reflections, 1062 reflections with $I > 3.00\sigma(I)$, $R = 2.19\%$.

Cp*Ir(pin) (6). A 20 mL vial was charged with a stir bar, [Cp*IrCl$_2$]$_2$ (340 mg, 0.427 mmol), pinacol (102 mg, 0.863 mmol), and THF (10 mL). To the resulting orange solution was added, dropwise with stirring, a THF slurry (5 mL) of KN(TMS)$_2$ (343 mg, 1.72 mmol). Over the course of the addition, the mixture became homogeneous and turned dark red-purple. The vial was capped, and the solution was stirred for 2 h at room temperature. The solution was then reduced to dryness under vacuum to yield a red powder, which was extracted with benzene (20 mL) to yield a red-purple extract and brown-yellow residue. The extract was reduced to dryness under vacuum, and recrystallization of the resulting red residue from ether (4 mL) at −30 °C yielded **6** as 295 mg of dark red needles (80% yield). ^{1}H NMR (C$_6$D$_6$): δ 1.48 (s, 12H), 1.41 (s, 15H) ppm. ^{13}C{^{1}H} NMR: δ 85.54 (s, O*C*Me$_2$), 81.61 (s, *C*$_5$Me$_5$), 27.44 (s, OC*Me*$_2$), 10.10 (s, C$_5$*Me*$_5$) ppm. IR (KBr): 1139 (s), 951 (m), 893 (m) cm^{-1}. Anal. Calcd for C$_{16}$H$_{27}$O$_2$Ir: C, 43.32; H, 6.16. Found: C, 43.24; H, 6.14.

Crystallographic Study of Cp*Ir(pin) (6). A red prism crystal having approximate dimensions 0.20 × 0.12 × 0.10 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. Data were collected using a SMART CCD area detector with graphite-monochromated Mo Kα radiation. Hydrogen atoms were included but not refined. The structure showed disorder similar to that observed for **4** (see above), and the structure given in Figure 3 is based on modeling of the central carbon atoms of the ligand as half-occupancy pairs of atoms with isotropic thermal parameters. Selected bond lengths are given in Figure 3. Crystallographic data are as follows: space group *Pnma*, $a = 17.028(1)$ Å, $b = 12.3059(9)$ Å, $c = 7.9491(6)$ Å, $V = 1665.6(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.77$ g/cm^3, μ(Mo Kα) = 80.35 cm^{-1}, 1645 unique reflections, 1225 reflections with $I > 3.00\sigma(I)$, $R = 1.8\%$.

(Cp*Co)$_2$(pin) (7). A 20 mL vial was charged with a stir bar, [Cp*CoCl]$_2$ (110 mg, 239 mmol), pinacol (29.0 mg, 246 mmol), and 5 mL of THF. To the resulting brown solution was added, dropwise with stirring, 5 mL of a THF solution of KN(TMS)$_2$ (95.9 mg, 482 mmol). Over the course of the addition, the mixture took on a greenish tint. The vial was capped, and the solution was stirred for 2 h at room temperature. The solution was then reduced under vacuum to yield a brownish green solid, which was extracted with 20 mL of benzene to yield a brownish green extract and a brown residue. The extract was reduced to dryness under vacuum, and recrystallization of the resulting brownish green solids from 2 mL of diethyl ether at −30 °C yielded (Cp*Co)$_2$(pin) as small brown-green crystals (85.1 mg, 70% yield). ^{1}H NMR (C$_6$D$_6$): δ 1.76 (s, 30H), 1.51 (s, 12H) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 87.82 (s, *C*$_5$Me$_5$), 84.26 (s, O*C*Me$_2$), 30.21 (s, OC*Me*$_2$), 10.36 (s, C$_5$*Me*$_5$) ppm. IR (KBr): 2975 (s), 1452 (s), 1378 (s), 1140 (m), 953 (m) cm^{-1}. EI-MS: *m*/*z* 504 ([(Cp*Co)$_2$(pin)]$^+$), 194 ([Cp*Co]$^+$). Anal. Calcd for C$_{26}$H$_{42}$O$_2$Co$_2$: C, 61.90; H, 8.39. Found: C, 61.74; H, 8.56.

