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Catalytic value addition of glycerol to lactic acid by chromium chloride and its corresponding pincer complex

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The 3d-metal salt chromium(III) chloride ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) and its corresponding pincer-Cr complexes were utilized to bring about the catalytic transfer dehydrogenation of glycerol (GLY) to lactic acid (LA) in the presence of a sacrificial hydrogen acceptor, acetone. Among the catalysts that were screened, the ($\text{C}^{\text{y}2}\text{NNN}$) CrCl_3 (0.5 mol%) catalyzed net transfer dehydrogenation of glycerol in the presence of 1.1 equivalents of NaOH at 160 °C afforded 94% lactic acid at 98% selectivity along with another value-added product isopropanol (IPA). Homogeneous molecular nature of the active catalyst in the reaction mixture was evident from the retention of catalytic activity in the presence of catalyst poisons such as PPh_3 , CS_2 and Hg. These homogeneous molecular species are likely to be based on Cr(II) as inferred from detailed mechanistic investigations involving EPR analysis, HRMS studies and Evan's magnetic moment experiments. Isotope labelling experiments indicate a KIE of 1.3.

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Introduction

The rapid depletion of fossil-fuel reserves has led to the increased utilization of biodiesel.¹ Biodiesel production is accompanied by a significant amount of waste generation such as glycerol (GLY).² This adds significantly to the global reservoirs already burdened by the glycerol contribution from a large number of industries involving cellulose hydrogenolysis^{3,4} and fermentation⁵ processes. Notably, GLY can serve as a starting material for numerous forms of specialty chemicals like lactic acid (LA), dihydroxyacetone and propanediol.^{6–8} GLY can also act as a potent hydrogen source as well as solvent in various metal aided catalysis owing to the presence of three hydroxyl groups.^{2,9,10} LA has a plethora of applications in diverse industries, which includes cosmetics, pharmaceuticals, food, green solvent production, biodegradable plastics, surfactants, chemical production and polylactic acid production (PLA).¹¹ Traditionally, GLY to LA conversion is carried out in two pathways which includes bacterial fermentation (*via* bioconversion)¹² and heterogeneous catalysis.^{3,8b,13} Special conditions required for bacterial survival apart from challenging product separation steps are the typical challenges associated with these classical

routes to LA.^{13m} Conversely, the use of homogeneous catalysts demands milder reaction conditions and hence provides better reactivity as well as selectivity.^{13d,n,14–22}

The Ir(I)-NHC catalyzed glycerol dehydrogenation in an acceptorless fashion was first demonstrated by Crabtree, where an impressive yield of LA (90%) was obtained at a very high selectivity (95%) with a high turnover number of 30 100.¹⁴ Tu then utilized a copolymer based Ir-NHC complex to perform the glycerol dehydrogenation to LA where a very high yield of LA (98%) was observed with a turnover number of 3266.¹⁵ Williams obtained a very high turnover number of 1 057 172 with a good yield of LA when glycerol was treated with an Ir(I) complex based on a bidentate (pyridylmethyl) imidazolium carbene ligand.¹⁶ Voutchkova-Kostal introduced highly charged sulfonate functionalization to Ir(I), Ir(III) and Ru(II) NHC complexes which rendered a turnover number of 45 592 under microwave conditions.^{17a} Very recently, Li studied the conversion of glycerol to lactic acid in water in high yields (*ca.* 99%) and with excellent selectivity (*ca.* 99%) that was catalyzed by a water-soluble piano-stool iridium complex.^{17b} Very recently, Kumar and Weller have reported PNP-Ir catalyzed glycerol to LA transformation, where 96% yield of LA was achieved at a high selectivity of 99% with a TON of 65 000.^{18a}

In the first report with catalytic systems based on Ru, Beller reported PNP pincer-Ru catalysed glycerol to LA transformation with an LA yield of 67% with 67% selectivity with a high turnover number of 270 000.^{18b} We have demonstrated the activity of 2,6-bis(benzimidazole-2-yl)pyridine based pincer-Ru towards dehydrogenating glycerol

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to LA. Under the optimized conditions, up to 90% yield of LA could be obtained with 98% selectivity.^{19a} Recently, the research group of Daw have demonstrated that 78% yield of lactate was obtained from a mixture of glycerol, ethylene glycol and methanol (1:1:5) in the presence of NNN pincer-Ru (1 mol%) and KOH (3.5 equivalents) in *t*-BuOH (1 mL) at 120 °C in 72 h.^{19b} Thus, it is evident that the catalytic systems based on Ir and Ru have enjoyed great success in accomplishing the dehydrogenative transformation of glycerol to lactic acid. However, in recent times, significant emphasis has been laid to accomplishing these transitions using earth-abundant first-row transition elements (Fig. 1).

The first report on the use of a 3d metal for the GLY to LA transformation again came from Crabtree who along with Hazari performed this reaction utilizing a PNP pincer-Fe complex which afforded a turnover number of 880 at 20% conversion of glycerol and 80% selectivity towards LA.^{20a} Fu have reported a highly reactive pincer-Mn complex, which afforded high yield of LA (96%) with high selectivity (96%).^{20b} Very recently, we have reported a catalytic system based on a simple base metal salt CoCl₂ which could accomplish the glycerol dehydrogenation to LA at 93% yield with a selectivity of 96% in the presence of acetone as a hydrogen acceptor.^{22a} The CoCl₂^{22a} based system was one of the very few examples of catalysts derived from earth-abundant, readily available 3d metals apart from the report on catalytic systems based on pincer-Mn by Fu^{20b} and pincer-Fe by Crabtree and Hazari.^{20a} In our recent report, we have demonstrated (Ph₂NNN)MnCl₂ (0.5 mol%) catalyzed transfer dehydrogenation of glycerol in the presence of acetone, where we could achieve 92% yield of LA with 99% selectivity in the presence of 1 equivalent NaOH at 140 °C.^{21a} We have also accomplished this reaction using an Fe complex based on the same bis(imino)pyridine ligand where excellent yield of LA (91%) at 99% selectivity was afforded in the

presence of 1.2 equivalents NaOH at 140 °C.^{21b} To the best of our knowledge, there are no other reports on homogeneous 3d-metal GLY dehydrogenation catalytic systems reported for the production of LA.

Taking a cue from the previous success on achieving alcohol dehydrogenation using commercially available chromium(III) chloride^{22b} and its corresponding pincer complexes,^{22b,j} we attempted the conversion of GLY to LA using CrCl₃·6H₂O and its corresponding pincer-Cr complexes based on bis(imino)pyridine ligands.^{22b,j} To our delight, in the presence of acetone, we could achieve LA in 94% yield at a selectivity of 98% along with the formation of isopropanol as a net transfer dehydrogenation product in the (Cy²NNN)CrCl₃ catalyzed reaction of glycerol with acetone at 160 °C after 24 h.

Results and discussion

Studies on the pincer-Cr catalyzed net transfer dehydrogenation of glycerol to lactic acid using acetone

For the proposed studies on the net transfer dehydrogenation of GLY **1** to LA **3** using acetone **2a**, CrCl₃·6H₂O and its corresponding NNN pincer-Cr complexes based on bis(imino)pyridine ligands^{22b,j} of the type (R²NNN)CrCl₃ (**5a**; R = Ph, **5b**; R = Cy, **5c**; R = ⁱPr and **5d**; R = ^tBu) were used as potential catalysts. During the course of the synthesis of the considered pincer-Cr complexes using our previously reported protocol, we were able to obtain crystals of **5a** which were suitable for single-crystal XRD analysis (Table S1). Green crystal was obtained for complex **5a** in a solution of MeOH and H₂O *via* slow evaporation. SC-XRD analysis of **5a** revealed that Cr is in an octahedral environment, to which the pincer ligand is bound in meridional geometry with one chloride *trans* to pyridyl-N and the other two chlorides are *trans* to each other (Fig. 2b). Complex **5a** has crystallized in the P2₁/n space group. The Cr–N(pyridyl) bond distance is 1.994(8) Å (Table S1). Both the Cr–N(imine) bonds are comparable (2.108(9) Å and 2.099(8) Å) in length with the pyridyl(N)–Cr–N(imine) bond angles of 77.0(4) and 77.4(4), respectively.

