1
Introduction

Transition metal complexes serve as catalysts in pivotal chemical transformations, including hydrogenation, oxidation, and polymerization reactions, facilitating the efficient synthesis of essential chemicals, fuels, and materials. Furthermore, their contribution extends to the development of superconductors, semiconductors, and magnetic materials, underpinning modern technological innovations. Biologically, transition metal ions, such as iron in oxygen transport and cobalt in enzymatic co-factors, are fundamental to life processes.[1-2]

Owing to their unparalleled chemical versatility, researchers are developing myriad transition metal complexes to address global problems like elevated carbon dioxide levels in the atmosphere, antimicrobial resistance caused by bacteria, etc., as an effective solution. Tremendous research endeavours directed towards the synthesis of novel organometallic complexes with meticulous ligand design have unveiled novel pathways in homogeneous catalysis for carbon dioxide hydrogenation to value-added products like formic acid/ formate, methanol and potential antibacterial agents. The major contribution came from the conventional precious noble metals for decades. The dominance of these metals stems from their efficiency, predictable two-electron redox processes and stability under a variety of conditions.[3-8]

The soaring demand, high-cost and potential toxicity for noble metal precursors triggered a growing interest towards their replacement with abundant, non-noble metal complexes. In this regard, much attention has been paid to the development of complexes derived from earth-abundant base metals (iron, cobalt, manganese, nickel) because of their lower cost, easy-availability, and often low-toxicity.[9-12] Here in this section we will discuss carbon dioxide hydrogenation to formic acid/formate with a particular emphasis on reports using 3d metal complexes, along with group VI metals Cr, Mo and W. We will also take a brief overview of the biological application of transition metals focusing mainly on 3d metal complexes.

1.1 Carbon Dioxide: General Introduction

CO_2 constitutes one of the major greenhouse gases resulting from fossil fuel combustion among various other sources like destruction of biomass. The atmospheric level of CO_2 has reached a value of more than 400 ppm in comparison to 280 ppm at the beginning of industrial revolution because of human activities.[13-17] The effect of CO_2 on climate change is irrefutable and has garnered worldwide attention owing to abnormal environmental changes, such as raising in the temperature of our climatic system, rise in sea-level, and unusual weather conditions.[18] To circumvent these environmental issues, the scientific community and chemical industries have realised an impelling need of the following steps: pursuit of sustainable energy sources and alternative fuels to meet the world's growing energy need, search for sustainable supply of raw materials, mitigating the anthropogenic CO_2 emission.

In fact, the urge to alleviate carbon footprint in the biosphere has prompted great endeavours to explore viable technologies. Many efforts have been planned and implemented to reduce the level of CO_2, such as by capturing it and storing in deep sedimentary reservoirs

(Carbon Capture and Storage, CCS). Carbon Capture and Utilization (CCU) offers huge potential to exploit CO_2 as a feedstock for chemical transformations although the issue of global warming cannot be tackled by only chemical use of carbon dioxide.[19-22] Nonetheless, in the context of ''sustainability'' CO_2 is a highly attractive renewable raw material as it is abundant, nontoxic, cheap and valuable C1 replacement to industrially applied hazardous chemicals like phosgene and CO etc.[23] Moreover, the use of CO_2 as renewable feedstock to produce valuable chemicals and energy carriers also paves the way for an effective circular economic model.[24-25]

The necessary energy for CO_2 transformation can be harnessed from renewable sources like solar energy leading to an overall carbon neutral cycle and successful renewable energy storage. It is surprising to note that utilization of CO_2 as C1 source in current laboratory and industrial practices is confined to certain organic compounds namely urea, salicylic acid, and cyclic carbonates.[26-28] On account of thermodynamic stability and kinetic inertness of CO_2 it is difficult to activate and thus limits its use in an extensive manner. Large energy input is necessary to transform CO_2 to other chemicals because of the completely oxidized form of the carbon atom in the CO_2 molecule and the energy consumption increases with a decrease in the carbon oxidation state in the product. Despite this, tremendous research efforts in the last years have been directed towards carbon dioxide valorisation and manifested in numerous excellent reviews.[29-33] Remarkably, the achievement in this area is made possible particularly by use of 'catalyst' that can overcome the kinetic barrier of CO_2 in most cases.

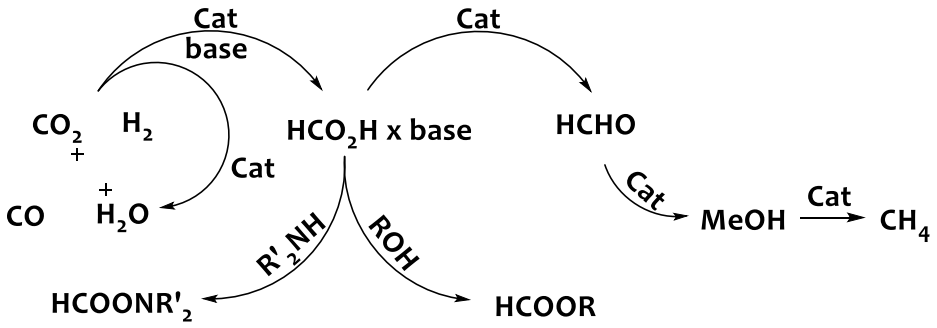
Catalytic CO_2 reduction to synthesize value-added chemicals and alternative fuels has emerged as an attractive protocol for the synthetic community as inter alia it also has the potential in exploring green and renewable energy as fossil fuels surrogate.[34-36] While in nature CO_2 is consumed and reduced during photosynthesis process, artificially borohydride reagents, hydrosilane, and molecular hydrogen can be used for the reduction of CO_2. Conventional reduction reactions with the use of reactive metal-hydride reagents in stoichiometric amounts are associated with painstaking procedures yielding noxious waste materials. Lately, catalytic hydrogenation, hydroboration, hydrosilylation, reactions of CO_2 have been developed.[38-42]

1.2 CO_2 Hydrogenation

Catalytic reduction of CO_2 using molecular hydrogen (hydrogenation) is an atom-economic, environmentally benign, and sustainable synthetic process; hydrogen can be obtained from renewable resources, such as solar energy driven water splitting.[43-44] Elegant reviews in this area of catalytic hydrogenation have been published by Noyori,[38] Jessop,[39] Leitner,[45] Beller,[46] and others,[47-49] using either homogeneous or heterogeneous catalysts. Hydrogenation of CO_2 can lead to formation of formic acid, carbon monoxide, methanol, and/or methane, which are all entropically disfavoured compared to CO_2 and H_2 (Scheme 1.1). Hence designing a suitable catalyst that enables selective synthesis of either of the products is highly appealing.

In the context of selectivity and designing of catalysts, 'homogeneous-catalysis' can play pivotal roles. Homogeneous catalysed reactions quite often operate under milder condition, resulting in better selectivity. Also, in solution experimental mechanistic understanding may give the notion to choose appropriate ligand-based complexes in executing the targeted task.
In fact, development on homogeneous CO_2 hydrogenation using well-defined transition metal-based complexes is noteworthy.[38,45,46] However, noble-metal based catalysts are still prevalent in this domain. There are several drawbacks associated with these metal complexes such as high cost, low earth-abundance and toxicity that limit their use, particularly in pharmaceutical industries. Hence in the pursuit of sustainability, utilization of earth-abundant, low-toxicity, non-precious 1st row transition metal-based complexes are of utmost importance.
Indeed, past few years have witnessed significant progress towards the exploitation of first-row transition metals in homogeneous catalysis.[50-57] Furthermore, 3d transition metals prefer one electron redox process in contrast to noble metals that undergo two electrons redox process.[57]

Hence shifting to base-metal catalysts also offers possibility for novel catalytic transformations, new catalytic selectivity, and even enhanced performance in comparison with expensive metal catalysts. Several reviews on CO_2 hydrogenation catalysed by complexes of first row transition metals have appeared in literatures.[58-59] Our group has summarised base metal catalysed *N*-formylation reaction using CO_2 and amines in the presence of H_2.[60]



Scheme 1.1 Possible CO_2 hydrogenation products.

Among various products obtained via hydrogenation of CO_2 (Scheme 1.1), methanol and formic acid are of significant interest because besides their utilization as chemical precursors, they can be used directly as fuels or to generate H_2 on demand at low temperatures, making them attractive hydrogen carriers.[61-63] They have high volumetric energy densities and are easily transportable, unlike hydrogen. To explore CO_2 as a C1 synthon towards formic acid and methanol products is also relevant to circular chemistry.

1.2.1 Hydrogenation of CO_2 and Bicarbonate to Formates

Formic acid is an essential chemical used in the leather and textile industries for tanning and dyeing, silage production, reducing agent in synthetic industries, and in pharmaceuticals. Formic acid is also employed as a coagulating agent in the production of latex rubber, electroplating of various materials, and for the production of resins, varnishes, plasticizers, and glass.[64] Lately formic acid (FA) has drawn considerable attention as a potential renewable hydrogen storage material because of various advantages. FA is a kinetically stable liquid at room temperature, has low toxicity, can be handled and stored easily. Though theoretical hydrogen storage capacity of FA is 4.4 wt% under ambient conditions, which is lower than the target set by the U.S. Department of Energy for 2020 (5.5 wt%), it is still currently an attractive material among liquid storage and transport media for H_2[65-68] as it produces only H_2 and CO_2 gaseous products, thereby obviating the accumulation of byproducts. Moreover, the dehydrogenation process to produce H_2 and CO_2 is thermodynamically favorable ($\Delta G = -32.9$ kJ/mol) at room temperature. In fact, remarkable attempts have successfully focused on formic acid fuel-cell as a source for public transportation. [69-70]

Worldwide demand for formic acid is growing rapidly with a production of more than 500 thousand tons' per annum at present. It is produced on a large scale by the chemical industry as well as by biomass fermentation.[71] The most widely used commercial method of producing formic acid is based on the carbonylation of methanol with carbon monoxide to methyl formate followed by hydration of the ester with water. The homogeneous hydrogenation of CO_2 to formic acid is as an attractive, sustainable, atom efficient protocol compared to existing routes as well as from the perspective of closed-cycle economy. Although the reaction of CO_2 and H_2 is exothermic in the 'gas phase' ($\Delta H_0 = -31.5$ kJ mol^{-1}), it is an endergonic process ($\Delta G°_{298} = +32.8$ kJ mol^{-1}) because of the unfavorable entropy conditions.

