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A Highly Efficient Catalyst for Selective Oxidative Scission of Olefins to Aldehydes: Abnormal-NHC–Ru(II) Complex in Oxidation Chemistry

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Supporting Information

ABSTRACT: The utility and selectivity of the catalyst [Ru(COD)($\mathbf{L^1}$)Br_2] (**1**) bearing a fused π-conjugated imidazo[1,2-*a*][1,8]naphthyridine-based abnormal N-heterocyclic carbene ligand $\mathbf{L^1}$ is demonstrated toward selective oxidation of C=C bonds to aldehydes and C≡C bonds to α-diketones in an EtOAc/CH_3CN/H_2O solvent mixture at room temperature using a wide range of substrates, including highly functionalized sugar- and amino acid-derived compounds.

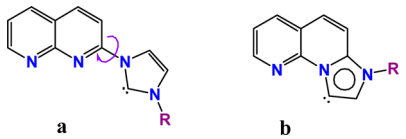
Oxidative cleavage of olefins is a useful reaction to fragment large compounds and introduce oxygen functionality.[1] Ozonolysis is a widely used method to obtain aldehydes or carboxylic acids depending upon reductive or oxidative workup.[2] However, major safety concerns and inconvenience associated with ozone generation has prompted researchers to develop catalytic metal-based systems. Olefin oxidation is carried out with OsO_4 and a variety of co-oxidants [H_2O_2, TBHP, oxone, $PhI(OAc)_2$, $NaIO_4$] in different solvent systems.[3] $RuCl_3$ with $NaIO_4$ as the oxidant in a 2:2:3 CCl_4/CH_3CN/H_2O solvent system was reported by Sharpless for oxidative cleavage of olefins.[4] Subsequently, several other $RuCl_3$/oxidant/solvent combinations have been developed.[5] However, high catalyst loading and overoxidation of aldehydes to the corresponding acids are the major drawbacks associated with these protocols.

Metal salts, nanoparticles, or oxides are often the choice for oxidation catalysts without the application of ligands. Most ligands are not stable under oxidative conditions and hence are not suitable for use. Only a handful of discrete Ru compounds bearing N-donor ligands have been employed for oxidative olefin cleavage.[6] N-Heterocyclic carbene (NHC) ligands form robust metal–C bonds and are presumably less susceptible to decomposition under harsher conditions.[7] We argued that stronger σ-donating ability would make C4/C5-bound mesoionic or abnormal NHCs (*a*NHCs) superior candidates for oxidation chemistry.[8] Further, π delocalization in annulated systems may provide higher conjugational stability and enhanced σ-donating ability compared with their nonannulated analogues.[9]

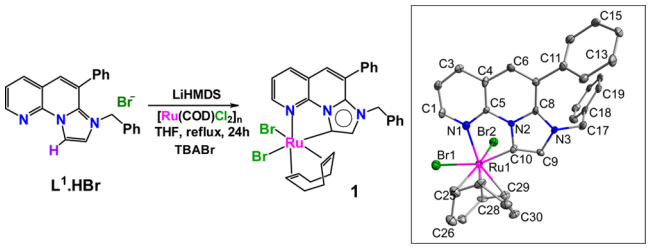
Multifaceted coordination of naphthyridine-functionalized NHC (NP-NHC) ligands to a variety of metal ions, due to free C–N rotation, was recently demonstrated (Scheme 1a).[10] To prevent rotational flexibility, a rigid π-conjugated fused imidazo[1,2-*a*][1,8]naphthyridine (Scheme 1b) was designed that could be considered as an *a*NHC analogue of 1,10-phenanthroline. The rigid system ensures directed metal binding. An electron-rich Ru^{II}(COD)(*a*NHC)Br_2 complex (COD = 1,5-cyclooctadiene) was synthesized and proved to be a superior catalyst for oxidative scission of olefins to aldehydes in terms of both efficiency and selectivity. The substrate scope ranging from simple olefins to sugar and amino acid derivatives was examined. Kinetic and density functional theory (DFT) studies indicated that [3 + 2] cycloaddition is the key step in the four-electron olefin oxidation process.

