

# Cobalt-Catalyzed Acceptorless Dehydrogenation of Alcohols to Carboxylate Salts and Hydrogen

Deepak Ranjan Pradhan,<sup>†</sup> Sandip Pattanaik,<sup>†</sup> Jugal Kishore, and Chidambaram Gunanathan\*



Cite This: <https://dx.doi.org/10.1021/acs.orglett.0c00193>



Read Online

ACCESS |



Metrics & More

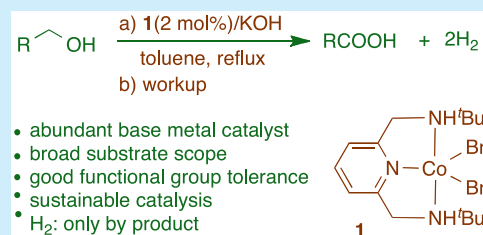


Article Recommendations



Supporting Information

**ABSTRACT:** The facile oxidation of alcohols to carboxylate salts and H<sub>2</sub> is achieved using a simple and readily accessible cobalt pincer catalyst (NNN<sup>HtBu</sup>CoBr<sub>2</sub>). The reaction follows an acceptorless dehydrogenation pathway and displays good functional group tolerance. The amine–amide metal–ligand cooperation in cobalt catalyst is suggested to facilitate this transformation. The mechanistic studies indicate that in-situ-formed aldehydes react with a base through a Cannizzaro-type pathway, resulting in potassium hemiacetolate, which further undergoes catalytic dehydrogenation to provide the carboxylate salts and H<sub>2</sub>.



The oxidation of primary alcohols to carboxylic acid is one of the fundamental transformations in organic synthesis, which finds interest in basic research, complex molecular synthesis, and industrial production. In conventional methods, the oxidation of alcohols to carboxylic acids is carried out with metal oxidants such as potassium permanganate, pyridine dichromate, chromium oxide, and sodium hypochlorite.<sup>1</sup> These traditional methods require excessive toxic oxidants, and such synthesis produces a stoichiometric amount of organic and inorganic waste. Often, these synthetic procedures are not compatible with other functional groups and undergo deleterious side reactions. In the last two decades, the acceptorless dehydrogenative oxidation of alcohols has received great attention because the process is greener, and dihydrogen and water are the only byproducts.<sup>2</sup>

In recent years, homogeneous noble metals such as Rh, Ru, and Ir complexes have been developed for the oxidation of alcohols to carboxylic acids. Grützmacher and coworkers have reported a diolefin-amido-tridentate-ligated rhodium catalyst for the oxidation of alcohols to acid salts using sacrificial acceptors such as cyclohexanone, 1-hexene, or O<sub>2</sub>/DMSO.<sup>3</sup> Elegant and robust ruthenium complexes containing tridentate ligands,<sup>4–6</sup> N-heterocyclic carbene (NHC) ligands,<sup>7</sup> and bidentate ligands<sup>8</sup> catalyzed the acceptorless dehydrogenation of alcohols under convenient experimental conditions. Cp\*Ir(III)<sup>9</sup> and bidentate phosphine or NHC-ligated iridium complexes<sup>10</sup> have been reported in which the reaction proceeded in neutral water and basic solution, respectively.

Very recently, Ni,<sup>11</sup> Fe,<sup>12</sup> and Mn<sup>12,13</sup> pincer complexes and ZnO<sup>14</sup>-catalyzed oxidation of alcohols to carboxylic acids have been reported. Thus the development of nontoxic, cheap, and abundant base metal catalysts bearing different nonsensitive donor atoms for this important transformation is desirable. The cobalt-catalyzed oxidation of alcohols to carboxylic acids is limited to two reports, which suffer from the use of excess

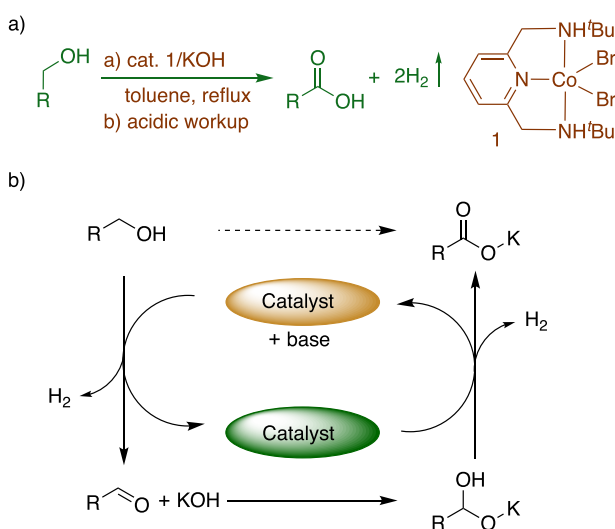
stoichiometric oxidant, a high catalyst load, and the use of a heterogeneous catalyst with a limited substrate scope.<sup>15</sup> Notably, there is no report on the cobalt-catalyzed oxidation of alcohols to carboxylic acids that follows the borrowing hydrogen methodology. Recently, we have reported a readily accessible cobalt catalyst **1** prepared from NNN<sup>HtBu</sup> (N,N'-(pyridine-2,6-diylbis(methylene))bis(2-methylpropan-2-amine)) and its catalytic application in the synthesis of disiloxanes and monohydrodisiloxanes.<sup>16</sup> Our group is interested in developing sustainable catalytic transformations using alcohols. Using ruthenium and manganese catalysis, we have reported the alkylation and olefination of nitriles and ketones,<sup>17,18</sup> cross-coupling of secondary alcohols,<sup>19</sup> ketazine synthesis from secondary alcohols,<sup>20</sup> and selective deuteration of primary and secondary alcohols.<sup>21</sup> In a continuation of these efforts, herein we report the simple cobalt-complex-**1**-catalyzed oxidation of alcohols to carboxylic acids (Scheme 1a) in which the process is empowered by an acceptorless dehydrogenation methodology (Scheme 1b).

