

Supporting Information

Conversion of CO₂ from Air into Formate Using Amines and Phosphorus-Nitrogen PN³P-Ru(II) Pincer Complexes

Chao Guan^{+[a]}, Yupeng Pan^{+[a]}, Eleanor Pei Ling Ang,^[a] Jinsong Hu^[a], Changguang Yao^[a], Mei-Hui Huang^[a], Huafeng Li^[a], Zhiping Lai^[a], Kuo-Wei Huang^{[a]*}

^[a] King Abdullah University of Science and Technology (KAUST), Division of Physical Sciences and Engineering (PSE), Thuwal 23955-6900, Saudi Arabia

Table of Contents

SI Pages

1. General Analytical and Experimental Information -----	S2
2. Preparation of Ruthenium Complexes -----	S3
3. Procedures for Catalytic Tests and Optimization -----	S18
4. CO ₂ Capture and Conversion -----	S25
5. X-Ray Crystallography -----	S32
6. References -----	S34

1. General Analytical and Experimental Information

All experiments (unless stated otherwise) with metal complexes were carried out under an atmosphere of dry argon in a glovebox or using standard Schlenk techniques. All other chemicals were commercially available and used as received. ^1H , ^{31}P and ^{13}C NMR spectra for proton, phosphorus and carbon were recorded on a Bruker 400 MHz at 400, 162 and 100 MHz, or on a Bruker 600 MHz spectrometer at 600, 243 and 125 MHz, respectively. Column chromatography was performed on silica gel (200-300 mesh). HRMS spectra were recorded on a Finnigan MAT 95 system. Elemental analyses were carried out on a Flash 2000 elemental analyzer. The X-ray diffraction data were collected using a Bruker-AXS KAPPA-APEXII CCD diffractometer. The metal leaching was detected by a PerkinElmer Inductively Coupled Plasma Optical Emission Spectrometry. Results of the GC analysis for gas mixture was obtained with Techcomp GC7890II equipped with a TCD and a FID. The aromatized and dearomatized ruthenium complexes **1**, **2** and **3** were synthesized according to literature procedures.^[1] TON and TOF were calculated according to literature procedures.^[2]

2. Preparation of Ruthenium Complexes

a) Synthesis and characterization of complex 1

In an argon glovebox, PN³P (N,N'-bis(diphenylphosphino)-2,6-diaminopyridine) ligand (955 mg, 2 mmol) was added to a suspension of RuHCl(CO)(PPh₃)₃ (953 mg, 1 mmol) in THF (15 ml). The flask was sealed and heated to 65 °C overnight. The reaction mixture was then cooled to room temperature. After removal of the solvent in vacuo, a pale white residue remained. The residue was purified by column chromatography using CH₂Cl₂/MeOH (20:1-10:1) as the eluent to yield complex **1** (617 mg, 70%). Single crystals of complex **1'** were obtained by slowly evaporating the CH₂Cl₂/MeOH solution in air. ¹H NMR (600 MHz, DMSO-*d*₆): δ (ppm) = 9.88 (br, 4H), 7.81 (m, 8H), 7.65-7.30 (m, 35H), 7.21 (t, *J* = 7.5 Hz, 4H), 7.04 (t, *J* = 7.0 Hz, 8H), 6.86–6.40 (m, 12H), 5.97 (t, *J* = 8.1 Hz, 1H), 5.10 (br, 2H), 4.47 (d, *J* = 8.1 Hz, 2H), -7.39 (dt, *J* = 94.9, 22.4 Hz, 2H). ³¹P {¹H} NMR (243 MHz, C₆D₆): δ (ppm) = 93.64 (br, 4P), 54.55 (br, 2P). ¹³C NMR (151 MHz, DMSO-*d*₆): δ (ppm) = 204.10, 159.02, 152.02 and 142.03 (t, *J* = 26.4 Hz) 141.44, 136.97 and 134.51 (t, *J* = 26.9 Hz), 132.12–128.13 (m), 103.15, 101.03. ESI-MS (+ve): *m/z* 846.63 [M-2Cl]²⁺. Anal. Calcd. for C₈₉H₇₇Cl₂N₉O₂P₆Ru₂: C, 60.62; H, 4.40; N, 7.15. Found: C, 60.17; H, 4.52; N, 7.63.

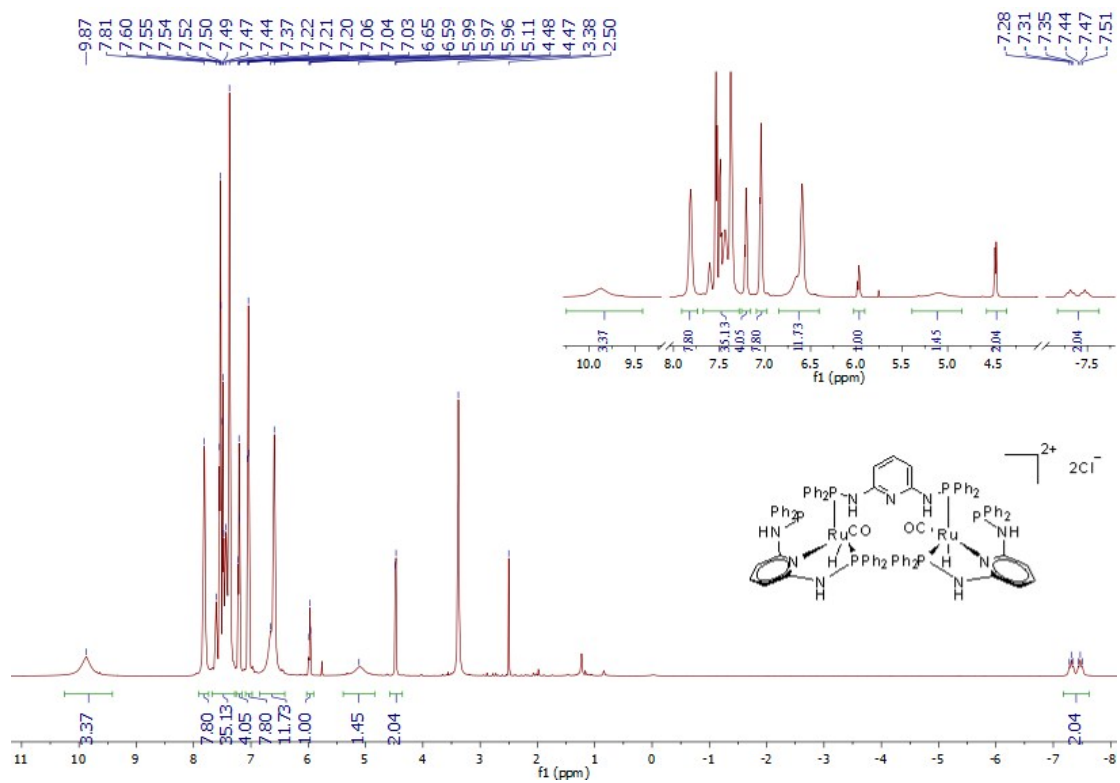


Figure S1. ^1H NMR spectrum of complex 1.

