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Chromium Catalyzed Transfer Hydrogenation of CO_2 to Formate Using Isopropanol Under Ambient Pressure

Research Article based on this study:
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3.1 Introduction

The surge in fossil fuel consumption to meet world's energy demand is currently a menace to the globe owing to their limited availability and a large amount of greenhouse gases release into the atmosphere causing 'Global warming'.[13-15] In this context, the effect of major greenhouse gas carbon dioxide on climate change is indisputable seeking global awareness.[18] The atmospheric level of CO_2 exceeded a value of 400 ppm since industrial revolution because of human activities.[17] Hence there is a compelling need to look for alternative sustainable energy sources and mitigate the anthropogenic CO_2 emission. In fact, the urge to curb the carbon footprint in the biosphere advocates research strives to explore viable technologies for carbon capture, storage, and utilization.[19-22,273] CO_2 being abundant, nontoxic, cheap C1 feedstock, constitutes a sustainable and cost-effective raw material for chemical transformations[28,35] and offers potential as valuable surrogate to commercially applied hazardous chemicals like CO and phosgene.[23] Additionally, exploration of CO_2 as renewable feedstock to acquire value-added chemicals and hydrogen storage materials lay the foundation for an effective circular economic model.[24-25]

In this regard catalytic CO_2 reduction has emerged as an attractive protocol for the synthetic community.[29-33,34,36] In particular, catalytic hydrogenation of CO_2 has received considerable attention on account of atom-economy and eco-friendly process.[13] However, this strategy relies on H_2 production from industrial reforming of non-renewable natural gas. Research endeavours to supply the necessary hydrogen for CO_2 reduction from renewable sources such as solar energy driven water splitting or renewable biomass are being made to address the goal of 'carbon neutrality'.[43,274-277] Nevertheless, the requirement of high pressurized CO_2 and flammable H_2 gases poses challenges demanding specialized set up, thus making the overall process cumbersome, and invokes safety issues. In recent years' efforts directed towards ambient/low pressure CO_2 reduction utilizing hydrogen from renewable resources is noteworthy.[278-281] In this regard, espousal of 'transfer hydrogenation' strategy[135-138] employing readily accessible biomass derived feedstock alcohols as hydrogen source is gaining momentum.[139-142]

The catalytic transfer hydrogenation of CO_2 to formic acid/formate is appealing not only for its versatile application in chemical industry but also as potential renewable hydrogen storage material.[143-145] While hydrogenation of CO_2 to formic acid/formate has been extensively marked by homogeneous catalysts under high pressure of H_2 and CO_2[37-39,49,77,86,87,94,102,111,112,116,117,121,122,126,133,202,204,205,219], only a handful of transition metal complexes appeared in literatures for transfer hydrogenation of CO_2 to formate.[146-154] Peris and co-workers reported transfer hydrogenation of CO_2 using iridium and ruthenium-based N-heterocyclic carbene complexes (Figure 3.1) and isopropanol as hydrogen source under harsh reaction conditions (200 ^oC and 50 bar CO_2) achieving a formate TON of upto 874.[146,147] Subsequently

water soluble Ir-carbene complexes catalyzed CO_2 transfer hydrogenation was also reported by them.[148] Aresta et al. demonstrated stoichiometric reduction of CO_2 mediated by Ru-complex(Figure 3.1) using aqueous glycerol as hydrogen source.[149] Beller described an excellent catalytic CO_2-transfer hydrogenation route with methanol as hydrogen donor under low 5 bar CO_2 pressure using Ru-macho complex.[150] Voutchkova-Kostal group used glycerol as hydrogen surrogate for executing transfer hydrogenation of CO_2 using water soluble Ru-NHC complex and recorded formate TON of 1065.[151] Chaudhary in 2019 disclosed the transfer hydrogenation of CO_2 under milder pressure of 1 bar and documented a formate TOF of 90 h^{-1} using iridium aNHC complex.[152] Later on, Ikariya revealed CO_2 transfer hydrogenation at 80 °C under 1 bar gaseous pressure exploiting Ir(III)Cp^* as catalyst and attained a TON of 655 in carbon dioxide transfer hydrogenation using aqueous isopropanol. Jang and coworkers demonstrated Ir-NHC based complex catalyzed CO_2 transfer hydrogenation and a very high TOF of 10000 h^{-1} was reported at 200 ^oC.[153] In 2022 a comprehensive review by Choudhury compiled the developments of CO_2 transfer hydrogenation reactions.[154]

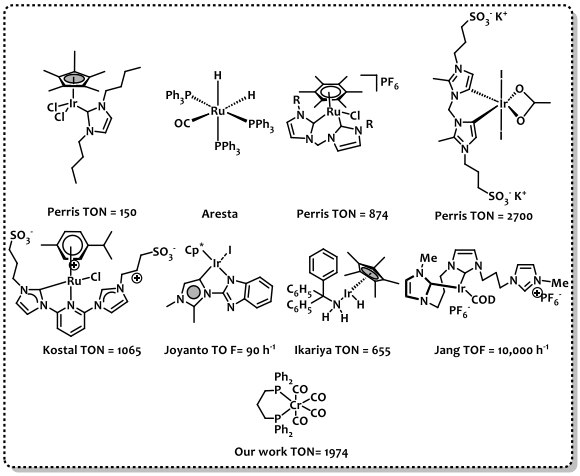


Fig. 3.1 Selected Catalysts for CO_2 transfer hydrogenation to formate.