Benzyl alcohol was taken as a model substrate to optimize the oxidation of alcohols to carboxylate salts using cobalt catalyst **1** and potassium hydroxide base (taken in a stoichiometric amount to balance the chemical reaction). The use of other bases such as NaOH, CsOH, and LiOH was not compatible in this catalytic system because they caused a parallel self-condensation reaction. For example, with aliphatic alcohols like ethanol and hexanol, the formation of unidentified higher chain alcohols (gas chromatography (GC) analysis) was observed. A preliminary experiment using benzyl alcohol (1

Received: January 14, 2020

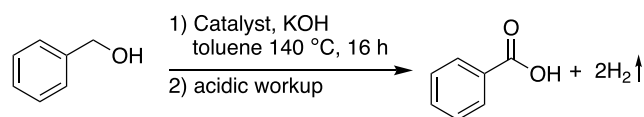


### Scheme 1. Catalytic Approach in Acceptorless Dehydrogenation of Alcohols



mmol) and KOH (1.2 mmol) with catalyst **1** at 140 °C for 24 h provided the benzoic acid in 49% yield upon acidic work-up (entry 1, Table 1). Furthermore, an increase in the base load

**Table 1. Optimization for Catalytic Dehydrogenation of Alcohol Catalyzed by **1**<sup>a</sup>**



entry	cat (mol %)	base (equiv)	time (h)	yield (%) <sup>b</sup>
1	<b>1</b> (1)	1.2	24	49
2	<b>1</b> (1)	1.5	24	81
3	<b>1</b> (2)	1.2	16	73
4	<b>1</b> (2)	1.5	16	93
5 <sup>c</sup>		1.5	24	3
6	CoBr <sub>2</sub> (2)	1.5	24	7

<sup>a</sup>Reaction conditions: Alcohol (1 mmol), catalyst, base, and toluene (2 mL) were taken in a sealed tube and heated to 140 °C. <sup>b</sup>Isolated yield of product after acidic work-up with 1 M HCl. <sup>c</sup>Control reaction performed without catalyst.

from 1.2 to 1.5 equiv enhanced the yield of benzoic acid to 81% (entry 2, Table 1). Performing a similar catalytic reaction using 2 mol % of catalyst **1** and 1.2 equiv of KOH resulted in a diminished yield (73%, entry 3, Table 1). Thus an experiment using 2 mol % of catalyst **1** and 1.5 equiv of KOH was performed, which provided benzoic acid in 93% yield (entry 4, Table 1). Without a catalyst, the reaction of alcohols with a base alone was performed, which failed to provide carboxylic acid in an appreciable amount (entry 5, Table 1), and this control experiment confirmed the necessity for a catalyst in this transformation. Furthermore, the use of simple CoBr<sub>2</sub> (2 mol %) as a catalyst provided benzoic acid in 7% yield, reiterating the importance of the designed cobalt pincer catalyst **1**.

With the optimized reaction condition in hand, an assortment of alcohols were subjected to the oxidation to develop the scope of the reaction as well as to identify the limitation of this catalytic protocol (Table 2). Aryl methanols with electron-donating groups such as *p*-methyl, *p*-isopropyl, and *p*-*tert*-butyl provided the corresponding carboxylic acids