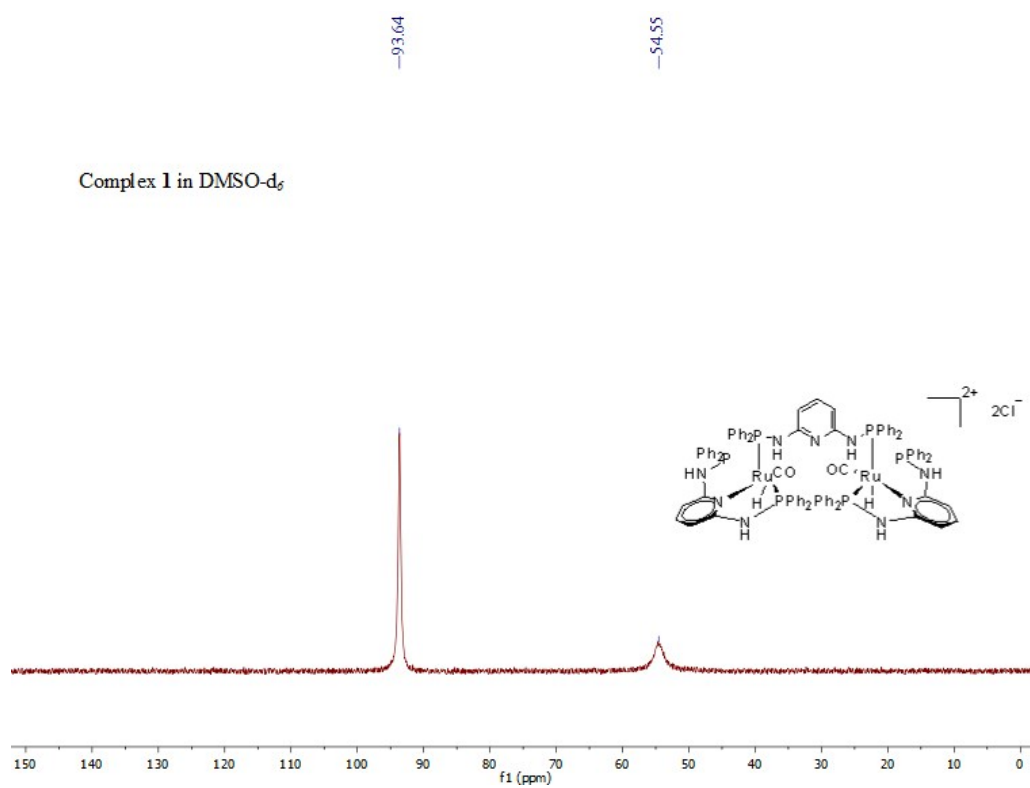
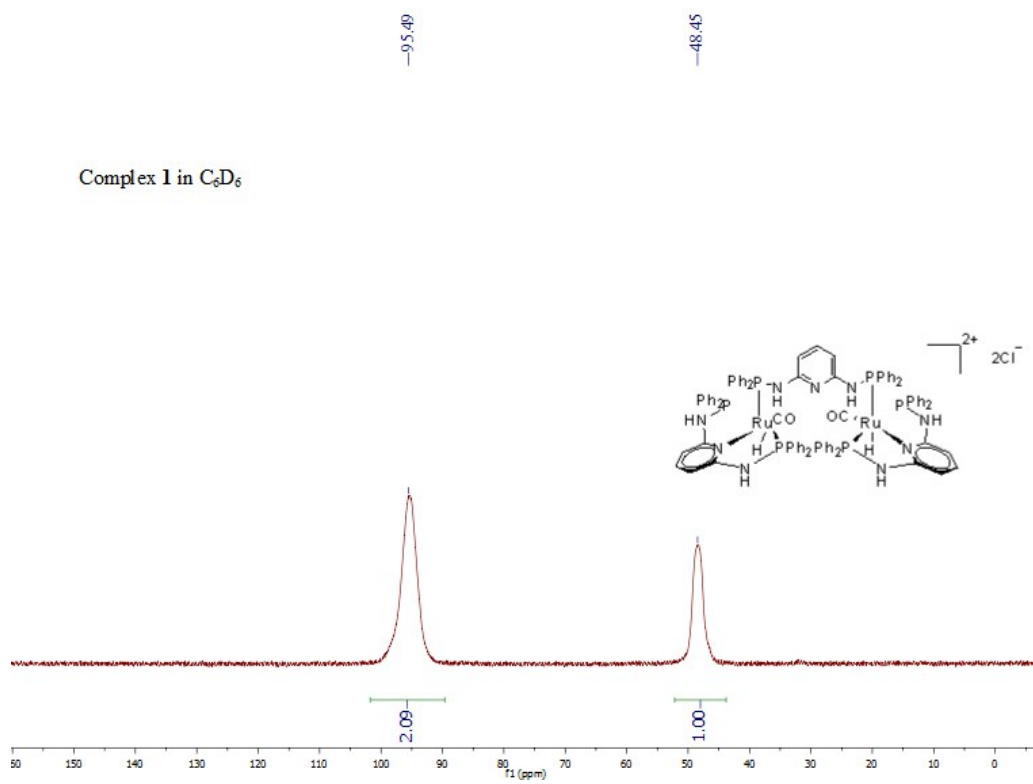


Figure S2. ^{31}P NMR spectra of complex 1.

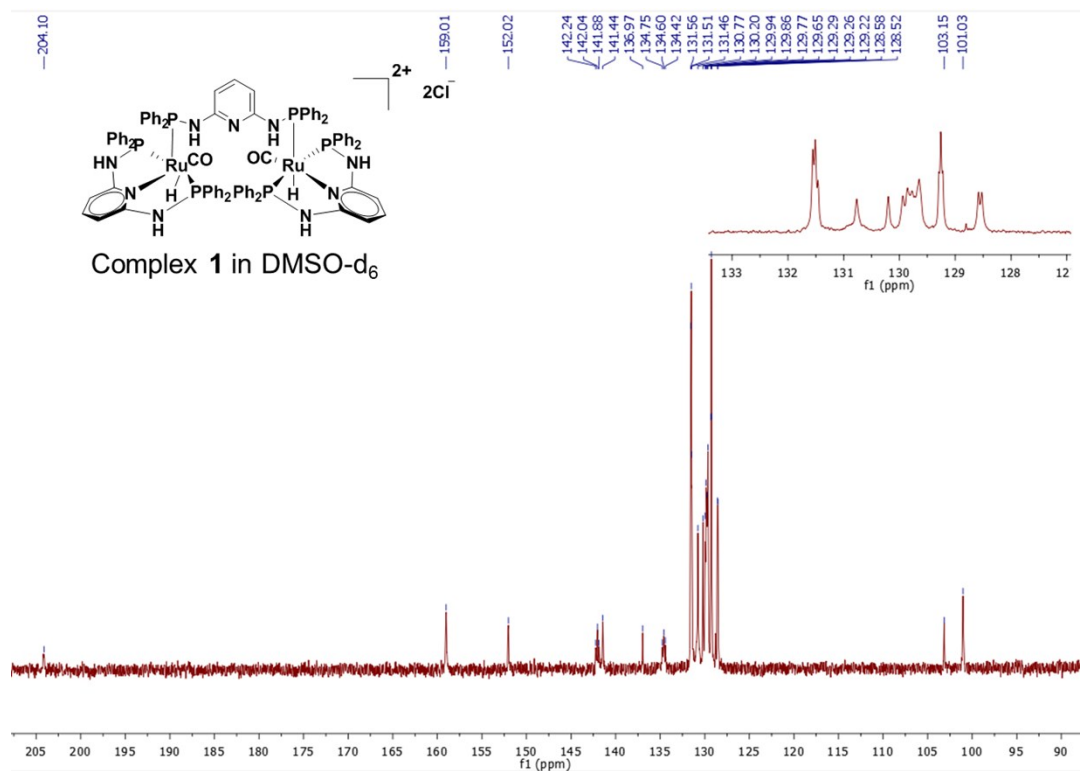
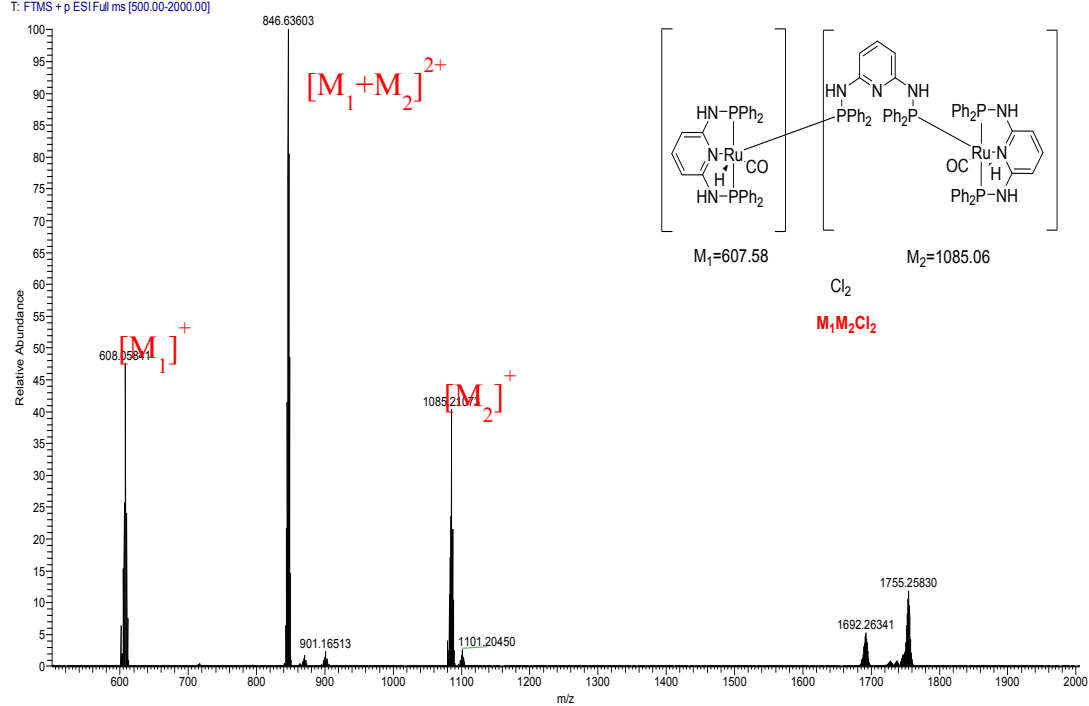


Figure S3. ¹³C NMR spectra of complex 1.

PH-PN3P_1 #2-22 RT: 0.03-0.56 AV: 21 NL: 3.52E7
T: FTMS + p ESI Full ms [500.00-2000.00]**Figure S4.** LTQ-Orbitrap MS full scan: +ve ESI for complex 1.

b) Synthesis and characterization of complex 2

In an argon glovebox, KO^tBu (22.4 mg, 0.2 mmol) was added to a solution of **1** (176.3 mg, 0.1 mmol) in THF (6.0 mL), then the mixture was stirred at room temperature for 2 hours. Removal of the solvent in vacuo resulted in a green solid. THF-*d*₈ (5 mL) was added to the solid. The suspension was filtered, yielding a white solid, which was dried in vacuo to obtain complex **2** (155.5 mg, 92%). ¹H NMR (600 MHz, DMSO-*d*₆): δ (ppm) = 7.89-7.86 (m, 8H), 7.58 (s, 8H), 7.24-7.21 (m, 9H), 7.12-7.10 (m, 5H), 7.04-6.96 (m, 17H), 6.84 (t, J = 7.1 Hz, 9H), 6.67 (t, J = 7.8 Hz, 2H), 6.49 (t, J = 8.7 Hz, 8H), 6.07 (d, J = 7.8 Hz, 4H), 5.65 (t, J = 8.0 Hz, 1H), 4.19 (d, J = 8.0 Hz, 2H), -7.61 (dt, J = 100.0, 21.1 Hz, 2H). ³¹P{¹H} NMR (243 MHz, DMSO-*d*₆): δ (ppm) = 85.70 (br, 4P), 50.09 (br, 2P). ¹³C NMR (176 MHz, THF-*d*₈): δ (ppm) = 204.77, 151.67, 135.46, 135.36, 133.07, 129.38, 128.23, 128.17, 126.40-125.12 (m), 99.76. ESI-MS (+ve): m/z 1692.27 [M+H]⁺.

