Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Recent developments in first-row transition metal complex-catalyzed CO_2 hydrogenation

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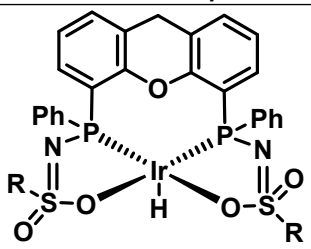
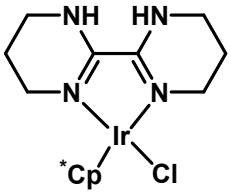
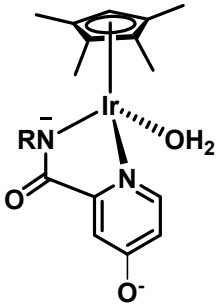
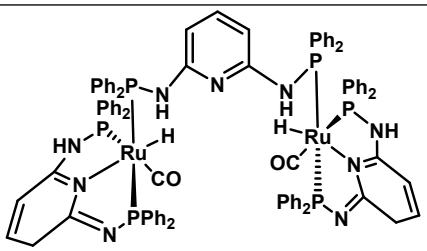
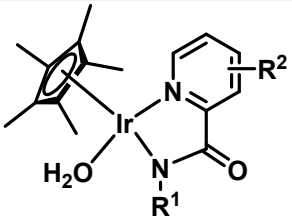
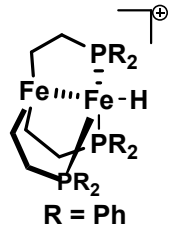
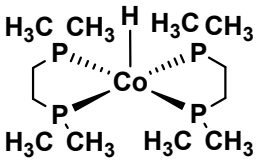
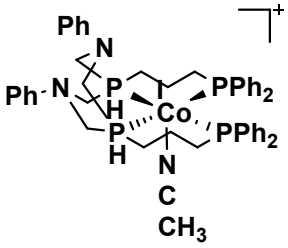
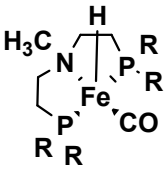
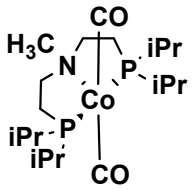
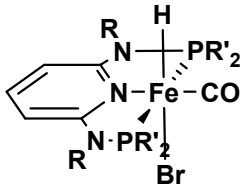
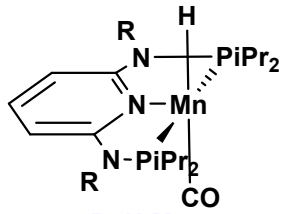
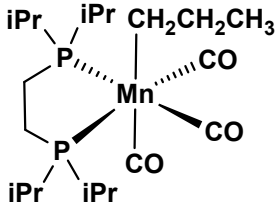
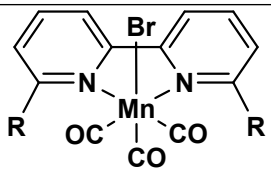
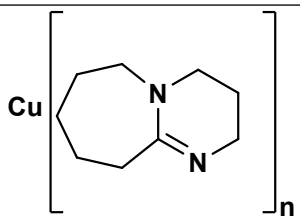
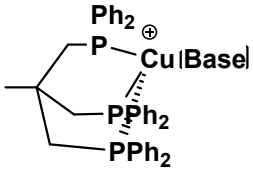
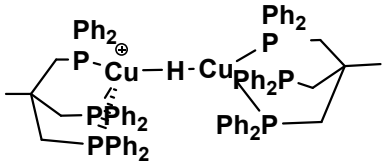
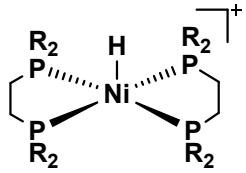
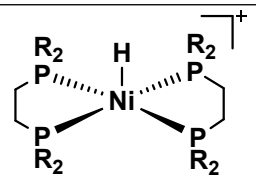
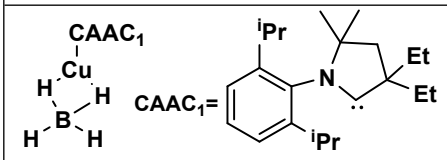
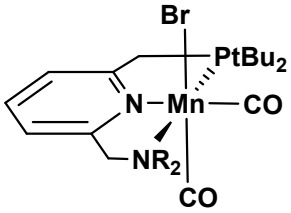
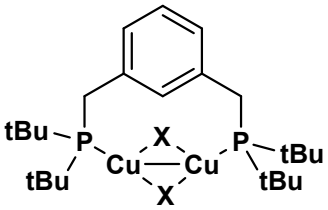
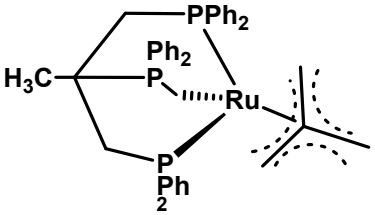
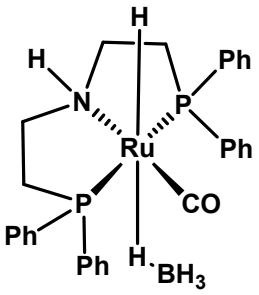
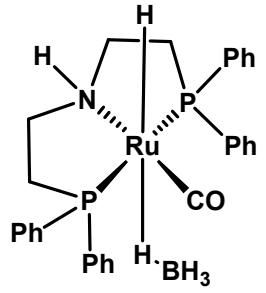
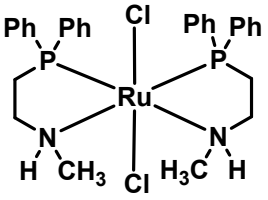
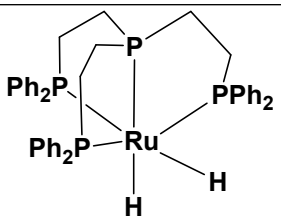
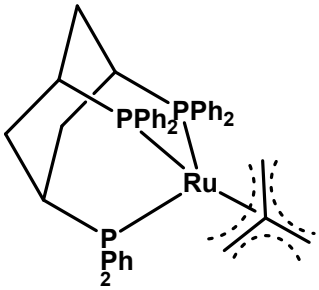
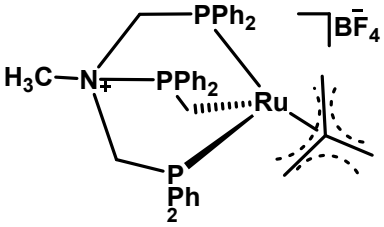
Table S1. The structure, reaction conditions, and catalytic performance of different CO_2 hydrogenation catalysts.