**2b–d** in very good yield. *p*-Methoxybenzyl alcohol and 3,5-dimethoxybenzyl alcohol provided the products **2e** and **2f** in 95 and 86% yield, respectively. Notably, *p*-methylthiobenzyl alcohol was tolerated by cobalt catalysis, which resulted in *p*-methylthiobenzoic acid **2g** in 78% yield. The electron-withdrawing group on arylmethanols diminished their reactivity toward the oxidation reaction, which resulted in comparatively low yields of the corresponding carboxylic acids. Thus *m*-chloro, *p*-bromo, and *p*-fluorobenzyl alcohols were subjected to the cobalt-catalyzed oxidation reaction and the products **2h–j**, obtained in 61–82% yield. Aryl halides are known to undergo a reduction reaction to the corresponding arenes when subjected to transition-metal catalysis. However, no such arene formation was observed under this catalytic condition (entries 8–10, Table 2). Similarly, the reaction of *p*-trifluoromethyl- and *p*-nitrobenzyl alcohol provided the carboxylic acids **2k** and **2l** in 71 and 55% yields, respectively. Despite the low yield observed for *p*-nitrobenzoic acid (**2l**), it is gratifying to note that the nitro functionality is tolerated; nitro compounds are incompatible in iridium-catalyzed oxidation reactions and are under-investigated in this transformation. Biaryl methanols are also tolerated. When 1-naphthalenemethanol was subjected to the reaction, 1-naphthalene carboxylic acid (**2m**) was isolated in 67% yield. Heteroarene functionalities are susceptible to a hydrogenation reaction under the acceptorless oxidation, where the catalyst can utilize the hydrogen liberated from alcohol oxidation. Remarkably, heteroarylmethanol compounds are well tolerated in the cobalt-catalyzed oxidation reaction, although the observed reactivity is low in comparison with that of other arylmethanols. When 2-pyridinemethanol and 4-pyridinemethanol were subjected to oxidation, the corresponding carboxylate salts **2n** and **2o** were isolated in 59 and 67% yield, respectively. Furfuryl alcohol and *p*-aminobenzyl alcohol provided the corresponding carboxylic acids **2p** and **2q** in poor yield. The cobalt catalysis is very well compatible with diols. Phthalic acid (**2r**) and terephthalic acid (**2s**) were obtained from the corresponding diols in good yield. However, 2,6-pyridinedimethanol provided the dicarboxylate salt **2t** in only 49% yield.

Furthermore, the scope of the reaction was explored with a variety of aliphatic primary alcohols in the catalytic synthesis of carboxylic acid. A variety of aliphatic primary alcohols provided moderate to good yields (Table 3). When ethanol and 1-propanol were subjected to catalysis, potassium acetate and potassium propanoate salts **3a** and **3b** were obtained in 67 and 73% yield, respectively. Long-chain linear alcohols such as 1-hexanol and 1-heptanol underwent facile oxidation to provide the carboxylic acids **3c,d** in good yield. Similarly, cyclobutylmethanol, cyclohexylmethanol, and bicyclo[2.2.1]heptylmethanol were oxidized to the corresponding carboxylic acids **3e–g** in good yield. Phenethyl alcohol and 3-phenylpropanol were transformed to phenylacetic acid (**3h**) and 3-phenylpropanoic acid (**3i**) in 75 and 81% yield, respectively. Iridium catalysts were not compatible with alkene compounds.<sup>10</sup> Although ruthenium catalysts were tolerated, the olefin functionality underwent in situ hydrogenation.<sup>5,6,8</sup> On the contrary, when cinnamyl alcohols were reacted with cobalt catalyst **1** and a base, cinnamic acid (**3j**) was isolated in 78% yield. Such selective oxidation of alcohol functionality by catalyst **1**, even in the presence of a competing olefin motif, is remarkable. 1,5-Pentane diol and hexamethylene diol were also

Table 2. Cobalt-Catalyzed Synthesis of Carboxylic Acid Using Aryl Methanols<sup>a</sup>

entry	Alcohols	Acids	Yield (%) <sup>b</sup>	entry	Alcohols	Acids	Yield (%) <sup>b</sup>
1			<b>2a</b> 93	11			<b>2k</b> 71
2			<b>2b</b> 89	12			<b>2l</b> 55
3			<b>2c</b> 78	13			<b>2m</b> 67
4			<b>2d</b> 85	14			<b>2n</b> 59
5			<b>2e</b> 95	15			<b>2o</b> 67
6			<b>2f</b> 86	16			<b>2p</b> 47
7			<b>2g</b> 78	17			<b>2q</b> 27
8			<b>2h</b> 77	18 <sup>c</sup>			<b>2r</b> 80
9			<b>2i</b> 61	19 <sup>c</sup>			<b>2s</b> 82
10			<b>2j</b> 82	20 <sup>c</sup>			<b>2t</b> 49

<sup>a</sup>Reaction conditions: Alcohol (1 mmol), catalyst **1** (2 mol %), base KOH (1.5 equiv), and toluene (2 mL) were taken in a sealed tube and heated to 140 °C. <sup>b</sup>Corresponds to isolated yield after acidic work-up using 1 M HCl. <sup>c</sup>Reaction performed with alcohol (1 mmol), catalyst **1** (4 mol %), and base KOH (3 equiv).

oxidized, and the corresponding dicarboxylic acids **3k** and **3l** were isolated in 79 and 83% yield, respectively.

