Polyhedron 207 (2021) 115375

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Ru catalyzed hydrogenation of CO_2 to formate under basic and acidic conditions

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ARTICLE INFO

Keywords:
Hydrogenation
CO_2
Ru
(tris)phosphine

ABSTRACT

The hydrogenation of CO_2 to MeOH is pertinent to advance future energy schemes. Towards this end, phosophine-ligated Ru catalysts have been shown to achieve this transformation under either acidic or basic conditions. In this manuscript, we screen catalytic conditions for a novel tris(phosphine) ligand with Ru to see if it can facilitate the conversion of CO_2 to MeOH under both acidic and basic conditions. With both sets of conditions, we observe hydrogenation of CO_2 to formate. This work shows that the same catalytic system can function under both reaction types but is limited to formate production.

1. Introduction

The development of catalysts that interconvert CO_2 and H_2 to formic acid or MeOH is pertinent to future energy schemes. Such systems would allow for the recycling of CO_2 to fuels, storage of H_2, and advancement of fuel cell technologies.[1–2] While there are numerous catalysts that can hydrogenate CO_2 to formate, very few can hydrogenate CO_2 to MeOH.

Towards hydrogenation of CO_2 to MeOH, three strategies have been employed. The first encompasses cascade catalysts, whereby a sequence of three catalysts work together to achieve i) hydrogenation of CO_2 to formic acid (FA), ii) FA esterification to give a formate ester, and iii) hydrogenation of the formate ester to provide MeOH (Fig. 1, top).[3–4] The second approach is a direct reduction of CO_2 to MeOH at a single catalyst (Fig. 1, middle). Now, the proposed sequence encompasses i) CO_2 insertion into M−H gives M−OCHO, ii) subsequent hydride/proton transfer furnishes a hydroxymethanolate, M−OCH_2OH, iii) hydrogenation generates M−OMe and water, and iv) H_2-mediated protonation releases the MeOH and regenerates the starting M−H .[5–9] This approach was first developed with triphos-ligated Ru (Fig. 1, top box),[5] and was shown to proceed in the absence of alcohols and additives.[6] Modification of the triphos-ligand to give a cationic species results in enhanced rates of MeOH production in the presence of Lewis acids and alcohols; a slightly different reaction sequence is proposed (Fig. 1, middle).[9] More recently, triphos-ligated Co was shown to also mediate the hydrogenation of CO_2 to MeOH in the presence of alcohol and a Lewis acid.[7] While the Co and Ru systems are postulated to occur at a single metal and necessitate solvent, a multi-nuclear Ir catalyst has also been shown to mediate this transformation in the gas-phase.[8] Finally, amine-assisted reduction of CO_2 (or carbamates) to MeOH has been achieved (Fig. 1, bottom). This sequence is thought to involve i) hydrogenation of CO_2 to FA, ii) formation of an amide via amine attack of FA, and iii) reduction of the amide to give MeOH and regenerate the amine.[10–15] This approach is conceptually different than the previous one as now catalysis occurs under basic conditions. Curiously, while this strategy has been achieved at Ru,[10,12–13,15] Mn,[11] and Fe,[14] it appears that the ability to undergo metal–ligand cooperativity (MLC) is needed. Hence, H_2 activation occurs across the metal and ligand, with hydride transfer occurring to the metal, and proton transfer to the ligand, as exemplified in Fig. 1 (bottom box). Formally, this changes the central N ligand from being LX- to L-type, which may have electronic structure ramifications.

Our research program aims to develop an understanding of why seemingly similar catalysts perform differently for hydrogenation reactions. As part of this effort, we developed a tris(phosphine) scaffold that features a pendent amine (Chart 1).[16] Given the flexible nature of the ligand, as exemplified from solid-state structures on Co, we envision that it may serve as a *fac*-coordinating surrogate to triphos (Chart 1), with the pendent amine serving as a proton relay and/or a CO_2 binding site. This could be advantageous because it is hypothesized that medium-assisted proton-transfer is pertinent in the triphos-ligated Ru system that takes CO_2 to MeOH.[6] Moreover, if protonated, the amine could give a cationic catalyst, which was found in another study to be advantageous.[9] The incorporation of the pendent amine may also