The catalytic investigations were initiated using 5 mmol of glycerol **1**, 5 mmol of acetone **2a**, 0.5 mol% CrCl₃·6H₂O and KOH (0.5 equivalents with respect to glycerol) where 25% glycerol conversion was observed that resulted in 23% lactate **3'** with 92% selectivity at 160 °C in 24 hours (entry 1,

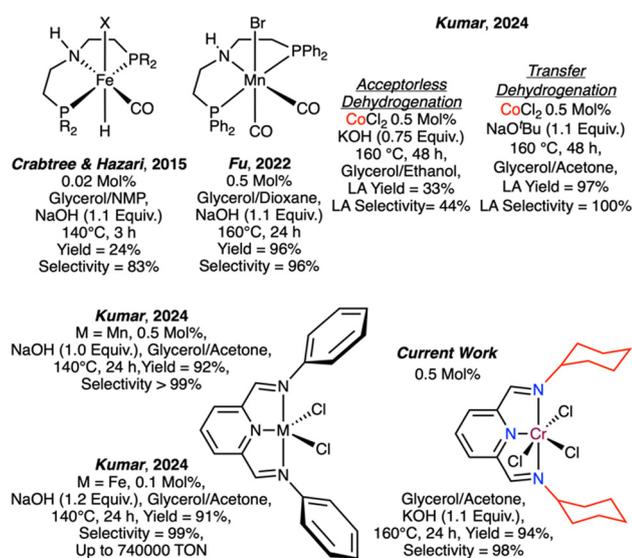


Fig. 1 Homogeneous 3d-metal based molecular catalytic systems reported for the transformation of GLY to LA.

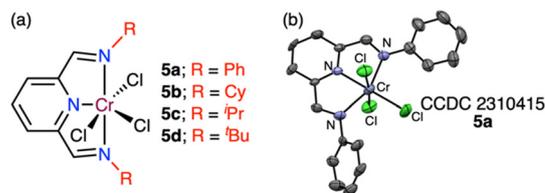


Fig. 2 (a) The considered catalysts **5a**–**d**. (b) The molecular structure of **5a** is provided as ORTEP drawn at 50% probability. All of the hydrogen atoms on **5a** are omitted for the sake of clarity.

Table 1 Glycerol net transfer dehydrogenation to lactic acid catalyzed by CrCl₃·6H₂O and its corresponding pincer complexes under varying conditions^a

Entry	Cr catalyst (<i>X</i> mol%)	Base (<i>Y</i> equivalents)	% conversion ^b 1	% yield ^b 3'	% selectivity ^c 3'	% yield ^b 4a	
1	CrCl ₃ ·6H ₂ O (0.5)	KOH	0.5	25%	23%	92%	19%
2	CrCl ₃ ·6H ₂ O (0.5)	KOH	0.75	40%	40%	100%	38%
3	CrCl ₃ ·6H ₂ O (0.5)	KOH	1	51%	50%	98%	42%
4 ^d	CrCl ₃ ·6H ₂ O (0.5)	KOH	1.1	62 ± 2%	62 ± 1%	>99%	55 ± 1%
5 ^d	CrCl ₃ ·6H ₂ O (0.5)	KOH	1.2	62 ± 2%	61 ± 3%	98%	57 ± 1%
6 ^d	CrCl ₃ ·6H ₂ O (0.5)	KOH	1.3	67 ± 1%	66 ± 1%	98%	60 ± 2%
7	CrCl ₃ ·6H ₂ O (0.75)	KOH	1.1	70%	68%	97%	68%
8	CrCl ₃ ·6H ₂ O (0.25)	KOH	1.1	63%	62%	98%	54%
9	CrCl ₃ ·6H ₂ O (0.1)	KOH	1.1	58%	58%	100%	51%
10	CrCl ₃ ·6H ₂ O (0.075)	KOH	1.1	55%	53%	96%	49%
11	CrCl ₃ ·6H ₂ O (0.05)	KOH	1.1	55%	54%	98%	40%
12	CrCl ₃ ·6H ₂ O (0.025)	KOH	1.1	60%	58%	97%	48%
13	CrCl ₃ ·6H ₂ O (0.01)	KOH	1.1	55%	54%	98%	54%
14	CrCl ₃ ·6H ₂ O (0.0075)	KOH	1.1	55%	55%	100%	45%
15	CrCl ₃ ·6H ₂ O (0.005)	KOH	1.1	51%	50%	98%	38%
16	CrCl ₃ ·6H ₂ O (0.0025)	KOH	1.1	50%	49%	98%	31%
17 ^e	CrCl ₃ ·6H ₂ O (0.0025)	KOH	1.1	60%	59%	98%	53%
18 ^d	CrCl ₃ ·6H ₂ O (0.5)	NaOH	1.1	88 ± 2%	84 ± 1%	95%	67 ± 1%
19 ^f	CrCl ₃ ·6H ₂ O (0.5)	NaOH	1.1	82%	81%	99%	52%
20 ^d	CrCl ₃ ·6H ₂ O (0.5)	NaO ^t Bu	1.1	40 ± 1%	39 ± 1%	99%	5 ± 1%
21 ^d	CrCl ₃ ·6H ₂ O (0.5)	KO ^t Bu	1.1	27 ± 1%	26 ± 1%	99%	21 ± 1%
22 ^d	CrCl ₃ ·6H ₂ O (0.5)	NaOEt	1.1	26 ± 1%	26 ± 1%	>99%	24 ± 1%
23	CrCl ₃ ·6H ₂ O (0.5)	Na ₂ CO ₃	1.1	Trace	Trace	Trace	Trace
24	CrCl ₃ ·6H ₂ O (0.5)	K ₂ CO ₃	1.1	Trace	Trace	Trace	Trace
25	CrCl ₃ ·6H ₂ O (0.5)	NaHCO ₃	1.1	0	0	0	0
26	CrCl ₃ ·6H ₂ O (0.5)	KHCO ₃	1.1	0	0	0	0
27	5a (0.5)	NaOH	1.1	92%	91%	99%	67%
28	5b (0.5)	NaOH	1.1	96 ± 1%	94 ± 1%	98%	79 ± 1%
29	5c (0.5)	NaOH	1.1	86%	84%	98%	53%
30	5d (0.5)	NaOH	1.1	78%	75%	96%	43%
31	5b (0.75)	NaOH	1.1	87%	86%	99%	76%
32	5b (0.25)	NaOH	1.1	75%	73%	95%	38%
33	5b (0.05)	NaOH	1.1	68%	67%	98%	28%
34	5b (0.005)	NaOH	1.1	61%	57%	91%	26%
35	5b (0.00125)	NaOH	1.1	56%	53%	95%	13%
36 ^g	5b (0.5)	NaOH	1.1	73%	72%	99%	47%
37 ^h	5b (0.5)	NaOH	1.1	63%	61%	97%	48%
38 ⁱ	5b (0.5)	NaOH	1.1	26%	24%	92%	20%
39	No Catalyst	NaOH	1.1	21%	19%	90%	Trace

^a Reaction conditions: 5 mmol glycerol, *X* mol% Cr catalyst, base (*Y* equivalents with respect to glycerol), 5 mmol **2a**, at 160 °C, in a 15 mL pressure tube, under air. ^b Determined from ¹H NMR analysis using sodium acetate as the standard. ^c Selectivity of lactic acid = (yield of lactic acid/conversion of glycerol) × 100. ^d Average of two runs. ^e Reaction was done for 96 h. ^f 0.555 mL acetone was used (1.5 equivalents with respect to glycerol). ^g Reaction was done at 140 °C. ^h Reaction was done at 120 °C. ⁱ Reaction was done at 100 °C.