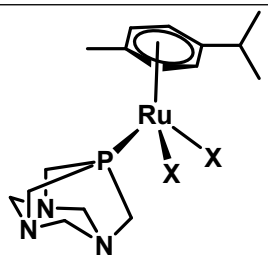
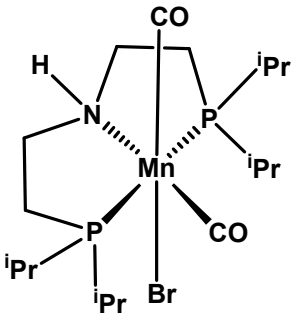
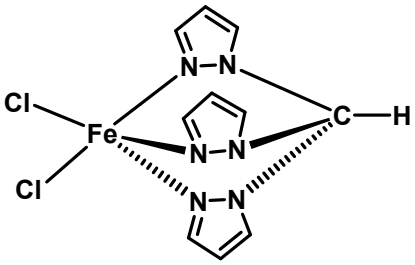
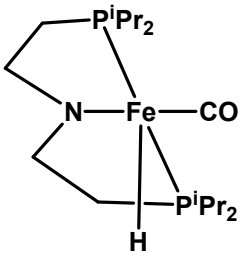
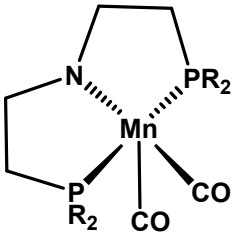
Catalyst [ref]	Pressure (CO_2 :H_2)	TON	TOF(h^{-1})	Solvent	Temperature	additives
 1. Reek, 2016	50 bar (1:1)	685	-	DMSO	100°C	DBU
 2. Li, 2016	5.0 MPa (1:1)	10,000	13,0000	H2O	40°C	-----
 3. Himeda, 2017	0.1 MPa	14700	167	H2O	25°C	-----
 4. Huang, 2018	$P_{(CO2)}$= 200 psi $P_{(H2)}$= 400 psi	33000	13,0000	THF/H_2O	110°C	--------
 5. Himeda, 2020	0.1 MPa (1:1)	---	198	H_2O	25°C	-------