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https://doi.org/10.1016/j.poly.2021.115375
Received 1 April 2021; Accepted 15 July 2021
Available online 21 July 2021

mimic ligands that undergo MLC when bound to the metal. Dubois and coworkers have shown such a strategy to be effective at P_2N_2 ligands that allow for electrocatalytic H_2 production and oxidation.[17] The flexibility of the ligand design allows for *mer*-coordination akin to the pincer ligands that can undergo MLC, though now there is no electronic structure changes. We thus hypothesize that Ru complexes of our ligands may allow for CO_2 reduction to MeOH under both acidic (route 2) and basic (route 3) conditions. To the best of our knowledge, no report compares the same ligand/metal combination under these two distinct one-pot approaches to produce MeOH. Herein we describe hydrogenation reactions that test this hypothesis. We found that CO_2 can be hydrogenated under both sets of conditions, but only produce formate or ethyl formate. The results are contextualized in comparison to related systems that can achieve hydrogenation to MeOH.

2. Material and methods

Unless noted, all experiments were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Glassware was oven-dried for at least 24 h prior to use at 140 °C. Molecular sieves were activated at 280 °C under vacuum for 48 h and stored in the glovebox. All non-deuterated solvents were sparged and stored under nitrogen then collected from a Pure Process Technology solvent purification system to remove oxygen and water, stored over activated 3 Å molecular sieves in a glovebox, and tested with ketyl radical before use. NMR solvents were obtained from Cambridge Isotope Labs, subjected to 3 freeze–pumpthaw cycles, and stored under nitrogen in the glovebox over sieves. $Ru(acac)_3$,[18] $Ru(PPh_3)_3(CO)(Cl)(H)$,[19] and $^{Me}P_3$ [20] were prepared according to literature protocol. $^{NHtBu}P_3$ was prepared from PhP_3H [21] (see Scheme 1) akin to the synthesis of other $^{R}P_3$ analogues.[16] Ethanol used in acidic hydrogenations was dried with sodium ethoxide and stored over sieves. All other reagents were purchased from Sigma Aldrich or Oakwood Chemical and used without further purification.

NMR spectra of all samples were recorded on a Unity 300, Inova 400 spectrometer or Bruker neo500 spectrometer. ^{31}P NMR spectra were referenced to H_3PO_4 and ^{1}H NMR spectra referenced to advantageous solvent. Spectra were analyzed using MestReNova software.

2.1. Synthesis of $^{NHtBu}P_3NtBu$.

In a glovebox, PhP_3H was massed into a 50 mL Schlenk flask (0.500 g, 0.902 mmol). Paraformaldehyde was massed in a scintillation vial (35.7 mg, 1.19 mmol), and transferred to the 50 mL Schlenk flask with dichloromethane (DCM). To a 250 mL Schlenk flask, *tert*-butylamine was added (100 μL, 0.947 mmol) and 40 mL of DCM. This solution was chilled to −78 °C on a Schlenk line. The PhP_3H and paraformaldehyde solution was added dropwise to the 250 mL flask, stirred for 30 min, and left to warm to room temperature overnight. After stirring overnight, the reaction mixture was heated to 35 °C for several hours. The solvent was removed under vacuum which afforded a sticky white solid. This was washed several times with pentanes and toluene (0.9187 g, 21.4%). **^{1}H NMR (400 MHz, benzene-d_6, δ):** 7.38 – 7.13 (m, 22H, ArH), 7.01 – 6.82 (m, overlap with toluene solvent, ArH), 3.20 (d, 2H, PCH_2NH^tBu, J = 4.4 Hz), 0.81 (s, 9H, ^{t}Bu). **^{31}P NMR (121 MHz, benzene-d_6, δ):** −14.23 (overlapping d, 2P, J = 140.4 Hz), −28.33 (dd, 1P, J = 144.7 Hz, 134.9 Hz).

2.2. Attempt to isolate ($^{NHtBu}P_3$)Ru(H)(Cl)(CO).

Equimolar solutions of ligand and $(PPh_3)_3Ru(H)(Cl)(CO)$ in THF were combined and allowed to stir at room temperature. After two weeks, one major product was observed (see Fig. 2).

2.3. Attempt to isolate ($^{Me}P_3$)Ru(TMM) (TMM = trimethylenemathane).

Equimolar solutions of ligand and (COD)Ru(2-methylallyl)$_2$ were combined in toluene and allowed to stir at 85 °C for 24 h. An incomplete reaction was observed (see Fig. 3).