Table 1). A higher yield of **3'** (40%) was observed at a higher KOH loading of 0.75 equivalents (entry 2, Table 1). In the presence of one equivalent of KOH, 50% yield of lactate **3'** was obtained at 98% selectivity (entry 3, Table 1).

The yield of lactate further increased to 62 ± 1% when 1.1 equivalents of KOH was used (entry 4, Table 1). On further increasing the equivalents of the base, comparable yield of lactate **3'** was observed (entries 5 and 6, Table 1). Further optimization was hence carried out using 1.1 equivalents of KOH. While increasing the loading of CrCl₃·6H₂O to 0.75 mol% led to comparable yield of lactate **3'** (68%, entry 7,

Table 1), further lowering the catalyst loading resulted in lactate yields that were in the range of 60–50% after 24 hours of reaction (entries 8–16, Table 1). Notably, with a very low loading of 0.0025 mol% CrCl₃·6H₂O, 59% yield of lactate **3'** which corresponds to an unprecedented turnover number of 23 600 TON was obtained in 96 hours (entry 17, Table 1).

To investigate the effect of various bases, the GLY to LA transformation reaction was done using 5 mmol glycerol, 5 mmol acetone, 0.5 mol% CrCl₃·6H₂O, and 1.1 equivalents of base at 160 °C for 24 hours (entries 18–26, Table 1). A very good yield of lactate **3'** (*ca.* 84 ± 1%, entry 18, Table 1) was

obtained in the presence of NaOH. Use of NaO^tBu gave lower yield of lactate 3' (39 ± 1%, entry 20, Table 1). Both KO^tBu and NaOEt have shown poor efficiency giving rise to similar yield of 3' (26 ± 1%, entries 21 and 22, Table 1). The carbonate and bicarbonate salts of neither sodium nor potassium were active (entries 23–26, Table 1). Increasing the amount of acetone hardly improved the productivity of 3' (entry 18 vs. 19, Table 1).

Under the optimized conditions (entry 18, Table 1), the transfer dehydrogenation of glycerol with acetone was repeated using pincer-Cr complexes based on bis(imino)pyridine ligands^{22b,j} of the type (^{R2}NNN)CrCl₃ (**5a**; R = Ph, **5b**; R = Cy, **5c**; R = ⁱPr and **5d**; R = ^tBu) which were previously reported by our group.^{22b,j} To our delight, complexes **5a** and **5b** have shown better reactivity than the precursor CrCl₃·6H₂O in terms of productivity of lactate 3' (entry 18 vs. entries 27 and 28, Table 1). In particular, 91% lactate 3' was obtained with 99% selectivity, when glycerol (5 mmol) was treated with 0.5 mol% **5a** in the presence of acetone (5 mmol) and NaOH (1.1 equivalents with respect to glycerol) (entry 27, Table 1). Under similar conditions, slightly better reactivity was demonstrated by **5b** compared to **5a** (entry 27 vs. entry 28, Table 1) where 94 ± 1% lactate 3' yield was obtained with 98% selectivity along with 79 ± 1% of isopropanol. Meanwhile, slightly lower yield of lactate (84%, entry 29, Table 1) but still at high selectivity (98%) was observed upon the use of catalyst **5c** under identical conditions.

The optimization of the loading of **5b** was then investigated. On increasing the loading of **5b** to 0.75 mol%, 86% yield of lactate 3' with 99% selectivity was obtained, which is slightly lower compared to that of 0.5 mol% **5b** (compared entry 31 with 27, Table 1) which may be attributed to the lower solubility of the higher amount of the catalyst. On lowering the loading of **5b** to 0.25 mol%, a decrement in the yield of lactate 3' was observed (73% with 95% selectivity, entry 32, Table 1). Further sequential lowering of **5b** loading led to gradual decrement in lactate 3' yield however with good turnover numbers (entries 33–35, Table 1).

To investigate the effect of the temperature, the reaction was performed at lower temperatures also. On lowering the temperature from 160 °C to 140 °C, a lower yield of lactate 3' (72%, entry 36, Table 1) was obtained which drops to 61% at 120 °C (entry 37, Table 1). The yield of lactate 3' further dropped to 24% at 100 °C (entry 38, Table 1). One would observe that in all entries in Table 1, the yield of IPA **4a** is slightly lower than 3', which apparently can be attributed to the secondary dehydrogenation of **4a** back to **2a** along with the generation of hydrogen. Accordingly, hydrogen was detected in GC measurements for representative examples (see Fig. S1a–f for H₂ detected from entries 4, 28, and 31–34, Table 1). Alternatively, the possibility of a competing aldol reaction of **2a** with the corresponding aldol products acting as hydrogen acceptors can also explain the lower yield of **4a**. A similar argument could explain the lower yields of **4a–4q** in Table 2 relative to 3'.

Table 2 Glycerol net transfer dehydrogenation to lactic acid catalyzed by **5b** using various acceptors^a

Entry	Acceptor	% conversion ^b 1	% yield ^b 3'	% selectivity ^c 3'	% yield ^b 4a–4q
1 ^d	Acetone (2a)	96 ± 1%	94 ± 1%	98%	67 ± 1%
2 ^e	Acetone (2a)	0%	0%	0%	0%
3 ^f	Acetone (2a)	18%	18%	100%	0%
4	Acetophenone (2b)	76%	74%	97%	72%
5	Benzaldehyde (2c)	31%	30%	97%	49%
6	4'-Chloroacetophenone (2d)	78%	76%	97%	32%
7	4'-Methylacetophenone (2e)	90%	89%	93%	84%
8	Cyclopentanone (2f)	74%	72%	97%	45%
9	4'-Nitroacetophenone (2g)	32%	18%	56%	Trace
10	Benzophenone (2h)	54%	50%	93%	47%
11	3'-Methoxyacetophenone (2i)	75%	73%	97%	56%
12	4-Acetylpyridine (2j)	48%	45%	94%	6%
13	4'-Bromoacetophenone (2k)	87%	84%	96%	22%
14	4'-Fluoroacetophenone (2l)	7%	6%	86%	0%
15	4'-CF ₃ -Acetophenone (2m)	47%	45%	96%	15%
16	4'-Methoxyacetophenone (2n)	74%	73%	98%	51%
17	4'- <i>tert</i> -Butylacetophenone (2o)	25%	23%	92%	0%
18	2-Acetylthiophene (2p)	65%	62%	95%	49%
19	4'-Hydroxyacetophenone (2q)	15%	12%	50%	Trace
20 ^g	No acceptor	10%	8%	80%	0%

^a Reaction conditions: 5 mmol glycerol, 0.5 mol% **5b**, NaOH (1.1 equivalents with respect to glycerol), 5 mmol acetone (1 equivalent with respect to glycerol), at 160 °C, in a 15 mL pressure tube, under air. ^b Determined from ¹H NMR analysis using sodium acetate as the standard. ^c Selectivity of lactic acid = (yield of lactic acid/conversion of glycerol) × 100. ^d Average of two runs. ^e Reaction was done in the absence of a base. ^f Reaction was done in the absence of **5b**. ^g Reaction was done in the absence of any acceptor.