 R = Ph 6. Beller 2012	$P_{(H2)}$= 60 bar	>7500	750	Methanol	>100°C	NEt_3
 7. Linehan, 2013	20 atm(1:1)	9400	74000	THF	21°C	Verkade's base
 8. Linehan, 2017	1.7 atm (1:1)	-	150(20)	acetonitrile	25°C	^{t}BuTMG
 R = iPr, Cy 9. Hazari, Bernskoeter, 2015	69 atm (1:1)	[tertiary amine =60,000], [secondary amine= 9000]	-	THF	80°C	LiOTf, DBU
 10. Bernskoeter, 2016	1000 psi(1:1)	29000	5700	THF	45°C	LiOTf, DBU
 R= H, Me, R'=iPr 11. Gonsalvi, 2016	$P_{(H2)}$= 90 bar	1964 (for R=H), 1036 (for R=Me)	-	H_2O: THF (4:1)	80°C	NaOH, DBU

 R=H,Me 12. Gonsalvi, 2017	80 bar(1:1)	30,000	-	H_2O: THF	80°C	DBU,LiOTf
 13. Gonsalvi, 2021	75 bar (1:1)	~2000	-	THF	80°C	DBU, LiOTf
 R=H,OH,OMe,NH_2 14. Khusnutdinova, 2017	60 bar(1:1)	>6000	-	acetonitrile	65°C	DBU
 15. Ikariya, 2015	20 (1:1)	167	-	1,4-dioxane	100°C	DBU
 16. Appel, 2015	40 (1:1)	500	25	acetonitrile	140°C	DBU
 17. Appel, 2016	40 atm (1:1)	-	7.5	CD_3CN	25°C	DBU
 18. Appel, 2017	34 atm(1:1)	-	$4.0(5) \times 10^{-1}$	H_2O	80°C	$NaHCO_3$

 18. Appel, 2017	$P_{(CO2)}$= 30 atm $P_{(H2)}$= 30 atm	58	-	0.082 mole fraction of water in acetonitrile	22°C	$[NEt_4HCO_3]$
 19. Bertrand, 2018	60 bar (1:3)	1881	-	THF	100°C	DBU, BCF
 20. Milstein, 2019	60 bar(1:1)	-	-	THF	110°C	KOH
 X = Cl, Br, I, CN 21. Rath, 2021	1 atm (1:1)	-	$10.65x10^5$	1,4-dioxane	80°C	DBU
 22, Walter leitner, 2012	10 bar/30ar	63	-	THF	140°C	EtOH
 23, Sanford, 2015	$P_{(H2)}$= 50 bar	550	-	THF	155°C	$NHMe_2$ K_3PO_4

 24, Prakash, 2016 & 2020	$P_{(H2)}$= 70 bar	520	-	biphasic 2-MTHF/water system	145°C	K_3PO_4
 25, Wass, 2017	$P_{(CO2)}$= 10 bar $P_{(H2)}$= 30 bar	8900	4500	Toluene	100°C	NaOEt
 26, Golderg, 2019	In the first step $H_2 : CO_2$ = 900 psi And in the second step 1200 psi	430	-	1,4-dioxane/EtOH	120°C	$Sc(OTf)_3$
 27, Klankarmayer, 2020	$P_{(CO2)}$= 30 bar $P_{(H2)}$= 90 bar	Upto 2100	-	EtOH	140°C	$(Al(OTf)_3$
 28, Wildner, 2020	$P_{(CO2)}$= 15 bar $P_{(H2)}$= 45 bar	240	23	EtOH	90°C	-

 **29, Rath, 2021**	$P_{(CO2)}$= 1 atm $P_{(H2)}$= 3 atm	4752	-	THF	60ºC	EtOH
[Co(Triphos)(L)n]$^{m+}$ **Beller, 2017**	20 bar/70 bar	50	-	THF/EtOH	100°C	$HNTf_2$
 **30. Prakash, 2017**	60 bar/60bar	36	-	THF	110°C	K_2CO_3
 **31. Pombeiro, 2017**	75 atm (1:3)	2387	66	Solvent- or amine-free	80°C	K_3PO_4
 **32. Bernskoeter, 2019**	100 psi/900 psi and 0/1150 psi from formamide	590	-	THF	100°C	DBU and LiOTf.
 **33. Leitner, 2021**	5 bar/160 bar	160	-	methanol and 1,4-dioxane	150°C	$(Ti(O^iPr)_4$ and $Sc(O^iPr)_3)$