2.4. General considerations for hydrogenation experiments.

All high pressure/ high temperature reactions were carried out using a Parr Model 5000 multichannel reactor with six 75 mL HASTC alloy vessels with stirring, pressurized gas inlet valves, and pressure / temperature monitoring. The system is controlled using a model 4871 process controller and SpecView version 2.5 software. Bone dry CO_2 (99.9%; 10 ppm H_2O) and ultrahigh purity (UHP) H_2 (99.999%; 1 ppm

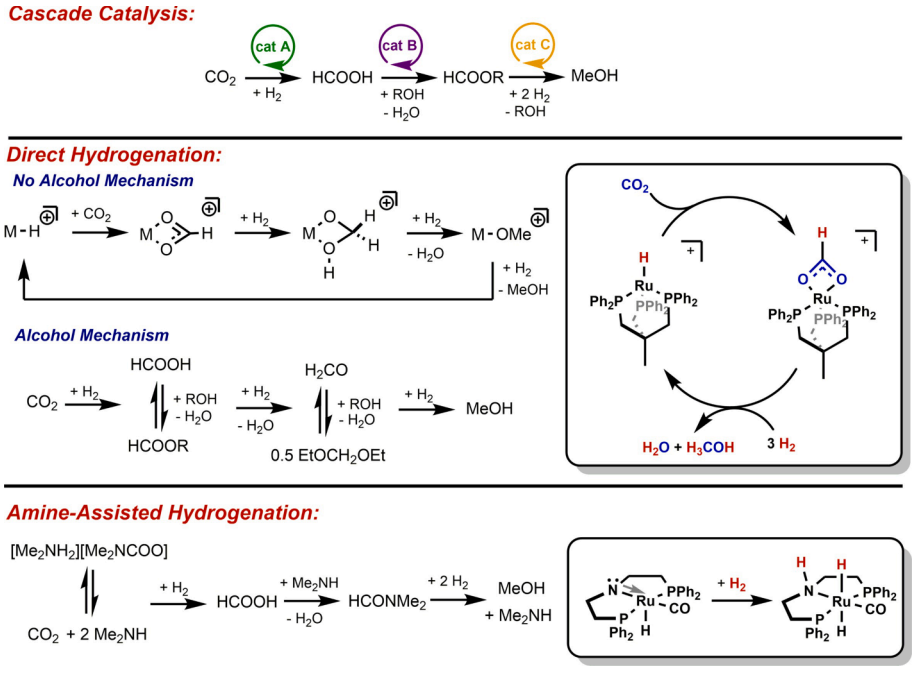


Fig. 1. Strategies for hydrogenation of CO_2 to MeOH. Boxes show exemplary catalysts for direct and amine-assisted hydrogenations.

O_2, 1 ppm H_2O, 0.5 ppm THC, 1 ppm CO, 1 ppm CO_2, 5 ppm N_2) gases were purchased from Airgas. Products were quantified using a Thermo Scientific Integrion Dionex HPIC and referenced to a formate calibration curve, and an Agilent 5890B GC and 5975C MS referenced to a methanol and ethyl formate calibration curve. Errors correspond to the standard deviation from duplicate runs, and average turnover numbers (TON) are reported.

2.5. Hydrogenations under basic conditions.

Conditions were adapted from the literature.[12] For a standard experiment, 100 equivalents of base was added to reaction vessel containing a stir bar by massing the difference. To the vessel, 200 μl of 0.025 M (5 μmol) ligand, 400 μl of 0.0125 M (5 μmol) $Ru(PPh_3)_3(CO)(Cl)(H)$, and 200 μl of 2.5 M (500 μmol) dimethylammonium dimethylcarbamate (DMAH.DMC) was added via manual pipette. Stock solutions were made in THF. To the base/catalyst solution, THF was added to give a final volume of 10 mL. The vessel was sealed with 6 screws and taken out of the glovebox and transferred immediately to the reactor block. The thermocouple, pressure sensor, and gas inlet were attached. Before the vessel was opened to any gas, the lines were vented, evacuated, and purged with relevant gas 3 times. Each vessel was then pressurized with 50 bar H_2 at room temperature. Stirring was turned on, the vessel was heated using a temperature ramp to 155 °C and kept at this temperature for 20 h. After the reaction was complete, it was cooled to room temperature, then further cooled by placing vessel in dry ice for at least 15 min. The vessel was slowly depressurized by opening the venting valve. For formate detection, 8.0 mL of reaction mixture was diluted to 100.0 mL in water. The sample solution was tested by IC. A formate calibration curve with a method detection limit of 1 ppm was prepared. For product detection by GCMS, an aliquot of the reaction mixture was injected.