Under the optimized conditions but in the absence of a base, no reactivity was observed (entry 2, Table 2), while in the absence of **5b**, only 18% yield of **3'** was observed with 100% selectivity towards **3'** (entry 3, Table 2). The GLY to LA transformation was then performed in the presence of various acceptors under the optimized reaction conditions (entry 28, Table 1), to understand the effect of acceptors on the productivity of lactate **3'** (Table 2).

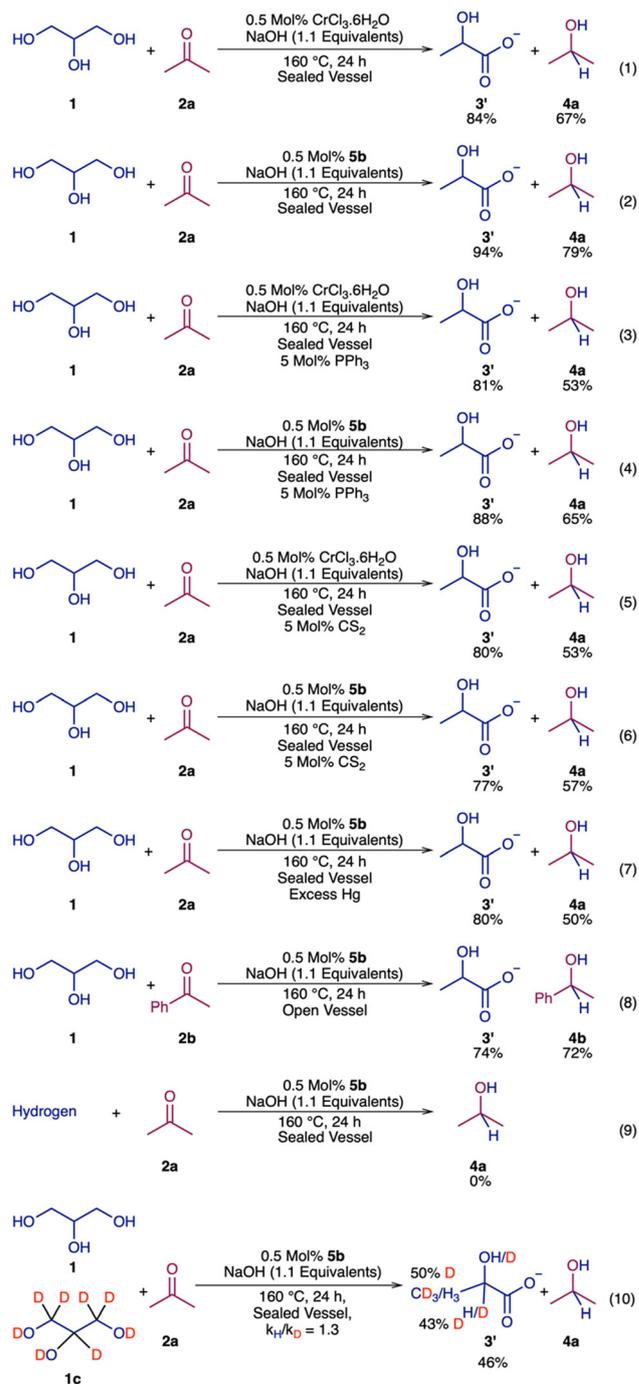
In the presence of acetophenone **2b** as an acceptor, moderate yield of lactate **3'** (74%) was observed (entry 4, Table 2). In the presence of benzaldehyde **2c**, poorer yield of lactate **3'** was obtained (30%, entry 5, Table 2). Hence, further studies were continued with various derivatives of acetophenone.

A very poor yield of lactate **3'** (6%) was obtained when **2l** with a strong electron withdrawing *p*-fluoro group was employed as an acceptor (entry 14, Table 2). The yield of **3'** improved to 45% when the *p*-fluoro group was replaced by a *p*-trifluoromethyl group in **2m** (entry 15, Table 2). In the presence of **2d** containing a poor electron-withdrawing chloro group, comparable yield of lactate **3'** (76% at 97% selectivity) was observed in comparison to **2b** that results in 70% yield of **3'** (entry 4 vs. entry 6, Table 2). Similarly, **2i** containing an poor electron withdrawing methoxy group in the *meta* position shows comparable reactivity yielding 73% of lactate to **2b** (entry 4 vs. entry 11, Table 2). Acceptor **2k** with a relatively less electron withdrawing *p*-bromo substituent resulted in 84% yield of lactate **3'** (entry 13, Table 2). Based on the observation, it is evident that the yield of lactate **3'** systematically decreased on increasing the electron deficiency and followed the trend *p*-Br > *p*-Cl ~ *m*-OMe > *p*-CF₃ > *p*-F. When the reaction was performed in the presence of **2e**, which contains an electron-donating methyl group, a much higher yield of 89% lactate **3'** with 93% selectivity was obtained (entry 7, Table 2).

When cyclopentanone **2f** was used as an acceptor, a lower reactivity was observed when compared to the corresponding activity with another aliphatic acceptor acetone (compared entry 8 with entry 1, Table 2). It might be attributed to the fact that cyclopentanone is more sterically crowded than acetone. Poor yield of lactate **3'** (18%) was observed in the presence of a nitro derivative of acetophenone **2g** (entry 9, Table 2) along with the formation of ethylene glycol EG (3%) and formic acid FA (11%), ultimately resulting in very low selectivity towards LA (56%). When benzophenone **2h** was used, 50% yield of lactate **3'** was obtained (entry 10, Table 2).

Mechanistic investigation on the pincer-Cr catalyzed net transfer dehydrogenation of glycerol to lactic acid using acetone

To check the homogeneity of the reaction, three well-established catalyst poisons²³ involving PPh₃, CS₂ and mercury were used. Negligible lowering of reactivity towards production of **3'** was observed when the transfer dehydrogenation of GLY catalyzed by CrCl₃·6H₂O and **5b**



Scheme 1 Control experiments.

(compared eqn (1) with eqn (3) and eqn (2) with eqn (4), Scheme 1) was performed in the presence of PPh₃. Similar observation was made in the presence of CS₂ (compared eqn (1) vs. eqn (5), Scheme 1 and eqn (1) vs. eqn (6), Scheme 1). Considering the fact that PPh₃ or CS₂ can poison both homogeneous and heterogeneous catalysts,^{23d} a confirmatory mercury poisoning test was also performed, where slight lowering of yield was observed (compared eqn (2) vs. eqn (7), Scheme 1). These observations draw evidence of the reaction being mostly homogeneous. Interestingly,

the high reactivity under open vessel conditions (compared entry 4, Table 2 vs. eqn (8), Scheme 1) in the presence of acetophenone (the boiling point is 202 °C) under the optimized reaction conditions gives an indication of the involvement of both hydrogenolysis and alcoholysis.

From the EPR analysis of the reaction mixture (entry 28, Table 1) at 0 h and 1 h, it is evident that at 0 h Cr(III) species ($g = 2.0006$)²⁴ is involved, whereas at 1 h Cr(II) species ($g = 1.9843$)²⁴ is involved (Fig. 3). HRMS analysis (Fig. 4) of the reaction mixture demonstrated the presence of several pincer-Cr mono-glyceroxide and pincer-Cr bis-glyceroxide species. Magnetic moment measurement (via Evan's method)^{24b} of **5b** in the absence and presence of a base in 2% ^tBuOH in D₂O (Fig. 5) bodes well with the observation from EPR (Fig. 3) of the reaction mixture. A magnetic moment of 3.42 BM of the reaction mixture before the addition of a base corresponds to Cr(III) species,^{24b} which converts to a Cr(II) species with a magnetic moment of 4.5 BM in the presence of a base.^{24b} Subjecting a mixture of glycerol (2.5 mmol) and glycerol-d₈ (2.5 mmol) to the optimized reaction conditions (eqn (10), Scheme 1) resulted in a modest KIE of 1.3 along with 46% lactate **3'**. This KIE gives an indication of the involvement of C–H activation as a part of the catalytic cycle, but it might not be a part of the rate determining step. Kinetic studies indicate that the reaction demonstrates a first-order dependence of rate on the concentration of **5b** and NaOH (Fig. 6). Thus, from the control experiments, it may be inferred that well-defined molecular pincer-Cr(II) complexes are involved in the catalytic cycle with a likely contribution from the alcoholysis and/or a Meerwein–Ponndorf–Verley type pathway (Scheme 2).

