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ARTICLE TYPE

Rh₂(esp)₂-Catalyzed Allylic and Benzylic OxidationsYi Wang,^a Yi Kuang^a and Yuanhua Wang^{a*}

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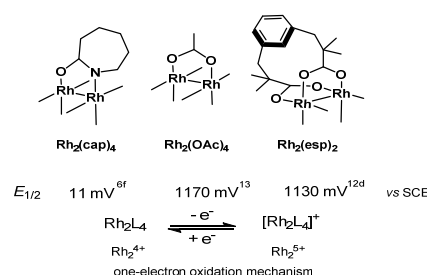
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The dirhodium(II) catalyst Rh₂(esp)₂ allows direct solvent-free allylic and benzylic oxidations by T-HYDRO with the remarkably low catalyst loading. This method is operationally simple and scalable at ambient temperature without the use of any additives. The high catalyst stability in these reactions may be attribute to a dirhodium(II,II) catalyst resting state, which is less prone to decompose.

In the past decade the scientific world witnessed a dramatic improvement in the methods used for selective C-H functionalization.¹ Select oxidations of C-H bonds are attractive as synthetic transformations and can convert relatively cheap hydrocarbons into value-added oxyfunctionalized products.² For example, a desirable synthetic goal would be the direct transformation of a methylene group into a ketone.³ Among these transformations, benzylic and allylic oxidations are fundamental functional transformations in synthetic chemistry.^{2a,4} Although organocatalytic benzylic and allylic oxidations have been reported,⁵ traditionally such oxidation reactions have relied upon metal complexes that are capable of carrying out one-electron redox processes mediated by oxidant *tert*-butyl hydroperoxide (TBHP),⁶ such as Fe²⁺/Fe³⁺,^{6m-o} Cu⁺/Cu²⁺,^{6p-q} Rh₂⁴⁺/Rh₂⁵⁺,^{6f-k} Co²⁺/Co³⁺.^{6l-m} These procedures provided a feasible approach for benzylic and allylic oxidations that showed moderate to good reactivities. However, despite the advances, drawbacks still exist in this transformation, such as the decomposition of the metal catalysts during the process, the lack of regio- and stereoselectivity, exothermic reactions, etc.^{6,7} Thus, there is an ongoing interest in finding more potent catalysts involving new mechanisms that enable this catalytic transformation to take place under more practical, environmentally friendly conditions.

Doyle and coworkers have demonstrated bimetallic paddlewheel catalyst dirhodium(II) caprolactamate Rh₂(cap)₄ as an excellent catalyst in activating TBHP in allylic and benzylic oxidation.^{6f,j} This catalyst's success is due to it readily engaging using a one-electron oxidation mechanism ($E_{1/2} = 11$ mV, in CH₃CN, vs Ag/AgCl).^{6f} In contrast to Rh₂(cap)₄, the common Rh₂(OAc)₄ displays a higher oxidation potential $E_{1/2}$ of 1170 mV and for that reason has limited activity in the allylic oxidation of olefins (Scheme 1).⁸ During our study of the application of selective allylic oxidations of cyclic olefin 3,5,5-trimethyl-2-cyclohexen-1-one (α -isophorone, α -1) to 3,5,5-trimethyl-2-cyclohexen-1, 4-dione (ketoisophorone, **2**), we were surprised to find that even dirhodium(II) complexes with higher oxidation

potentials still occur in allylic oxidation. These unexpected results appear to indicate that the requirement of dirhodium(II) catalysts with lower oxidation potentials in allylic and benzylic oxidations can be lifted.^{6k} In order to clarify the possible reaction pathway, we therefore directed our efforts towards the investigation of this interesting phenomenon.



Scheme 1 Half-Wave Potential for Dirhodium(II) Catalyst.