Treatment of Cp*Co(pin) Photolysis Intermediate with Cp*Co(pin) (4). In the glovebox, **4** (2.0 mg, 6.5 μmol) was dissolved in C$_6$D$_6$ to yield a bright green solution which was transferred to a J. Young tube. The tube was irradiated for 60 min, after which time the solution was purple, and monitoring of the reaction by ^{1}H NMR spectroscopy showed that acetone (δ 1.54 (s, 2 × 6H) ppm) was the only NMR-active product. (When such purple, irradiated samples were allowed to stand in the dark at room temperature, they turned brown over the course of 24 h and yielded only broad, noisy ^{1}H NMR spectra.) In the box, more Cp*Co(pin) (2.0 mg, 6.5 μmol) was added to the purple solution, and it was left in the dark at 20 °C for 2 days. The reaction was monitored by ^{1}H NMR spectroscopy, which indicated formation of **7** in 80% yield. ^{1}H NMR (C$_6$D$_6$): δ 1.76 (s, 30H), 1.51 (s, 12H) ppm.

Photolysis of Cp*Co(pin) (4) in C$_6$D$_{12}$ with 2,3-Dimethylbutadiene. In the glovebox, **4** (5.8 mg, 18.8 μmol) and 2,3-dimethylbutadiene (10 μL, 120 μmol) were dissolved in C$_6$D$_{12}$ and the solution was transferred to a J. Young NMR tube. The tube was irradiated for 40 min, after which time ^{1}H NMR spectroscopy indicated complete conversion to acetone and the product **8**. Removal of volatile materials under vacuum yielded 5.0 mg of spectroscopically pure **8** as a brown solid (93% yield). ^{1}H NMR (C$_6$D$_{12}$): δ 1.96 (s, 2 × 6H, acetone), 1.81 (s, 6H), 1.74 (s, 15H), 0.89 (br, 2H), −0.70 (br, 2H) ppm. ^{1}H NMR (C$_6$D$_6$): δ 1.80 (s, 6H), 1.69 (s, 15H), 1.06 (br, 2H), −0.41 (br, 2H) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 88.62 (s, *C*$_5$Me$_5$), 87.64 (s, CH$_2$*C*Me), 38.63 (s, *C*H$_2$CMe), 17.29 (CH$_2$C*Me*), 9.98 (C$_5$*Me*$_5$) ppm. (Lit.[20] ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 88.6, 87.6, 38.6, 17.3, 10.0 ppm. No ^{1}H NMR data were included in the reference.)

Photolysis of Cp*Co(pin) (4) with 2,3-Dimethylbutadiene in C$_6$D$_6$. In the glovebox, **5** (6.9 mg, 22.2 μmol) and 2,3-

dimethylbutadiene (15 μL, 180 μmol) were dissolved in C_6D_6, and the solution was transferred to a J. Young NMR tube. The tube was irradiated for 40 min, and ^{1}H NMR spectroscopy indicated acetone (δ 1.54 ppm) was the only NMR-active product. Although the starting material was completely consumed, no diene had been consumed. The reaction was allowed to continue at 20 °C in the dark for 2 days, after which time monitoring by ^{1}H NMR spectroscopy showed that the product **8** had been formed in 80% yield. Complex **8** was isolated as a brown solid by recrystallization from pentane at −30 °C (3.9 mg, 64% yield).

(Cp*Rh)$_2$(pin) (11). In the glovebox, **5** (50.7 mg, 143 μmol) was dissolved in pentane (50 mL) in a 100 mL glass bomb. This was exposed to ambient light for 1 week, over which time a color change from purple to maroon occurred. The solution was then reduced under vacuum to a dark oily material, which was recrystallized repeatedly from diethyl ether to yield **11** as a black solid (23.1 mg, 54% yield). ^{1}H NMR (C_6D_6): δ 1.75 (s, 30H), 1.51 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 87.86 (s, OCMe$_2$), 86.91 (d, J_{Rh-C} = 8.6 Hz, C_5Me$_5$), 29.95 (s, OCMe_2), 11.42 (s, C$_5$$Me_5$) ppm. IR (KBr): 2957 (s), 1452 (m), 1376 (s), 1139 (s), 950 (m), 890 (m) cm^{-1}. EI-MS: *m*/*z* 592 ([(Cp*Rh)$_2$(pin)]$^+$), 373 ([Cp*$_2$Rh]$^+$), 238 ([Cp*Rh]$^+$). Anal. Calcd for $C_{26}H_{42}O_2Rh_2$: C, 52.71; H, 7.15. Found: C, 52.63; H, 7.06.

Treatment of (Cp*RhOMe)$_2$ (12) with Pinacol. In the glovebox, (Cp*RhOMe)$_2$ (4.2 mg, 7.8 μmol) and pinacol (2.0 mg, 17.0 μmol) were dissolved in C_6D_6. The resulting purple solution was transferred to a J. Young NMR tube, which was subsequently heated at 45 °C for 1 h. After this time, the solution was maroon. Monitoring of the reaction by ^{1}H NMR spectroscopy indicated quantitative conversion to product **11** and methanol (δ 3.05 (s, 2 × 3H) ppm). Recrystallization of the product from ether yielded **11** as a black solid (1.9 mg, 39% yield).