Accessing discrete Ru^{II}(COD) compounds is a challenging task since COD is often replaced by stronger ligands. Only a handful of such compounds are known.[11] Although the newly synthesized NHC precursor[12] $\mathbf{L^1}$·HBr (Scheme 2) turned out to be a difficult ligand for metalation with different metal ions, the complex [Ru(COD)($\mathbf{L^1}$)Br_2] (**1**) was isolated in high yield (81%) via the reaction of $\mathbf{L^1}$·HBr with Li[$N(SiMe_3)_2$] followed by 1 equiv of $\{Ru(COD)Cl_2\}_n$ and subsequent treatment with 1 equiv of $^nBu_4NBr$. To the best of our knowledge, this is the first report of a Ru–NHC complex (normal or abnormal) that

Scheme 1. (a) Multifaceted NP-NHC and (b) Annulated NP-aNHC Ligands



Scheme 2. Synthesis and X-ray Structure of 1



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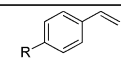
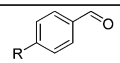
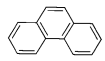
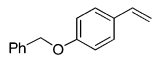
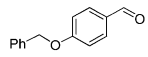
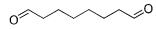
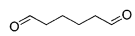
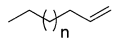
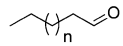
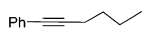
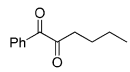
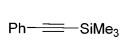
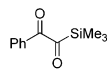
contains COD, a potentially labile ligand under oxidative conditions (vide infra). The ^{1}H NMR spectrum of **1** exhibited sets of multiplets for COD protons (4.11−0.81 ppm). The carbene carbon was observed at 164 ppm in the ^{13}C NMR spectrum. Electrospray ionization mass spectrometry (ESI-MS) showed a signal at m/z 624 (z = 1) assigned for $[\mathbf{1} - \mathrm{Br}]^+$ (Figure S6 in the Supporting Information). The molecular structure of **1** confirms chelate binding of the ligand involving the carbene carbon and the nitrogen atom of the naphthyridine unit. The Ru1−C10 and Ru1−N1 bond distances are 2.042(8) and 2.177(7) Å, respectively. One COD and two *cis* bromides complete the octahedral coordination sphere around the metal.

The catalytic utility of **1** was evaluated for olefin oxidation. The use of **1** (0.01 mmol) with styrene (1 mmol), $NaIO_4$ (2.1 mmol), and water (1 mL) in 3 mL of dichloroethane (DCE) at room temperature afforded 66% conversion to benzaldehyde. Increasing the temperature to 80 °C improved the yield to 95%. To our delight, no traces of dihydroxy, epoxide, α-hydroxy ketone, α-dione, or acid were observed in the reaction. Screenings of solvents and various oxidants were carried out with the model reaction (1 mmol of styrene, 1 mol % catalyst **1**, 2.1 mmol of oxidant; Table S2 in the Supporting Information). Quantitative conversion to benzaldehyde was achieved at room temperature within 30 min in a 2:2:1 ethyl acetate/acetonitrile/water solvent combination. Other oxidants such as hydroperoxides and oxygen were found to be ineffective (Table S2).

Subsequently we examined the substrate scope under the optimized conditions at room temperature (Table 1). Styrene and the electron-rich styrene derivatives *p*-methyl- and *p*-methoxystyrene afforded quantitative conversions to the corresponding aldehydes (entries 1−3), but electron-deficient styrenes (*p*-fluoro- and *p*-chlorostyrene) gave lower yields (92 and 94%, respectively) under identical conditions (entries 4 and 5). The protocol was extended to internal alkenes and substituted alkene derivatives. *cis*-Stilbene and *trans*-stilbene afforded 86% and 92% conversions to benzaldehyde, respectively (entries 6 and 7). *trans*-β-Methylstyrene gave a 78% yield of benzaldehyde (entry 8) without any undesired dihydroxy or epoxide side products. Oxidation of the least aromatic ring of phenanthrene to give biphenyl-2,2′-dicarbaldehyde, albeit in moderate yield, clearly revealed the effectiveness of the catalyst (entry 9). Although the reagent is strong enough to disrupt an aromatic system, it is selective enough not to overoxidize an aldehyde to the corresponding carboxylic acid. Benzylic carbons are susceptible to oxidation. To check the catalyst selectivity, *p*-benzyloxystyrene and allylbenzene (entries 10 and 11) were employed under identical conditions and afforded high yields (98% and 96%, respectively) of the corresponding aldehydes, in which the benzylic positions remained unaffected. Aliphatic cyclic substrates such as *cis*-cyclooctene and cyclohexene were readily cleaved to the corresponding dialdehydes (entries 12 and 13). Long-chain 1-hexene and 1-octene gave the corresponding scission products in good yields but contained overoxidized acid (entries 14 and 15), perhaps because electron-rich monoaldehydes are more likely to undergo oxidation than dialdehydes. The substrate scope was further extended to internal alkynes. Diphenylacetylene gave a quantitative yield of benzil within 30 min (entry 16). Under identical conditions 1-phenyl-1-hexyne and 1-trimethylsilyl-2-phenylacetylene showed excellent conversions (100 and 96%, respectively) to the corresponding α-diketone derivatives (entries 17 and 18).