Selective oxidation of isophorone (**1**) to **2** is an important reaction since the product **2** is not only an important substance in flavoring, but a key intermediate in the synthesis of pharmaceuticals, especially for vitamin E.⁹ The direct oxidation of readily available α -1 to **2**, avoiding the intermediate isomerization of α -1 to β -1 (3,5,5-trimethyl-3-cyclohexen-1-one), is particularly attractive.¹⁰ However, α -1, with the conjugated system of double bond and carbonyl group is the more stable isomer thermodynamically, which makes the current oxidation method from α -1 to **2** suffer drawbacks such as low conversions, long reaction times, harsh conditions, and low chemoselectivity.¹¹ After considerable experimentation, we found that the chelating Du Bois' catalyst Rh₂(esp)₂,¹² with higher oxidation potential ($E_{1/2} = 1130$ mV),^{12d} allowed for the direct solvent-free oxidation of α -1 into the corresponding **2**. This had a 91% conversion at room temperature, with catalyst loadings as low as 0.1 mol% without detecting any other unwanted side products, and yielded TON up to 910 (Table 1, entry 1). Solvent-free green oxidation reactions were achieved through dissolving catalysts directly into the substrate α -1 with T-HYDRO (70% *tert*-butyl hydroperoxide in water) as an oxidant, without any additives necessary. The results obtained during the optimization process are summarized in Table 1.

There was no conversion to the desired product **2** in the absence of a metal catalyst or T-HYDRO oxidant (Table 1, entries 2-3). If organic solvents like DCE (1, 2-dichloroethane) were added, a lower conversion resulted (Table 1, entry 4). When TBHP (5-6 M solution in decane) was used, the results

showed less promise than the T-HYDRO oxidant (Table 1, entries 5-6), which indicated water was crucial for this reaction. Reducing the amount of T-HYDRO from 5 eq to 1 or 3 eq gave a significantly lower conversion (Table 1, entries 7-8). We also screened the reaction temperature and found the conversion rate dropped significantly when the temperature was raised (Table 1, entries 9-10). Subsequent experimentation proved dioxygen did not play a role in the reaction system (Table 1, entry 11). Hence, we next focused our attention on the efficiency of the different dirhodium(II) catalysts without solvents. By replacing the $\text{Rh}_2(\text{esp})_2$ with $\text{Rh}_2(\text{OAc})_4$ which had exhibited a similar oxidation potential ($E_{1/2} = 1170 \text{ mV}$),¹³ the reaction occurred with only 31% conversion to the desired product (Table 1, entry 12). When the $\text{Rh}_2(\text{OAc})_4(\text{IMes})$ catalyst combination was employed,⁸ the reaction was still less efficient (Table 1, entry 13). Doyle's catalyst $\text{Rh}_2(\text{cap})_4$ ^{6f-j} dissolved in the α -1 substrate but provided only 49% conversion after 24 hr (Table 1, entry 14). Poor results were obtained when the reaction was carried out with other structurally chelating dirhodium(II) catalysts (Table 1, entries 15-18).¹⁴ Notably, as the prototype of $\text{Rh}_2(\text{esp})_2$, the Taber's catalyst $\text{Rh}_2(\text{MPDP})_2$ ^{14b} only gave a trace amount of the desired enedione **2** (Table 1, entry 15). Interestingly, the color of the reaction mixture stayed green until the end of the reaction under the standard condition, while it was previously reported to have a brilliant red color due to one-electron oxidized dirhodium(II,III).^{12d-e} In addition, the $\text{Rh}_2(\text{esp})_2$ catalyst did not degrade and was recovered from the reaction mixture at the end of this reaction.

Next, in order to explore the possible mechanism, we used UV/visible spectroscopy to allow for the assessment of metal oxidation states in dirhodium(II) chemistry, so that we could monitor the change of the $\text{Rh}_2(\text{esp})_2$ catalyst during the oxidation reaction (Figure 1).¹⁵

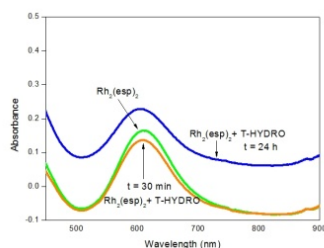


Figure 1 UV/Vis spectrum of $\text{Rh}_2(\text{esp})_2$ catalyst during the oxidation.