There are several strategies that have been adopted to surmount the thermodynamic barrier for the hydrogenation of CO_2 to HCOOH such as use of a stoichiometric base to stabilize HCOOH as a formate salt improving the enthalpy of CO_2 hydrogenation. However, the added

base has to be removed from the resultant adducts and the formation of large amounts of salt waste makes the overall operation complex. In this regard, several efforts have also been demonstrated such as hydrogenation of CO_2 under acidic conditions.[72-74] Use of polar solvents like DMSO,[75-76] water, use of ionic liquids, supercritical CO_2 to stabilize the free HCOOH have also been explored.[77-78] This is probably due to hydrogen bonding effecting the entropy of reactants and products. The solvation effect can significantly influence the thermodynamics of the hydrogenation. The hydrogenation reaction is exergonic in the aqueous phase ($\Delta G°_{298} = -4.0$ kJ mol^{-1}) and generally hydroxides, bicarbonates, and carbonates are used for the reaction in water. Thus, despite endergonic nature of this reaction under standard conditions, there are several efficient catalytic systems available enabling high yields of formic acid/formate. The synthesis of formic acid/formate salt by the hydrogenation of CO_2 was first discovered by Farlow and Adkins in 1935 using heterogeneous Raney nickel as the catalyst.[79] Several reviews on heterogeneously catalysed hydrogenation of CO_2 to formic acid have been published.[46,77-80] However, heterogeneous catalytic systems are still in their infancy in terms of the catalytic efficiency and stability in comparison to homogeneous catalysis.

In 1976, Inoue et al. reported the first homogenously catalyzed hydrogenation of carbon dioxide using Group VIII transition metal complexes in combination with trimethylamine and water, under mild conditions.[81] Since then homogeneous hydrogenation of CO_2 to formate or formic acid has attracted increasing attention, and a number of reviews have summarized significant progress in the last two decades.[82-83] The majority of the catalysts described are complexes of noble metals (e.g. Ru, Rh, and Ir). In this section we will discuss the studies on homogeneous catalytic systems for the hydrogenation of CO_2, bicarbonate to formic acid or formate based on first row transition metal complexes Fe, Co, Ni, Cu and Mn. Additionally, we will discuss reports based upon Cr, Mo and W with regards with CO_2 hydrogenation to formate.

1.2.2 Fe-based Catalysts

Seminal studies on the hydrogenation of CO_2 based on non-noble, non-precious iron complex (**C-1**) (Figure 1.1) was reported by the group of Evans and Newell in 1978 without using base in alcoholic solvent resulting in the formation of formate ester. Under the optimised condition (175 °C, 20.7 bar H_2 and CO_2 each in MeOH) the methyl formate was obtained with a turnover number of up to 6 and very low TOF (0.06 h^{-1}) (Table 1.1, entry 1) using complex $[N(PPh_3)_2]^+[HFe_3(CO)_{11}]^-$ (**C-1**).[84] In 2003, Jessop and coworkers described by high-throughput screening that the combination of $FeCl_3$ with 1,2-bisdicyclohexylphosphinoethane(dcpe) (**C-2)**, (Table 1.1, entry 2) generated active catalysts for the reduction of carbon dioxide with a turnover number of 113. The reaction proceeded in the presence 0.5 equivalents of the DBU base in DMSO at 100 bar total pressure of CO_2 and H_2 at 50 °C.[85]

In 2010 Laurenczy and Beller reported reduction of carbon dioxide using an in situ formed iron-based catalyst bearing tetradentate $P(CH_2CH_2PPh_2)_3$ (PP_3) ligand. The $Fe(BF_4)_2 \cdot 6H_2O/PP_3$ (**C-3**) combination yielded methyl formate in the presence of NEt_3 and methanol at 100 °C after 20 h and a maximum TON of 585 was achieved (Table 1.1, entry 3). The in situ generated $[FeH(PP_3)]BF_4$ and $[FeH(H_2)(PP_3)]BF_4$ hydride complexes under the reaction conditions were identified as the active species.[86] Besides, the reduction of biologically relevant but challenging sodium bicarbonate was also realized using the same (**C-3)** catalyst combination. Sodium formate was obtained by hydrogenation of $NaHCO_3$ with a TON = 610 and 88% yield at 80 °C (Table 1.1, entry 4). Based on in situ high pressure NMR spectroscopy, isolation of intermediate complexes, X-ray analysis of $[FeH(PP_3)]BF_4$ complex, the authors proposed a catalytic cycle as shown in Scheme 1.2.

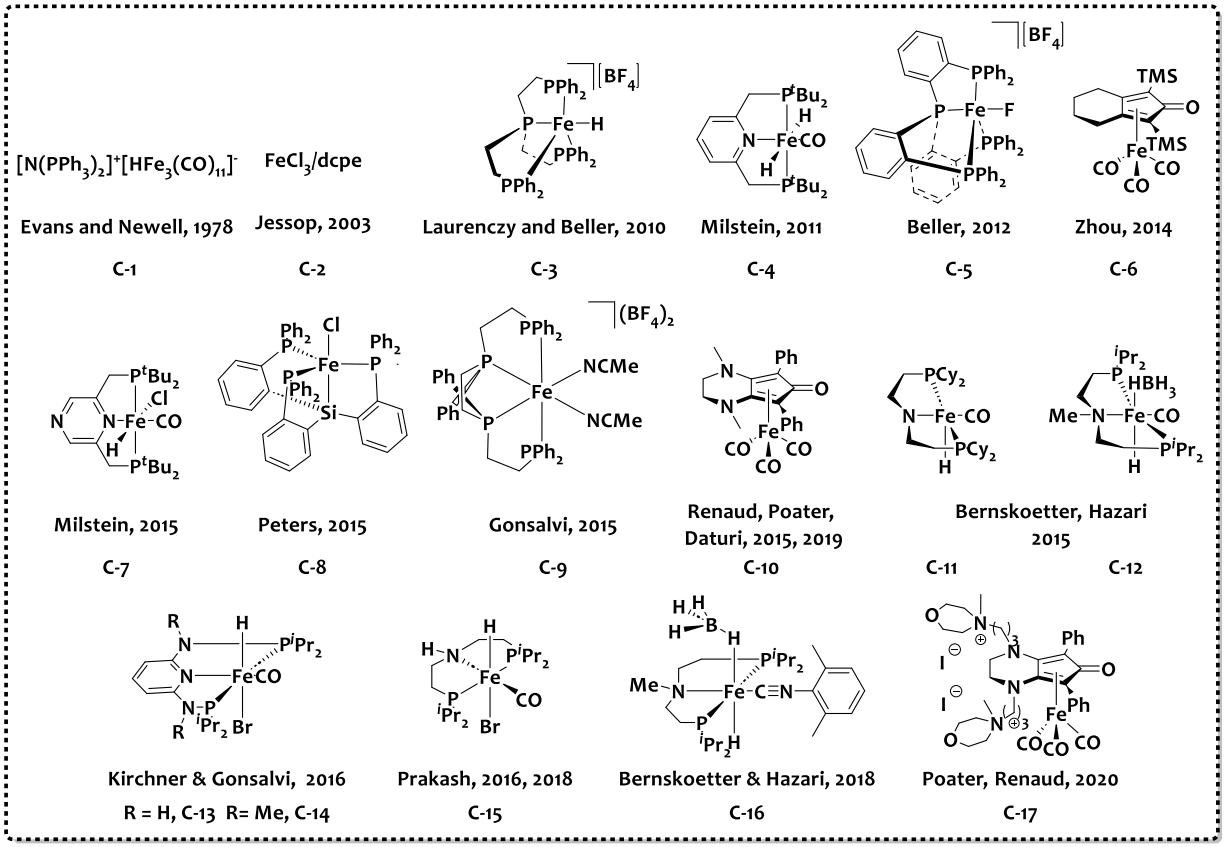
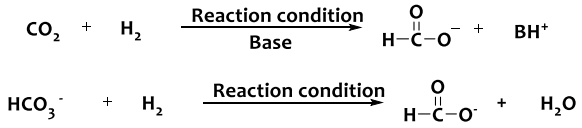


Figure 1.1 Fe catalysts explored for hydrogenation of CO_2 and bicarbonate to formic acid/formate.

In 2011, Milstein group designed well defined Fe(II) dihydride *Trans*-(tBu-PNP)Fe(H)$_2$(CO)] pincer complex (**C-4**, Table 1.1) that can hydrogenate carbon dioxide and sodium bicarbonate to yield formates under low pressure, which displays similar activity to a noble metal catalyst. Turn over numbers of upto 788 for CO_2 hydrogenation and 320 for $NaHCO_3$ hydrogenation were achieved at 80 °C using only 6-10 bar pressures of CO_2/H_2 (Table 1.1, entries 5 and 6). Based on X-ray analysis of a hydrido formate complex formation, it was proposed by the author that the reduction occurs via straight attack of hydride on carbon dioxide and subsequent displacement of formate moiety by water molecule (Scheme 1.3).[87]
Beller group subsequently reported a thermally stable and more active iron(II) catalyst (**C-5)** (Figure 1.1), which hydrogenated sodium bicarbonate to produce sodium formate with a TON of upto 7546 at 100 °C under 60 bar H_2 (Table 1.1, entry 8).[88] Hydrogenation of CO_2 in methanol in the presence of water gave formic acid in 16.7% yield with a TON of 1897 after 20 h (Table 1.1, entry 7).