2.6. Hydrogenations under acidic conditions.

Conditions were adapted from the literature.[5] For a standard experiment, 25 μmol of $Ru(acac)_3$ and 50 μmol of ligand was added to the reaction vessel containing a stir bar. To the vessel, 10 mmol of ethanol (0.584 mL), 1.0 mL of a 0.039 M (3.7 mg/mL) methane sulfonic acid (MSA) solution (1.5 eq.), and THF was added to give a final volume of 10 mL. The vessel was sealed with 6 screws and taken out of the glovebox and transferred immediately to the reactor. The thermocouple, pressure sensor, and gas inlet were attached. Before the vessel was opened to any gas, the lines were vented, evacuated, and purged with relevant gas 3 times. Each vessel was pressurized with 20 bar CO_2 then H_2 was added to a total pressure of 80 bar, at room temperature. Stirring was turned on, then the vessel was heated using a temperature ramp to 140 °C and kept at this temperature for 20 h. After the reaction was complete, it was cooled to room temperature, then further cooled by placing vessel in dry ice for at least 15 min. The vessel was slowly depressurized by opening the venting valve. For formate detection, 1.0 mL of reaction mixture was diluted to 10.0 mL in water. The sample solution was tested by IC. A formate calibration curve with a method detection limit of 1 ppm was prepared. For product detection, an aliquot of reaction mixture was tested via GCMS.

3. Results

3.1. Basic hydrogenation reactions.

Table 1 shows the results of the catalysis screening run under basic conditions. The conditions employed are modified from the literature.[12] Briefly, 1:1 mixtures of the ligand and $Ru(PPh_3)_3(CO)(Cl)(H)$ were dissolved in THF. This mixture was placed in the reactor along with 100 equiv of base and 100 equiv of dimethylammonium dimethylcarbamate (DMAH.DMC), the latter of which serves as a source of CO_2; at the reaction temperatures, CO_2 is released.[12] The reactor was pressurized to 50 bar H_2 and allowed to stir at 155 °C for 20 h, after which the solution phase was analyzed by IC (formate) and GCMS (all other products).

In the absence of both Ru and ligand, very little formate is produced (entry 2). $(PPh_3)_3Ru(H)(Cl)(CO)$ itself can hydrogenate DMAH.DMC to formate, yielding a TON of 40 (entry 1). However, addition of either $^{Me}P_3$ or $^{NHtBu}P_3$ ligand affords enhanced formate production, both giving a TON of 90 (entries 4 and 7). Hence, the tris(phosphine)ligands double the TON. Use of the *fac*-coordinating triphos as the ligand decreases the TON to 20. With either of the $^{R}P_3$ ligands, no formate is produced in the absence of added base. GCMS shows no formation of MeOH or DMF. When CO_2 is used as the carbon source instead of DMAH.DMC, lower TONs are observed (entries 8–9).