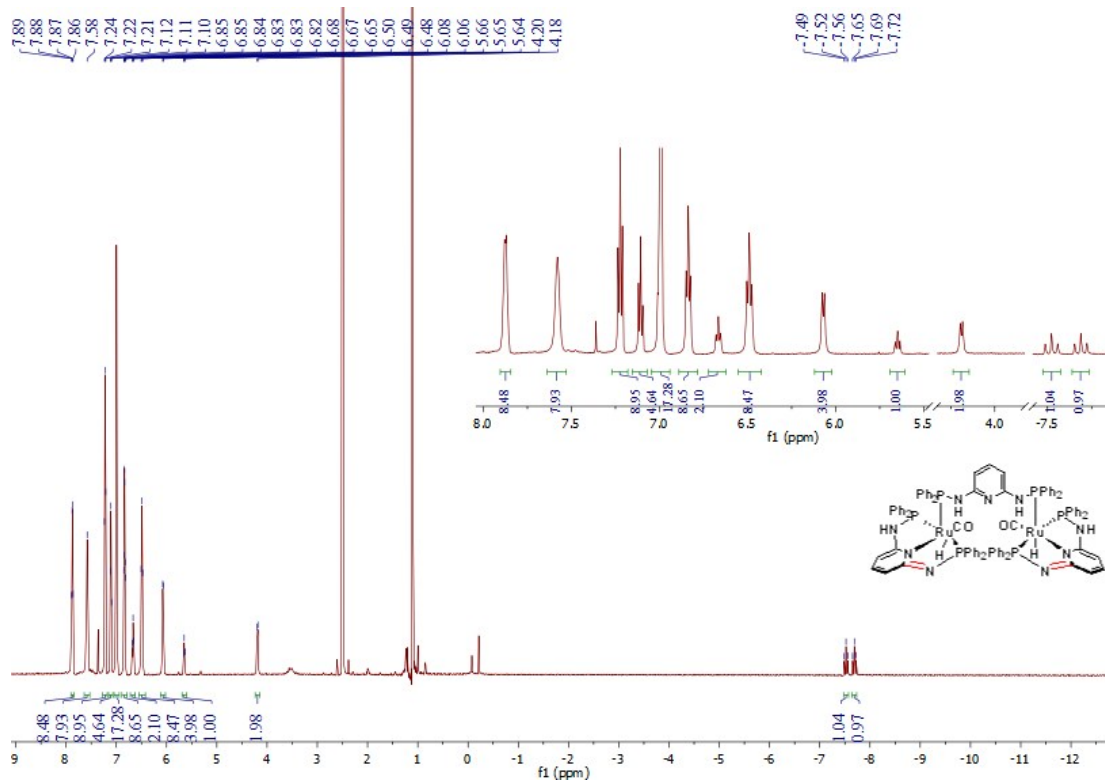


Figure S5. ^1H NMR spectrum of complex 2.

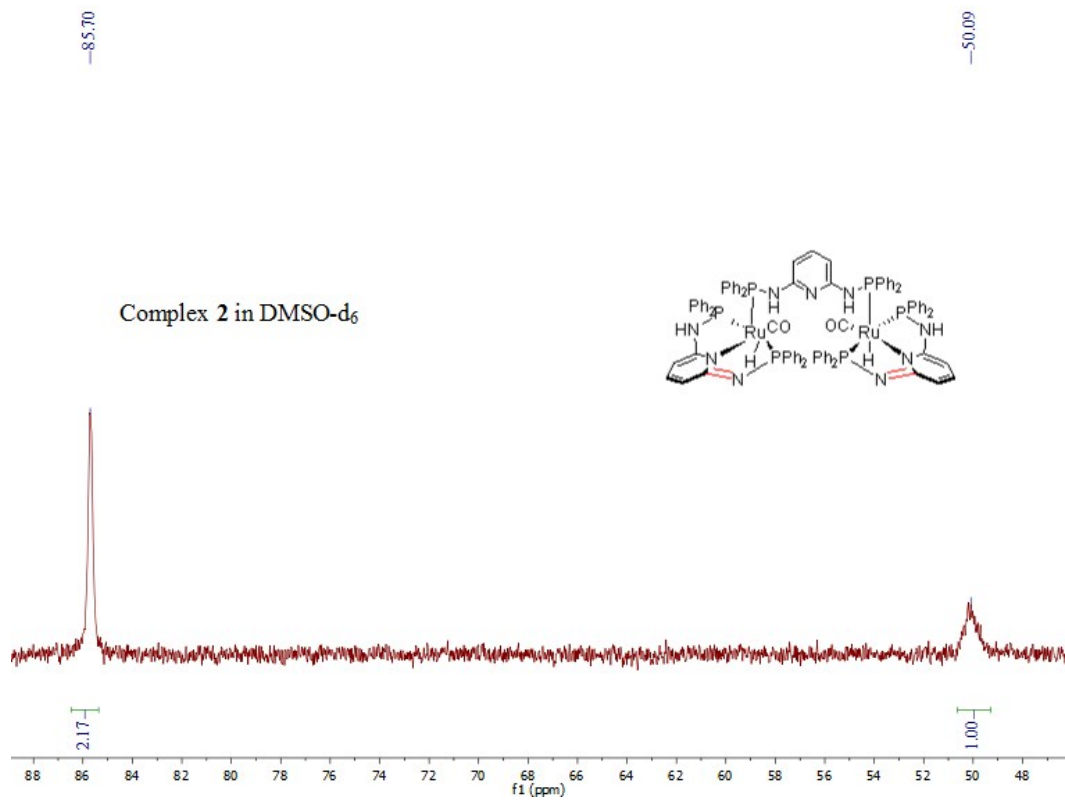


Figure S6. ³¹P NMR spectrum of complex 2.

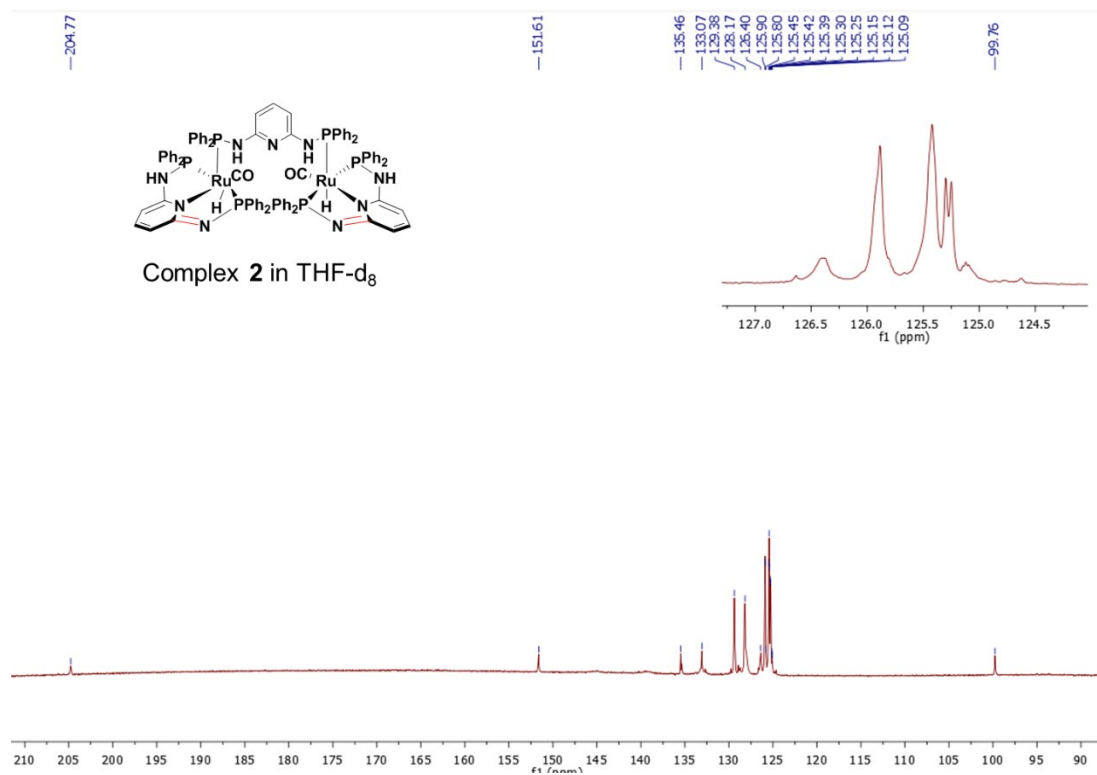


Figure S7. ¹³C NMR spectrum of complex 2.