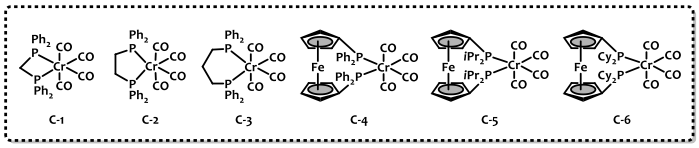


Fig. 3.2 Chromium complexes tested for CO_2 transfer hydrogenation.

Nonetheless, aforesaid reports primarily utilized high pressure of CO_2 (except reports by Choudhury and Ikariya) and exploitation of precious noble metal catalysts suffering from high-cost, availability, and toxicity issues. Hence, the development of efficient and robust homogeneous earth-abundant catalysts for the CO_2-transfer hydrogenation process working under ambient pressure is highly desirable. Research efforts to investigate economical, less noxious and abundant 3d transition metal complexes in the realm of homogeneous catalysis has garnered significant attention among the scientists over the years and remarkable progress has already been made.[50-53,56] Exploring low-valent chromium in this context is equally appealing on account of its biocompatibility and earth abundance.[182] Reports including dehydrogenative coupling of alcohols and amines, N-alkylation of amines, β-alkylation of secondary alcohols are recently documented by Kempe, and others.[222-226] Catalytic homogeneous hydrogenation reactions using Cr complexes were established to carry out hydrogenation of ketones, aldehyde, polycyclic aromatics and semi-hydrogenation of alkynes.[228-232] Chromium complexes are also known to catalyze transfer hydrogenation reactions of ketones and aldehydes.[282] Lately Topf and co-workers studied the transfer hydrogenation of aldehyde and ketones by applying $Cr(CO)_6$ as catalyst.[268] In 1984 Darensbourg observed CO_2 hydrogenation using hydridocarbonyl

complex of chromium as catalyst, and alkyl formate was obtained with a low TON of 14.[128] Recently we discovered efficient Cr catalyzed hydrogenation of CO_2 to formate in THF/H_2O mixture under 30 bar H_2 pressure.[134] Encouraged by these pioneering low-valent chromium carbonyl complexes on transfer hydrogenation and CO_2 hydrogenation reactions, we were instigated to probe diphosphine ligands supported Cr complexes in CO_2 transfer hydrogenation reactions. To the best of our knowledge there are no reports on CO_2 transfer hydrogenation to formate using non-noble 3d metals thus far.

3.2 Results and Discussion

Our study commenced by evaluating the catalytic efficiency of various diphosphine-based low-valent tetracarbonyl chromium complexes (Figure 3.2, **C-1 - C-6**) with varied bite-angles. Complexes **C-1** to **C-6** were synthesized by following the literature protocols.[236,237,210] Initially 2.6 μmol of DPPM-based **C-1** was screened for CO_2 transfer hydrogenation in the presence of 20 mmol NaOH at 130 °C in THF/H_2O (1:10) solvent mixture and 2 ml isopropanol as hydrogen source (DPPM=1,1Bis(diphenylphosphino)methane, β_n=72°), affording a TON of 28 (Table 3.1, entry 1). Taking 1.7 μmol Cr(DPPE)$(CO)_4$ (DPPE=1,2-Bis(diphenylphosphino)ethane, β_n=85°) **C-2** as catalyst yielded formate with a TON of 7.5 (Table 3.1, entry 2). Excitingly, DPPP (1,3-Bis(diphenylphosphino)propane, β_n=91°) anchored complex Cr(DPPP)$(CO)_4$ (0.43 μmol, **C-3**) catalyzed CO_2 transfer hydrogenation furnishing formate with a maximum TON of 1974 (Table 3.1, entry 3). However, Cr(DPPF)$(CO)_4$ **C-4**, (DPPF = 1,1′-Bis(diphenylphosphino)ferrocene, 1.8 μmol, , β_n = 96°) gave trace amount of formate (Table 3.1, entry 4). As anticipated, no formate was detected upon carrying out the reaction without any catalyst (Table 3.1, entry 5). Cr(DiPPF)$(CO)_4$ **C-5** (1.63μmol, β_n=103.6° DiPPF = 1,1′-Bis(diisopropylphosphino)ferrocene) and Cr(DCPF)$(CO)_4$ (1.27 μmol, β_n=102.4° DCPF = 1,1′-Bis(dicyclohexylphosphino)ferrocene) **C-6** were also probed as catalysts. **C-5** didn't exhibit any catalytic activity and product was obtained in trace amount (Table 3.1, entry 6) while TON of 43 was recorded in case of **C-6** (Table 3.1, entry 7). **C-3** turned out to be the most active catalyst among various employed catalysts, suggesting crucial role of phosphine substituent and bite angles of the ligands.