Zhou group in 2014 demonstrated CO_2 and bicarbonate hydrogenation using phosphine free Knölker's iron complex (**C-6**). A loading of 0.1 mol% catalyst in the presence of NaOH utilizing 30 bar H_2 and 20 bar CO_2 pressure after 24 h at 120 °C yielded formate (30.7%) with a TON of 307 in EtOH/H_2O mixture (Table 1.1, entry 9). TON upto 447 was recorded when hydrogenation was carried out using $NaHCO_3$ and 30 bar H_2 giving sodium formate.[89] Later in 2015, Milstein modified pyridine backbone with pyrazine moiety and synthesised pincer complex [Fe(H)(Cl)(CO)(tBu-PNzP)] (**C-7**), it was conveyed that 0.1mol% catalyst in aqueous media hydrogenated bicarbonates and carbon dioxide to formates at the expense of 6-7 bar H_2 pressure. TONs upto 149 and 388 were achieved, respectively (Table 1.1, entry 10). The author inferred the involvement of MLC in the reduction of carbon dioxide catalysed by iron systems using aqueous or non-aqueous solvent.[90]

Table 1.1 Optimum reactions conditions and TON/yields for the hydrogenation of CO_2 and bicarbonate to formic acid/formate catalysed by Fe.



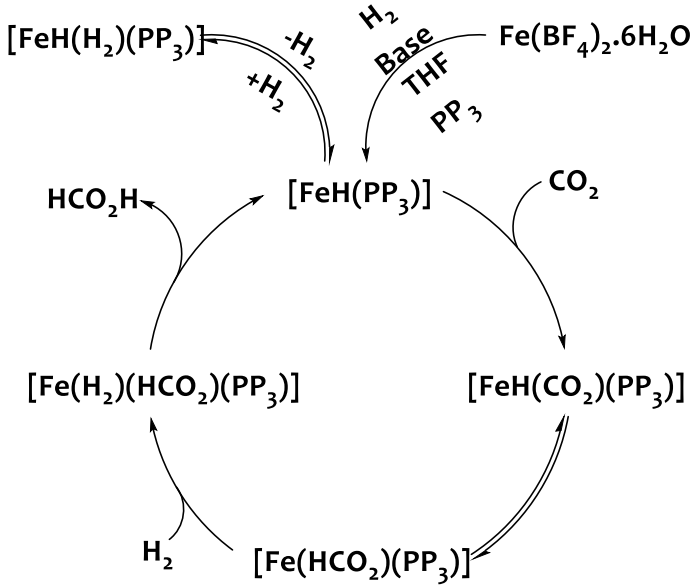
Entry	Catalyst	CO_2/H_2 pressure (bar)	T (°C)	Solvent	base	additive	TON (h)	TOF (h^{-1})	Yield
1	C-1	20.7/20.7	175	MeOH	-	-	6 (96)	0.06	5.8%
2	C-2	60/40	50	DMSO	DBU	-	113 (7.5)	15.1	-
3	C-3	30/60	100	MeOH	Et_3N	-	585 (20)	-	14%
4	C-3	-/60	80	MeOH	-	$NaHCO_3$	610 (20)	-	88%
5	C-4	3.33/6.66	30	H_2O/THF	NaOH	-	788 (5)	156	39.4%
6	C-4	-/8.3	80	H_2O/THF	-	$NaHCO_3$	320 (16)	-	32%
7	C-5	30/30	100	MeOH	Et_3N	H_2O	1897(20)		16.7
8	C-5	-/60	100	MeOH	-	$NaHCO_3$	7546 (20)	-	77%
9	C-6	20/30	120	EtOH/H_2O	NaOH	-	307 (24)	-	30.7%
10	C-7	6.3/3.3	30	H_2O/THF	NaOH	-	388 (16)	-	-
11	C-8	30/30	100	MeOH	Et_3N	-	200 (20)	-	-
12	C-9	-/60	80	MeOH	-	-	1229 (24)	-	12%
13	C-10	-/50	100	DMSO/H_2O	-	$NaHCO_3$	1246 (20)	-	-
14	C-10	20/40	100	DMSO/H_2O	TMG	MIL-53(Cr)	3006 (20)	-	60.1%
15	C-11	35/35	80	THF	DBU	LiOTf	8910(24)	1830	11%
16	C-12	35/35	80	THF	DBU	LiOTf	58990(24)	-	74%
17	C-13	-/90	80	Water/THF	-	$NaHCO_3$	4560 (24)	-	23%
18	C-14	4.25/4.25	80	EtOH	DBU	-	10275 (21)	-	21%
19	C-15	-/50	80	THF	-	NaOH	2706 (6.3)	428	98%
20	C-16	35/35	80	THF	DBU	LiOTf	5300 (24)	-	-
21	C-17	20/40	100	H_2O	TEOA	-	3343 (20)	-	66.9%
22	C-17	-/50	100	H_2O	-	$KHCO_3$	4234 (20)	-	-

Peters group in 2015 reported the CO_2 hydrogenation by testing a series of triphosphinoiron-based pre-catalysts systems having Si^-, C^-, PhB^-, N, B as apical unit in the ligand system. The authors communicated that (SiP^{ph}_3)FeCl (**C-8**) emerged as an effective catalyst for carrying out the hydrogenation. 0.1 mol% of catalyst in conjunction with triethyl amine at 100 °C after 20 h in methanol yielded triethylammonium formate along with methyl formate. TON upto 200 was achieved (Table 1.1, entry 11). Interestingly, no product formation took place upon changing solvent from methanol to THF.[91]

Gonsalvi group in 2015 prepared the linear tetraphosphine-based iron complex (**C-9**, Figure 1.1) and executed the bicarbonates hydrogenation. TON upto 1229 was recorded upon using the 0.001mmol of the catalyst, 60 bar of hydrogen after 24 h in methanol (Table 1.1, entry 12).[92] In 2015 Poater and Renaud demonstrated synthesis of a phosphine free cyclopentadienone iron carbonyl complex (**C-10)** (Figure 1.1) and explored the catalyst in the hydrogenation of sodium bicarbonate. The highest activity was obtained in a 1:1 solvent mixture of DMSO and water; a TON of 1246 was attained at 100 °C under 50 bar of hydrogen (Table 1.1, entry 13).[93]

The complex was also explored for CO_2 hydrogenation by Daturi and Renaud in 2019.[94] TON upto 1772 was obtained by taking the 1,1,3,3-tetramethylguanidine (TMG) base and 0.02 mol% catalyst at 100 °C. The activity of the catalyst towards CO_2 hydrogenation was further enhanced in the presence of MIL-53(Cr) (0.05 mol%) and TON's up to 3006 were reached in the presence of TMG base at 100 °C after 20 h with a catalyst loading of 0.02 mol% in DMSO/H_2O) mixture (Table 1.1, entry 14). However, the MOF has little influence to improve the activity of the catalyst in $NaHCO_3$ hydrogenation.

Hazari and Bernskoetter described several iron(II) PNP pincer carbonyl hydride complexes for hydrogenation of CO_2 in the presence of Brønsted base. The PNP ligands containing secondary N-H or tertiary N-Me moiety form complexes (**C-11)** and (**C-12)**, respectively (Figure 1.1). (**C-12)** was reported to be the most active catalyst. 0.30 micromol catalyst in presence of DBU as base and LiOTf as co-catalyst after 24 h at 80 °C in THF yielded formate with a TON of almost 60,000 after 24 h. For the secondary amine supported system (**C-11)**, turnover numbers of approximately 9000 for formate production were achieved (Table 1.1, entries 15 and 16).[95] In both cases a remarkable enhancement in catalytic activity was observed upon the addition of Lewis acid co-catalysts.

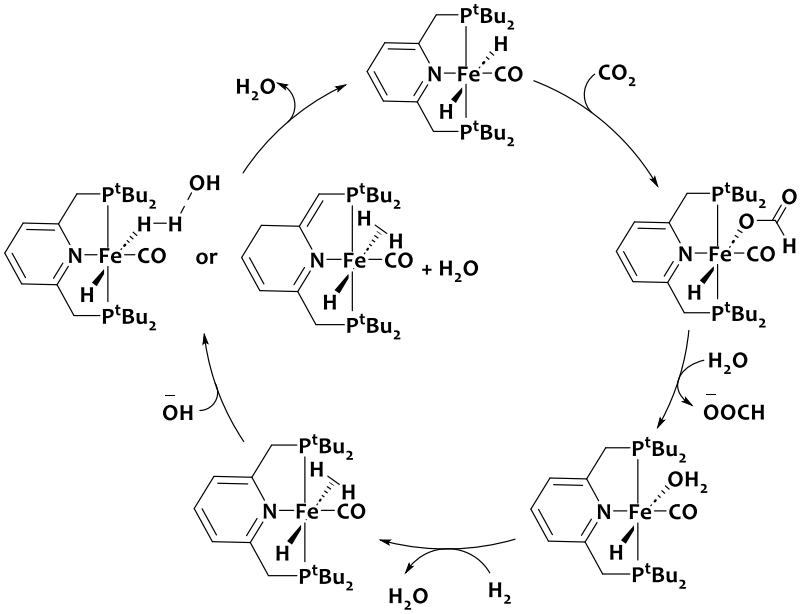


Scheme 1.2 Iron pincer complex **C-3** catalysed CO_2 hydrogenation to formate proposed by Beller.[86]

In 2016 Kirchner, Gonsalvi and co-workers delineated the CO_2 and sodium bicarbonate hydrogenation using Fe(II) hydrido PNP pincer complexes (**C-13)** and (**C-14)** bearing 2,6-diaminopyridine moiety (Figure 1.1). A maximum TON of 1220 was achieved when CO_2 was hydrogenated in the presence of NaOH base using (**C-13)** in THF/H_2O mixture at 80 °C under total 80 bar CO_2/H_2 pressure, whereas hydrogenation of $NaHCO_3$ gave TON of 4560 after 24 h and 90 bar H_2 pressure using same catalyst (Table 1.1 entry 17). On the other-hand a loading of 0.005 mol% catalyst at 80 °C in presence of 12.5 mmol DBU produces a TON of 10275 in ethanol using (**C-14)** (Table 1.1, entry 18). DFT studies revealed that the reactions proceeded via outer-sphere pathway.[96]

Olah and Prakash came up with an interesting recyclable system which was efficient in capturing and subsequent conversion of CO_2 to formate salts. They screened various Ru complexes along with the iron PNP pincer complex (**C-15**) and a TON of 255 was recorded in case of formate product when PEHA (pentaethylenehexamine) was used as capturing amine (Figure 1.1).[97] Subsequently they explored aqueous inorganic hydroxide solutions for CO_2 capture and hydrogenation employing the same (**C-15)** as catalyst.[98] A TON of 2706 was

achieved when NaOH was used as capturing agent followed by hydrogenation using 50 bar H_2 at 80 °C for 6 h (Table 1.1 entry 19).