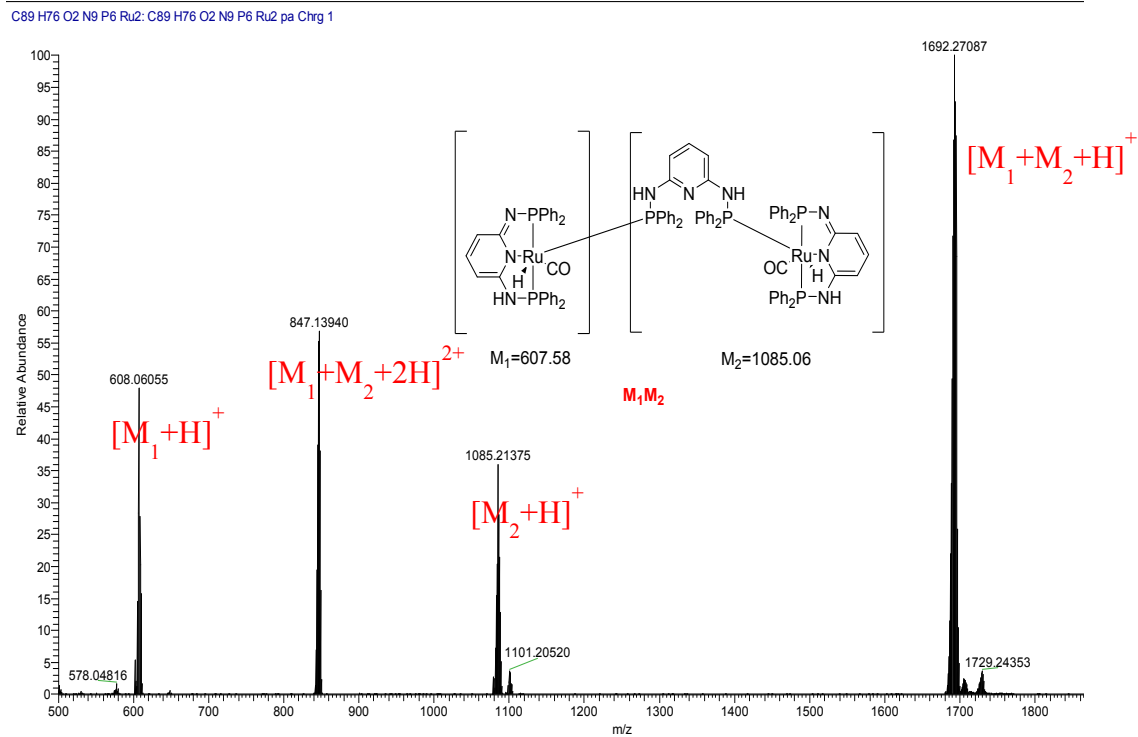


Figure S8. LTC-Orbitrap MS full scan: +ve ESI for complex 2.

c) Synthesis and characterization of complex **3**

In an argon glovebox, PPh_3 (57.7 mg, 0.22 mmol) was added to a solution of **2** (169.1 mg, 0.1 mmol) in THF (5.0 mL), and the mixture was stirred at room temperature for 6 hours. Removal of the solvent in vacuo resulted in a dark brown solid, to which Et_2O (5 mL) was added. The suspension was filtered, yielding a celadon solid that was dried in vacuo to obtain complex **3** (156.4 mg, 90%). ^1H NMR (600 MHz, C_6D_6): δ (ppm) = 8.42-8.40 (m, 2H, Ph), 7.93-7.85 (m, 2H, Ph), 7.75-7.66 (m, 2H, Ph), 7.33-7.23 (m, 6H, Ph), 7.09 (t, $J = 7.6$ Hz, 1H, py), 6.98-6.87 (m, 7H, Ph, py), 6.87-6.72 (m, 15H, Ph), 6.70 (t, $J = 7.7$ Hz, 2H, Ph), 5.08 (d, $J = 5.9$ Hz, 1H, py), 4.65 (br, 1H, NH), -6.74 (dt, $J_{\text{PH}} = 92.7, 22.4$ Hz, 1H, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ (ppm) = 91.26 (dd, $J_{\text{PP}} = 223.7, 18.6$ Hz, PNP), 88.14 (dd, $J = 223.7, 18.6$ Hz), PNP), 28.59 (t, $J = 18.6$ Hz, PPh_3). ESI-MS (+ve): m/z 870.1 $[\text{M}+\text{H}]^+$. Anal. Calcd. for $\text{C}_{48}\text{H}_{40}\text{N}_3\text{OP}_3\text{Ru}$: C, 66.35; H, 4.64; N, 4.84. Found: C, 65.86; H, 4.88; N, 4.35.

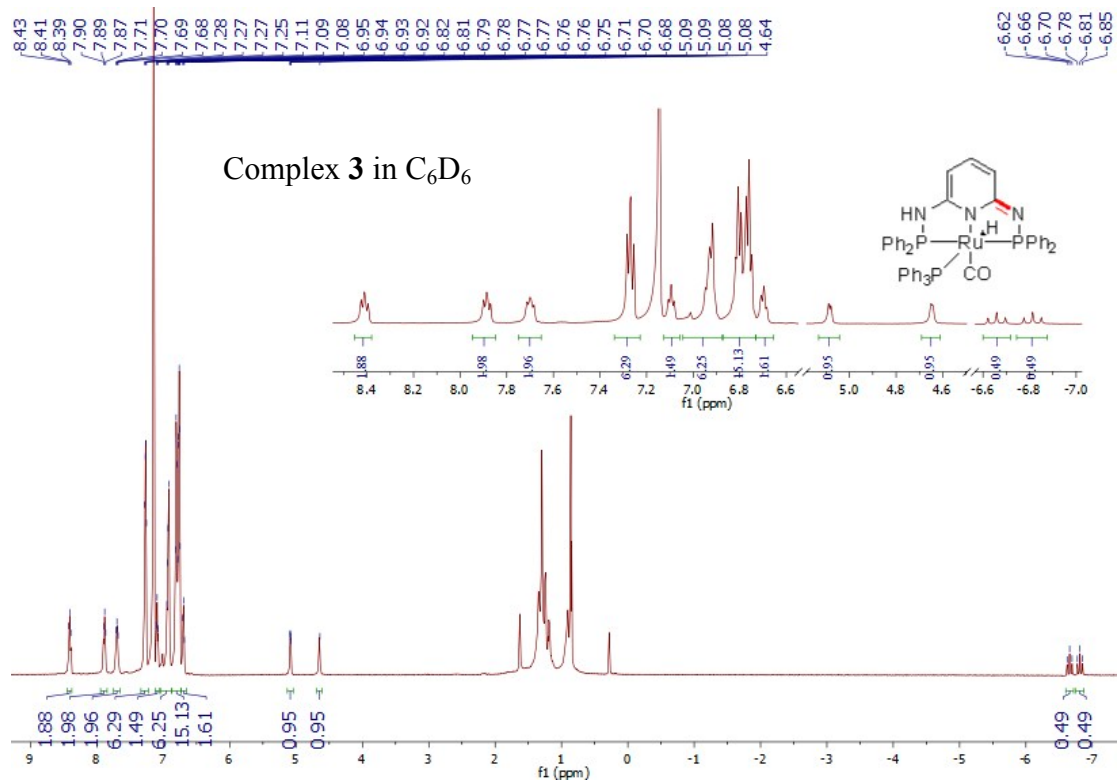


Figure S9. ¹H NMR spectrum of complex **3**.

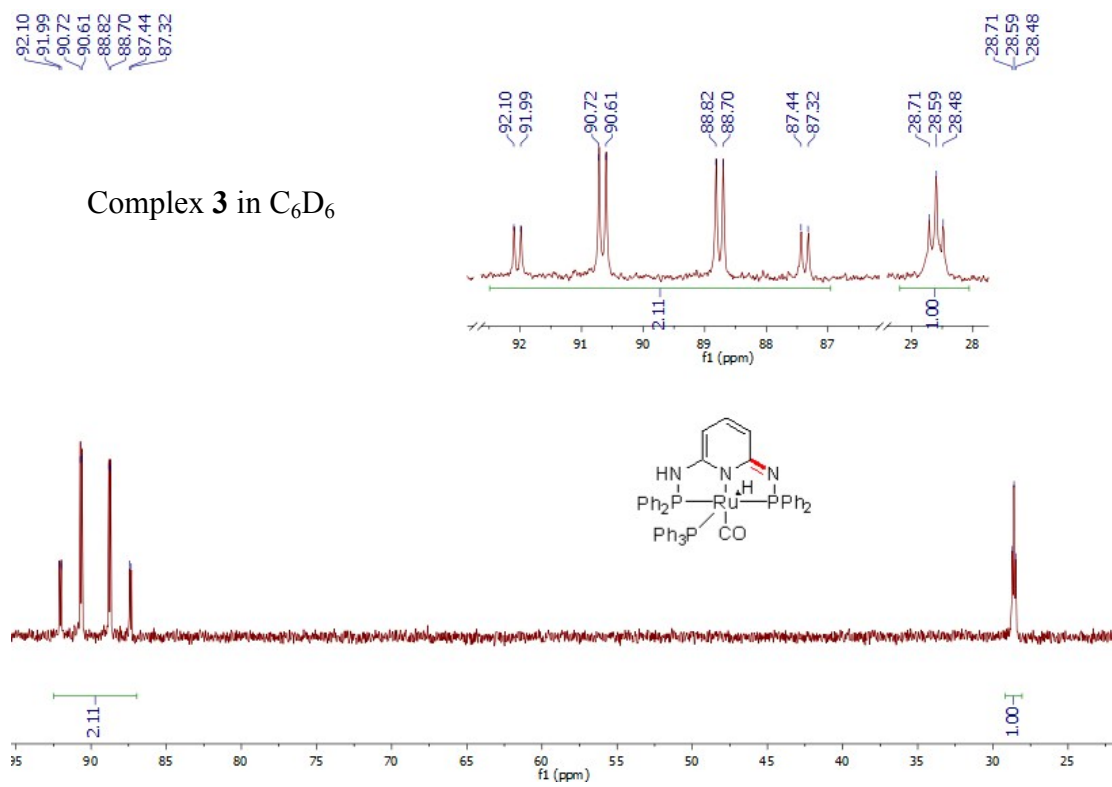


Figure S10. ^{31}P NMR spectrum of complex 3.