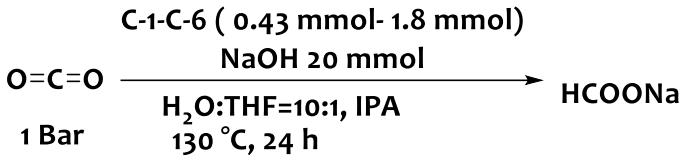
With the most efficient catalyst in hand, base optimization was carried out in order to get optimum catalytic activities. To our surprise trace amount of formate was obtained using Na_2CO_3, K_3PO_4 and ^{t}BuOK as bases (Table 3.1, entries 8-10). Using DBU as base resulted in formate formation with a TON of 41 (Table 3.1, entry 11). Screening Et_3N as base under optimum conditions yielded formate with a TON of 53 (Table 3.1, entry 12). Performing reaction in presence of KOH as base could not help in improving the TON and furnished a formate TON of 12 (Table 3.1, entry 13). Afterwards, screening of various other hydride donor molecules was carried out. To our delight, methanol can also be used as hydride source although formate was produced with a TON of 83 (Table 3.1, entry 14). Likewise, ethanol and 1,4 butanediol were also tested and formate TONs of 65 and 149 were recorded, respectively (Table 3.1, entries 15-16). Hydrazine hydrate furnished formate with a TON of 412 (Table 3.1, entry 17). The reaction worked comparatively better by taking glycerol as hydride surrogate TON of 1495 was attained in this case (Table 3.1, entry 18). Trace amount of formate was obtained when the reaction was performed in the absence of hydride donors (Table 3.1, entry 19).

Next, we performed the reaction in neat isopropanol, which resulted in formate formation with a TON of 119 (Table 3.1, entry 20) indicating the important role of solvent combination in the transfer hydrogenation reaction. Executing reaction in only water as solvent under optimum conditions provided a TON of 18 (Table 3.1, entry 21) We have also performed the transfer hydrogenation reaction in the presence of 0.1 mmol Me_3NO under optimum conditions giving a TON of 180 for the formate formation (Table 3.1, entry 22). The reaction also worked under lower basic conditions, and formate TON of 30 was recorded using 2mmol NaOH as base under optimum conditions (Table 3.1, entry 23). Increasing the reaction temperature to 150 °C, resulted in decrease of formate TON to 1700 (Table 3.1, entry 24)

probably due to catalyst decomposition at higher temperature. The formate TON increased to 2231 (Table 3.1, entry 25) upon utilizing 5 bar CO_2 pressure. So, the yield upto 4.8% and TON of 2231 was achieved in the transfer hydrogenation reaction prompted by the recent reports[18,26,27] on transfer hydrogenation of various bicarbonate and carbonates using iridium complexes, we were also interested to test the activity of **C-3** in sodium bicarbonate transfer hydrogenation. A loading of 1.7 μmol **C-3** in conjunction with 2.5 mmol NaOH, taking isopropanol as hydride source at 130 °C in THF/H_2O mixture converted sodium bicarbonate to sodium formate with only 13% yield after 36 h. **C-3** was also examined in the transfer-hydrogenation of ammonium carbonate and potassium carbonate. 1.7 μmol **C-3** in the presence of 2.5 mmol NaOH, and isopropanol at 130 °C in THF/H_2O mixture converted the carbonates to respective ammonium formate and potassium formate with 6% and 7% yields.

To understand the mechanism of the transfer hydrogen reaction of CO_2 catalyzed by Cr complexes, several stoichiometric experiments have been performed. Heating a solution of **C-3** in THF overnight at 130 ^oC did not reveal any changes in the ^{31}P NMR and IR spectra. However, when **C-3** was heated with 5 eq. NaOH in THF under analogous reaction condition, an orange solution was observed after 3 h. The reaction mixture displayed a new peak at 10.9 ppm in the ^1H NMR spectrum (Figure 3.3.2). A new signal at 32 ppm in the ^{31}P NMR was also observed. The newly formed complex was assigned as the metallacarboxylate **C-3a** (Scheme 3.1).[134,215-216]

Table3.1 Chromium catalyzed CO_2 transfer hydrogenation to formate.[a]



Entry	Base	Catalyst	Hydride donor	Solvent	TON[b,c]
1	NaOH	C-1	^{i}PrOH	THF:H_2O	28
2	NaOH	C-2	^{i}PrOH	THF:H_2O	7.5
3	NaOH	C-3	^{i}PrOH	THF:H_2O	1974
4	NaOH	C-4	^{i}PrOH	THF:H_2O	Trace
5	NaOH	-	^{i}PrOH	THF:H_2O	Trace
6	NaOH	C-5	^{i}PrOH	THF:H_2O	Trace
7	NaOH	C-6	^{i}PrOH	THF:H_2O	43
8	Na_2CO_3	C-3	^{i}PrOH	THF:H_2O	Trace
9	K_3PO_4	C-3	^{i}PrOH	THF:H_2O	Trace
10	^{t}BuOK	C-3	^{i}PrOH	THF:H_2O	Trace
11	DBU	C-3	^{i}PrOH	THF:H_2O	41
12	Et_3N	C-3	^{i}PrOH	THF:H_2O	53