Treatment of (Cp*Rh)$_2$(pin) (11) with MeOH. In the glovebox, a glass bomb was charged with a stir bar, **11** (3.1 mg, 5.2 μmol), and MeOH (1 mL). The maroon solution was stirred at room temperature for 3 days, during which time a slight darkening was observed. The solution was then reduced to dryness under vacuum, and C_6D_6 was added. The products were identified by ^{1}H NMR spectroscopy, which showed that **11** had been completely consumed and converted to (Cp*RhOMe)$_2$ (**12**) and pinacol, both in 60% yield. The product mixture was not clean, and the products were not isolated. Partial ^{1}H NMR (C_6D_6): δ 3.56 (s, 6H), 1.66 (s, 30H), 1.03 (s, 12H, pinacol C−CH_3) ppm. (Lit.[21] ^{1}H NMR (C_6D_6): δ 3.54 (s, 6H), 1.66 (s, 30H) ppm.)

(Cp*Rh)$_3$C$_6$H$_6$ (10) and (Cp*Rh)$_2$C$_6$H$_6$ (9). In the glovebox, a glass bomb was charged with **5** (150 mg, 0.423 mmol) and C_6H_6 (200 mL, 2 mM). The sample was irradiated for 16 h and reduced to dryness under vacuum to yield a brown solid. This was recrystallized from diethyl ether at −30 °C, and compound **10** was isolated as black, poorly formed crystals (30.1 mg, 27% yield). Complex **9** could not be cleanly separated from residual **10**; therefore, the spectroscopic assignments for **9** that follow are based upon spectra which included **10** as a ~20% impurity.

(Cp*Rh)$_3$C$_6$H$_6$ (10). ^{1}H NMR (C_6D_6): δ 7.64 (m, 2H, aryl), 4.36 (m, 2H, aryl), 2.23 (m, 2H, aryl), 2.06 (s, 15H, Cp*), 1.78 (s, 30H, Cp*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.74 (m,[43] aryl), 97.61 (d, J_{Rh-C} = 4.2 Hz, C_5Me$_5$), 97.40 (d, J_{Rh-C} = 4.3 Hz, C_5Me$_5$), 75.90 (d, J_{Rh-C} = 5.7 Hz, aryl), 71.48 (d, J_{Rh-C} = 17.0 Hz, aryl), 12.30 (s, C$_5$$Me_5$), 11.17 (s, C$_5$$Me_5$) ppm. IR (KBr): 2904 (s), 1376 (s), 1021 (m), 718.2 (m) cm^{-1}. EI-MS: *m*/*z* 792 ([(Cp*Rh)$_3$(C$_6$H$_6$)]$^+$), 373 ([Cp*$_2$Rh]$^+$). Anal. Calcd for $C_{36}H_{51}Rh_3$: C, 54.56; H, 6.49. Found: C, 54.95; H, 6.39.

(Cp*Rh)$_2$C$_6$H$_6$ (9). ^{1}H NMR (C_6D_6): δ 8.73 (m, 2H, aryl), 5.81 (m, 2H, aryl), 4.58 (m, 2H, aryl), 1.75 (s, 30H, Cp*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 184.59 (m,[38] aryl), 96.13 (t, J_{Rh-C} = 1.8 Hz, aryl), 94.50 (d, J_{Rh-C} = 4.8 Hz, C_5Me$_5$), 75.85 (d, J_{Rh-C} = 5.5 Hz, aryl), 10.82 (s, C$_5$$Me_5$) ppm.