Ph-PN3P-dearomatic-110X-ACN_1_1 #1-38 RT: 0.02-1.00 AV: 38 NL: 1.86E8
T: FTMS + p ESI Full ms [500.00-2000.00]

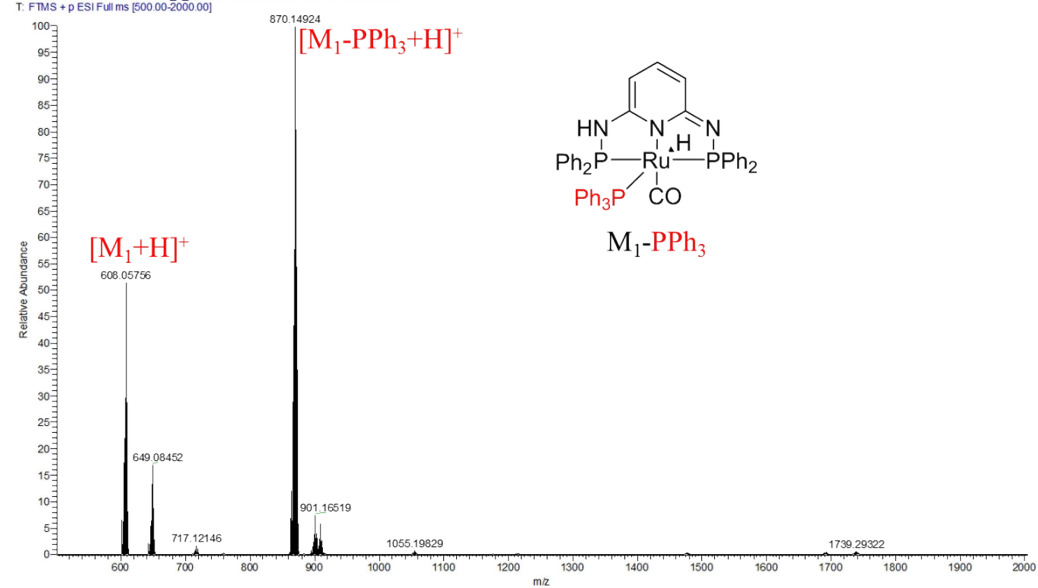


Figure S11. LTQ-Orbitrap MS full scan: +ve ESI for complex 3.

3. Procedures for Catalytic Tests and Optimization

a) General procedure for hydrogenation with or without gaseous CO₂^[2]

Complex **2**, a base (NaOH, Na₂CO₃ or NaHCO₃) and the solvent THF/H₂O (1:1, 20 mL) were added to a stainless steel autoclave (100 mL) equipped with a stir bar. After evacuation of the autoclave, a CO₂/H₂ mixture or pure H₂ was introduced at a given pressure. The reactor was stirred and heated for a certain period of time at the desired temperature (oil bath), then cooled down to room temperature. Water was added to the top layer of the biphasic reaction mixture until only one phase remained. Then, DMSO (0.1ml, 1.4 mmol) was added to the reaction mixture as an internal standard. An aliquot (0.4 mL) mixed with three drops of D₂O was analyzed by ¹H and ¹³C NMR spectroscopy. The reaction was repeated twice to confirm the reproducibility of the results.

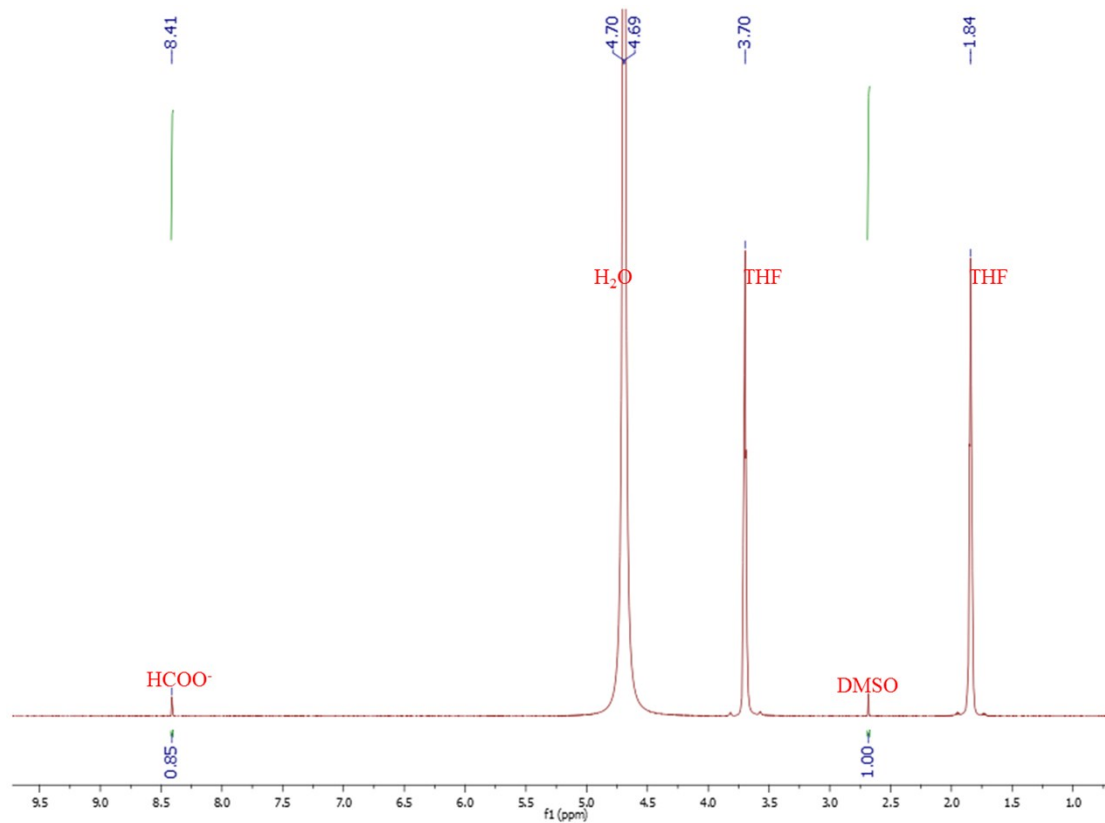


Figure S12. ^1H NMR spectrum of the reaction mixture obtained after hydrogenation of bicarbonate using complex **2**. Internal standard DMSO (1.4 mmol), pulse program=zgig30, D1=20s, NS=1631.

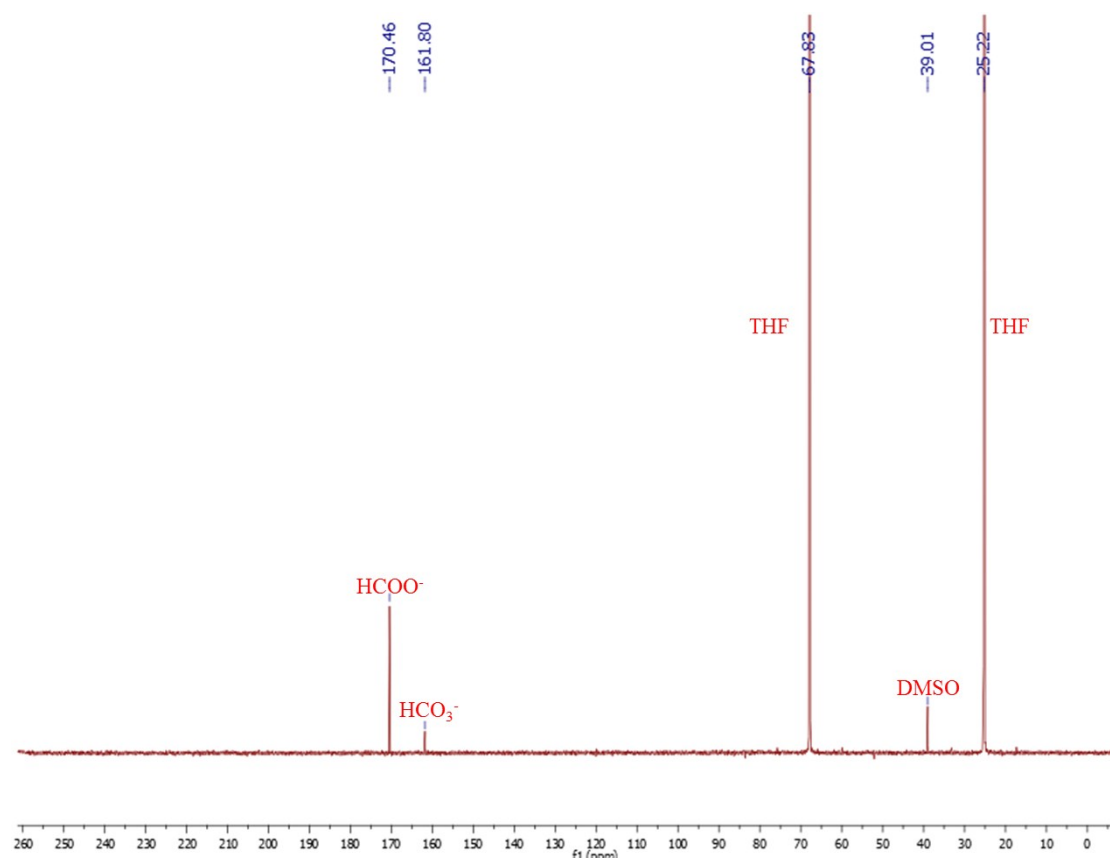


Figure S13. ^{13}C NMR spectrum of the reaction mixture obtained after hydrogenation of bicarbonate using complex **2**. Internal standard DMSO (1.4 mmol), pulse program=zgig30, D1=20s, NS=1631.