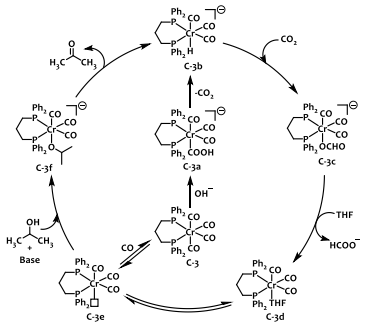
13	KOH	C-3	^{i}PrOH	THF:H_2O	12
14	NaOH	C-3	MeOH	THF:H_2O	83
15	NaOH	C-3	EtOH	THF:H_2O	65
16	NaOH	C-3	1,4BuOH	THF:H_2O	149
17	NaOH	C-3	$NH_2.NH_2$	THF:H_2O	412
18	NaOH	C-3	Glycerol	THF:H_2O	1495
19	NaOH	C-3	-	THF:H_2O	Trace
20	NaOH	C-3	^{i}PrOH	IPA	119
21	NaOH	C-3	^{i}PrOH	H_2O	18
22[d]	NaOH	C-3	^{i}PrOH	THF:H_2O	180
23[e]	NaOH	C-3	^{i}PrOH	THF:H_2O	30
24[f]	NaOH	C-3	^{i}PrOH	THF:H_2O	1700
25[g]	NaOH	C-3	^{i}PrOH	THF:H_2O	2231

[a]Reaction conditions: Unless and otherwise stated 130 °C, 1 bar CO_2, 24 h, ^{i}PrOH 2ml as hydrogen source, 20 mmol NaOH in 3ml water, certain mmol catalyst. [b]Yield based on ^{1}H NMR signals of sodium formate, with DMF used as an internal standard. [c]Turnover number = moles of sodium formate per mole of catalyst.[d] 0.1 mmol Me_3NO was used.[e] 2 mmol NaOH was used.[f] reaction was carried out at 150 °C.[g] 5 Bar CO_2 was used.

^{1}H NMR shift in the similar region for the hydroxycarbonyl ligand of related Ir and Pt complexes have been reported.[216] We have previously reported that we could not Hydride complex **C-3b** (Scheme 3.1) probably owing to conversion of C-3a to formate C-3c or poor solubility in $CHCl_3$ under the reaction conditions.[134] To our delight, weakly intense signal at -2.36 ppm with a $^{2}J_{PH}$ coupling constant of 45 Hz in ^{1}H NMR has been identified in DMSO d-6 corresponding to the hydride ligand of complex **C-3b** formed via decarboxylation of C-3a (Figure 3.3.3.), This observation is in accord with related reported molybdenum hydride complexes.[45] Carboxylate in DMSO d-6 cannot detected in DMSO d-6 probably due to exchange. Both hydride and carboxylate were detected together using HRMS spectrometry. Furthermore, after careful examination of IR data taken of reaction performed using 5 eq. NaOH after 3 hours we found that a weak signal at 1567 cm-1 merged with C=C stretching of dppp ligand was detected as hydride signal which was in sync with the simulated IR data. Further heating the reaction resulted in formate **C-3c** formation as confirmed from ^{1}H NMR spectrum (Figure 3.3.7). When the reaction was conducted in neat isopropanol in the presence of 5 eq. NaOH formate complex was detected in the ^{1}H NMR spectrum. Interestingly, in this case also we could identify very weak triplet signals at -1.74 (J=5 HZ) and -1.95 ppm (J=10 HZ) in the hydride region of the ^{1}H NMR spectrum. However, the coupling constants and slight downfield shift of the signals are not in accord with the hydride complex **C-3b**, generated via addition of NaOH to **C-3** in THF. However, this cannot exclude the formation of a in situ hydride species of type **C-3b** as solvent dependent changes in the hydridic nature of complexes has been well established.[126] In an alternative pathway we have also tried to regenerate the hydride species by performing the stochiometric reaction with **C-3** and

sodium isopropoxide. Unfortunately, we could not detect any isopropoxide complex nor the hydride complex in this case.

. However, catalyst decomposition was also observed in this case, indicating crucial role of THF in stabilizing the complex. We have also performed the stochiometric reaction with NaOD also, heating the **C-3** with 5 eq. NaOD at 130 °C after 24 h yielded a mixture of peaks at 10.06 ppm and 8.24ppm in ^{2}H NMR confirming the formation of carboxylate and formate-D species (Figure 3.3.11) Based on our experimental findings and literature precedents,[128,134,127,285,217-218] we proposed a mechanism as illustrated in Scheme 3.1. Initially a metallacarboxylate species **C-3a** is formed[127,285] through the nucleophilic attack of NaOH. Decarboxylation of **C-3a** leads to the formation of hydride complex **C-3b**, which is considered as the active species for catalytic cycle. Subsequent CO_2 insertion into the **C-3b** resulted in the formation of formato complex **C-3c**. Release of formate product with THF coordination generates **C-3d**. Complex C-3d is converted to isopropoxide coordinated complex **C-3f** in the presence of iPrOH and base via an unsaturated 16 e$^-$ species **C-3e**. Concomitant β-hydride elimination from **C-3e** regenerates the active hydride complex C-3b and closes the catalytic cycle. Alternatively, formation of an unsaturated complex **C-3e** via CO elimination followed by formation of **C-3f** cannot be excluded.[217-218]



Scheme 3.1 Proposed mechanism for C-3 catalyzed CO_2 transfer hydrogenation.