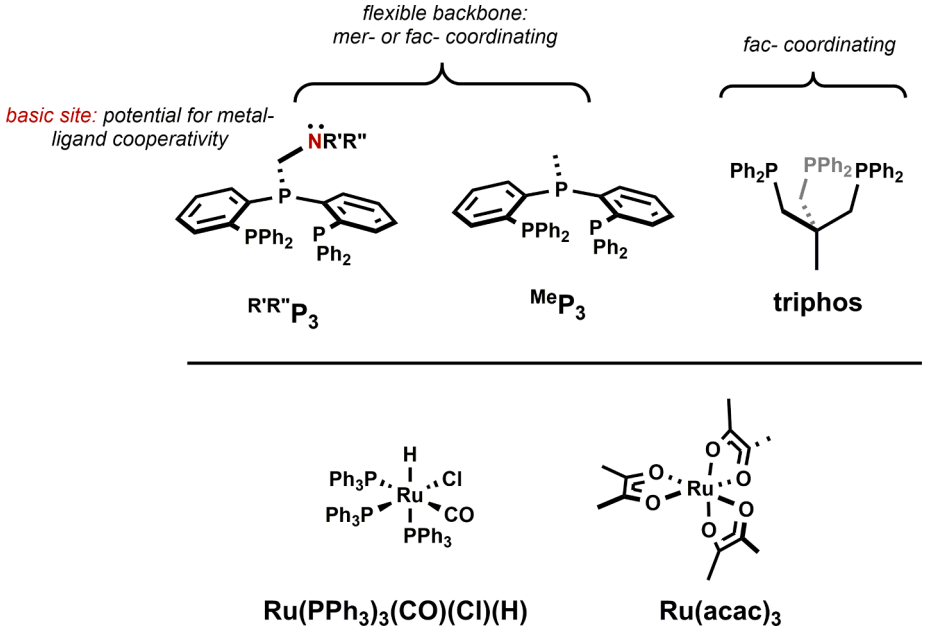
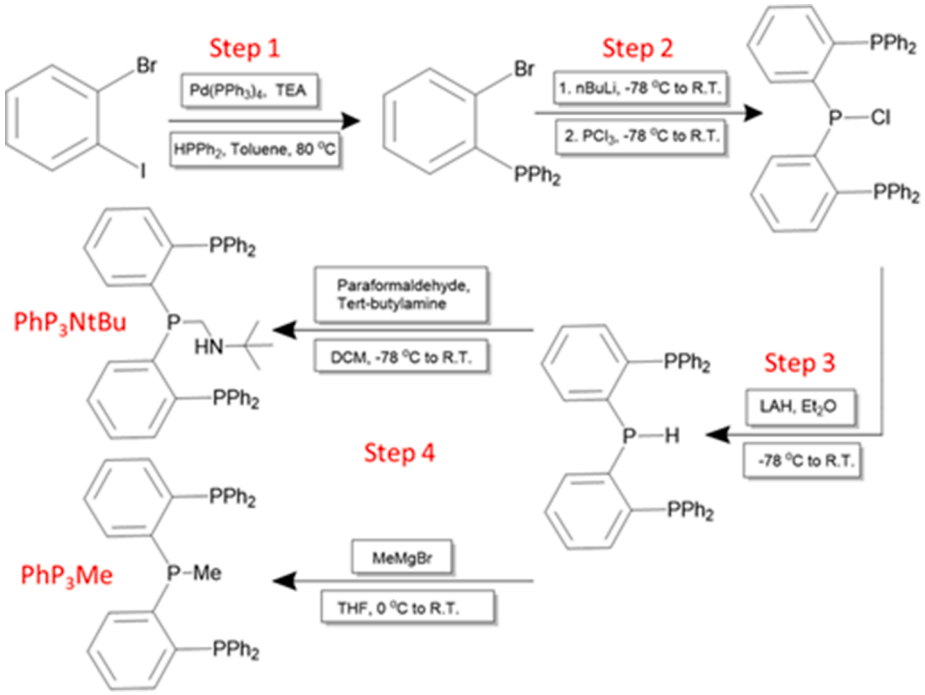


Chart 1. Ligands employed in the study.



Scheme 1. Synthetic strategy to prepare $^{NHtBu}P_3$.