b) Optimization of reaction conditions for hydrogenation of bicarbonate using complex 2

Different temperatures, catalyst loadings, concentrations of bicarbonate and H₂ pressures were screened to determine the optimal conditions (Figure S14-S17). In Figure S14, the results showed that when the temperature was greater than 130 °C, the average TOF during the first 30 mins actually decreased, presumably due to the decomposition of catalyst. In Figure S15 and S16, the rates became faster with the increasing concentration of bicarbonate and pressure of H₂, suggesting the reaction rate law involves the concentrations of base and H₂. Accordingly, the final conditions for the best reaction activity were 130 °C, catalyst loading of 0.1 μmol and 1600 psi H₂. The variation in TON as a function of the reaction time is plotted in Figure S18; the maximum TON of 33,000 was achieved in approximately 50 hours.

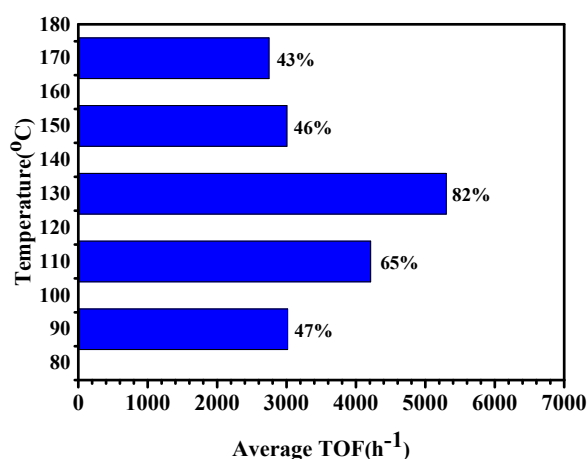


Figure S14. Catalytic performance of complex 2 at different temperatures. Reaction conditions: 10.4 mmol NaHCO₃, THF/H₂O (1:1, 20 mL), n(2)=1 μmol, 1600 psi H₂, Time= 0.5h, internal standard DMSO (1.4 mmol). TOF is an average value and calculated in the 30 mins.

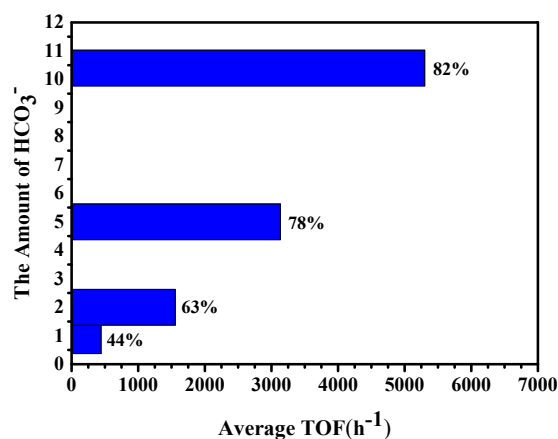


Figure S15. Catalytic performance of complex **2** with different concentrations of NaHCO_3 . Reaction conditions: THF/ H_2O (1:1, 20 mL), $n(\mathbf{2})=1.0 \mu\text{mol}$, 1600 psi H_2 , $T=130 \text{ }^\circ\text{C}$, time=0.5 h, internal standard DMSO (1.4 mmol). TOF is an average value and calculated in the 30 mins.

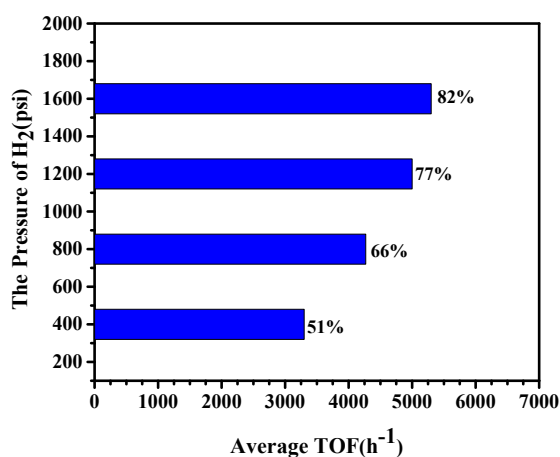


Figure S16. Catalytic performance of complex **2** under different H_2 pressures. Reaction conditions: 10.4 mmol NaHCO_3 , THF/ H_2O (1:1, 20 mL), $n(\mathbf{2})=1 \mu\text{mol}$, $T=130 \text{ }^\circ\text{C}$, time=0.5 h, internal standard DMSO (1.4 mmol). TOF is an average value and calculated in the 30 mins.

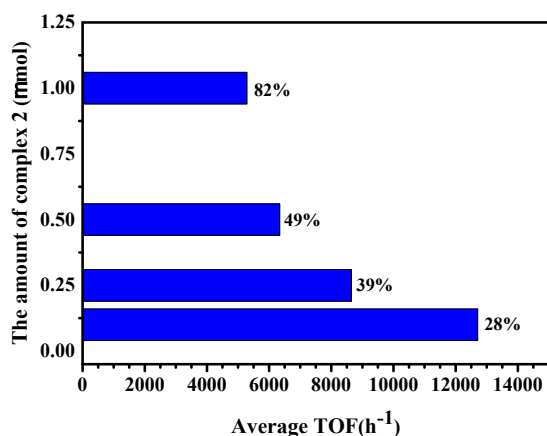


Figure S17. Catalytic performance of complex **2** with different catalyst loadings. Reaction conditions: 10.4 mmol NaHCO₃, THF/H₂O (1:1, 20 mL), T=130 °C, 1600 psi H₂, Time=0.5 h, internal standard DMSO (1.4 mmol). TOF is an average value and calculated in the 30 mins.

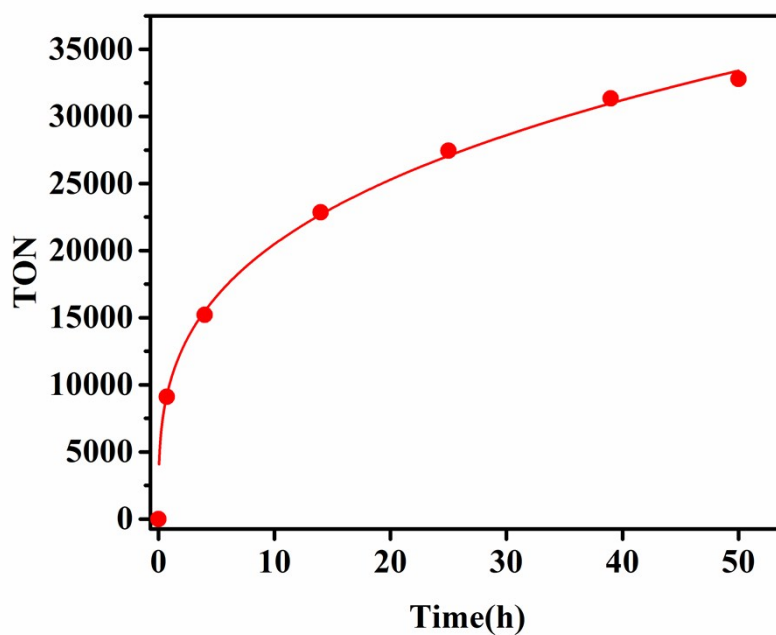


Figure S18. The relation between TON and reaction time during bicarbonate hydrogenation using complex **2**. Reaction conditions: 10.4 mmol NaHCO₃, THF/H₂O (1:1, 20 mL), n(**2**)=0.1 μmol, 1600 psi H₂, T=130 °C, 1600 psi H₂, internal standard DMSO (1.4 mmol).

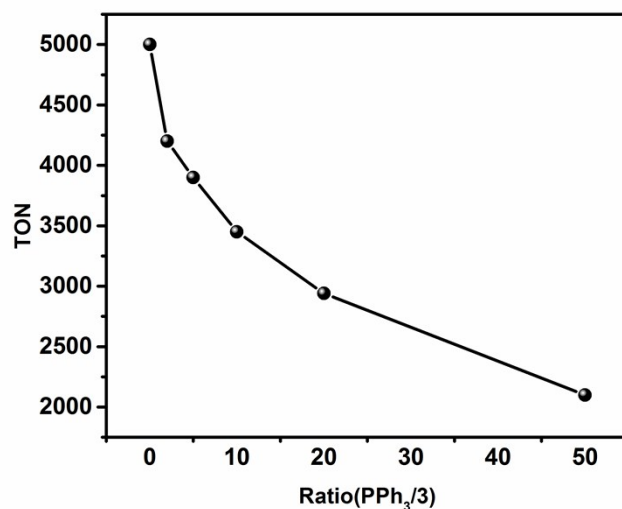


Figure S19. Catalytic performance of complex **3** with different amounts of PPh₃. Reaction conditions: 10.4 mmol NaHCO₃, THF/H₂O (1:1, 20 mL), n(**3**)=2 μmol, 1600 psi H₂, T=130 °C, time=1 h, internal standard DMSO (1.4 mmol).