The first step in the pincer-Cr catalyzed net transfer dehydrogenation of glycerol to lactic acid using acetone involves the generation of the active Cr(II) species **6** from the Cr(III) precursor (**5b**) in the presence of a base (Scheme 2). Subsequent salt metathesis of **6** with NaOH in the presence of glycerol **1** will generate the alkoxide species **7** along with loss of water. This will be followed by a β -hydride elimination at **7** which will give rise to the hydride species **9** via **TS-8** along with the extrusion of a molecule of glyceraldehyde **1'**. Glyceraldehyde **1'** will follow a series of base mediated reactions which involves dehydration of **1'** to **10** and a subsequent tautomerization of **10** to **11**. Ultimately, a base

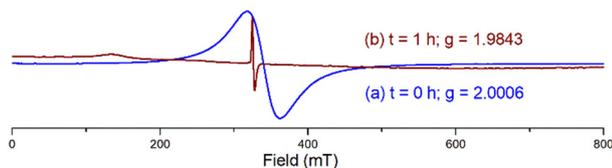


Fig. 3 EPR analysis of the reaction mixture obtained from the optimized transfer dehydrogenation of glycerol (entry 28, Table 1 and eqn (2), Scheme 1) (a) at 0 h in the absence of NaOH and (b) at 1 h in the presence of NaOH. The X-band EPR spectra were recorded in methanol on a JESFA200 ESR spectrometer at 78 K with a microwave power of 0.998 mW and a microwave frequency of 9.14 GHz.

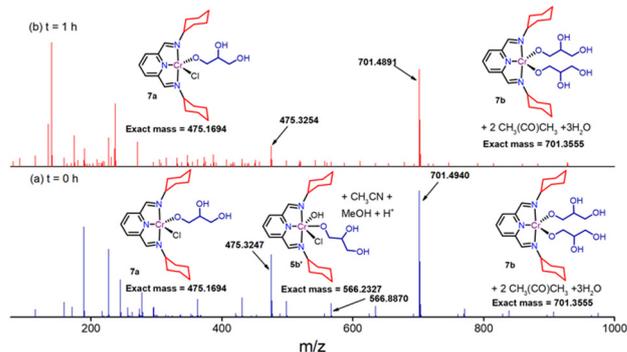


Fig. 4 HRMS analysis of the reaction mixture obtained from the optimized transfer dehydrogenation of glycerol (entry 2, Table 2 and eqn (2), Scheme 1) at (a) $t = 0$ h at room temperature and (b) $t = 1$ h at 160 °C (also see Fig. S2a–c).

mediated intramolecular Cannizzaro reaction in **11** leads to the final lactate **3'**.

The pincer-Cr-hydride species **9** has three paths (path A–C) at its disposal (Scheme 2). Along path A, the Cr–H bond in **9** would undergo a σ -bond metathesis with the O–H bond of glycerol **1** leading to the regeneration of alkoxide species **7** via **TS-12** along with the extrusion of H₂. Notably, hydrogen was detected from the headspace of the reaction mixture (eqn (1) and (2), Scheme 1 and Fig. S1a and b). However, entry 20 in Table 2 indicates that the contribution (*ca.* 8% yield of **3'**) from acceptorless path A is very minor.

Along path B, **2a** would insert into the Cr–H bond in **9** to give the pincer-Cr isopropoxide **14** while going through **TS-13**. Species **14** can undergo a σ -bond metathesis (alcoholysis) with the O–H bond of glycerol **1** leading to the regeneration of alkoxide species **7** via **TS-15** while generating isopropanol **4a** (Scheme 2). Reactivity under open-vessel conditions (eqn (8), Scheme 1) is suggestive of the involvement of the alcoholysis along path B. Alternatively, if the pincer-Cr isopropoxide species **14** undergoes a σ -bond metathesis (hydrogenolysis) with

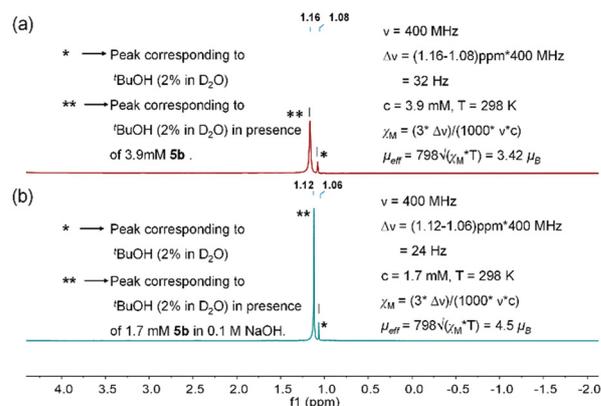


Fig. 5 Magnetic moment determination via Evan's method of a) **5b** before addition of NaOH and b) **5b** after addition of NaOH at room temperature.