A series of experiments were performed to identify the possible intermediates involved in the catalytic cycle. The catalytic oxidation of benzyl alcohol with KOH in the presence of mercury provided benzoic acid **2a** in 82% yield (against 93% yield in the absence of mercury; see Scheme 2a and Table 2), indicating that the reaction proceeds with molecular intermediates. Furthermore, GC analysis of the gas phase collected from the catalytic reaction of alcohol with catalyst **1** confirmed the liberation of molecular hydrogen (Scheme 2b). The amount of dihydrogen liberated from the catalytic oxidation of alcohol was quantified by reacting 1 mmol of benzyl alcohol in the presence of catalyst **1** with a stoichiometric amount of KOH, which resulted in 46 mL of

water displacement in a gas buret that is equivalent to 2 mmol of dihydrogen (Scheme 2c). Furthermore, the possible involvement of a Cannizzaro reaction pathway was investigated using both aromatic and aliphatic aldehydes. The reactions of benzaldehyde and 1-hexanal with KOH in the absence of catalyst **1** were tested, which provided benzoic acid and 1-hexanoic acid in 69 and 67% yield, respectively (GC analyses, Scheme 2d,e). These results indicate that the oxidation processes by cobalt catalysis perhaps follow the Cannizzaro-type reaction pathway. The reaction between benzaldehyde and benzyl alcohol under catalytic conditions provided only 9% formation of benzyl benzoate (GC analysis, Scheme 2f), further indicating the possible involvement of the Cannizzaro pathway. When benzaldehyde was subjected to optimized experimental conditions, a major amount of benzoic acid

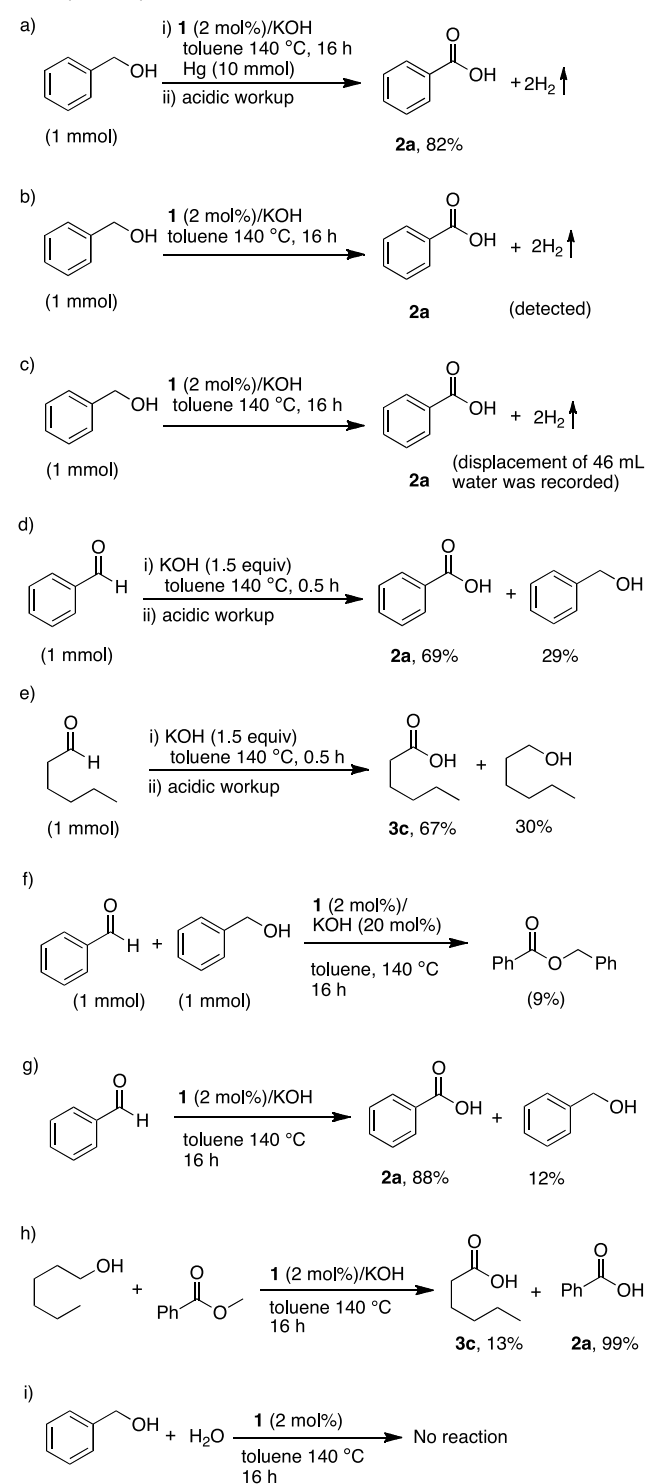
**Table 3. Cobalt-Catalyzed Synthesis of Carboxylic Acid from Aliphatic Primary Alcohols<sup>a</sup>**

entry	Alcohols	Acids		Yield (%) <sup>b</sup>
	$R-CH_2OH$	$R-COOH$	$+ 2H_2 \uparrow$	
	1) <b>1</b> (2 mol%), KOH, toluene 140 °C, 16 h 2) acidic workup			
1			<b>3a</b>	67
2			<b>3b</b>	73
3			<b>3c</b>	82
4			<b>3d</b>	74
5			<b>3e</b>	73
6			<b>3f</b>	75
7			<b>3g</b>	86
8			<b>3h</b>	75
9			<b>3i</b>	81
10			<b>3j</b>	78
11 <sup>c</sup>			<b>3k</b>	79
12 <sup>c</sup>			<b>3l</b>	83

<sup>a</sup>Reaction conditions: Alcohol (1 mmol), catalyst **1** (2 mol %), base KOH (1.5 equiv), and toluene (2 mL) taken in a sealed tube were heated to 140 °C. <sup>b</sup>Corresponds to isolated yield after acidic work-up using 1 M HCl. <sup>c</sup>Reaction performed using diol (1 mmol), catalyst **1** (4 mol %), and base KOH (3 equiv).