4. CO₂ Capture and Conversion

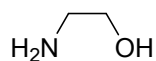
a) General procedure for CO₂ capture from air or gas cylinder (1 bar)^[2]

After dissolving the base in 15 mL of water in a 25 mL vial, 200 mL/min of either synthetic air (N₂:O₂ = 80:20) containing CO₂ (409 ppm), or CO₂ from a gas cylinder (1 bar) was bubbled into the aqueous solution through a needle for a given period of time. The reaction mixture was then sparged with nitrogen for an hour at room temperature. Subsequently, DMSO or imidazole (1.4 mmol) was added as an internal standard. The resultant solution was analyzed by ¹³C NMR with decoupled-NOE, relaxation delay=20 s (rd>20s did not change the integration), pulse angle=30°, scans=1000-2000 and acquisition time=1.36 s.

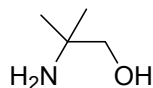
NaOH
(pKa=15.7)

Na₂CO₃
(pKa=10.3)

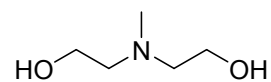
NH₄OH
(pKa=13.7)



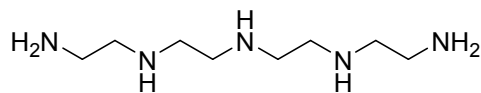
MEA (pKa=12.85)



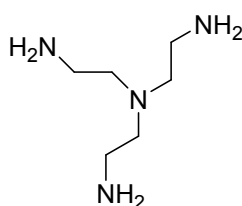
AMP (pKa=12.91)



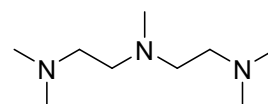
MDEA (pKa=8.52)



TEPA (pKa=10.07)



NTEA (pKa=10.00)



PMDTA (pKa=8.84)

Figure S20. Bases used for CO₂ capture in water during this study. The pKa values given here are in water.

Table S1. CO₂ capture using different bases*.

Entry	n(base) (mmol)	CO ₂ source	Absorption time (h)	Salt formed	n(CO ₂) absorbed (mmol)	Absorption efficiency (%)
1	NaOH (15)	air	50	Carbonate	3.7	25
2	NaCO ₃ (7.5)	air	50	/	/	/
3	NH ₄ OH (7.5)	air	50	/	/	/
4	MEA (7.5)	air	140	Carbamate/B icarbonate	1.3	17
5	AMP (7.5)	air	140	Carbamate	0.54	7
6	MDEA (7.5)	air	140	Bicarbonate	0.65	9
7	TEPA (7.5)	CO ₂ (1bar)	24	Carbamate/B icarbonate	14.5	38(1.93eq)
8	NTEA (7.5)	CO ₂ (1bar)	24	Carbamate/B icarbonate	17.7	59(2.36eq)
9	PMDTA (7.5)	CO ₂ (1bar)	24	Bicarbonate	8.7	39(1.16eq)

*Conditions: The base was dissolved in 15 ml H₂O, and air or CO₂ was bubbled through the solution at room temperature. The salt formed in the aqueous solution was analyzed by quantitative ¹³C NMR (pulse program=zgig30, D1=20 s, NS=1000-2000).

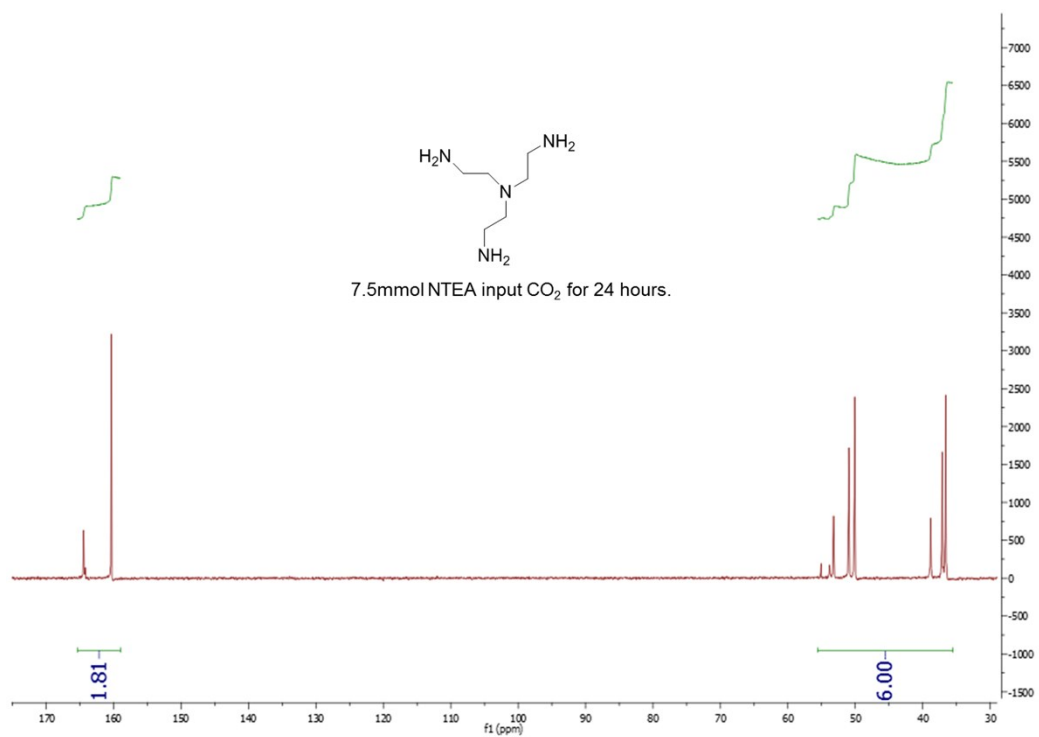


Figure S21: ¹³C NMR spectrum of the reaction mixture obtained after CO₂ capture CO₂ with amine NTEA. Pulse program=zgig30, D1=20 s, NS=1500.

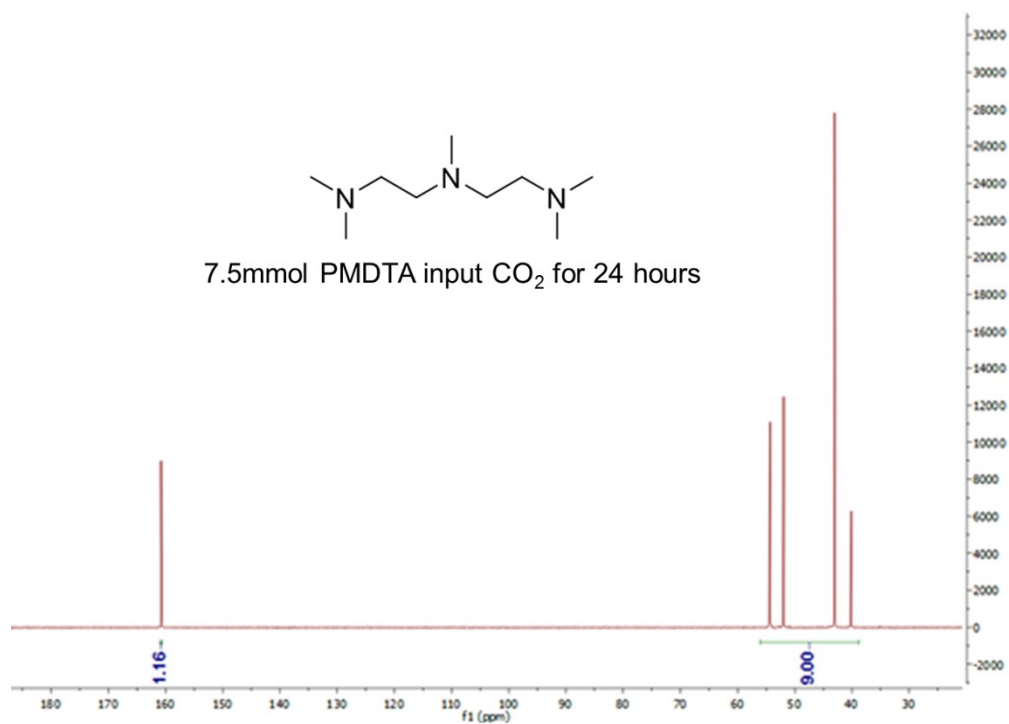


Figure S22: ¹³C NMR spectrum of the reaction mixture obtained after CO₂ capture with amine PMDTA. Pulse program=zgig30, D1=20 s, NS=1300.

b) General procedure for hydrogenation of CO₂ captured by base^[3]

After CO₂ was captured from air or gas cylinder by the base, the total volume of the base/water mixture was reduced to 5 mL by water evaporation. This was followed by transferring the mixture using ~5 mL water into a Monel Parr reactor (100 mL), equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer, in a N₂ chamber. Next, complex **2** and THF (10 mL) were added into the reaction mixture, and H₂ was introduced at a given pressure (e.g. 400 psi). After stirring and heating for a certain period of time at the desired temperature (oil bath), the reactor was cooled down to room temperature. A biphasic solution was obtained first; then, water was added until a homogeneous solution was achieved. Then, DMSO or imidazole (1.4 mmol) was added to the reaction mixture as an internal standard. An aliquot (0.4 mL) mixed with three drops of D₂O was analyzed by ¹H and ¹³C NMR spectroscopy.