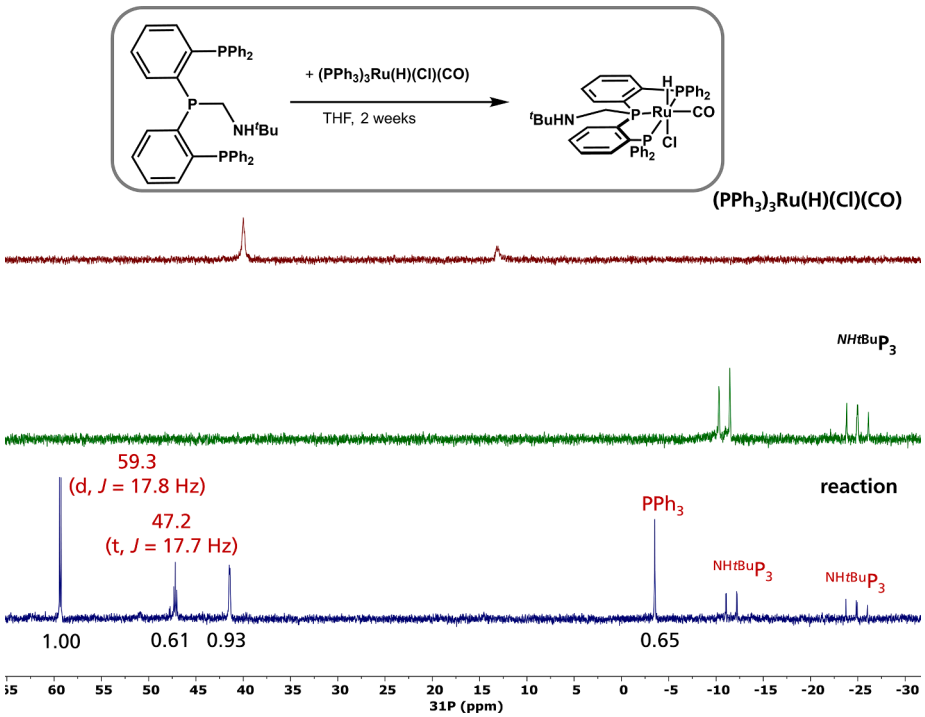


Fig. 2. ^{31}P NMR (121 MHz, Benzene-d_6) δ 59.3 (d, J = 17.8 Hz), 47.2 (t, J = 17.7 Hz). Peaks associated with ligand and free triphenylphosphine are labelled. The peak at 41.4 ppm could not be readily identified and may be derived from triphenylphosphine. Heating the solution did not alter the composition.

3.2. Acidic hydrogenation reactions.

Hydrogenation of CO_2 was also explored using acidic conditions. For these studies, Ru(acac)$_3$ was mixed with the ligand; the mixture of Ru(acac)$_3$ and triphos has been shown to give identical catalytic results when compared to pre-made triphos-ligated Ru(II).[5] Now, the reactions are run in a THF:EtOH solvent mixture with methanesulfonic acid (MSA) under H_2 and CO_2 gas. These conditions are a slight modification of those found in the literature; the catalyst loading and moles employed remain the same, but we used more solvent (more dilute conditions) to allow for accurate product quantification from our reactors.

As shown from Table 2, using the triphos ligand with these more dilute conditions gives a TON of 111 for MeOH after 20 h. This value is comparable to the TON of 135 obtained in the literature under more concentrated conditions (after 24 h).[5] When $^{Me}P_3$ is used as the ligand,

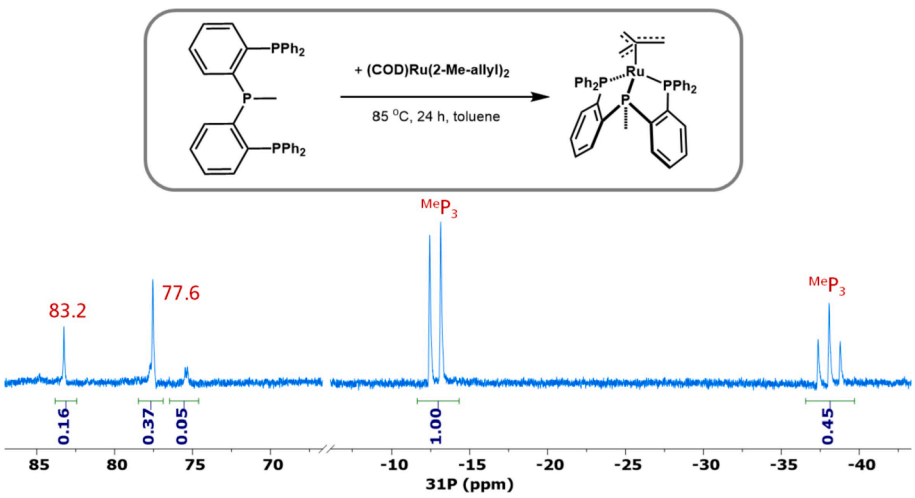
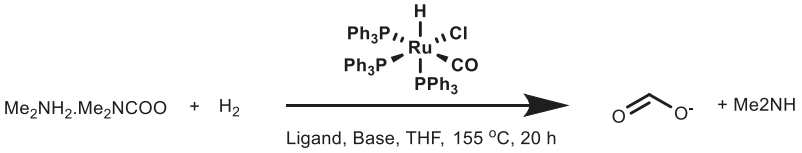


Fig. 3. ^{31}P NMR (121 MHz, Benzene-d_6). Starting ligand is present, and two pairs of resonances are also present. The major species product gives two singlets that integrate 1:2. A minor species appears to be comprised of a doublet at 75.4 (J = 29.6 Hz) and a multiplet that overlaps with the resonance at 77.6 ppm.