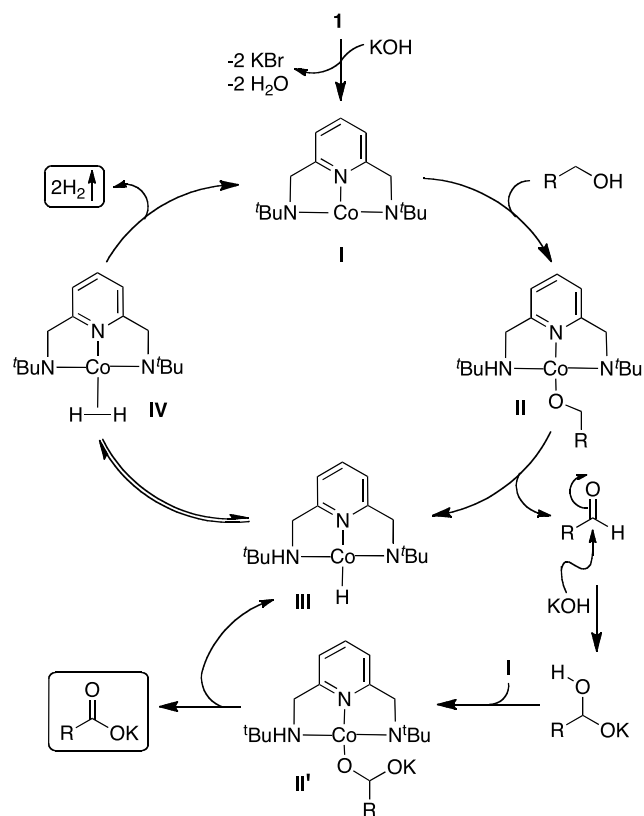
(88%) and a minor amount of benzyl alcohol (12%) were isolated (Scheme 2g). Furthermore, the noninvolvement of ester formation was inferred from <sup>1</sup>H NMR and GC monitoring of this reaction progress, implying that the reaction via Tishchenko pathway is unlikely (Scheme 2g). Ester functionalities are not compatible in this dehydrogenation process. Under standard experimental conditions, the reaction of 1-hexanol and methylbenzoate provided only 13% formation of 1-hexanoic acid and the complete formation of benzoic acid (99%) resulting from ester hydrolysis (Scheme 2h). Furthermore, the oxidation of alcohol in the presence of water (instead of KOH) failed to provide the desired carboxylic acid product (Scheme 2i), indicating that KOH acts as an oxygen source for the formation of a carboxylate salt through a Cannizzaro-type reaction.

**Scheme 2. Mechanistic Studies for Oxidation of Alcohol Catalyzed by **1****



Although more data are required, a plausible mechanism for the oxidation of alcohols to carboxylic acid using catalyst **1** is presented in Scheme 3. Upon reaction with a base, catalyst **1** underwent dehydrohalogenation to provide coordinatively unsaturated intermediate **I**. The formation of intermediate **I** from catalyst **1** was previously established by us.<sup>16</sup> Furthermore, intermediate **I** reacts with alcohol, resulting in O–H bond activation, and generates alkoxy-ligated intermediate **II**. One of the amide arms in intermediate **I** acts as

**Scheme 3. Plausible Mechanism for Acceptorless Dehydrogenation of Alcohols Catalyzed by 1**



proton acceptor, which facilitates O–H bond activation and becomes an amine arm in **II**. The  $\beta$ -hydride elimination of the alkoxy ligand in intermediate **II** provides monohydrido cobalt intermediate **III** and aldehyde. Intermediate **III** is probably in equilibrium with the nonclassical hydrogen-coordinated **IV**, and in the process, the amine donor in **III** becomes an amide donor in **IV**. Intermediate **IV** liberates molecular hydrogen to regenerate **I** and completes one loop in a catalytic cycle. The amine–amide metal–ligand cooperation<sup>22,23</sup> operating in the catalyst facilitates both bond activation and formation and allows the cobalt to exist in the same oxidation state (+2) in intermediates **I**–**IV**. Free aldehyde reacts with the base and undergoes a Cannizzaro-type reaction to generate potassium hemiacetalate salt. The activated alcohol motif in potassium hemiacetalate can react with **I** to generate an alkoxy-coordinated intermediate **II'**, similar to that of **II**. Possible  $\beta$ -hydride elimination from **II'** provides potassium carboxylate salt and intermediate **III**. Overall, two equivalents of hydrogen are liberated (estimated experimentally) from this catalytic transformation.