We set the reaction time to 30 min for all substrates to make a meaningful comparison. In fact, complete conversions were

Table 1. Substrate Scope of Catalyst 1[a]

Entry	Substrate	Product	Yield (%)
1-3 R= H, Me, OMe			100[c], 100[c], 100[c]
4-5 R= F, Cl			92[c], 94[c]
6	*trans*-stilbene		92[c]
7	*cis*-stilbene		86[c]
8			78[c]
9			45[c]
10			98[c]
11			96[c]
12	*cis*-cyclooctene		68[d]
13	cyclohexene		100[d]
14-15 n=1,3			72(18), 80(14)[d,e]
16			100[b,c]
17			100[b,c]
18			96[b,c]

[a]Reaction conditions: 1 mmol of substrate, 1 mol % catalyst **1**, 2.1 mmol of $NaIO_4$, 2:2:1 CH_3CN/EtOAc/H_2O solvent, 25 °C, 30 min, unless otherwise noted. [b]The solvent was 3:1 CH_3CN/(0.1 M H_2SO_4) H_2O. [c]Isolated yield. [d]GC-MS yield using dodecane as an internal standard. [e]Acid formation was observed.

achieved for less-reactive substrates (e.g., *p*-chlorostyrene and *cis*-stilbene) when the reaction was carried out for a longer time, whereas *p*-methoxystyrene gave quantitative conversion in less time (Figure S35). The time−conversion profiles revealed that the potency of the catalyst remained undiminished over a period of time.

Catalyst **1** clearly performs better than the discrete catalyst systems reported to date. We are aware of a Ru−NHC catalyst[7] that was employed for olefin oxidation but showed low conversion (23−58%) and required longer reaction times (24 h) for styrene and stilbene derivatives. The catalyst $[\mathrm{Ru^{II}(dmp)_2(H_2O)_2}]^{2+}$ (dmp = 2,9-dimethylphenanthroline)[6b] was effective but required longer reaction times (2 and 8 h respectively). The $RuCl_3/NaIO_4$ combination[5b] required a high catalyst loading (3.5 mol %) to afford moderate yields of oxidative cleaved products. Encouraged by the performance of **1**, we further expanded its scope using highly functionalized substrates that are more realistic in synthetic organic chemistry.

Sugar derivatives are important precursors for biologically significant compounds such as glycosidase inhibitors, antitumor products,[13] etc. Oxidative cleavage of olefins appended to sugar units gives the corresponding aldehydes, which are important synthons for further structural elaboration. Ozonolysis often fails for highly functionalized systems with sensitive protecting groups. Catalyst **1** was tested in the formation of a number of

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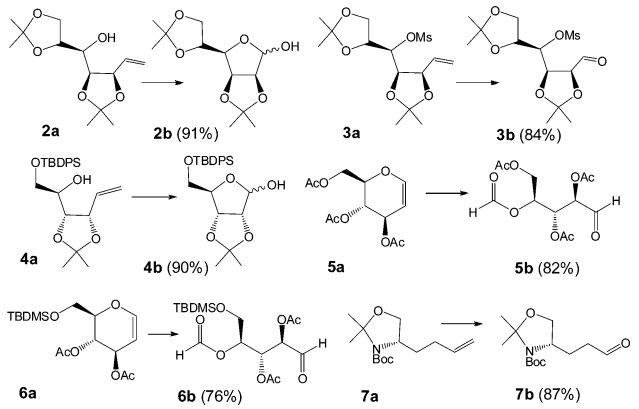
sugar-derived aldehydes from the corresponding olefins. The diacetonoid derivative of mannose (**2a**; Scheme 3) was tested