Photolysis of Cp*Rh(pin) (5) in C$_6$D$_6$. (a) Various Light Sources. In the glovebox, a stock solution of **5** (18.1 mg, 51.0 μmol) in C_6D_6 (2.5 mL, 20 mM) was prepared and divided roughly evenly among four Pyrex J. Young NMR tubes and a quartz Schlenk cuvette. The quartz cuvette (1) and one tube (2) were irradiated directly with the mercury lamp, another tube (3) was irradiated through a uranium glass filter, and another (4) was irradiated through an amber filter. After 20 min of irradiation, the contents of the cuvette were transferred to an NMR tube in the glovebox, and ^{1}H NMR spectra of all the tubes were acquired. At this point, no starting material remained in the solution irradiated through quartz. The other tubes 2−4 (showing approximately 50, 40, and 30% conversion, respectively) were irradiated as before and monitored every 10 min by ^{1}H NMR spectroscopy until no starting material remained. The fourth tube was exposed to ambient light in the laboratory and monitored by ^{1}H NMR spectroscopy periodically until no starting material remained. All were subsequently irradiated for an additional 24 h, and ^{1}H NMR spectroscopy after this time revealed no significant change in any of the product mixtures. Relative product concentrations were determined by ^{1}H NMR spectroscopy and reported in Table 1 as proportions of the total Cp* resonances. Only the Cp* resonances reported for **9** and **10** were observed. Compound **10** was isolated from the combined product mixture by recrystallization from ether (2.0 mg black solid, 11% yield), and a mass spectrum was obtained. EI-MS: *m*/*z* 798 ([(Cp*Rh)$_3$(C$_6$D$_6$)]$^+$), 373 ([Cp*$_2$Rh]$^+$).

(b) Irradiation Carried Out using Low Concentration of 5. In the glovebox, a 20 mL vial was charged with **5** (0.4 mg, 1.1 μmol) and C_6H_6 (10 mL, 0.1 mM). The faint purple solution was left exposed to ambient light and observed every 20 min. Within 60 min, the color had changed to a pale yellow that did not change visibly over the next 1 h. The solution was reduced to dryness under vacuum, and the brown residue was dissolved in C_6D_6 and transferred to an NMR tube. The product ratio was determined and reported as described above.

(c) Early Conversion with Mercury-Lamp Irradiation. In the glovebox, **5** (2.5 mg, 7.1 μmol) was dissolved in C_6D_6, and the solution was transferred to a J. Young NMR tube. The tube was irradiated for 2 min, and a ^{1}H NMR spectrum was acquired which showed < 5% conversion of **5** to only products **11** (40%), **9** (60%), and acetone. The tube was then irradiated for 40 min, and ^{1}H NMR spectroscopy showed complete conversion of **5** to predominantly **10** and **9**.

(d) Early Conversion with Ambient Light. In the glovebox, **5** (2.5 mg, 6.8 μmol) was dissolved in C_6D_6, and the solution was transferred to a J. Young NMR tube. The tube was exposed to ambient light for 2 h, and a ^{1}H NMR spectrum was acquired which showed <5% conversion of **5** to only products **11** (60%), **9** (40%), and acetone. The tube was exposed to ambient light for 2 more days, after which ^{1}H NMR spectroscopy showed complete conversion of **5** to predominantly **11** and **10**.

Photolysis of Cp*Rh(pin) (5) in C$_6$D$_{12}$. In the glovebox, **5** (2.4 mg, 6.8 μmol) was dissolved in C_6D_{12} and the purple solution was transferred to a J. Young NMR tube. The tube was irradiated for 40 min to yield a maroon solution, and ^{1}H NMR spectroscopy indicated complete conversion to the products. The solution was then reduced to dryness under vacuum, and C_6D_6 was added. Subsequent ^{1}H NMR spectroscopy confirmed the product to be **11.** ^{1}H NMR (C_6D_{12}): δ 1.96 (s, 2 × 6H, acetone), 1.75 (s, 30H), 1.21 (s, 12H) ppm. ^{1}H NMR (C_6D_6): δ 1.75 (s, 30H), 1.51 (s, 12H) ppm.

Photolysis of Cp*Rh(pin) (5) with 2,3-Dimethylbutadiene. In the glovebox, **5** (5.2 mg, 14.6 μmol) and 2,3-dimethylbutadiene (10 μL, 120 μmol) were dissolved in C_6D_6 and the solution was transferred to a J. Young NMR tube. The

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[43] This multiplet has a complex pattern that indicates coupling to multiple rhodium nuclei but is otherwise unhelpful in assigning the structure.

tube was irradiated for 40 min, and ^{1}H NMR spectroscopy indicated complete conversion to acetone and the brown diene adduct **13**. The diene adduct was subsequently isolated by recrystallization from pentane as red-brown crystals (3.1 mg, 66% yield). ^{1}H NMR (C_6D_6): δ 1.83 (s, 15H), 1.75 (s, 6H), 1.74 (br, 2H), 0.53 (br, 2H) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.83 (s, 15H), 1.72 (s, 6H), 1.51 (br, 2H), 0.06 (br, 2H) ppm. (Lit.[44] ^{1}H NMR (CD_2Cl_2): δ 1.83 (s, 15H), 1.72 (s, 6H), 1.51 (br, 2H), 0.06 (br, 2H) ppm.)