In summary, we have developed a highly efficient and simple cobalt catalyst for the acceptorless dehydrogenative oxidation of alcohols to carboxylate salts using KOH as a base. The evolved two equivalents of hydrogen are the only byproducts observed. The mechanistic investigation indicates that KOH acts as a source for the second oxygen of the carboxylate salt, and the reaction follows the Cannizzaro-type pathway. This catalytic protocol is applicable to a wide range of alcohols including aromatic, aliphatic, and heteroaromatic alcohols. Highly sensitive and competing functional groups such as pyridyl, nitro, and olefin are well tolerated and retained in products. Such selectivity and functional group tolerance are

notable. Remarkably, ethanol was oxidized to potassium acetate, and the diols were successfully converted to dicarboxylic acids. This phosphine-free simple catalytic system can be a potential alternative to precious noble-metal catalysts for the oxidation of alcohols to carboxylic acids.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c00193>.

Experimental procedures, spectral data, and copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

**Chidambaram Gunanathan** – School of Chemical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar 752050, India; [orcid.org/0000-0002-9458-5198](https://orcid.org/0000-0002-9458-5198); Email: [gunanathan@niser.ac.in](mailto:gunanathan@niser.ac.in)

### Authors

**Deepak Ranjan Pradhan** – School of Chemical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar 752050, India

**Sandip Pattanaik** – School of Chemical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar 752050, India

**Jugal Kishore** – School of Chemical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar 752050, India

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.orglett.0c00193>

### Author Contributions

<sup>†</sup>D.R.P. and S.P. contributed equally to this work.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank SERB New Delhi (EMR/2016/002517), DAE, and NISER for financial support. D.R.P. thanks DAE for a research Fellowship, and S.P. thanks CSIR for a research fellowship.

## ■ REFERENCES

- (1) (a) *Oxidation of Primary Alcohols to Carboxylic Acids: A Guide to Current Common Practice*; Tojo, G., Fernandez, M., Eds.; Springer: New York, 2007. (b) Freeman, F. Chromic Acid. In *Encyclopedia of Reagents for Organic Synthesis*; Wiley: Chichester, U. K., 2001. (c) Piancatelli, G. Pyridinium Dichromate. In *Encyclopedia of Reagents for Organic Synthesis*; Wiley: Chichester, U. K., 2001. (d) Lee, D. G.; Ribagorda, M.; Adrio, J. Potassium Permanganate. In *Encyclopedia of Reagents for Organic Synthesis*; Wiley: Chichester, U.K., 2001. (e) Fatiadi, A. J. The Classical Permanganate Ion: Still a Novel Oxidant in Organic Chemistry. *Synthesis* **1987**, *1987*, 85–127.
- (2) Reviews for acceptorless dehydrogenation of alcohols: (a) Crabtree, R. H. Homogeneous Transition Metal Catalysis of Acceptorless Dehydrogenative Alcohol Oxidation: Applications in Hydrogen Storage and to Heterocycle Synthesis. *Chem. Rev.* **2017**, *117*, 9228–9246. (b) Gunanathan, C.; Milstein, D. Bond Activation and Catalysis by Ruthenium Pincer Complexes. *Chem. Rev.* **2014**, *114*, 12024–12087. (c) Gunanathan, C.; Milstein, D. Applications of Acceptorless Dehydrogenation and Related Transformations in

Chemical Synthesis. *Science* **2013**, *341*, 1229712. (d) Trincado, M.; Banerjee, D.; Grützmacher, H. *Energy Environ. Sci.* **2014**, *7*, 2464–2503.

(3) (a) Zweifel, T.; Naubron, J.; Grützmacher, H. Catalyzed Dehydrogenative Coupling of Primary Alcohols with Water, Methanol, or Amines. *Angew. Chem., Int. Ed.* **2009**, *48*, 559–563. (b) Annen, S.; Zweifel, T.; Ricatto, F.; Grützmacher, H. Catalytic Aerobic Dehydrogenative Coupling of Primary Alcohols and Water to Acids Promoted by a Rhodium(I) Amido N-Heterocyclic Carbene Complex. *ChemCatChem* **2010**, *2*, 1286–1295. (c) Trincado, M.; Grützmacher, H.; Vizza, F.; Bianchini, C. Domino Rhodium/Palladium-Catalyzed Dehydrogenation Reactions of Alcohols to Acids by Hydrogen Transfer to Inactivated Alkenes. *Chem. - Eur. J.* **2010**, *16*, 2751–2757. (d) Gianetti, T. L.; Annen, S. P.; Santiso-Quinones, G.; Reiher, M.; Driess, M.; Grützmacher, H. Nitrous Oxide as a Hydrogen Acceptor for the Dehydrogenative Coupling of Alcohols. *Angew. Chem., Int. Ed.* **2016**, *55*, 1854–1858.