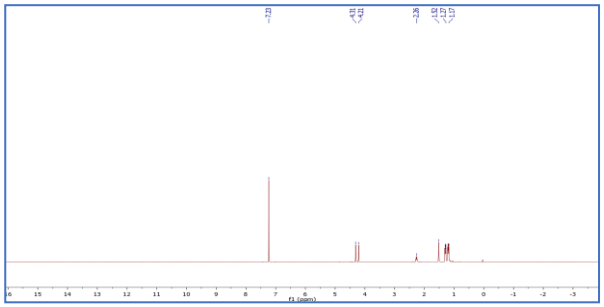
3.3 Experimental Section

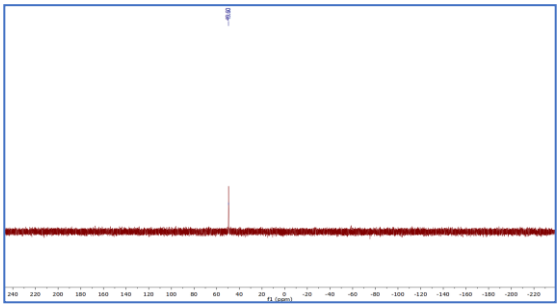
The complexes **C-1** to **C-6** were synthesized by charging the Schlenk flask with $Cr(CO)_6$ and toluene solution of respective phosphine based ligands in equimolar ratio inside the glove box. Reaction mixture was heated at 120 °C for 48 hours. Afterwards, reaction was stopped, cooled and solvent was dried under vacuum, solid powder thus obtain was characterized and the obtained data was as par with the reported data.[210,236-237] The experimental data of **C-1** to **C-5** has been added already in the chapter 2(b) in sections 2(b).3.1 to 2(b).3.4 and 2(b).3.8.

3.3.1 Representative Characterization Data for Complex C-6

$CrDCPF(CO)_4$ (**C-6**)
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.31 (4H), 4.21 (4H), 2.26 (4H), 1.52 (4H), 1.27 m(20H), 1.17 m (16H).
^{31}P{^{1}H}-NMR (203.0 MHz, $CDCl_3$) δ 49.60 (2P).

(a)

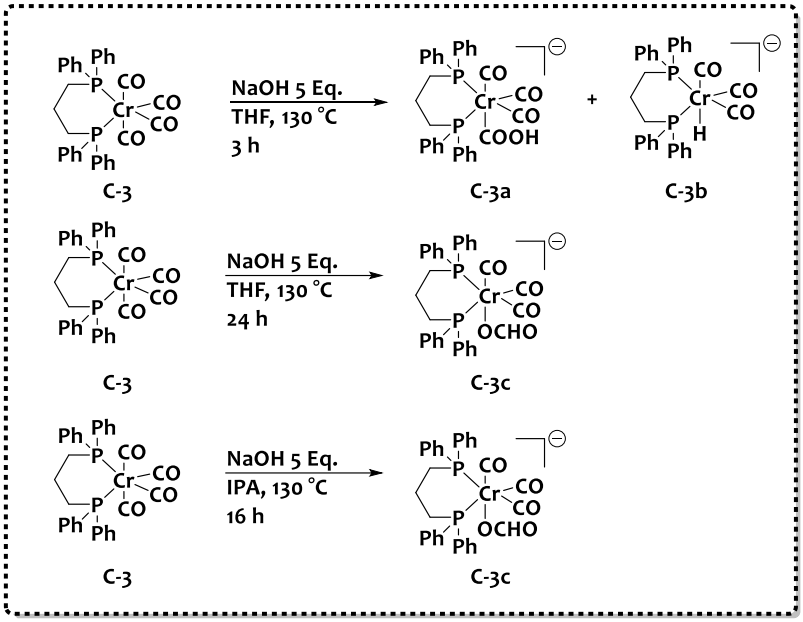




(b)

Fig. 3.3.1 (a) ^{1}H NMR Spectrum, **(b)** ^{31}P Spectrum for **C-6** complex.

3.2.2 Mechanistic Experiments



Scheme 3.2 Scheme for mechanistic experiments.