Treatment of (Cp*Rh)$_2$(pin) (11) with Pinacol and Oxygen. In the glovebox, **11** (1.3 mg, 2.2 μmol) and pinacol (4.4 mg, 37 μmol) were dissolved in C_6D_6 to yield a maroon solution which was transferred to a J. Young tube. The tube was then freeze−pump−thawed twice on the vacuum line and pressurized with O_2 (223 Torr). The reaction was monitored by ^{1}H NMR spectroscopy. After 36 h, all of the starting material was gone and the product **5** was evident in 72% yield. Only a small amount of pinacol (approximately 0.5 equiv for every 1 equiv of **5** produced) was consumed.

Treatment of (Cp*Rh)$_2$(pin) (11) with Pinacol and *tert*-Butyl Hydroperoxide. In the glovebox, **11** (1.5 mg, 2.5 μmol) and pinacol (3.6 mg, 31 μmol) were dissolved in C_6D_6 to yield a maroon solution which was transferred to a J. Young tube. *tert*-Butyl hydroperoxide (0.40 μL, 2.1 μmol) was later added as a C_6D_6/nonane solution, and the tube was shaken and left at room temperature. The reaction was monitored by ^{1}H NMR spectroscopy and found to be complete within 10 min. A total of 70% of the starting material was consumed, and **5** was produced in 70% yield based on the amount of **11** consumed. *tert*-Butyl alcohol (δ 1.05 (s, 9H) ppm) was also produced. Only a small amount of pinacol (approximately 0.5 equiv for every 1 equiv of **5** produced) was consumed.

Catalytic Conversion of Pinacol to Acetone Using Oxygen. Specific quantities for this reaction are given in Table 2. In the glovebox, the catalyst (see Table 2) and pinacol were dissolved in 300 μL of the appropriate solvent, and the solution was transferred to a J. Young tube. The tube was then moved to the vacuum line where the solution was twice freeze−pump−thawed. The line was then charged with oxygen, the NMR tube (at room temperature) was opened to the line, and the pressure in the system was noted. The tube was then closed, shaken vigorously for several seconds, and irradiated for 16−20 h. After this time, the number of turnovers was determined using ^{1}H NMR spectroscopy by noting the change in the pinacol methyl resonance (δ 1.03 (s, 12H) ppm). The values thus obtained were always in good agreement with the amount of acetone (δ 1.54 (s, 6H) ppm) produced. Results are reported in Table 2, and turnover values for experiments in which **11** was used as a catalyst are corrected for the fact that it includes two rhodium centers.

Catalytic Conversion of Pinacol to Acetone Using Nitrous Oxide. In the glovebox, the catalyst (3.5 mg, 10 μmol) and pinacol (24.0 mg, 203 μmol) were dissolved in C_6D_6 (0.25 mL) and the solution was transferred to a J. Young tube. The tube was then moved to the vacuum line where the solution was twice freeze−pump−thawed. The line was then charged with 761 Torr of nitrous oxide, and the NMR tube (at room temperature) was opened to the line and then closed. The tube was shaken vigorously for several seconds and irradiated for 12 h with additional shaking every 2 h. After this time, ^{1}H NMR spectroscopy showed that >95% of the starting pinacol (δ 1.03 (s, 12H) ppm) had been consumed relative to internal standard, and acetone (δ 1.54 (s, 6H) ppm) accounting for 85% of the pinacol had been produced.

Treatment of Cp*Rh(pin) (5) with Catechol. In the glovebox, **5** (11.8 mg, 33.3 μmol) was dissolved in THF-d_8. No internal standard was used. To the purple solution was added catechol (3.7 mg, 34 μmol), resulting in an immediate color change to intense blue. The reaction was monitored by ^{1}H NMR spectroscopy, and product was found to have formed in quantitative yield. The solution was then reduced to dryness under vacuum and recrystallization from ether at −30 °C afforded product **14** as dark crystals (8.0 mg, 70% yield). ^{1}H NMR (THF-d_8): δ 6.50 (m, 2H), 6.71 (m, 2H), 1.92 (s, 15H), ppm. ^{1}H NMR ($CDCl_3$): δ 6.82 (m, 4H), 1.95 (s, 15H), ppm. (Lit.[27] ^{1}H NMR ($CDCl_3$): δ 6.80 (m, 4H), 1.95 (s, 15H) ppm.)

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Supporting Information Available: Data collection and refinement details and listings of atomic coordinates, thermal parameters, and bond lengths and bond angles of all three crystallographically characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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