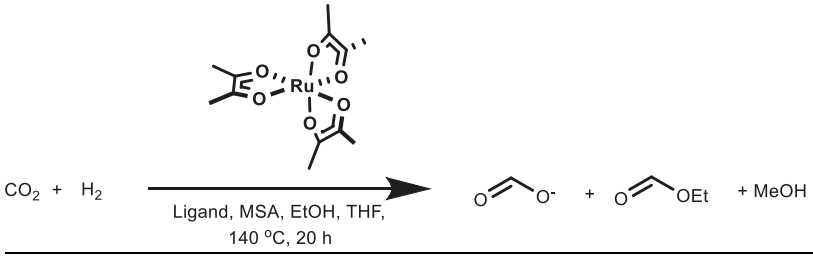
Table 1



Entry[a]	Ligand	Ru salt (μmol)	Base	Formate(TON)	MeOH(TON)
1	n/a	5	K_3PO_4	40	n/d[b]
2	n/a	n/a	K_3PO_4	2[c]	n/d
3	$^{NHtBu}P_3$	5	n/a	0.7 ± 0.3	n/d
4	$^{NHtBu}P_3$	5	K_3PO_4	90 ± 15	n/d
5	triphos	5	K_3PO_4	20[d]	n/d
6	$^{Me}P_3$	5	n/a	0.3 ± 0.1	n/d
7	$^{Me}P_3$	5	K_3PO_4	90 ± 28	n/d
8[e]	$^{NHtBu}P_3$	5	n/a	8[d]	n/d
9[e]	$^{NHtBu}P_3$	5	K_3PO_4	11 ± 2	n/d

[a] Reaction conditions: equal equivalences of $Ru(PPh_3)(CO)(Cl)(H)$ & ligand were used (5 μmol), all reactions were run for 20 h, under 50 bar of H_2, and 100 eq. of DMA-DMC. Turnover numbers (TON) correspond to the moles of product divided by the moles of ligand (or Ru) added. [b]Not detected. [c]TON determined relative to 1% of K_3PO_4. [d]Reaction not duplicated. [e]Reactions used 20 bar of CO_2 instead of DMA-DMC.

Table 2



Entry[a]	ligand	Acid (equiv.)	Formate(TON)	MeOH(TON)	Ethyl formate
1	triphos	MSA (1.5)	6.5	111	5.1
2	$^{Me}P_3$	MSA (1.5)	9 ± 4	n/d[b]	12 ± 8
3	$^{NHtBu}P_3$	MSA (1.5)	7.1 ± 0.7	n/d	2.2 ± 0.7
4[c]	$^{NHtBu}P_3$	MSA (1.5)	7	n/d	1
5[d]	$^{NHtBu}P_3$	MSA (1.5)	n/d	n/d	n/a[e]
6[d]	$^{Me}P_3$	MSA (1.5)	n/d	n/d	n/a

[a] Reaction conditions: $Ru(acac)_3$ (25 μmol) & ligand (50 μmol) used as catalyst, THF (9.0 mL), EtOH (10 mmol), 140 °C, 60 bar H_2, 20 bar CO_2, for 21 h. TON calculated relative to moles of Ru. [b]Not detected. [c]Used $(COD)Ru(methylallyl)_2$ instead of $Ru(acac)_3$. [d]Ethyl formate used instead of CO_2 as a carbon source (100 equiv). [e]Not applicable.

no MeOH is observed, but rather formate and ethyl formate. This is true whether $Ru(acac)_3$ or $(COD)Ru(meallyl)_2$ was used as the Ru source (entries 3–4).[5] The TON for formate is comparable to when triphos is employed, but the TON for ethyl formate is ~ double that when triphos is used. Using $^{NHtBu}P_3$ also gave no MeOH, and a comparable TON for formate as when triphos is employed as the ligand. Curiously, the ethyl formate yield is decreased, suggesting that esterification is inhibited. To test whether ethyl formate can be hydrogenated to methanol, ethyl formate was employed as the substrate (entries 5–6). No methanol was detected, suggesting that the catalysts cannot hydrogenate ethyl formate.

4. Discussion

The tris(phosphine) ligands were designed to allow MLC to occur, as well as to have a flexible binding motif to the metal. With regards to the potential for MLC, we sought to compare the performance of the ligand with those that are known to undergo MLC in the hydrogenation of DMA-H.DMC and hence used identical catalytic conditions.[12] These systems make use of (L)Ru(H)(Cl)(CO), where L is a *mer*-coordinating tridentate pincer ligand, and the carbonyl is the fourth ligand that comprises the plane with the pincer ligand. Though we have not isolated analogous $(^{R}P_3)Ru(H)(Cl)(CO)$ species, we sought to determine if they may form under catalytic conditions. Treatment of $^{tBuNH}P_3$ with $(PPh_3)_3Ru(H)(Cl)(CO)$ generates a single species, as determined by ^{31}P NMR spectroscopy (Fig. 2). An AB_2 splitting pattern is observed, with a doublet at 59.3 integrating to 2P atoms and a triplet at 47.2 integrating to 1P atom ($J = 17.7$ Hz). Such a configuration is consistent with the structure shown in Fig. 2.