Scheme 1.3 Iron pincer complex **C-4** catalysed CO_2 hydrogenation to formate proposed by Milstein.[87]

In 2018 Hazari and Bernskoetter group synthesized series of the $PN^{Me}P$ based iron complexes bearing isonitrile as ligand. Complex ($^{iPr}PN^{Me}P$)Fe(H)(HBH_3)(CNR) (**C-16**) possessing 2,6-dimethyl phenyl arm with isonitrile ligand proved to be most effective catalyst in hydrogenating carbon dioxide. TON upto 5300 was reported after 24 h reaction at 80 °C using DBU along with LiOTf as co-catalyst (Table 1.1, entry 20).[99] Recently, in 2020, Albert Poater and Jean-Luc Renaud developed an efficient, stable and phosphine free cyclopentadienoneirontricarbonyls catalyst system (**C-17)** for reduction of CO_2 to fomate in pure water. This system was also utilized in reduction of hydrogencarbonates and carbonates. The bifunctional (**C-17)** catalyst was found to be an efficient catalyst in carbon dioxide reduction and bicarbonate hydrogenation with a TONs more than 3300 were reported (Table 1.1, entries 21 and 22). DFT studies were also performed in order to deduce the mechanism and role of the base.[100]

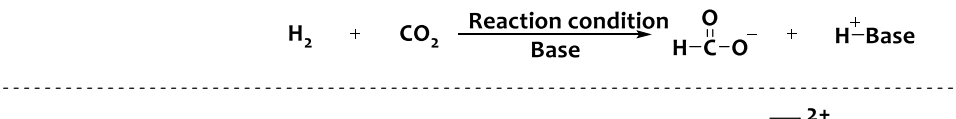
1.2.3 Co-based Catalysts

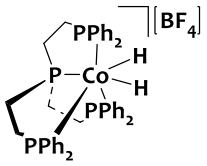
One of the very first examples of cobalt catalysed CO_2 hydrogenation was reported by Beller group in 2012. They successfully utilized cobalt-based complex to reduce carbon dioxide and bicarbonates. The catalyst was formed in combination of $Co(BF_4)_2.6H_2O$ with $P(CH_2CH_2PPh_2)_3$ (PP_3) ligand (**C-18**). After 20 h reaction at 120 °C, sodium formate was achieved as hydrogenated product of $NaHCO_3$ with 71% yield and a TON of 3877 (Table 1.2, entry 1). On the other hand, hydrogenation of CO_2 in MeOH at 100 °C after 20 h gave methyl formate with a maximum TON of 659 (Table 1.2, entry 2). Well defined complex $[Co(H_2)PP_3]^+BPh_4^-$ provided similar results when applied separately as catalyst, which is suggested as the active species.[101]
In 2013 Linehan et al. reported $Co(dmpe)_2H$ (dmpe: 1,2-bis(dimethylphosphino)-ethane) complex (**C-19**) is highly active for the hydrogenation of CO_2 in THF. In the presence of a very strong Verkade's base at room temperature, the high TOFs of 3400 and 74 000 h^{-1} were achieved under 1 and 20 atm of CO_2/H_2 (1:1), respectively (Table 1.2, entries 3 and 4).[102]

Based on experimental evidences and detection of deactivation compounds a mechanistic study using DFT calculations suggested a probable reaction pathway as shown in (Scheme 1.4).[103] Muckerman, Himeda and Fujita in 2013 demonstrated pentamethylcyclopentadienylcobalt(III) based complexes bearing proton responsive dihydroxy

bipyridine ligands are active for CO_2 hydrogenation in aqueous sodiumbicarbonate. Complex (**C-20)** (Table 1.2) found to be effective in hydrogenating carbon dioxide to formate with a TOF upto 39 h^{-1} was recorded after 1-hour reaction at 100 °C (Table 1.2, entry 5).[104]

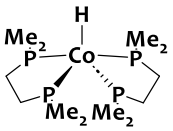
Table 1.2 Optimum reactions conditions and TON/yields for the hydrogenation of CO_2 and bicarbonate to formic acid/formate catalysed by Co.





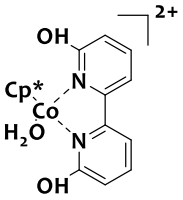
Beller. 2012

C-18



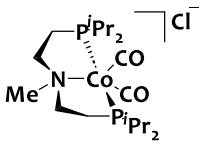
Linehan, 2013

C-19



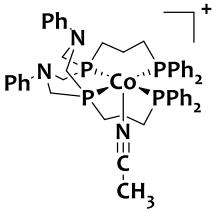
Fujita, 2013

C-20



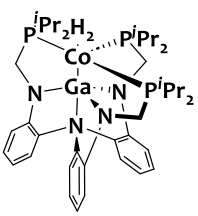
Bernskoetter, 2016

C-21



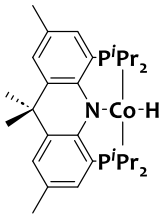
Linehan, 2017

C-22



Lu, 2020

C-23



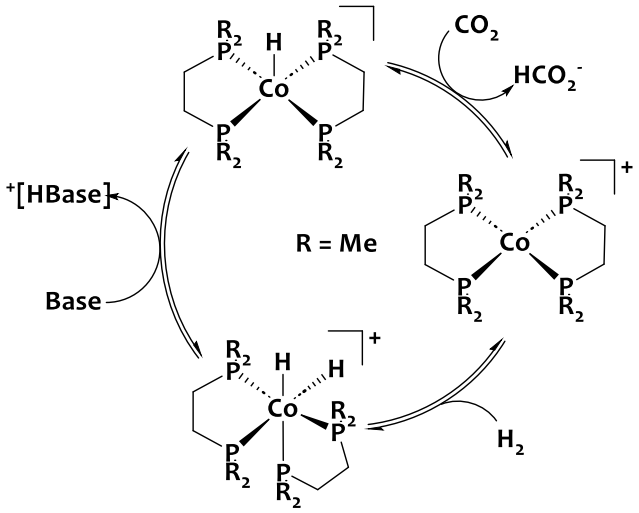
Lee, 2020

C-24

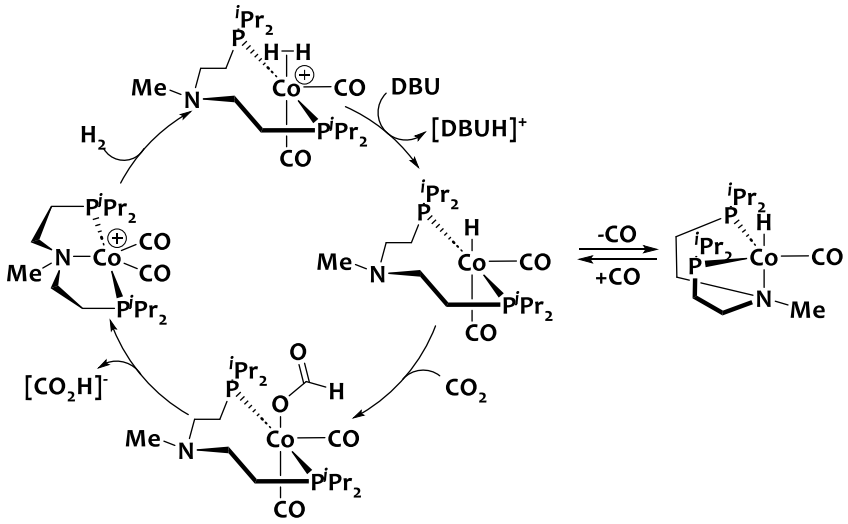
Entry	Catalyst	CO_2/H_2 pressure (bar)	T (°C)	Solvent	base	additive	TON	TOF	Yield
1	C-18	0/60	120 °C	MeOH	Et_3N	$NaHCO_3$	3877	-	71%
2	C-18	30/60	100 °C	MeOH	Et_3N	-	659	-	16%
3	C-19	1/1	21 °C	THF	Verkade's Base	-	2100	3400	-
4	C-19	10/10	21 °C	THF	Verkade's Base	-	9400	74000	-
5	C-20	20/20	80 °C	H_2O	$NaHCO_3$	-	39	39	-
6	C-21	35/35	80 °C	THF	DBU	LiOTf	30000	-	13%
7	C-22	1/1	25 °C	CH_3CN	^{t}BuTMG	-	-	150	-
8	C-23	17/17	20 °C	THF	Verkade's Base	-	12000	27000	98%
9	C-24	20/20	100 °C	THF	DBU	LiOTf	1600	4200	-

In 2016 Bernskoetter and co-workers came up with several Co(I) complexes to hydrogenate CO_2. Dicarbonylcobalt complex $[(^{iPr}PNP)Co(CO)_2]^+[Cl^-]$ (**C-21**) turned out to be an efficient catalyst in combination with Lewis acid lithium triflate at 1000 psi and 45 °C to produce formate with TON of almost 30000 (Table 1.2, entry 6).[105] The mechanism proposed by the authors is depicted in (Scheme 1.5). In 2017 Linehan described that CO_2 can be hydrogenated at room temperature using cobalt catalyst. The author proposed that tetra phosphine cobalt complex $[Co(L')-(CH_3CN)]BF_4$, L′ =1,5-diphenyl-3,7-bis(diphenylphosphino)-propyl-1,5-diaza-3,7-(**C-22**) diphosphacyclooctane convert CO_2 to formate at room temperature upon utilizing the low pressure of 1.7 atm in presence of ^{t}BuTMG as base. TOF upto 150(20) h^{-1}

was reported (Table 1.2, entry 7).[106] Lu and co-workers in 2020 menifested CO_2 hydrogenation by using cobalt and group 13 bimetallic species. Co complex bearing gallium metalloligand (**C-23**, Table 1.2) turned out to be most efficient catalyst. Formate was obtained upto 98% yield upon carrying the reaction for 1.5 h at 20 °C. Moreover, TOF upto 27000 was reached (Table 1.2, entry 8).[107] Lee group almost at the same time hydrogenated CO_2 using PNP pincer catalyst of cobalt (**C-24**). TOF upto 4200 h^{-1} was achieved using the catalyst along with LiOTf as co-catalyst in presence of DBU at 100 °C in THF solvent and 40 bar of CO_2 and H_2 mixture (Table 1.2, entry 9).[108]