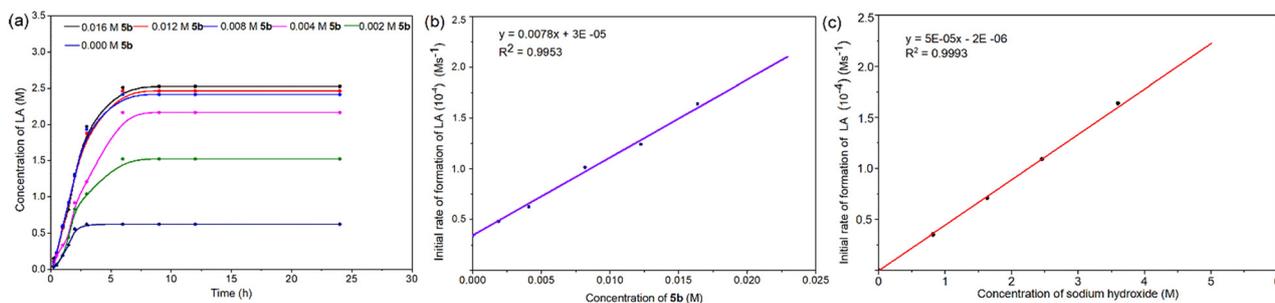
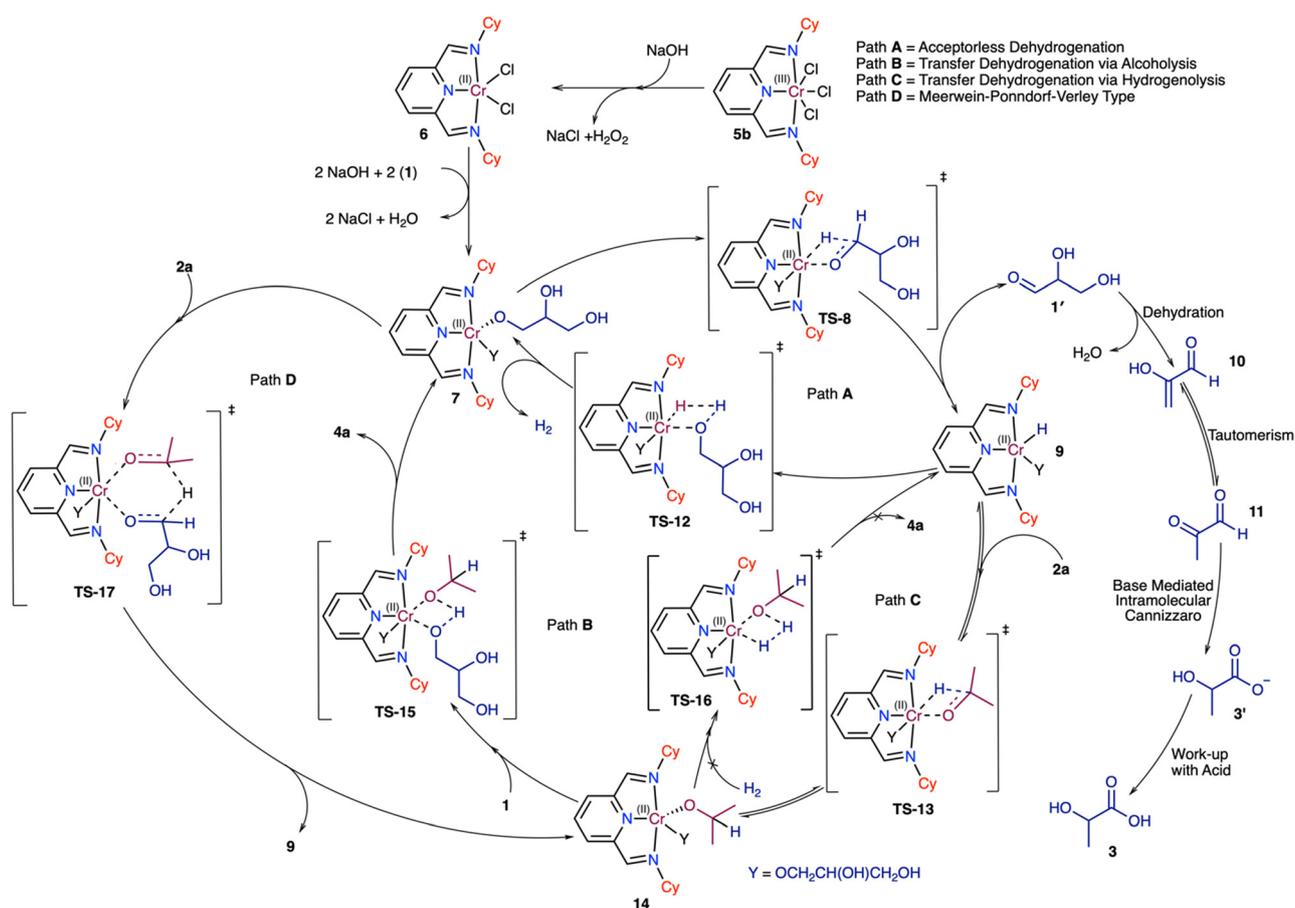


Fig. 6 (a) Time-profile of transfer hydrogenation of glycerol in an open vessel using glycerol (0.460 g, 5 mmol, 3.3 M), NaOH (0.2198 g, 5.4956 mmol, 3.6 M), acetophenone (1.2 g, 10 mmol, 6.6 M), at 160 °C, in the presence of **5b** (0.0013–0.0114 g, 0.003–0.025 mmol, 0.002–0.016 M). (b) Dependence of the initial rate of transfer hydrogenation of the glycerol reaction on the concentration of **5b** (extracted from the data at 15 minutes in Fig. 6a). (c) Dependence of the initial rate of transfer hydrogenation of the glycerol reaction on the concentration of NaOH (extracted from the data at 15 minutes in Fig. S59). Reaction conditions: glycerol (0.460 g, 5 mmol, 3.3 M), **5b** (0.0114 g, 0.025 mmol, 0.016 M), acetophenone (1.2 g, 10 mmol, 6.6 M), at 160 °C, in the presence of NaOH (0.05–0.22 g, 1.25–5.5 mmol, 0.8–3.6 M).



Scheme 2 Plausible mechanism involved in the **5b** catalyzed net transfer hydrogenation of glycerol to lactic acid.

hydrogen, the pincer-Cr hydride **9** would be regenerated along with the formation of **4a**. Notably, though hydrogen is detected from the headspace of the reaction mixture (eqn (1) and (2), Scheme 1 and Fig. S1a and b), the hydrogenolysis through path C is unlikely to contribute to the observed catalysis, as independent experiments with molecular hydrogen under the optimized reaction conditions yielded no product (eqn (9), Scheme 1).

In alternative path **D**, the pincer-Cr glyceroxide species **7** would interact with **2a** to initiate a direct transfer of the β -hydrogen *via* Meerwein–Ponndorf–Verley type **TS-17** leading to the extrusion of glycerolaldehyde **1'** and formation of pincer-Cr isopropoxide species **14** (Scheme 2). Species **14** upon alcoholysis would regenerate **7** and produce **4a**. Notably, while path **B** has a sequence of β -hydride elimination and insertion steps, path **D** has a concerted

β -hydride transfer step prior to the alcoholysis step that is common to both the paths.

Experimental

Materials and methods

All the complexes were synthesized in anhydrous THF under argon using the Schlenk technique at room temperature. All the reactions were performed in a sealed vessel under air. Kinetic experiments were performed in an open vessel under air. Glycerol, NaOH, KOH, Na₂CO₃, K₂CO₃, NaHCO₃, and KHCO₃ were purchased from Himedia. Deuterated glycerol-d₈, D₂O, NaO^tBu, KO^tBu and NaOEt were purchased from Sigma-Aldrich. The ketones were purchased from MERCK or Sigma-Aldrich or SRL or Alfa Aesar or TCI and used as such.

Physical measurements

¹H, ¹³C {¹H} and ²H NMR were performed either on a Bruker ASCEND 600 operating at 600 MHz for ¹H and ²H and 151 MHz for ¹³C or on a Bruker AVANCE 400 operating at 400 MHz for ¹H. Chemical shifts (δ) are reported in ppm, spin-spin coupling constants (J) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet and q = quartet. HRMS measurements were recorded using an Agilent Accurate-Mass QTOF ESI-MS 6520. The X-band EPR spectra were recorded on a JESFA200 ESR spectrometer.

General procedure for transfer dehydrogenation of glycerol to lactic acid using **5b**

In a 15 mL sealed tube, glycerol (0.460 g, 5 mmol, 6.8 M) followed by sodium acetate (0.05 g, 0.6095 mmol, 0.8 M), NaOH (0.2198 g, 5.4956 mmol, 7.5 M), **5b** (0.0114 g, 0.025 mmol, 0.02 M) and acetone (0.37 mL, 5 mmol, 6.8 M) were added. The reaction mixture was heated in a preheated oil bath at 160 °C for 24 hours. After 24 hours, the reaction mixture was brought to room temperature. Subsequently, 0.5 mL H₂O was added to the reaction mixture and was allowed to homogenize under continuous stirring for 10 minutes. An aliquot was drawn and submitted for NMR analysis in D₂O as the NMR solvent. The yield of lactate (**3'**) was determined as 94% from ¹H NMR using sodium acetate as an internal standard.