Both $^{R}P_3$ ligands gave comparable results with respect to TON for formate and neither produced DMF or MeOH. Thus, the secondary amine has no impact on catalytic performance. The amine has also been shown to have no effect when $^{R}P_3CoCl$ is used to hydrogenate CO_2 in the presence of KO^tBu.[16] The combination of ligand and catalyst can also hydrogenate CO_2 to formate, albeit the TON are low.

As stated in the introduction, catalysts that undergo MLC coordinate *mer*- to the metal. When *fac*-enforcing triphos is used as the ligand, the TON is decreased relative to adding no ligand. This suggests that catalysis may ensue more readily from a *mer*-coordinating configuration, as suggested in Fig. 2.

Triphos-ligated Co and Ru has also been shown to hydrogenate CO_2 to MeOH under acidic conditions.[5,7] Given that the $^{R}P_3$ scaffold can coordinate metals in a *fac* manner,[16] it is anticipated that similar results would be obtained. Additionally, we have shown that $^{R}P_3CoCl$ can electrocatalytically reduce CO_2 to formate and MeOH in the presence of water.

Using the triphos ligand, we do observe MeOH with TON that are comparable to that reported in the literature. Switching to the $^{R}P_3$ ligands results in no MeOH being detected. Given that both are tris (phosphine) scaffolds, with mixed aryl/alkyl substituents, the different in reactivity is likely due to different geometries enforced. Whereas the triphos ligand is strictly *fac*-coordinating, the $^{R}P_3$ ligands developed are flexible, and from solid-state structures obtained on Co can adopt both *mer*- and *fac*- geometries.[16] This suggests that to obtain MeOH, a strict *fac*-coordinating ligand may be required. To glean more insight into the coordination of $^{R}P_3$ under these conditions, the synthesis of $(^{R}P_3)Ru(TMM)$ was attempted. This species is analogous to the pre-catalyst (triphos)Ru(TMM), which performs similarly to that mixing $Ru(acac)_3$ with triphos under the acidic conditions.[5] As shown in Figure 3, incomplete conversion occurs. Figure 3 nonetheless indicates that a novel Ru species forms.

Whereas the basic conditions gave comparable results between the two ligands, under the acidic conditions distinct TON are obtained for ethyl formate, with less being produced with $^{NHtBu}P_3$. It is conceivable that under acidic conditions, the pendent amine is protonated. It has been shown that using a cationic ligand that mimics triphos, enhanced MeOH production is observed.[9] This has been attributed to an electric field effect, which may not carry over in this system. Notably, while the triphos-derived system can hydrogenate ethyl formate, that with $^{R}P_3$ cannot (Table 2, entries 5–6).

5. Conclusions

Herein we screened mixtures of Ru salts and two $^{R}P_3$ ligands for the hydrogenation of CO_2 under both acidic and basic conditions. Under acidic conditions, no MeOH was observed, and only mixtures of ethyl formate and formate were produced. This contrasts with the results obtained with the triphos ligand that produces MeOH. This suggests that the strict *fac*-coordination of triphos may be necessary for MeOH production. Under acidic conditions we saw slightly increased activity for the ligand that lacks the pendant amine. Under basic conditions, we only observed formate, with similar TON for both ligands. This suggests that the amine employed is not sufficiently basic to engage in a meaningful MLC manner. This work shows that CO_2 hydrogenation to formate can be achieved with the same metal/ligand combination under both acidic and basic conditions. To our knowledge, this is the first study that explores the hydrogenation of CO_2 under both acidic and basic conditions with the same ligand at Ru.

CRediT authorship contribution statement

Austin T. Cannon: Methodology, Formal analysis, Investigation, Writing – original draft. **Caroline T. Saouma:** Conceptualization, Methodology, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

We thank Ms. Fang Wang for helpful discussions. This work was funded by the NSF CAREER (1945646) and NSF REU (1659579).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115375.

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