(4) (a) Balaraman, E.; Khaskin, E.; Leitus, G.; Milstein, D. Catalytic Transformation of Alcohols to Carboxylic Acid Salts and H<sub>2</sub> Using Water as the Oxygen Atom Source. *Nat. Chem.* **2013**, *5*, 122–125. (b) Hu, P.; Ben-David, Y.; Milstein, D. General Synthesis of Amino Acid Salts from Amino Alcohols and Basic Water Liberating H<sub>2</sub>. *J. Am. Chem. Soc.* **2016**, *138*, 6143–6146.

(5) (a) Choi, J.-H.; Heim, L. E.; Ahrens, M.; Prechtel, H. G. Selective Conversion of Alcohols in Water to Carboxylic Acids by in situ Generated Ruthenium trans Dihydrido Carbonyl PNP Complexes. *Dalton Trans.* **2014**, *43*, 17248–17254. (b) Zhang, L.; Nguyen, D. H.; Raffa, G.; Trivelli, X.; Capet, F.; Desset, S.; Paul, S.; Dumeignil, F.; Gauvin, R. M. Catalytic Conversion of Alcohols into Carboxylic Acid Salts in Water: Scope, Recycling, and Mechanistic Insights. *ChemSusChem* **2016**, *9*, 1413–1423. (c) Dahl, E. W.; Louis-Goff, T.; Szymczak, N. K. Second Sphere Ligand Modifications Enable a Recyclable Catalyst for Oxidant-Free Alcohol Oxidation to Carboxylates. *Chem. Commun.* **2017**, *53*, 2287–2289.

(6) (a) Dai, Z.; Luo, Q.; Meng, X.; Li, R.; Zhang, J.; Peng, T. Ru(II) Complexes Bearing 2,6-Bis(benzimidazole-2-yl)pyridine Ligands: A New Class of Catalysts for Efficient Dehydrogenation of Primary Alcohols to Carboxylic Acids and H<sub>2</sub> in the Alcohol/CsOH System. *J. Organomet. Chem.* **2017**, *830*, 11–18. (b) Dai, Z.; Luo, Q.; Jiang, H.; Luo, Q.; Li, H.; Zhang, J.; Peng, T. Ni–N'NN' Pincer Complexes Catalyzed Dehydrogenation of Primary Alcohols to Carboxylic Acids and H<sub>2</sub> Accompanied by Alcohol Etherification. *Catal. Sci. Technol.* **2017**, *7*, 2506–2511.

(7) (a) Malineni, J.; Keul, H.; Möller, M. A Green and Sustainable Phosphine-Free NHC-Ruthenium Catalyst for Selective Oxidation of Alcohols to Carboxylic Acids in Water. *Dalton. Trans.* **2015**, *44*, 17409. (b) Ventura-Espinosa, D.; Vicent, C.; Baya, M.; Mata, J. A. Ruthenium Molecular Complexes Immobilized on Graphene as Active Catalysts for the Synthesis of Carboxylic Acids from Alcohol Dehydrogenation. *Catal. Sci. Technol.* **2016**, *6*, 8024–8035. (c) Santilli, C.; Makarov, I. S.; Fristrup, P.; Madsen, R. Dehydrogenative Synthesis of Carboxylic Acids from Primary Alcohols and Hydroxide Catalyzed by a Ruthenium N-Heterocyclic Carbene Complex. *J. Org. Chem.* **2016**, *81*, 9931–9938.

(8) Sarbjana, A.; Dutta, I.; Daw, P.; Dinda, S.; Rahaman, S. M. W.; Sarkar, A.; Bera, J. K. Catalytic Conversion of Alcohols to Carboxylic Acid Salts and Hydrogen with Alkaline Water. *ACS Catal.* **2017**, *7*, 2786–2790.

(9) Fujita, K.; Tamura, R.; Tanaka, Y.; Yoshida, M.; Onoda, M.; Yamaguchi, R. Dehydrogenative Oxidation of Alcohols in Aqueous Media Catalyzed by a Water-Soluble Dicationic Iridium Complex Bearing a Functional N-Heterocyclic Carbene Ligand without Using Base. *ACS Catal.* **2017**, *7*, 7226–7230.

(10) Cherepakhin, V.; Williams, T. J. Iridium Catalysts for Acceptorless Dehydrogenation of Alcohols to Carboxylic Acids: Scope and Mechanism. *ACS Catal.* **2018**, *8*, 3754–3763.

(11) Dai, Z.; Luo, Q.; Jiang, H.; Luo, Q.; Li, H.; Zhang, J.; Peng, T. Ni(ii)-NNNPincer Complexes Catalyzed Dehydrogenation of

Primary Alcohols to Carboxylic Acids and H<sub>2</sub> Accompanied by Alcohol Etherification. *Catal. Sci. Technol.* **2017**, *7*, 2506–2511.

(12) Nguyen, D. H.; Morin, Y.; Zhang, L.; Trivelli, X.; Capet, F.; Paul, S.; Desset, S.; Dumeignil, F.; Gauvin, R. M. Oxidative Transformations of Biosourced Alcohols Catalyzed by Earth Abundant Transition Metal. *ChemCatChem* **2017**, *9*, 2652–2660.