Scheme 3. Substrate Scope with Olefins Bearing Sugar and Amino Acid Scaffolds

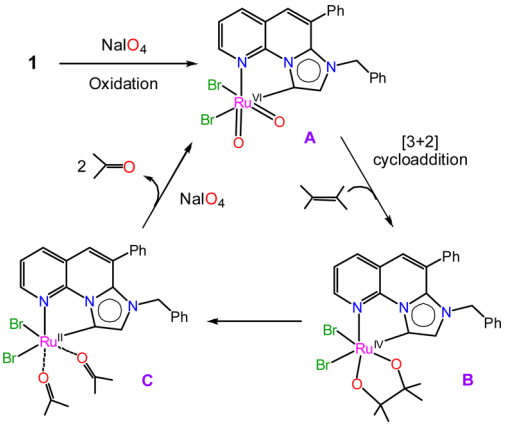


under the optimized protocol and readily gave cyclized lactol **2b** in 91% yield. It is likely that initially the olefin is oxidatively cleaved to give the aldehyde, which subsequently undergoes cyclization to afford **2b**. To prove this point, mannose derivative **3a** with the interfering hydroxyl group protected as a mesylate was used, and the reaction yielded acyclic diacetonoid aldehyde **3b** with the mesyl group intact. The acid-sensitive TBDPS-protected ribose derivative **4a** also afforded the corresponding lactol **4b** in excellent yield (90%). Electron-rich glucal derivatives, which are widely used for the synthesis of different natural products in carbohydrate chemistry, were subjected to the oxidation reaction. Formylesteraldehyde **5b** was obtained from the oxidative cleavage of 3,4,6-tri-*O*-acetyl-D-glucal (**5a**) in high yield (82%). This is significantly higher than the moderate 50% yield obtained from **5a** with Yang's catalyst.[5b] Also, the TBDMS-protected glucal derivative **6a** afforded formylester-aldehyde **6b** in good yield without affecting the protecting groups. Boc-protected oxazolidine ring **7a** prepared from L-glutamic acid was also examined with this protocol and gave the corresponding aldehyde **7b** in good yield.

Selective olefin oxidation under mild conditions is the most remarkable aspect of catalyst **1**. The metal−oxo, −peroxo, and/or −hydroperoxo are the range of intermediates encountered in oxidation reactions. Selective aldehyde formation suggests a high-valent Ru−oxo species as an intermediate. Che and co-workers reported that a Ru−*cis*-dioxo compound stabilized by the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) can cleave alkenes to aldehydes stoichiometrically.[6a] Neumann and co-workers showed that $[cis\text{-}Ru^{VI}(dmp)_2(O)_2]^{2+}$ is the active species for regioselective oxidation of alkenes to carbon−carbon bond-cleaved products.[6b] Furthermore, the formation of α-diketones from internal alkynes by **1** with $NaIO_4$ supports a four-electron-oxidized Ru−dioxo intermediate.[6a,14] Moreover, the use of $NaIO_4$ as an oxidant with Ru complexes leads to high valent Ru−oxo species, as exemplified by Griffith's complex $[Ru^{VI}(O)_2(bipy)\{IO_3(OH)_3\}]$ (bipy = 2,2′-bipyridyl).[15]

Accordingly, we propose a mechanism that involves high-valent Ru−oxo species. Complex **1** reacts with the terminal oxidant $NaIO_4$ to form a Ru^{VI}−*cis*-dioxo intermediate (Scheme 4).[16] Electrophilic attack on the C=C bond by the high-valent dioxo intermediate affords a Ru^{IV} cycloadduct via a concerted [3 + 2] cycloaddition reaction. The σ-donating *a*NHC ligand

Scheme 4. Proposed Mechanism for Olefin Oxidation by 1



renders the Ru^{IV} center fairly electron-rich to further undergo two-electron reduction and cleaves the C−C bond to give the carbonyl product.

In order to gain insight into the proposed intermediates, we carried out the stoichiometric reaction between complex **1** and $NaIO_4$(aq) at 0 °C in acetonitrile, and immediate recording of the IR spectrum in solution showed the appearance of two new absorptions at 866 and 802 cm^{-1} (Figure S37) attributable to asymmetric and symmetric stretching of a Ru−*cis*-dioxo species.[6d] However, we failed to identify the intermediate by other spectroscopic techniques. In view of the high reactivity of the catalyst (most reactions were over within 30 min), it is not surprising that the intermediate was short-lived and hence difficult to isolate and characterize. We further examined whether the "Ru−*a*NHC" moiety was retained in the catalyst after alkene oxidation with $NaIO_4$. A stoichiometric reaction of complex **1**, $NaIO_4$(aq), and styrene (1:1:1.5 molar ratio) in acetonitrile was carried out for 1 h. The reaction mixture was then filtered, and all of the volatiles were removed. An acetonitrile solution of the residue was subjected to ESI-MS analysis, which showed a signal at m/z 598 (z = 1) corresponding to $[Ru(\mathbf{L}^1)Br(CH_3CN)_2]^+$ (Figure S38). The presence of metal-bound $\mathbf{L}^1$ after completion of the oxidation suggests that the molecular integrity of the catalyst is maintained during the catalysis.