General procedure for kinetic studies

(a) Variation in the loading of **5b.** To each of the five round-bottom flasks, glycerol (0.460 g, 5 mmol, 3.3 M) followed by sodium acetate (0.05 g, 0.6095 mmol, 0.4 M), NaOH (0.2198 g, 5.4956 mmol, 3.6 M) and acetophenone (1.2 g, 10 mmol, 6.6 M) were added in the presence of **5b** (0.0013–0.0114 g, 0.003–0.025 mmol, 0.002–0.016 M). The reaction mixture was heated at 160 °C. Aliquots (10 μ L) were collected at regular intervals. The yield of lactate (**3'**) was determined from ¹H NMR analysis using sodium acetate as an internal standard and D₂O as the NMR solvent.

(b) Variation in the loading of NaOH. To each of the four round-bottom flasks, glycerol (0.460 g, 5 mmol, 3.3 M) followed by sodium acetate (0.05 g, 0.6095 mmol, 0.4 M), **5b** (0.0114 g, 0.025 mmol, 0.016 M) and acetophenone (1.2 g, 10 mmol, 6.6 M) were added in the presence of NaOH (0.05–0.22 g, 1.25–5.5 mmol, 0.8–3.6 M). The reaction mixture was heated at 160 °C. Aliquots (10 μ L) were collected at regular intervals. The yield of lactate (**3'**) was determined from ¹H NMR analysis using sodium acetate as an internal standard and D₂O as the NMR solvent.

Conclusions

Commercially available first-row transition metal salt CrCl₃·6H₂O and its corresponding pincer complexes in the presence of a sacrificial hydrogen acceptor, acetone, is found to accomplish the transfer dehydrogenation of glycerol (GLY) to lactic acid (LA). In particular, the pincer-Cr complex, (Cy²NNN)CrCl₃ (0.5 mol%) was found to efficiently bring about the catalytic net transfer dehydrogenation of glycerol in the presence of 1.1 equivalents of NaOH, at 160 °C to afford 94% lactic acid at 98% selectivity along with another value-added product isopropanol (IPA). The scope of the studies on the GLY to LA conversion under transfer dehydrogenation conditions has been extended to include various carbonyl compounds (16 examples) as acceptors. The acceptor 4'-methylacetophenone with an electron donating methyl group has shown the best result with 89% yield of lactate.

While reactions with catalyst poisons such as PPh₃, CS₂ and elemental mercury revealed the homogeneous molecular nature of the catalyst, EPR studies and magnetic moment measurements using Evan's method revealed that these homogeneous molecular species are likely to be based on Cr(II). Detailed mechanistic studies are indicative of the sole contribution of the alcoholysis path towards the observed reactivity with a KIE of 1.3.

Author contributions

H. N. performed all the experiments. S. D. provided intellectual inputs. A. K. conceptualized the project, analyzed the data and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI).

Supplementary information: detailed experimental procedure, NMR of the reaction mixtures, GC and HRMS analysis (PDF). See DOI: <https://doi.org/10.1039/d5cy01041a>.

CCDC 2310415 contains the supplementary crystallographic data for this paper.²⁵

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Notes and references

- 1 F. Cherubini, *Energy Convers. Manage.*, 2010, **51**, 1412–1421.
- 2 R. H. Crabtree, *ACS Sustainable Chem. Eng.*, 2019, **7**, 15845–15853.
- 3 P. D. Vaidya and A. E. Rodrigues, *Chem. Eng. Technol.*, 2009, **32**, 1463–1469.
- 4 D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem. Soc. Rev.*, 2012, **41**, 8075–8098.
- 5 P. T. Anastas and J. B. Zimmerman, *Innovations in Green Chemistry and Green Engineering: Selected Entries from the Encyclopedia of Sustainability Science and Technology*, Springer Science & Business Media, 2012.
- 6 (a) D. B. Lao, A. C. E. Owens, D. M. Heinekey and K. I. Goldberg, *ACS Catal.*, 2013, **3**, 2391–2396; (b) D. D. Falcone, J. H. Hack, A. Y. Klyushin, A. Knop-Gericke, R. Schlögl and R. J. Davis, *ACS Catal.*, 2015, **5**, 5679–5695; (c) X. Zhao, J. Wang, M. Yang, N. Lei, L. Li, B. Hou, S. Miao, X. Pan, A. Wang and T. Zhang, *ChemSusChem*, 2017, **10**, 819–824; (d) Q. Sun, S. Wang and H. Liu, *ACS Catal.*, 2017, **7**, 4265–4275; (e) M. Sherbi, A. Wesner, V. K. Wisniewski, A. Bukowski, H. Velichkova, B. Fiedler and J. Albert, *Catal. Sci. Technol.*, 2021, **11**, 6649–6653.
- 7 (a) R. M. Painter, D. M. Pearson and R. M. Waymouth, *Angew. Chem., Int. Ed.*, 2010, **49**, 9456–9459; (b) C. Crotti, J. Kašpar and E. Farnetti, *Green Chem.*, 2010, **12**, 1295–1300; (c) K. Chung, S. M. Banik, A. G. De Crisci, D. M. Pearson, T. R. Blake, J. V. Olsson, A. J. Ingram, R. N. Zare and R. M. Waymouth, *J. Am. Chem. Soc.*, 2013, **135**, 7593–7602; (d) S.-S. Liu, K.-Q. Sun and B.-Q. Xu, *ACS Catal.*, 2014, **4**, 2226–2230; (e) N. Gupta, O. Khavryuchenko, A. Villa and D. Su, *ChemSusChem*, 2017, **10**, 3030–3034.
- 8 (a) C. H. Lam, A. J. Bloomfield and P. T. Anastas, *ChemSusChem*, 2017, **19**, 1958–1968; (b) Z. Jiang, Z. Zhang, T. Wu, P. Zhang, J. Song, C. Xie and B. Han, *Chem. – Asian J.*, 2017, **12**, 1598–1604; (c) D. Ainembabazi, K. Wang, M. Finn, J. Ridenour and A. Voutchkova-Kostal, *Green Chem.*, 2020, **22**, 6093–6104.
- 9 (a) M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. Della Pina, *Angew. Chem., Int. Ed.*, 2007, **46**, 4434–4440; (b) F. Jérôme, Y. Pouilloux and J. J. C. C. Barrault, *ChemSusChem*, 2008, **1**, 586–613; (c) B. Katryniok, H. Kimura, E. Skrzyńska, J.-S. Girardon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul and F. Dumeignil, *Green Chem.*, 2011, **13**, 1960–1979; (d) A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**, 13–30; (e) P. Gallezot, *Catal. Today*, 2007, **121**, 76–91.
- 10 A. Wolfson, C. Dlugy, Y. Shotland and D. Tavor, *Tetrahedron Lett.*, 2009, **50**, 5951–5953.
- 11 (a) M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina and B. F. Sels, *Energy Environ. Sci.*, 2013, **6**, 1415–1442; (b) A. Komesu, J. A. R. de Oliveira, L. H. da Silva Martins, M. R. W. Maciel and R. Maciel Filho, *Bioresour.*, 2017, **12**, 4364–4383.
- 12 (a) S. J. Sarma, S. K. Brar, E. B. Sydney, Y. Le Bihan, G. Buelna and C. R. Soccol, *Int. J. Hydrogen Energy*, 2012, **37**, 6473–6490; (b) J. Tang, Z. Hu, Y. Pu, X. C. Wang and A. Abomohra, *J. Environ. Manage.*, 2024, **369**, 122372.
- 13 (a) A. C. C. De Souza and J. L. Silveira, *Renewable Sustainable Energy Rev.*, 2011, **15**, 1835–1850; (b) G. W. Huber, J. W. Shabaker and J. A. Dumesic, *Science*, 2003, **300**, 2075–2077; (c) D. L. King, L. Zhang, G. Xia, A. M. Karim, D. J. Heldebrant, X. Wang, T. Peterson and Y. Wang, *Appl. Catal., B*, 2010, **99**, 206–213; (d) S. H. Cho and D. J. J. Moon, *Nanosci. Nanotechnol.*, 2011, **11**, 7311–7314; (e) J. J. Wang, Z. J. Li, X. B. Li, X. B. Fan, Q. Y. Meng, S. Yu, C. B. Li, J. X. Li, C. H. Tung and L. Z. Wu, *ChemSusChem*, 2014, **7**, 1468–1475; (f) S. H. Siddiki, A. S. Touchy, K. Kon, T. Toyao and K. I. Shimizu, *ChemCatChem*, 2017, **9**, 2816–2821; (g) G. Dodekatos, S. Schünemann and H. Tüysüz, *ACS Catal.*, 2018, **8**, 6301–6333; (h) W. Oberhauser, C. Evangelisti, A. Liscio, A. Kovtun, Y. Cao and F. J. Vizza, *Catal.*, 2018, **368**, 298–305; (i) S. Feng, K. Takahashi, H. Miura and T. Shishido, *Fuel Process. Technol.*, 2020, **197**, 106202; (j) R. Palacio, D. López and D. J. Hernández, *J. Nanopart. Res.*, 2019, **21**, 1–13; (k) C. S. Lee, M. K. Aroua, W. A. Wan Daud, P. Cagnet, Y. Pérès and M. A. Ajeel, *Front. Chem.*, 2019, **7**, 110; (l) S. A. Zavrazhnov, A. L. Esipovich, S. Y. Zlobin, A. S. Belousov and A. V. Vorotyntsev, *Catalysts*, 2019, **9**, 231; (m) M. A. Abdel-Rahman and K. J. Sonomoto, *Biotechnol.*, 2016, **236**, 176–192; (n) A. Bisarya, S. Karim, H. Narjinari, A. Banerjee, V. Arora, S. Dhole, A. Dutta and A. Kumar, *Chem. Commun.*, 2024, **60**, 4148–4169.
- 14 L. S. Sharninghausen, J. Campos, M. G. Manas and R. H. Crabtree, *Nat. Commun.*, 2014, **5**, 5084.
- 15 Z. Sun, Y. Liu, J. Chen, C. Huang and T. Tu, *ACS Catal.*, 2015, **5**, 6573–6578.
- 16 Z. Lu, I. Demianets, R. Hamze, N. J. Terrile and T. J. A. Williams, *ACS Catal.*, 2016, **6**, 2014–2017.
- 17 (a) M. Finn, J. A. Ridenour, J. Heltzel, C. Cahill and A. Voutchkova-Kostal, *Organometallics*, 2018, **37**, 1400–1409; (b) X. Xu, H. You, B. Dong, Y. He and F. Li, *Inorg. Chem.*, 2024, **63**, 12929–12934; (c) K. Wang, J. Horlyck, N. An and A. Voutchkova-Kostal, *Green Chem.*, 2024, **26**, 3546; (d) B. Dong, Y. Ji, F. Zhou, N. T. Tung, Y. Fan and F. Li, *J. Catal.*, 2026, **453**, 116442.
- 18 (a) Vikas, L. Kathuria, C. N. Brodie, M. J. Cross, F. A. Pasha, A. S. Weller and A. Kumar, *Inorg. Chem.*, 2025, **64**,