(13) Shao, Z.; Wang, Y.; Liu, Y.; Wang, Q.; Fu, X.; Liu, Q. A General and Efficient Mn-Catalyzed Acceptorless Dehydrogenative Coupling of Alcohols with Hydroxides into Carboxylates. *Org. Chem. Front.* **2018**, *5*, 1248–1256.

(14) Monda, F.; Madsen, R. Zinc Oxide Catalyzed Dehydrogenation of Primary Alcohols into Carboxylic Acid. *Chem. - Eur. J.* **2018**, *24*, 17832–17837.

(15) (a) Das, S.; Punniyamurthy, T. Cobalt (II) Catalyzed Oxidation of Alcohols into Carboxylic Acids and Ketones with Hydrogen Peroxide. *Tetrahedron Lett.* **2003**, *44*, 6033–6035. (b) Shi, S.; Liu, M.; Zhao, L.; Wang, M.; Chen, C.; Gao, J.; Xu, J. Catalytic Oxidation of Alcohol to Carboxylic Acid with a Hydrophobic Cobalt Catalyst in Hydrocarbon Solvent. *Chem. - Asian J.* **2017**, *12*, 2404–2409.

(16) Pattanaik, S.; Gunanathan, C. Cobalt-Catalyzed Selective Synthesis of Disiloxanes and Hydrodisiloxanes. *ACS Catal.* **2019**, *9*, 5552–5561.

(17) (a) Thiyagarajan, S.; Gunanathan, C. Ruthenium-Catalyzed  $\alpha$ -Olefination of Nitriles Using Secondary Alcohols. *ACS Catal.* **2018**, *8*, 2473–2478. (b) Thiyagarajan, S.; Gunanathan, C. Facile Ruthenium(II)-Catalyzed  $\alpha$ -Alkylation of Arylmethyl Nitriles Using Alcohols Enabled by Metal–Ligand Cooperation. *ACS Catal.* **2017**, *7*, 5483–5490.

(18) (a) Gawali, S. S.; Pandia, B. K.; Gunanathan, C. Manganese(I)-Catalyzed  $\alpha$ -Alkenylation of Ketones Using Primary Alcohols. *Org. Lett.* **2019**, *21*, 3842–3847. (b) Gawali, S. S.; Pandia, B. K.; Pal, S.; Gunanathan, C. Manganese(I)-Catalyzed Cross-Coupling of Ketones and Secondary Alcohols with Primary Alcohols. *ACS Omega* **2019**, *4*, 10741–10754.

(19) (a) Thiyagarajan, S.; Gunanathan, C. Catalytic Cross-Coupling of Secondary Alcohols. *J. Am. Chem. Soc.* **2019**, *141*, 3822–3827. (b) Thiyagarajan, S.; Gunanathan, C. Ruthenium-Catalyzed Direct Cross-Coupling of Secondary Alcohols to  $\beta$ -Disubstituted Ketones. *Synlett* **2019**, *30*, 2027–2034.

(20) Kishore, J.; Thiyagarajan, S.; Gunanathan, C. Ruthenium(II)-Catalyzed Direct Synthesis of Ketazines Using Secondary Alcohols. *Chem. Commun.* **2019**, *55*, 4542–4545.

(21) Chatterjee, B.; Gunanathan, C. Ruthenium Catalyzed Selective  $\alpha$ - and  $\alpha,\beta$ -Deuteration of Alcohols Using D<sub>2</sub>O. *Org. Lett.* **2015**, *17*, 4794–4797.

(22) Reviews on metal–ligand cooperation: (a) Khusnutdinova, J. R.; Milstein, D. Metal–Ligand Cooperation. *Angew. Chem., Int. Ed.* **2015**, *54*, 12236–12273. (b) Gunanathan, C.; Milstein, D. Metal–Ligand Cooperation by Aromatization–Dearomatization: A New Paradigm in Bond Activation and “Green” Catalysis. *Acc. Chem. Res.* **2011**, *44*, 588–602. (c) Gunanathan, C.; Milstein, D. Bond Activation by Metal–Ligand Cooperation: Design of “Green” Catalytic Reactions Based on Aromatization–Dearomatization of Pincer Complexes. *Top. Organomet. Chem.* **2011**, *37*, 55–84.

(23) Similar amine–amide metal–ligand cooperation is also operative in catalysis by the Ru-MACHO catalyst. See the previous reports refs 17 and 19–21 and: (a) Krishnakumar, V.; Gunanathan, C. Ruthenium-Catalyzed Selective  $\alpha$ -Deuteration of Aliphatic Nitriles using D<sub>2</sub>O. *Chem. Commun.* **2018**, *54*, 8705–8708. (b) Krishnakumar, V.; Chatterjee, B.; Gunanathan, C. Ruthenium-Catalyzed Urea Synthesis by N-H Activation of Amines. *Inorg. Chem.* **2017**, *56*, 7278–7284. (c) Chatterjee, B.; Gunanathan, C. The Ruthenium-Catalyzed Selective Synthesis of mono-Deuterated Terminal Alkynes. *Chem. Commun.* **2016**, *52*, 4509–4512.