Scheme 1.4 Proposed cobalt **C-19** catalysed hydrogenation of CO_2 to formate.[103]



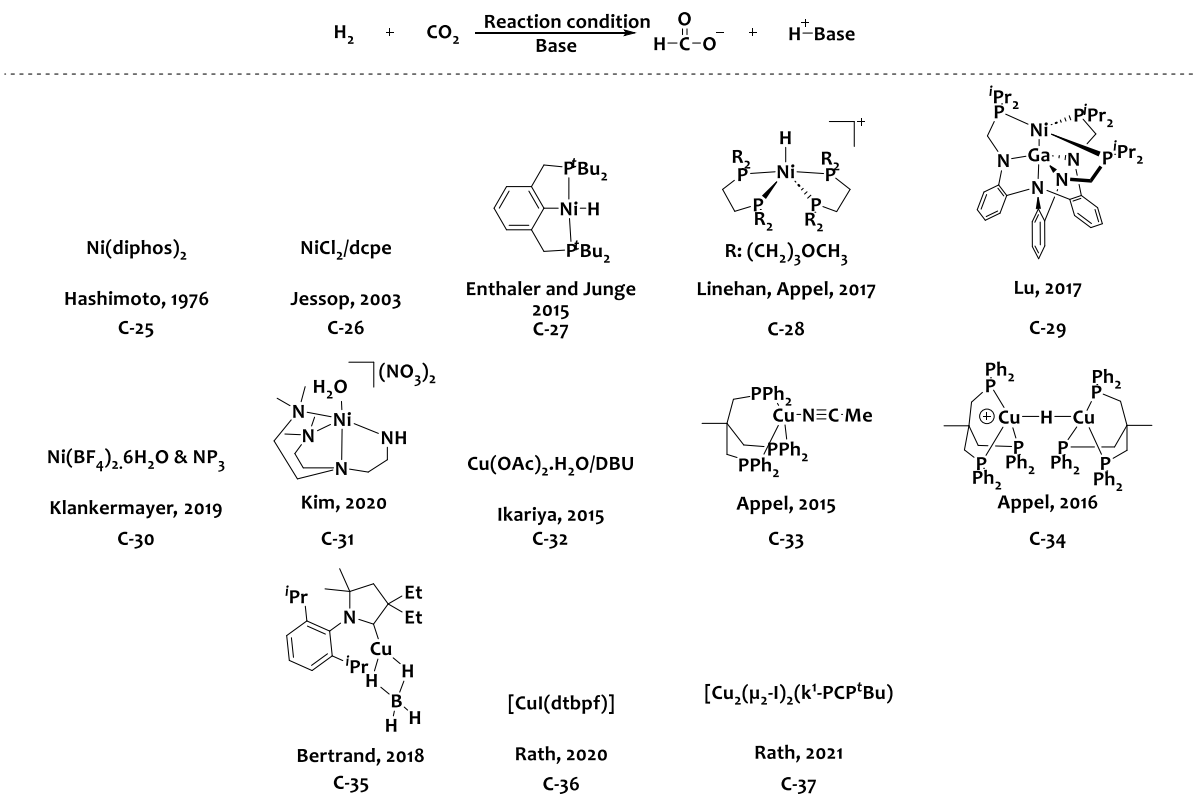
Scheme 1.5. Proposed mechanism by Bernskoetter et al. for cobalt (**C-21**) catalysed hydrogenation of CO_2 to formate.[105]

1.2.4 Ni and Cu-based Catalysts

Hydrogenation of CO_2 to formate was also explored using Ni and Cu complexes by several groups and are listed in Table 1.3. The first nickel catalysed CO_2 hydrogenation to formic acid was reported by Inoue et al. in 1976. A $Ni(dppe)_2$ catalyst (dppe = $Ph_2PCH_2CH_2PPh_2$) (**C-25**) in the presence of NEt_3 was found to be catalytically active under 25 atm H_2 and 25 atm CO_2. However, a low TON of 7 was achieved after 20 h of reaction time at room temperature (Table 1.3, entry 1).[109] In 2003, the Jessop group screened a series of metal salts and found the catalyst $NiCl_2$/dcpe (dcpe = $Cy_2PCH_2CH_2$-PCy_2) **(C-26)** with the base DBU (DBU=1,8-diazabicycloundec-7-ene) as an effective system, resulting in a TON of 4400 after 216 hours at 50 °C (Table 1.3, entry 2).[85]

In 2015 Enthaler and Junge reported a well-defined nickel PCP pincer hydride complex (**C-27**) that can catalyse hydrogenation of bicarbonate in methanol at 150 °C and 55 bar H_2 revealing catalytic activity with turnover numbers of up to 3000 for the hydrogenation reactions after 20 h (Table 1.3, entry 3).[110]

Table 1.3 Ni and Cu catalysed hydrogenation of CO_2 to formate.



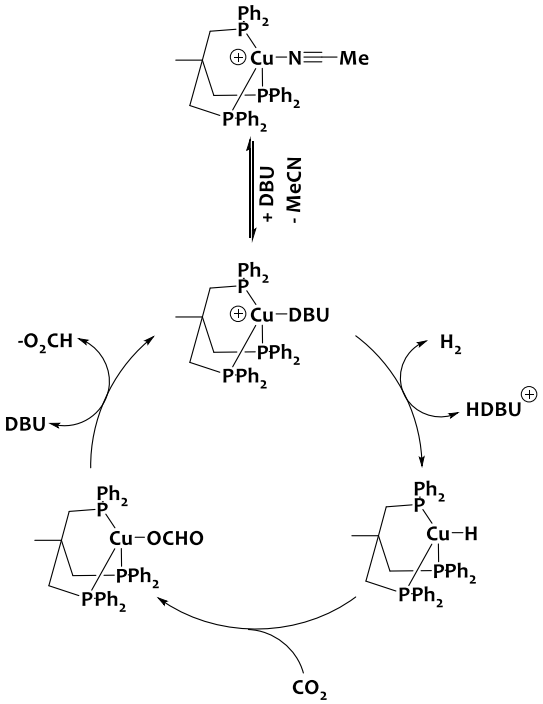
Entry	Catalyst	CO_2/H_2 pressure (bar)	T (°C)	Solvent	base	TON	TOF (h^{-1})	Yield
1	C-25	25/25	r.t.	water/benzene	Et_3N	7	-	7%
2	C-26	60/40	50 °C	DMSO	DBU	4400	-	-
3	C-27	30/30	150 °C	DMF	$NaHCO_3$	3000	-	-
4	C-28	17/17	80 °C	H_2O	$NaHCO_3$	-	0.4	-
5	C-29	17.5/17.5	20 °C	THF	vkd base	3150	6900	-
6	C-30	30/60	120 °C	CH_3CN	DBU	4650710	64593	-
7	C-31	30/30	r.t.	water	$NaHCO_3$	121	10	-
8	C-32	40/40	100 °C	1,4-dioxane	DBU	167	-	33%
9	C-33	20/20	140 °C	CH_3CN	DBU	500	25	-
10	C-34	20/20	83 °C	CH_3CN	DBU	-	7.5	-
11	C-35	15/45	100 °C	THF	DBU	1881	-	-
12	C-36	1/1	80 °C	DMF	DBU	$1.065 * 10^5$	98	-
13	C-37	1/1	80 °C	1,2-dioxane	DBU	8642	-	-

Linehan and Appel in 2017 synthesized the Nickel complex $[NiL'_2](BF_4)$ (L′= [bis(dimethoxypropyl)phosphino]ethane (**C-28**) and reported the carbon dioxide hydrogenation using it as catalyst. (**C-28)** is water soluble therefore it hydrogenated CO_2 in aqueous media using $NaHCO_3$ as sole basic additive. TOF upto 0.4 h^{-1} was recorded under 34 atm total pressure of CO_2 and H_2 at 80 °C (Table 1.3, Entry 4).[111] In the same year Lu documented the CO_2

hydrogenation using Nickel-gallium catalyst (**C-29**). 0.25 mmol catalyst in presence of verkade base upon utilizing 34 atm proportional mixture of CO_2 and H_2 at 20 °C produce formate with a TON of 3150 (Table 1.3, entry 5). The author proposed that gallium ion principally stabilized the nickel hydride species generated during the course of the reaction.[112]

Klankermayer group in 2019 came up with yet another CO_2 hydrogenation using nickel-based catalyst. Nickel precursor $Ni(BF4)_2$ in concoction with $N(CH_2CH_2PPh_2)_3$ (NP_3) ligand form the catalyst (**C-30**). Notably 0.002 micromol catalyst using DBU as base upon utilizing 90 atm mixture of H_2 and CO_2 in 2:1 ratio after 20 h at 120 °C in acetonitrile yielded formate. An outstanding TON of 4.65*106 was achieved (Table 1.3, entry 6).[113] In 2020 Kim synthesized air and moisture stable water-soluble nickel-azirane based catalyst (**C-31**) which is active for the hydrogenation of $NaHCO_3$. The best TON of 121 was obtained using the catalyst for the direct hydrogenation of bicarbonate to formate in aqueous medium. (Table 1.3, entry 7).[114]

In addition to Fe, Co, and Ni, few Cu based complexes have also been demonstrated as effective catalysts in the hydrogenation of CO_2 to formate. In 2015 Watari and Ikariya et al. reported catalytic activity of some Cu complexes towards hydrogenation of CO_2. The copper precursor $Cu(OAc)_2.H_2O$ in combination with DBU (**C-32**) in dioxane at 100 °C produces $[DBU-H]^+[HCO_2]^-$ upto 54% isolated yield. A TON of upto 167 was observed at 33% yield after 116 h (Table 1.3, entry 8). Notably it was mentioned that DBU provided stability to the catalyst during the course of reaction along with capturing formic acid.[115] Appel described that tripos ligand-based copper complex (**C-33)** efficiently catalysed CO_2 hydrogenation. A TON of 500 was reached using 0.1 mol% of catalyst at 140 °C after 20 h (Table 1.3, entry 9). The catalyst performed exceptionally well in comparison with the formerly reported copper catalyst. Furthermore, it was articulated that strong base like DBU direct the reaction towards high TON.[116] The catalytic mechanism proposed by the authors is described in Scheme 1.6.