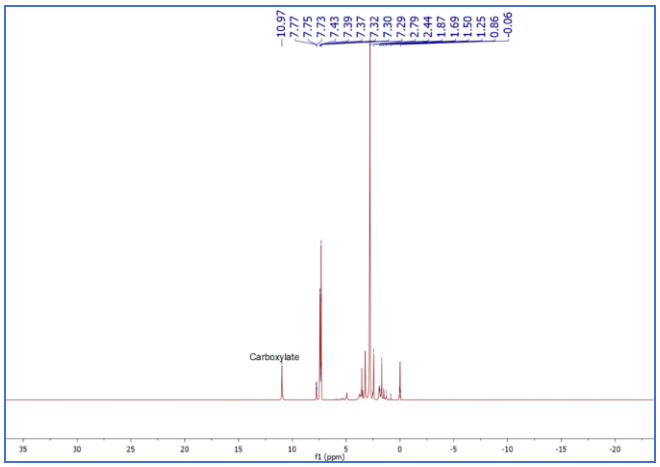


Fig. 3.3.2 ^{1}H NMR after 3 h of **C-3** heating in presence of 5 eq. NaOH in THF analyzed in THF-d_8.

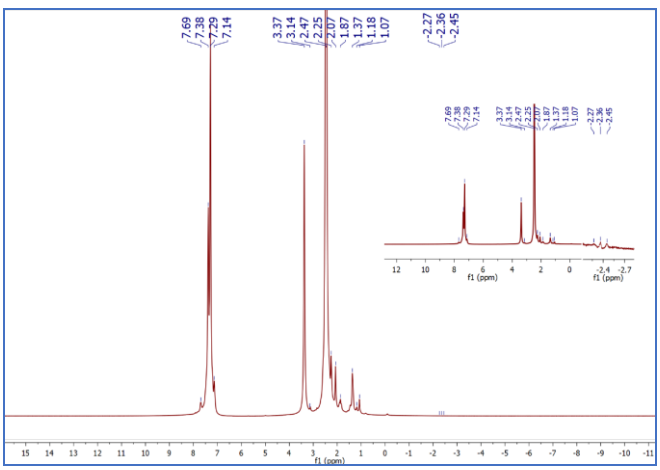


Fig. 3.3.3 ^{1}H NMR spectra after 3 h of **C-3** heating in presence of 5 eq. NaOH in THF analyzed in DMSO-d_6.

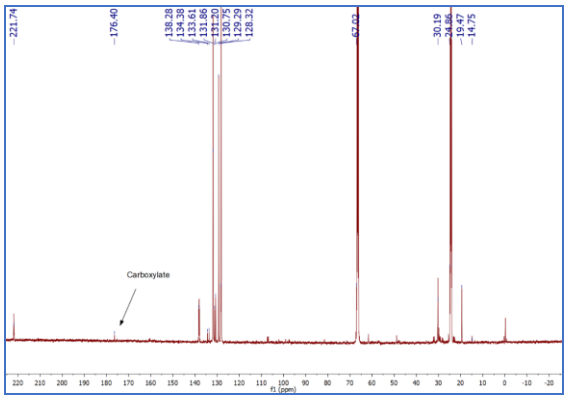


Fig. 3.3.4 ^{13}C NMR spectra after 3 h of heating of C-3 in presence of 5 eq. NaOH in THF analyzed in THF-d_8.

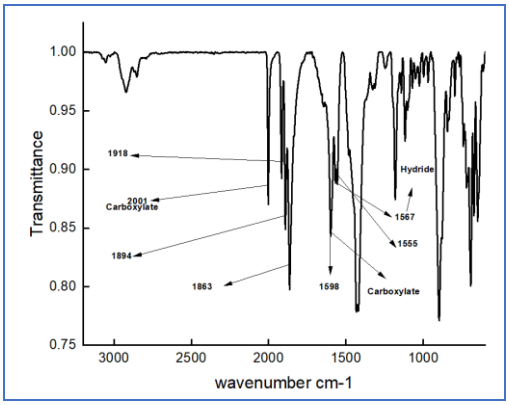


Fig. 3.3.5 IR spectra after 3 h of heating in the presence of 5 eq. NaOH in THF.

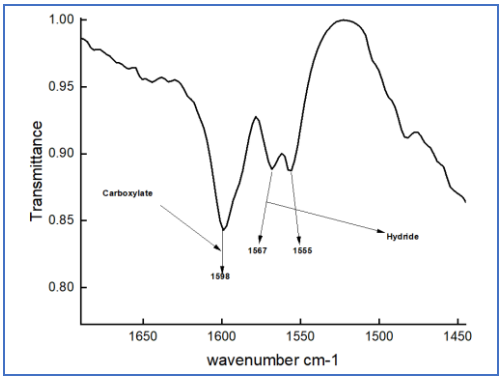


Fig. 3.3.6 Zoomed IR spectra after 3 h of heating in presence of 5 eq. NaOH in THF.