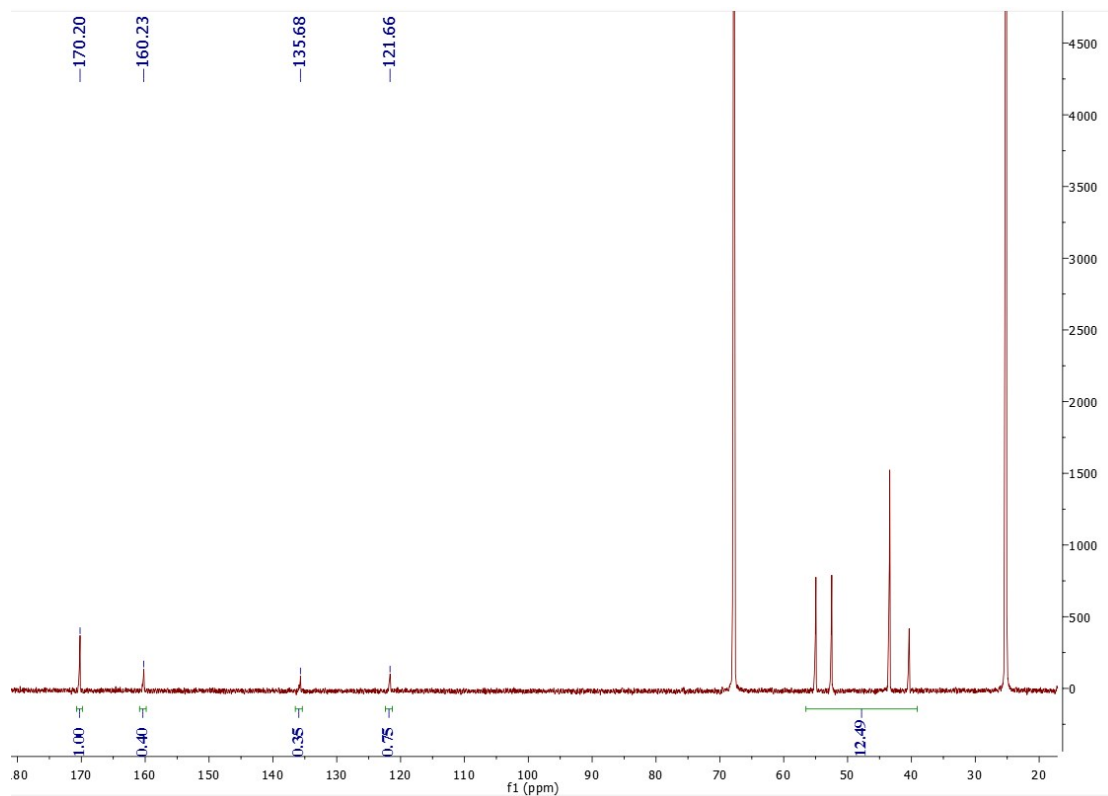


Figure S23: ^1H NMR spectrum of the reaction mixture obtained after hydrogenation of CO_2 captured from air by amine PMDTA using complex **2** ($2\ \mu\text{mol}$). 5.55 mmol amine + 10ml H_2O , 10 ml THF, $T=130\ ^\circ\text{C}$, 1h, 1600 psi H_2 , Internal standard imidazole (1.4 mmol), pulse program=zgig30, D1=20 s, NS=1631. TOF is an average value and calculated in the 1 hour.

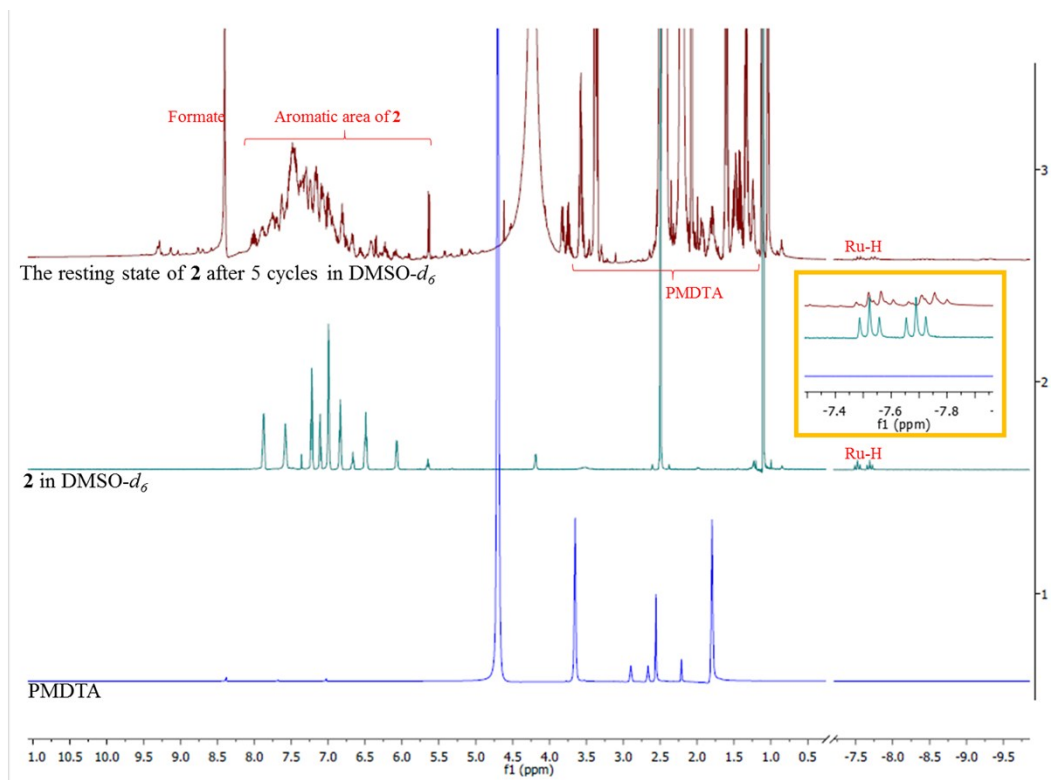


Figure S24: ^1H NMR spectrum of the organic layer of the biphasic reaction mixture after the evaporation of Me-THF using catalyst **2** in $\text{DMSO-}d_6$.

5. X-ray Crystallography

Table S2. Crystallographic data and refinement parameters for complex **1'**.

Identification code	Complex 1'
Empirical formula	C ₉₀ H ₇₈ N ₉ O ₅ P ₆ ClRu ₂
Formula weight	1789.02
Temperature/K	150.01
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	22.8345(7)
b/Å	15.0703(5)
c/Å	27.8444(9)
α/°	90
β/°	92.9260(10)
γ/°	90
Volume/Å ³	9569.4(5)
Z	4
ρ _{calc} /g/cm ³	1.242
μ/mm ⁻¹	4.169
F(000)	3664.0
Crystal size/mm ³	0.2 × 0.18 × 0.15
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	4.884 to 140.416
Index ranges	-17 ≤ h ≤ 17, -28 ≤ k ≤ 28, -35 ≤ l ≤ 35
Reflections collected	17969
Independent reflections	17969 [R _{int} = 0.05, R _{sigma} = 0.0570]
Data/restraints/parameters	17969/37/1020
Goodness-of-fit on F ²	1.081
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0597, wR ₂ = 0.1731
Final R indexes [all data]	R ₁ = 0.0679, wR ₂ = 0.1793
Largest diff. peak/hole / e Å ⁻³	3.26/-1.32

Table S3. Crystallographic data and refinement parameters for complex **3**.

Identification code	Complex 3
Empirical formula	C ₄₈ H ₄₀ N ₃ OP ₃ Ru
Formula weight	868.81
Temperature/K	180.0
Crystal system	triclinic
Space group	P-1
a/Å	12.2479(14)
b/Å	20.634(2)
c/Å	25.309(3)
α/°	106.192(4)
β/°	93.516(4)
γ/°	106.236(4)
Volume/Å ³	5829.8(12)
Z	4
ρ _{calc} /g/cm ³	0.990
μ/mm ⁻¹	0.380
F(000)	1784.0
Crystal size/mm ³	0.2 × 0.18 × 0.15
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.116 to 59.336
Index ranges	-17 ≤ h ≤ 17, - 8 ≤ k ≤ 28, -35 ≤ l ≤ 35
Reflections collected	140803
Independent reflections	32645 [R _{int} = 0.0618, R _{sigma} = 0.0618]
Data/restraints/parameters	32645/0/1002
Goodness-of-fit on F ²	1.060
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0770, wR ₂ = 0.1976
Final R indexes [all data]	R ₁ = 0.0990, wR ₂ = 0.2072
Largest diff. peak/hole / e Å ⁻³	1.47/-1.47

6. References

- [1] L.-P. He, T. Chen, D.-X. Xue, M. Eddaoudi, K.-W. Huang, *J. Organomet. Chem.* **2012**, 700, 202
- [2] J. Kothandaraman, A. Goepfert, M. Czaun, G. A. Olah, G. S. Prakash, *J. Am. Chem. Soc.* **2016**, 138, 778
- [3] J. Kothandaraman, A. Goepfert, M. Czaun, G. A. Olah, G. S. Prakash, *Green Chem.* **2016**, 18, 5831.