- 3760–3770; (b) Y. Li, M. Nielsen, B. Li, P. H. Dixneuf, H. Junge and M. Beller, *Green Chem.*, 2015, **17**, 193–198.
- 19 (a) M. Dutta, K. Das, S. J. Prathapa, H. K. Srivastava and A. Kumar, *Chem. Commun.*, 2020, **56**, 9886–9889; (b) S. T. Sahoo, A. Sinku and P. Daw, *RSC Adv.*, 2024, **14**, 37082–37086.
- 20 (a) L. S. Sharninghausen, B. Q. Mercado, R. H. Crabtree and N. Hazari, *Chem. Commun.*, 2015, **51**, 16201–16204; (b) C.-Q. Deng, J. Deng and Y. Fu, *Green Chem.*, 2022, **24**, 8477–8483.
- 21 (a) A. Bisarya, S. Dhole and A. Kumar, *Dalton Trans.*, 2024, **53**, 12698–12709; (b) B. Venkateshappa, A. Bisarya, P. G. Nandi, S. Dhole and A. Kumar, *Inorg. Chem.*, 2024, **63**, 15294–15310.
- 22 (a) H. Narjinari, S. Dhole and A. Kumar, *Chem. – Eur. J.*, 2024, **30**, e202302686; (b) H. Narjinari, N. Tanwar, L. Kathuria, R. V. Jasra and A. Kumar, *Catal. Sci. Technol.*, 2022, **12**, 4753–4762; (c) P. G. Nandi, P. Thombare, S. J. Prathapa and A. Kumar, *Organometallics*, 2022, **41**, 3387–3398; (d) P. G. Nandi, P. Kumar and A. Kumar, *Catal. Sci. Technol.*, 2022, **12**, 1100–1108; (e) K. Islam, Vikas, B. Nag and A. Kumar, *ChemCatChem*, 2022, e202200440; (f) M. Dutta, H. K. Srivastava and A. Kumar, *Comput. Chem.*, 2021, **42**, 1728–1735; (g) V. Arora, H. Narjinari, P. G. Nandi and A. Kumar, *Dalton Trans.*, 2021, **50**, 3394–3428; (h) V. Arora, H. Narjinari and A. Kumar, *Organometallics*, 2021, **40**, 2870–2880; (i) V. Arora, M. Dutta, K. Das, B. Das, H. K. Srivastava and A. Kumar, *Organometallics*, 2020, **39**, 2162–2176; (j) N. Tanwar, H. Narjinari, H. Sharma, S. Dhole, R. V. Jasra and A. Kumar, *Inorg. Chem.*, 2024, **63**, 3005–3018.
- 23 (a) S. Werkmeister, J. Neumann, K. Junge and M. Beller, *Chem. – Eur. J.*, 2015, **21**, 12226–12250; (b) D. H. Nguyen, Y. Morin, L. Zhang, X. Trivelli, F. Capet, S. Paul, S. Desset, F. Dumeignil and R. M. Gauvin, *ChemCatChem*, 2017, **9**, 2652–2660; (c) L. Chen, S. Ren and X. P. Ye, *React. Kinet., Mech. Catal.*, 2015, **114**, 93–108; (d) V. Artero and M. Fontecave, *Chem. Soc. Rev.*, 2013, **42**, 2338–2356.
- 24 (a) D. V. Azamat, A. Dejneka, J. Lančok, L. Jastrabik, V. A. Trepakov, Z. Bryknar, E. V. Neverova and A. G. Badalyan, *J. Appl. Phys.*, 2013, **113**, 174106; (b) J. E. Huheey, E. A. Keiter, R. L. Keiter and O. K. Medhi, *Inorganic Chemistry: Principles of Structure and Reactivity*, Pearson Education, 2006; (c) N. Y. Garces, N. C. Giles, L. E. Halliburton, K. Nagashio, R. S. Feigelson and P. G. Schunemann, *J. Appl. Phys.*, 2003, **94**, 75677570; (d) A. G. Avanesov, V. V. Badikov and G. S. Shakurov, *Solid State Phys.*, 2003, **45**, 1451–1454; (e) J. Telser, L. A. Pardi, J. Krzystek and L.-C. Brunel, *Inorg. Chem.*, 1998, **37**, 5769–5775; (f) D. Himmelbauer, B. Stöger, L. F. Veiros, M. Pignitter and K. Kirchner, *Organometallics*, 2019, **38**, 4669–4678.
- 25 CCDC 2310415: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2hk5js](https://doi.org/10.5517/ccdc.csd.cc2hk5js).