We further carried out substoichiometric reactions between **1**, $NaIO_4$, and styrene. It is evident from the kinetic plots (Figure S36) that the rate of the reaction is directly proportional to the concentrations of the catalyst and styrene but independent of the amount of $NaIO_4$. This suggests that the rate-limiting step does not involve $NaIO_4$ but depends on the concentrations of the active catalytic species and the alkene.

To obtain support for the proposed mechanism, competitive oxidation of para-substituted styrenes (p-$YC_6H_4CH{=}CH_2$; Y= OMe, Me, H, Cl, F) with the "**1** + $NaIO_4$" protocol was studied by GC−MS analysis. The relative reactivities of that para-substituted styrenes are in the order Y = OMe > Me > H > F > Cl. The least-squares fit to the plot of $[\log(k_X/k_H)]$ versus Hammett σ^+ constant gave a straight line with a ρ^+ value of −0.344 (Figure S32). The small negative ρ^+ value suggests little development of positive charge at the α-carbon atom of the styrene. This ρ^+ value is comparable to that for the stoichiometric oxidation of para-substituted styrenes by *cis*-$[(Me_3tacn)(CF_3CO_2)Ru^{VI}(O)_2]^+$ (ρ^+ = −1.05)[6a] but very different from those for reactions involving the formation of carbocations, for example, bromination (ρ^+ = −4.1) and hydration (ρ^+ = −3.5) of alkenes. The Hammett

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kinetic study thus supports a concerted [3 + 2] cycloaddition pathway.

The effect of temperature on the rate of the reaction of **1** with styrene was also examined. The activation parameters were determined from the plot of $\ln(k/T)$ versus $1/T$, which was linear over the temperature range studied (283−313 K) (Figure S34). The estimated entropy of activation ($\Delta S^{\ddagger}$) is −27.67 ± 1.64 cal mol^{-1} K^{-1}, and the enthalpy of activation ($\Delta H^{\ddagger}$) is 10.17 ± 0.49 kcal mol^{-1}. The large and negative $\Delta S^{\ddagger}$ value is consistent with a rate-limiting step that involves association of the ruthenium−*cis*-dioxo species with the alkene.[6a]

DFT calculations at the B3LYP level were carried out to gain insight into the reaction pathway.[17] The Ru^{VI}−*cis*-dioxo intermediate **A′** (Figure S39) is optimized with Ru−O bond distances of 1.758 and 1.726 Å and an O−Ru−O bond angle of 107°. These values are comparable to those for related isolated Ru^{VI}−*cis*-dioxo compounds.[6e] The concerted [3 + 2] cycloaddition of **A′** and ethylene affords metalladioxo-2,5-dioxolane intermediate **B′** (Ru−O = 1.91, 1.96 Å; C−O = 1.41, 1.42 Å; C−C = 1.53 Å). The transition state (TS) connecting **A′** and **B′** has one imaginary frequency of 172i cm^{-1} corresponding to simultaneous formation of two C−O bonds with an increase in the C═C and Ru═O bond lengths (Figure S40). The activation barrier of the transition state is 14.0 kcal/mol. Intermediate **B′** undergoes another two-electron oxidation across the C−C bond to yield two formaldehyde molecules.

In conclusion, an annulated imidazo[1,2-*a*][1,8]naphthyridine based *a*NHC ligand was designed that upon metalation affords a rare COD-bound electron-rich complex, Ru(*a*NHC)(COD)Br$_2$. The title compound is an excellent catalyst for selective C═C bond scission of olefins to aldehydes and alkyne C≡C bond oxidation to α-diketones in an aqueous/organic solvent mixture at room temperature. The catalyst displays clearly superior activity for highly functionalized substrates derived from sugars and amino acids. Activation parameters, kinetic Hammett studies, substoichiometric experiments, and DFT calculations point to a *cis*-dioxo intermediate that undergoes [3 + 2] cycloaddition with the olefin. This study underlines the general utility of the annulated *a*NHC ligand in organometallic catalysis and in particular oxidation chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) The CO analogue of **1** afforded only a 17% yield of benzaldehyde from styrene after 2 h under identical conditions. This led us to believe that COD is extruded from the metal under oxidative conditions.

(17) To reduce the computational cost, the benzyl group on the imidazolium nitrogen was replaced by a methyl group and the phenyl substituent at the 3-position of the naphthyridine moiety was replaced by a hydrogen.