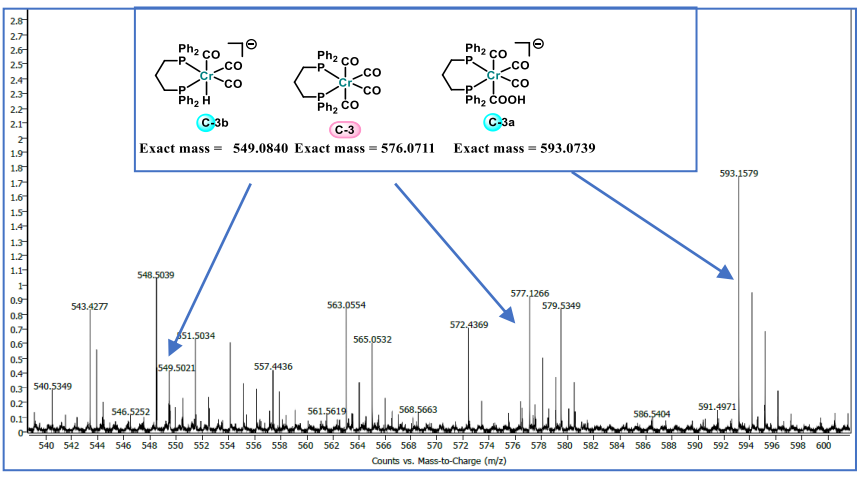


Fig. 3.3.7 HRMS data of the reaction mixture taken after 3 h of heating in presence of 5 eq. NaOH in THF.

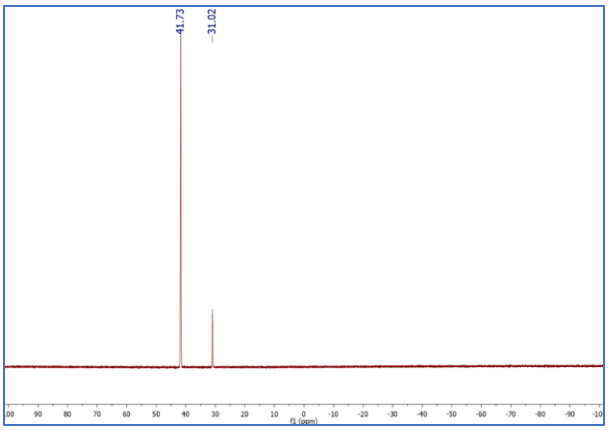


Fig. 3.3.8 ^{31}PNMR of reaction mixture heated for 3 h in presence of 5 eq. NaOH in THF-d_8.

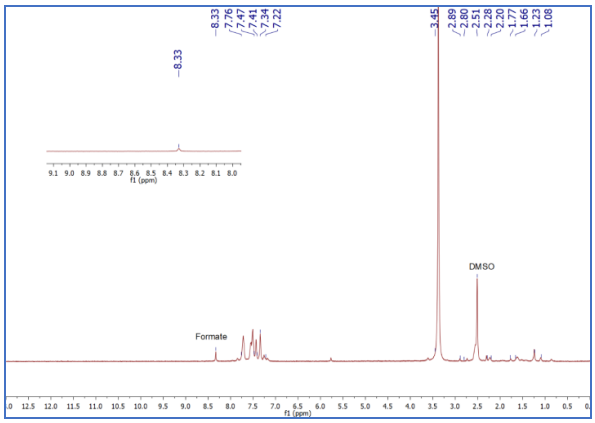


Fig. 3.3.9 ^{1}H NMR of **C-3** reaction mixture heated for 24 h in THF.

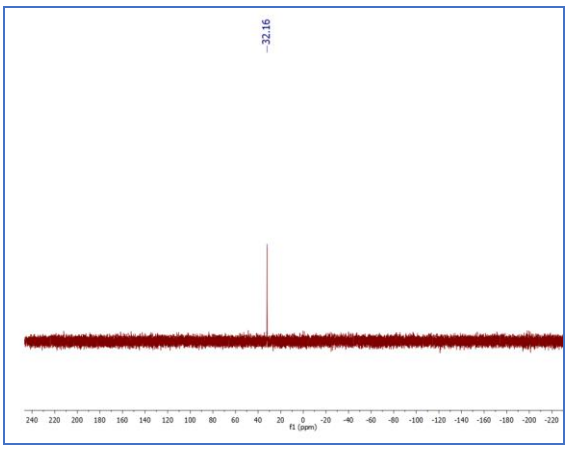


Fig.3.3.10 ^{31}P NMR of the **C-3** reaction mixture heated for 24 h in THF.

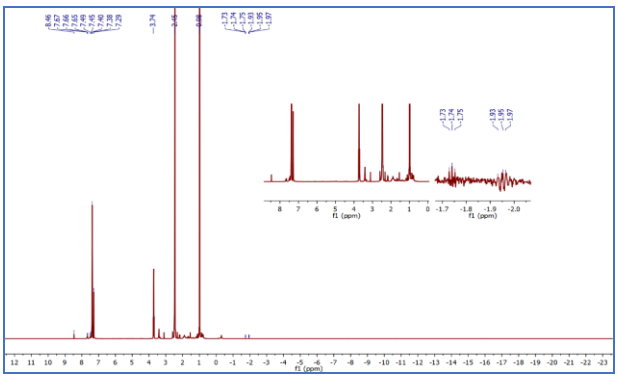


Fig.3.3.11 ^{1}H NMR spectra of **C-3** reaction mixture heated for 16 h in IPA.