Initially, the $\text{Rh}_2(\text{esp})_2$ catalyst directly dissolved in the substrate, α -1, which may also have functioned as the "solvent" (see supplementary material). The UV/visible spectrum of the obtained green clean solution revealed a representative adsorption of dirhodium(II,II) carboxylates. After T-HYDRO was added, no drastic change was observed in the electronic spectrum until the end of the reaction (Figure 1). As previously reported, the adsorption spectroscopy of the $\text{Rh}_2(\text{esp})_2^+$ catalyst showed the characteristic band of one-electron oxidized $\text{Rh}_2^{\text{II,III}}$ species at $\sim 800 \text{ nm}$.^{12d-e,15} The unchanged UV/visible spectroscopy indicated the $\text{Rh}_2(\text{esp})_2$, not the $\text{Rh}_2(\text{esp})_2^+$, is the catalyst resting state during the reaction.

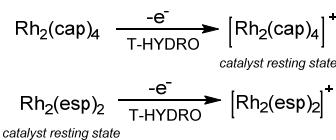
Given the nearly identical potentials of one-electron oxidation of $\text{Rh}_2(\text{esp})_2$ and $\text{Rh}_2(\text{OAc})_4$, the low conversion of the reaction

Table 1 Optimization of Reaction Conditions^a

Entry	Deviation from standard reaction conditions	Conversion(%) ^b
1	none	91
2	without $\text{Rh}_2(\text{esp})_2$	NR
3	without T-HYDRO	NR
4	DCE added	86
5 ^c	TBHP instead of T-HYDRO	72
6 ^{c,d}	TBHP instead of T-HYDRO and DCE added	39
7	1 equiv of T-HYDRO	17
8	3 equiv of T-HYDRO	36
9	40°C instead of r.t.	89
10	60°C instead of r.t.	67
11	N_2 instead of air	91
12	$\text{Rh}_2(\text{OAc})_4$ instead of $\text{Rh}_2(\text{esp})_2$	31
13	$\text{Rh}_2(\text{OAc})_4(\text{IMes})$ instead of $\text{Rh}_2(\text{esp})_2$	9
14	$\text{Rh}_2(\text{cap})_4$ instead of $\text{Rh}_2(\text{esp})_2$	49
15	$\text{Rh}_2(\text{MPDP})_2$ instead of $\text{Rh}_2(\text{esp})_2$	Trace
16	Dirhodium(II) catalyst I instead of $\text{Rh}_2(\text{esp})_2$	NR
17	Dirhodium(II) catalyst II instead of $\text{Rh}_2(\text{esp})_2$	Trace
18	$\text{Rh}_2(\text{MPDP})(\text{CO}_2\text{CF}_3)_2$ instead of $\text{Rh}_2(\text{esp})_2$	8

^a Unless otherwise noted, all reactions were performed by using α -1 (4.00 mmol), T-HYDRO (20 mmol), dirhodium catalyst (0.1 mol %). ^b Determined by GC (Gas chromatography). ^c 5-6 M solution in decane. ^d 2 mL DCE was added. cap = caprolactamate, esp = $\alpha, \alpha', \alpha'', \alpha'''$ -tetramethyl-1,3-benzenedipropionate, NR = no reaction