Scheme 1.6 Catalytic cycle for molecular Cu (**C-33**) catalysed hydrogenation of CO_2 to formate.[116]

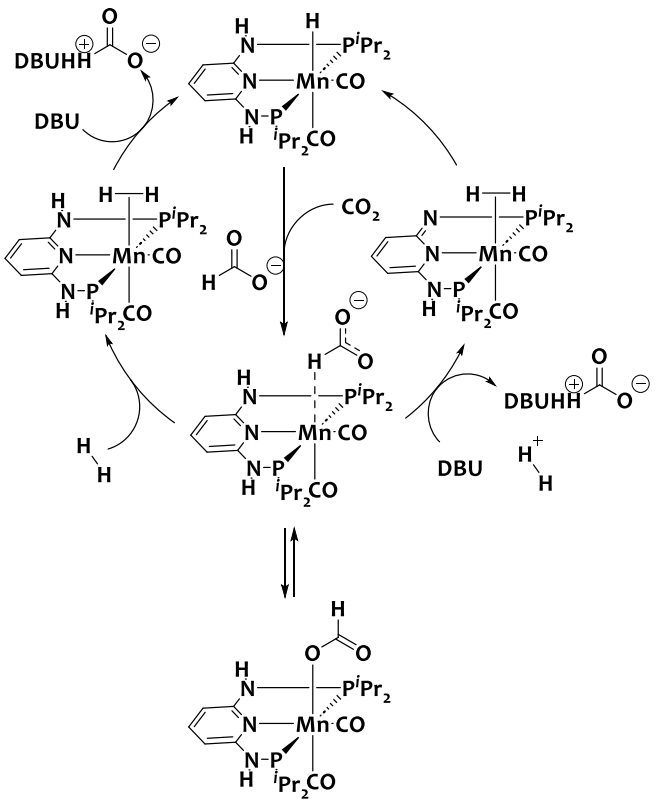
Appel group almost at the same time extended their earlier work and synthesized the dicopper hydride $[(L1\ Cu)_2H]PF_6$ complex (**C-34**) (Table 1.3) where L1= (1,1,1-tris(diphenylphosphinomethyl)ethane. The complex proved more or less equally efficient towards CO_2 hydrogenation when compared with earlier reported copper catalyst. Presence of strong bases like DBU proliferate the reactivity of complex towards carbon dioxide.

Accordingly, [L1CuH] was suggested as the active species.[117] Hu, Jazzar, Bertrand and co-workers in 2018 demonstrated catalytic hydrogenation of CO_2 using a borane stabilised cyclic alkyl amino carbene based copper hydride complex (**C-35**) in combination with Lewis pairs DBU/$B(C_6F_5)_3$. The Cu-H catalytic system activates CO_2 and works in tandem with the Lewis pairs that splits H_2 in a heterolytic fashion yielding formate with a TON of upto 1881 after 24 h at 100 °C at the expense of 15 bar CO_2 and 45 bar H_2 (Table 1.3, entry 11).[118]

Trivedi, Masram and Rath in 2020 successfully hydrogenated CO_2 by using [CuI(dtbpf)] complex (**C-36**) 0.002 mmol of catalyst at 80 °C after 48 h in presence of DBU produced formates in 98% yield in DMF with a TON of 1.065 × 105.[119] Subsequently in 2021 they synthesized several novel copper complexes and explored them in CO_2 hydrogenation. Copper complex (**C-37)** coordinated with PCP^{tBu} ligand turned out to be an efficient catalyst. A loading of 0.00025 mmol catalyst in presence of DBU after 48 h at 80 °C in dioxane yielded formate as product. A TON of upto 8642 was recorded (Table 1.3, entry 12).[120]

1.2.5 Mn-based Catalysts

Manganese catalysed hydrogenation of CO_2 to formate was also reported by several groups since 2017 when Nervi and Khusnutdinova demonstrated that 2,2′-bipyridine Mn(I) based catalyst (**C-38)** (Table 1.4) is capable of CO_2 hydrogenation to formate effectively. A loading of 0.005 mmol catalyst with DBU as base at 65 °C after 24 h in acetonitrile produces formates in 99% yield. TON upto 6250 was also reported (Table 1.4, entry 1).[121]



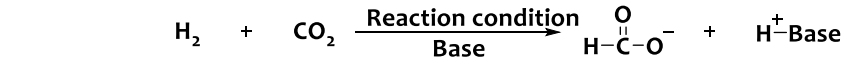
Scheme 1.7 Manganese **C-39** catalysed hydrogenation of CO_2 to formate proposed by Gonsalvi and Kirchner.[122]

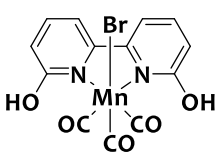
Gonsalvi and Kirchner also documented the CO_2 hydrogenation using manganese based PNP pincer hydride complex (**C-39**) (Table 1.4). Maximum TON of 9100 was recorded upon carrying the reaction for 24 h while keeping the temperature 80 °C using DBU as sole basic additive. Introduction of LiOTf in the form of co-catalyst escalated the TON upto 30000 (Table 1.4, entry 2).[122] The proposed catalytic cycle is depicted in Scheme 1.7. In 2018 group of Prakash came up with an integrated approach to capture CO_2 followed by hydrogenation to formate utilizing Ru, Mn, and Fe pincer complexes. The Mn complexes (**C-40**) and (**C-41**) revealed TON

of 1233 and 2258, respectively when the hydrogenation of CO_2 was carried out in the presence of NaOH base (Table 1.4, entries 3 and 4).[98]

Milstein group in 2019, demonstrated activation of CO_2 using Mn-PNP type pincer complexes via different modes of metal-ligand cooperation. They explored the reactivity of the complexes with CO_2 and revealed that (**C-42**) was able to hydrogenate CO_2 giving low yield of 23% at 110 °C in the presence of KOH (Table 1.4, entry 5).[123] Kirchner and Gonsalvi in 2021 reported the CO_2 hydrogenation using bidentate dippe ligand-based Mn complex (**C-43**) giving TON of upto 1988 in the presence of DBU as base and LiOTf as co-catalyst. The reaction was carried out in THF.[124] A mechanistic cycle as shown in (Scheme 1.8) was depicted by the authors. Saouma in the same year reported the hydrogenation of CO_2 using

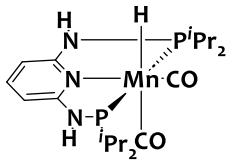
Table 1.4 Manganese catalysed hydrogenation of CO_2 and bicarbonate to formate.





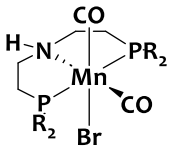
Khusnutdinova, 2017

C-38



Kirchner & Gonsalvi, 2017

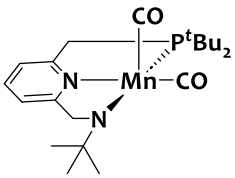
C-39



Prakash, 2018

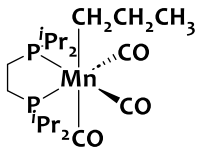
R = ^{i}Pr, C-40

R = Cy, C-41



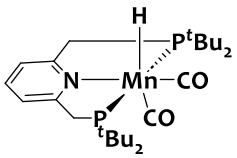
Milstein, 2019

C-42



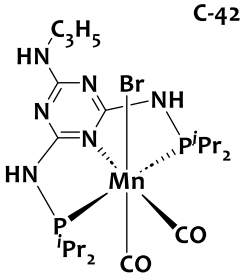
Kirchner & Gonsalvi, 2021

C-43



Saouma,2021

C-44



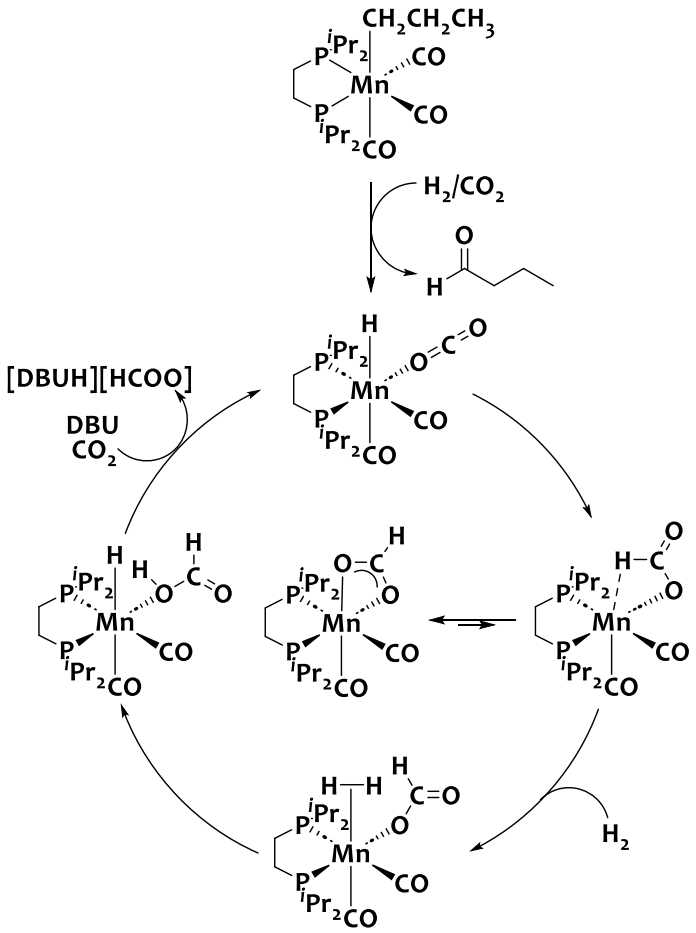
Sponholz, Junge, Beller 2022

C-45

Entry	Catalyst	CO_2/H_2 pressure (bar)	T (°C)	Solvent	base	additive	TON	TOF	Yield
1	C-38	30/30	65 °C	CH_3CN	DBU	-	6250	-	98%
2	C-39	40/40	80 °C	THF/H_2O	DBU	LiOTf	30000		60%
3	C-40	-/50	80 °C	THF	NaOH	-	1233	31	45%
4	C-41	-/50	80 °C	THF	NaOH	-	2258	33	82%
5	C-42	30/30	110 °C	H_2O	KOH	-	-	-	23%
6	C-43	50/25	80 °C	THF	DBU	LiOTf	1988	-	98.7%
7	C-44	15/15	100 °C	THF	KO^{t}Bu	-	58	-	-
8	C-45	20/60	115 °C	H_2O/THF	Lys	-	230000	-	92%