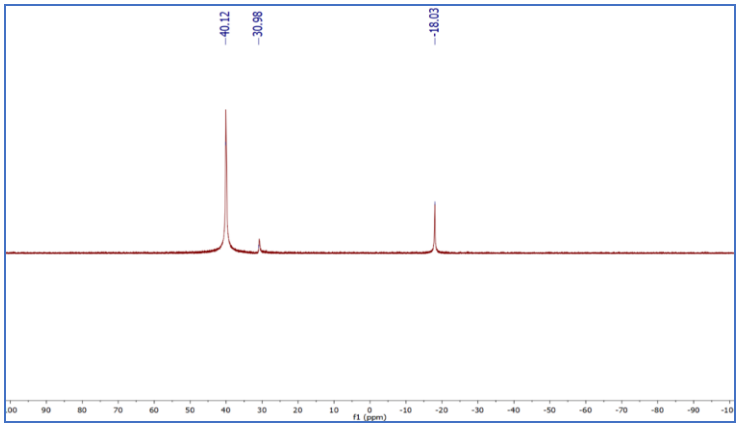


Fig.3.3.12 ^{31}P NMR spectra of **C-3** reaction mixture heated for 16 h in IPA.

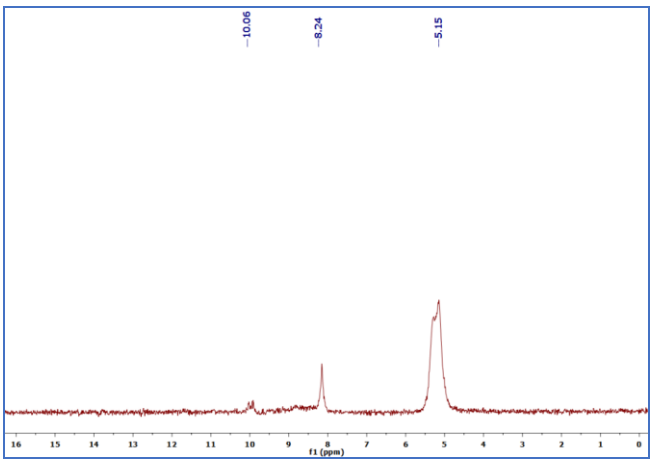


Fig.3.3.13 ^{2}H NMR of C-3 reaction mixture heated for 24 h in THF in presence of 5 eq. NaOD in D_2O solution at 130 °C.

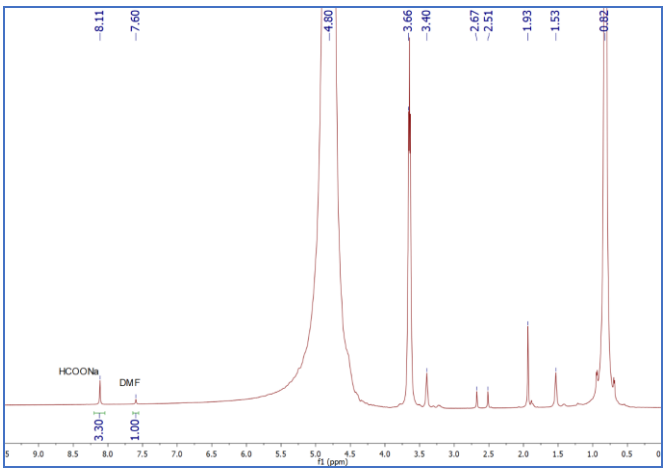


Fig.3.3.14 Representative ^{1}H NMR for Cr catalyzed transfer hydrogenation of CO_2 to formate.

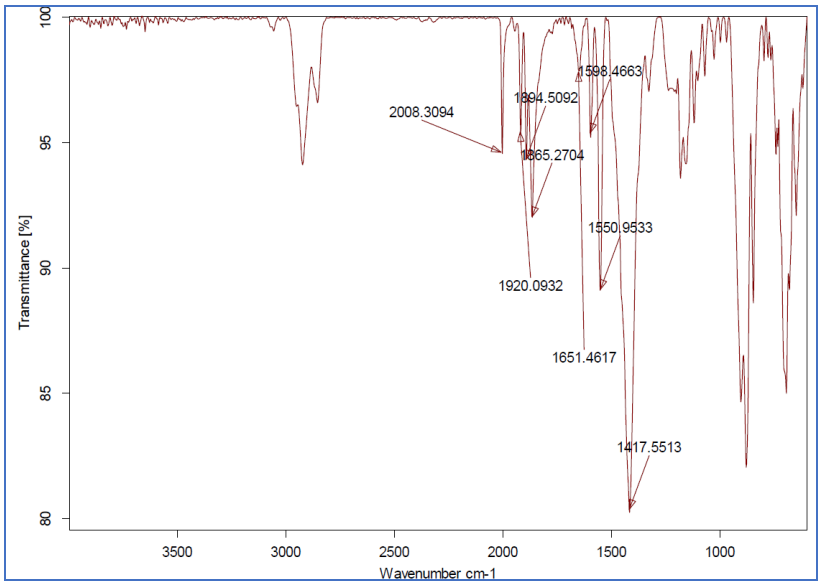


Fig.3.3.15 IR spectra of **C-3** reaction mixture heated for 24 h in THF.