catalyzed by $\text{Rh}_2(\text{OAc})_4$ (Table 1, entry 12) clearly indicated the chelating ligand of $\text{Rh}_2(\text{esp})_2$ was relevant with the oxidation mechanism and also excluded the possible mechanism proposed by Ren and coworkers (their diruthenium(II,III) catalyzed the oxygenation of organic sulfide, suggesting that a binuclear catalyst would act as oxygen transfer).¹⁶ In addition, none of product **2** was obtained when the H_2esp ligand alone was used in an attempt to catalyze this reaction. Based on our experimental results, we concluded $\text{Rh}_2(\text{esp})_2$ was the catalyst resting state in this green oxidation, which was different from the well-documented Doyle's catalyst $\text{Rh}_2(\text{cap})_4$.^{6f-j} In $\text{Rh}_2(\text{cap})_4$ catalyzed oxidation, the oxidized catalyst $\text{Rh}_2(\text{cap})_4^+$ was the resting state (Scheme 2).



Scheme 2 Different catalyst resting state.

Subsequently, we used gas chromatographic studies in order to investigate the different performances of these two catalysts in the oxidation reaction. The plots in Figure 2 revealed that the oxidation reaction catalyzed by $\text{Rh}_2(\text{esp})_2$ was more reactive than reaction catalyzed by $\text{Rh}_2(\text{cap})_4$. We observed that oxidative $\text{Rh}_2(\text{cap})_4$ resulted in 49% conversion, as opposed to the 91% conversion that resulted from using $\text{Rh}_2(\text{esp})_2$ under the same

experimental conditions, showing clearly the advantage of $\text{Rh}_2(\text{esp})_2$ in driving the α -1 oxidation. Further study revealed that even 0.01 mol % $\text{Rh}_2(\text{esp})_2$, in the presence of 5 eq T-HYDRO, lives for 10 days and catalyzes the reaction with impressive 88% conversion (see supplementary material). Given the fact that oxidative dirhodium(II,III) complexes have been shown to slowly degrade as the reaction proceeds,^{6i,12d-e,17} the dirhodium(II,II) catalyst resting state may keep the catalyst stability throughout the reaction, thus avoiding metal catalyst decomposition in the reaction.¹⁸ Next, we attempted catalyst recycling experiments in an operationally simple procedure.¹⁹ The $\text{Rh}_2(\text{esp})_2$ catalyst can be recovered through chromatographic purification. 94% conversion, 77% yield of **2** resulted after two cycles and NMR study confirmed the recovered $\text{Rh}_2(\text{esp})_2$ catalyst remained unchanged (see supplementary material).

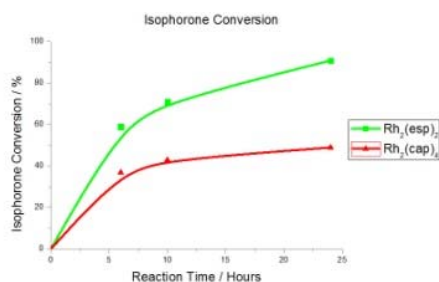


Figure 2 Evaluation of catalysts kinetic performance

With the optimized conditions in hand, we then turned our attention toward the scope and limitations of this unexpected process. The good solubility of the $\text{Rh}_2(\text{esp})_2$ catalyst in the selected substrates and T-HYDRO mixture rendered the possibility of performing the catalytic reactions without solvents (Table 2). In general, this solvent-free catalytic reaction was compatible with a wide range of the allylic substrate, and excellent regioselectivities in the oxidation at the secondary over primary carbon was achieved (Table 2, entries 1-5). The starting material in the fragrance and flavoring industry, like α -1, valencene (**3**), β -ionone (**5**), α -pinene (**7**), was transformed into the corresponding oxidized product with a good yield (Table 2, entries 1-4). These results indicate the potential industrial application of this process. Interestingly, (+)-3-carene (**9**) was transformed into enedione **10** under the reaction conditions (Table 2, entry 5). In addition, the present protocol was also successfully applied to a variety of representative benzylic substrates (Table 2, entries 6-13). Notably, a different reactivity was observed when 1,2,3,4-tetrahydronaphthalene (**13**) was used as substrate (Table 2, entries 7-8). Under the standard conditions, **13** oxidized to give enedione **16** as major product in moderate yield, along with α -tetralone (**14**) and an intermediate *tert*-butyl peroxy ether **15** that corresponded with the enedione (Table 2, entry 7). Meanwhile, this reaction resulted in **14** as a major product, with *tert*-butyl peroxy ether intermediate **17** when $\text{Rh}_2(\text{cap})_4$ was applied (Table 2, entry 8). Further experimentation confirmed that **14** would transform into the enedione **16** in good yield when catalyzed by $\text{Rh}_2(\text{esp})_2$ (Table 2, entry 12). We then focused on the substrates that possessed two benzylic positions in this reaction system. We also observed the formation of benzyl *tert*-butyl peroxides for the enediones in the oxidation of isochroman (**18**) and indane (**21**) (Table 2, entries 9-