PNP pincer complex of manganese (**C-44**) (Table 1.4). 0.0005 mmol of catalyst after 18 h in presence of ^{t}BuOK produced formates with a TON of upto 58. The author proposed that on account of hydricity of complex, it is less susceptable to insert CO_2 suggesting the reaction to follow different pathway.[125] Very recently Beller and co-workers reported a Mn-based PNP

pincer complex in combination with naturally occurring α-amino acid Lys (**C-45**) to yield formate upto 92% with TON 230000 (Table 1.4, entry 8). This catalytic system was found to be very much stable and reused various time to give TTON upto 2000000.[126]

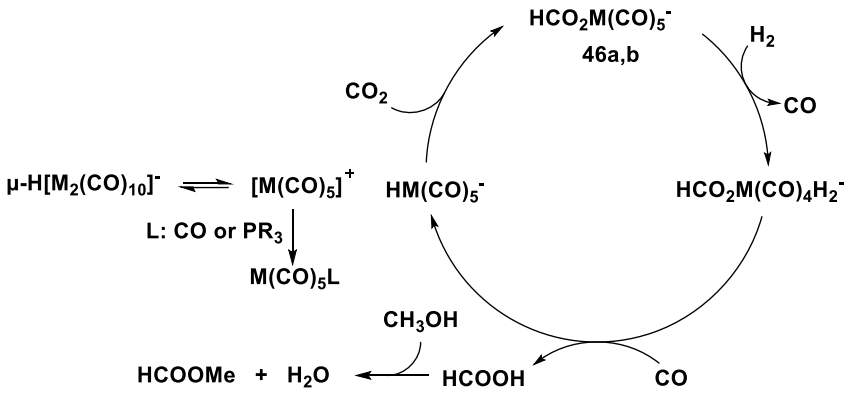


Scheme 1.8. Proposed mechanism for **C-43** catalysed hydrogenation of CO_2 to formate.[124]

1.2.6 Cr, Mo and W-based Catalysts

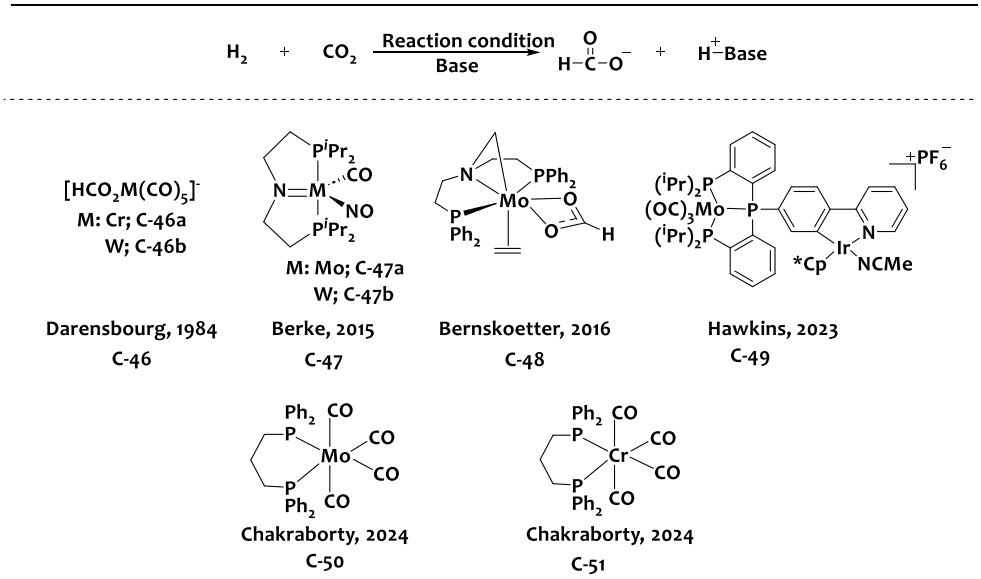
Although Group VI metal hydrides mediated reduction of CO_2 to formate was known[127] since 1981, their effective application in a catalytic manner was explored in 1984 by Darensbourg and co-workers.[128] Under 17 bar pressure of CO_2 and H_2 (each), $HM(CO)_5$- derived from μ-$HM_2(CO)_{10}$- and their CO_2 insertion products $HCO_2M(CO)_5$-, (M= Cr, W C-46a,b) (Table 1.5) served as active catalysts for the hydrogenation of CO_2 in presence of alcohols at 125 °C yielding alkyl formates. The catalytic cycle commences with the release of formic acid from the metal centre either by ligand-assisted heterolytic splitting of dihydrogen or reductive elimination of the hydrido formato ligands which leads to loss of formic acid from the so formed complex. Subsequently, this formic acid forms HCOOR upon reaction with alcohols (Scheme 1.9). Using tungsten analogue $HCO_2W(CO)_5$- (**C-46b**), the maximum TON of 16 was reported.

In 2015, Berke group[129] applied amido complexes (**C-47a,b**) for the hydrogenation of CO_2. A loading of 5 mol% of catalyst **C-47a**, in presence of $Na[N(SiMe_3)_2]$, CO_2 (10 bar) and H_2 (70 bar) yielded only a maximum of 4% yield of HCOONa (Table 1.5). On the other hand, when (**C-47b**) was used as catalysts, 2% yield of corresponding formate was obtained. The formation of stable carbamate complexes from the reaction of (**C-47**) with CO_2 was anticipated to block the reaction steps to be catalytic.



Scheme 1.9. Proposed mechanism for **C-46a, b** catalysed hydrogenation of CO_2 to formate.

Table 1.5 Cr, Mo and W catalysed hydrogenation of CO_2 and bicarbonate to formate.



Entry	Catalyst	CO_2/H_2 pressure (bar)	T (°C)	Solvent	base	additive	TON	TOF	Yield
1	C-46a	17/17	125 °C	-	-	-	14.6	-	-
2	C-46b	17/17	125 °C	MeOH	-	-	16.4	-	-
3	C-47a	10/70	140 °C	THF	$Na[N(SiMe_3)_2]$	-	-	-	4%
4	C-47b	10/70	140 °C	THF	$Na[N(SiMe_3)_2]$	-	-	-	2%
5	C-48	35/35	100 °C	1,4-dioxane	DBU	LiOTf	35	-	-
6	C-49	30/30	50 °C	MeCN	DBU	-	128	-	77%
7	C-50	10/30	130 °C	H_2O/THF	NaOH	-	975	-	-
8	C-51	10/30	130 °C	H_2O/THF	NaOH	-	259000	-	60%

Bernskoetter introduced a Mo triphos complex (κ^4 -$PN^{Me}P$)$Mo(C_2H_4)(\kappa^2$-$O_2CH)$ (**C-48**) (Table 1.5), which serves as a precatalyst for hydrogenation of CO_2 under basic condition. Using an autoclave, kept at 100 °C for 16 hours, under the 1:1 mixture of 69 atm CO_2 and H_2, and DBU solvent mixture, they were able to afford free formate in less than 1 equivalent quantity. However, the reaction was found to be catalytic in the presence of Lewis acid as additives. Addition of LiOTf (50 equivalent) and changing the solvent in the reaction mixture, a TON of 35 was reported.[130]

Recently, Zhuofeng and co-workers have theoretically designed a series of group VI metals based NHC complexes. These complexes have been studied computationally for the hydrogenation of CO_2 to formic acid.[131] Their computational results exhibit promising potentials of group VI metal NHC-based complexes in CO_2 hydrogenation catalyses owing to their relatively low electronegativity and low oxidation states. The potential of group VI metal complexes M(0) as good non-noble candidates for CO_2 hydrogenation or related catalytic transformations, can be explained by predicted energy barriers of 24.3-28.0 kcal/mol for Cr(0)/Mo(0)/W(0). Hawkins and co-workers reported heterobimetallic Mo/Ir catalyzed hydrogenation of CO_2 to formate and a TON of 128 was reported.[132] Lately our group reported Mo and Cr catalyzed hydrogenation of CO_2 to formate independently and achieved TONs of 975, 2,59000 respectively.[133-134]

1.3 CO_2 Transfer Hydrogenation to Formates

Espousal of 'transfer hydrogenation' strategy employing readily accessible biomass derived feedstock alcohols as hydrogen source is gaining momentum.[135-142] 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] 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 1.2) 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 1.2) 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]