Table 2 Oxidation by $\text{Rh}_2(\text{esp})_2$ /T-HYDRO under standard conditions^a

Entry	Substrate	Products	Yield ^b
1			78%
2			71%
3			54%
4 ^c			43%
5 ^c			60%
6 ^d			99%
7 ^d			8%(14)+19%(15) +40%(16)
8 ^{d,e}			25%(17)+44%(14)
9 ^d			48%(19)+30%(20)
10 ^d			46%(22)+19%(23)
11 ^d			65%(25)+7%(26)
12 ^d			78%
13 ^d			11%(28)+45%(29)

^a Unless otherwise noted, all reactions were performed by using α -1 (4.00 mmol), T-HYDRO (20 mmol), $\text{Rh}_2(\text{esp})_2$ (0.1 mol%), ^b Isolated yield. ^c 1 mol% $\text{Rh}_2(\text{esp})_2$ and 1 mL H_2O was added. ^d The reaction temperature was 40°C. ^e 0.1 mol% $\text{Rh}_2(\text{cap})_4$ instead.

10). Oxidation of N-tosyltetrahydroisoquinoline (**24**) afforded small amounts desired amide product **26**, and due to the decomposition of the peroxide being very slow in this case peroxide compound **25** was the major product (Table 2, entry 11). Though we did not detect a peroxide intermediate in the α -1 oxidation reaction, based on the above results from benzylic oxidation, we concluded that it is likely that *t*-BuOO• (*t*-butylperoxy radical) still forms and acts as an oxidant in this reaction system. The successfully tracing of the *tert*-butylperoxy radical revealed that the $\text{Rh}_2(\text{esp})_2$ catalyzed green process is a radical reaction. According to the allylic and benzylic oxidations

mechanism in dirhodium(II) chemistry outlined by Doyle and co-workers,^{6f,j} the most probable pathway was believed to be as follows: after T-HYDRO was added to the reaction mixture, the one-electron oxidation of Rh₂(esp)₂ to Rh₂(esp)₂⁺ occurred. Due to the high oxidation potential of the Rh₂(esp)₂ (*E*_{1/2} = 1130 mV), this oxidation is also a rate-limiting step and the very reactive Rh₂(esp)₂⁺ species would generate in this step. This activated species then underwent a much faster chemical transformation with substrate to the desired product. This would explain why the Rh₂(esp)₂ is the catalyst resting state during the reaction.²⁰ Furthermore, because the low conversion of the reaction catalyzed by Rh₂(OAc)₄, the details of how the chelating ligand of Rh₂(esp)₂ effect the catalyst remains to be investigated.

Conclusions

In summary, we have reported the low loading chelating dirhodium(II) complex Rh₂(esp)₂ catalyzing allylic and benzylic oxidations with good conversion under operationally simple, solvent-free, mild reaction conditions, a report which has potential applications in both the fine chemical and pharmaceutical industries. These reactions generally exhibit high catalyst stability because they have a dirhodium(II,II) catalyst resting state, which is less prone to decompose. Further experiments will be used to elucidate the mechanism in detail and to broaden the scope of the reaction.

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Notes and references

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