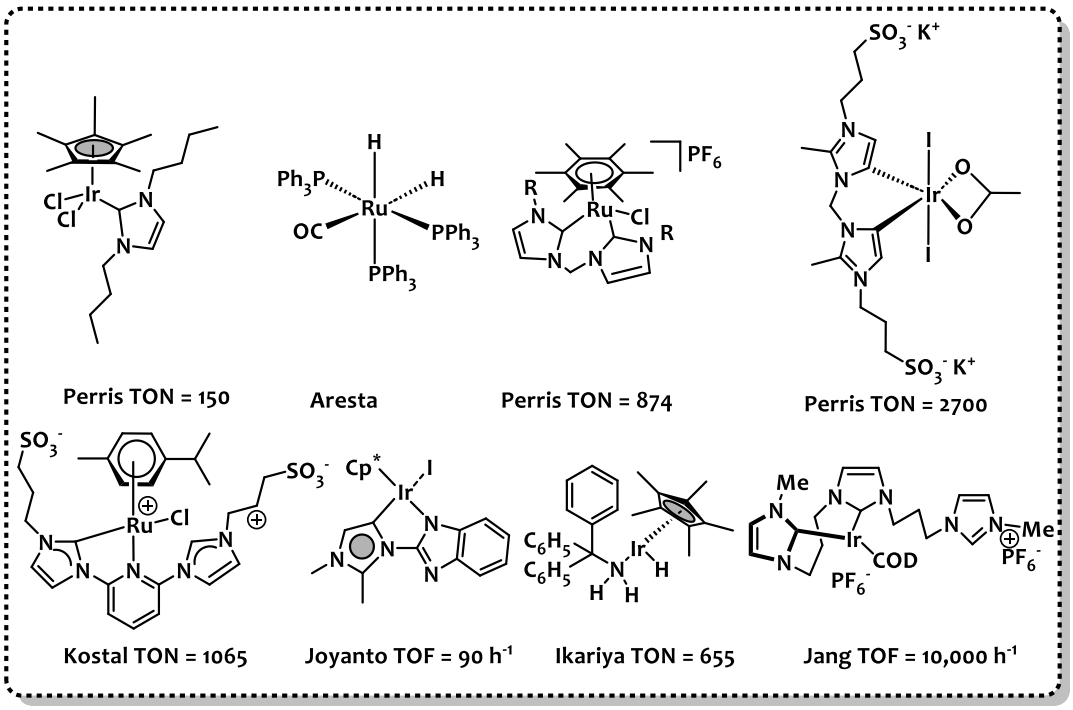


Figure 1.2 Selected Catalysts for CO_2 transfer hydrogenation to formates.

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 699 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 °C.[153] In 2022 a comprehensive review by Choudhury compiled the developments of CO_2 transfer hydrogenation reactions.[154]

1.4 Transition Metal Application as Antibacterial Agents

Resistance to antimicrobial drug is one of the global concerns as it hampers the global economy and civilization health at the broader scale since couple of decades. This dreaded trouble arises in human pathogens due to irrational and unbridled clinical usage of available antimicrobial agents as well as the haphazard intake of antibiotics in food and fodder industries. These deranged situations bring in demand discovery and development of new therapeutic interventions to control the world-wide problem of antibiotic resistance.[155-156] In this regards the bioinorganic chemistry provides the room to develop novel therapeutic drugs, over the years this domain is evolving expeditiously, utilizing transition metal complexes as potential therapeutic agents is gaining interest at rapid pace, infact landmark breakthrough has been made utilizing well defined metal complexes in medical chemistry like pioneering discovery of cisplatin for the treatment of cancer, ferroquine for curing malaria etc.[157-160]

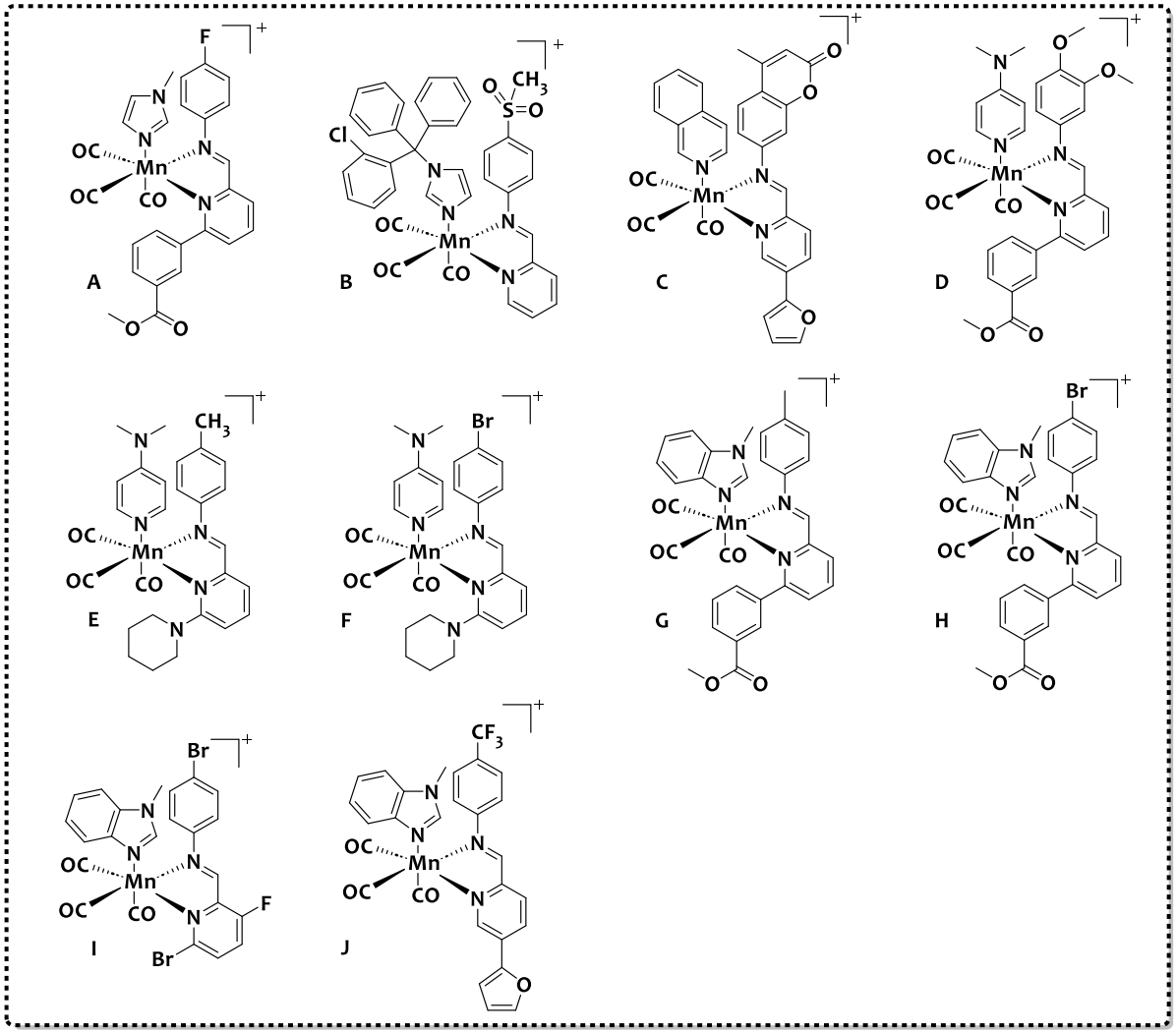


Figure 1.3 Mn Schiff base complexes screened by Angelo for the antibacterial properties.

Designing the diverse transition metal complexes with judicious selection of organic ligand scaffold, and exploring the unique properties of metal-specific modes of action that are not available for organic antibiotics led to design of new drugs for potential application in anti-bacterial and other diseases. Contextually, Schiff base supported complexes are highly interesting as these they have widespread utility in the arena of medicine and biology owing to the embedded bioactive azomethine motif, which raise the prospect of various nucleophilic and electrophilic attack at Nitrogen and carbon centers independently thereby facilitates to understand the mechanism of various phenomenon taking place in biological systems which includes racemization, trans-amination etc. Myriads of Schiff base supported complexes are known to display antibacterial activity. However, most of the complexes are based on precious platinum group metals, which are expensive, and potentially toxic. In this regard 3d transition metal complexes-based antibiotics are valuable alternatives because of their bio-compatibility, earth-abundance and cost-effectiveness. In fact, there are several reports on synthesis and biological evaluation based on first row metal complexes.[161-176] Lately, Angelo frei and co-workers screened 420 novel manganese complexes and evaluated them for antibacterial action, upon assessment 10 lead complexes were recognized and characterized thoroughly. The Mn compounds were highly active against gram positive bacteria. Patra group revealed some Cr complexes which performed well as antibacterial agent. Similarly, several chromium complexes are also known to display the antibacterial action.

1.5 Scope of the Thesis

The primary scope of this thesis is to develop and explore chromium (Cr) and molybdenum (Mo) complexes that demonstrate catalytic efficiency in CO_2 hydrogenation and potential biological applications. Given the urgent need to address climate change and mitigate greenhouse gas emissions, CO_2 hydrogenation represents a promising pathway for transforming CO_2 into valuable chemicals and fuels. This research aims to harness the unique catalytic properties of chromium and molybdenum complexes, investigating their role in efficient CO_2 conversion processes. CO_2 hydrogenation, particularly when catalyzed by transition metal complexes, has the potential to contribute to sustainable energy solutions by converting CO_2 into methanol, formic acid, and other hydrogen-rich compounds. Chromium and molybdenum, as abundant transition metals with relatively low toxicity compared to heavier metals, offer an attractive alternative for catalysis. This thesis will focus on synthesizing and characterizing a variety of Cr and Mo complexes, each designed to optimize CO_2 hydrogenation under different conditions. Parameters such as ligand design, oxidation states, coordination environment, and reaction conditions will be systematically varied to identify key factors that enhance catalytic efficiency and selectivity.

In addition to their catalytic applications, chromium and molybdenum complexes hold promise in the field of biological activity. Transition metal complexes are increasingly being explored for applications such as antimicrobial, anticancer, and enzyme-mimetic activities. This research investigates the bioactivity profiles of a novel Cr complex to understand its potential in medicinal chemistry. The dual focus of this thesis—CO_2 hydrogenation and biological activity—will provide a comprehensive view of the versatility of Cr and Mo complexes, potentially leading to developments that benefit both environmental sustainability and health sciences. This study will include detailed structural, spectroscopic, and mechanistic investigations to elucidate the catalytic pathways and bioactive mechanisms of Cr and Mo complexes. By integrating fundamental chemistry with applied research, the thesis aims to contribute to the growing field of sustainable catalysis and expand the understanding of transition metal complexes in biological applications. Ultimately, this work could open new vistas for utilizing chromium and molybdenum as environmentally friendly and versatile materials in both energy and healthcare sectors.