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H_2 Production Mediated by CO_2 via Initial Reduction to Formate

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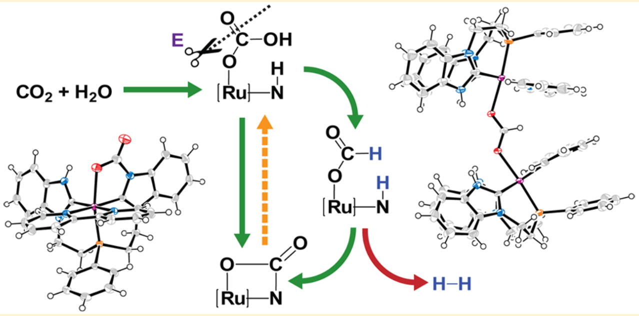
Ⓢ *Supporting Information*

ABSTRACT: A Ru(NH-NHC) complex with an open coordination site on the metal center adjacent to ligand N−H moieties has been synthesized and characterized. This complex exhibits unique reactivity upon reaction with either CO_2 or $NaHCO_3$, yielding a formate-bridged bimetallic complex via a spontaneous deoxygenation reaction and formal reduction at carbon. Dehydrogenation of the formate complex leads to a Ru−carbamate species following carbon−nitrogen bond formation between the CO_2 moiety and the NHC ligand. This reactivity opens up new pathways for CO_2 reduction and is relevant to H_2 storage.



Increased global energy demand, along with concerns of CO_2 as a contributor to climate change, have spurred intense research into alternative energy sources that do not result in greenhouse gas emissions. Hydrogen gas is a clean fuel that does not produce CO_2 as a product of combustion; however, the main source of H_2 on an industrial scale is the re-forming of natural gas, which results in significant CO_2 generation.[1] Thus, if H_2 is to be used as an alternative fuel, its source must be water, and the need to pressurize and transport H_2 requires advances in storage. Alternatively, the CO_2 generated from burning fossil fuels could be captured and reduced back to a useful form.[2] A number of electrochemical and hydrogenation systems have been studied that reduce CO_2 to CO,[3] formate/formic acid,[2c,4] and methanol.[5] The continued challenge is finding catalysts that operate under ambient conditions for these transformations. An interesting proposition that combines the use of H_2 as a clean-burning fuel with CO_2 reduction is the storage of H_2 in formic acid as a transportable liquid, followed by dehydrogenation to retrieve the H_2.[6] This strategy still requires H_2 that is not produced by the re-forming of natural gas and also only remains carbon neutral if the CO_2 formed in the dehydrogenation reaction is recaptured and recycled.[7]

In order to understand and exploit CO_2 chemistry, complexes that interact with CO_2 in unique or unconventional ways and that are capable of multifaceted CO_2 transformations are necessary. In biology, for example, [NiFe] CO dehydrogenase enzymes utilize a push−pull mechanism to activate CO_2, where Ni acts as a Lewis base and Fe^{2+} serves as a Lewis acid.[8] Several studies have utilized multimetallic complexes or metal−ligand cooperation to achieve new and unique reactivity with CO_2, including studies of bifunctional Co(salen-R)M complexes,[9] Zr/Co heterobimetallic complexes where CO_2 oxidatively adds across the two metal centers,[10] a Cu^I dimer/tetramer that reduces CO_2 to oxalate,[11] and Ru(PNP)[12] and Ru(PNN)[13] complexes that involve cooperative activation of CO_2 between a redox-active ligand and metal center.

Recently, we reported the synthesis of a new tridentate bisimidazole-phosphine ligand and metalation with Ru salts.[14] We hypothesized that a Ru complex with an accessible coordination site next to the protic NH-NHC ligands (Figure 1) could exhibit interesting metal−ligand reactivity with CO_2. This led us to the synthesis of a Ru−solvent complex, $[\mathbf{1\text{-}OH_2}]^{2+}$, which indeed demonstrates unique reactivity with both CO_2 and HCO_3^-; facilitating the reduction of either substrate to formate at room temperature or direct activation across the M−L scaffold at elevated temperature. In the case of substrate

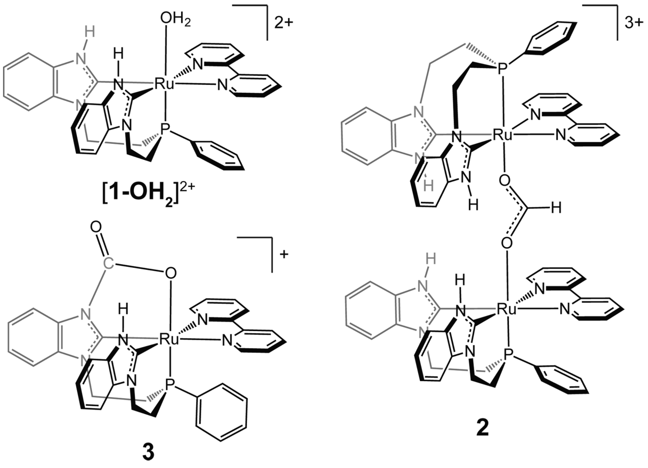


Figure 1. Ru(NH-NHC) complex with an open coordination site $[\mathbf{1\text{-}OH_2}]^{2+}$, the formate-bridged bimetallic complex **2**, and the carbamate complex **3**.

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reduction, the formate complex (**2**) undergoes spontaneous dehydrogenation in solution to yield H_2 and the product of direct M–L activation, a Ru–carbamate complex (**3**) where the CO_2 remains activated and added to the ligand scaffold.

Synthesis of the phosphine ligand PhP(Etbim)$_2$ was carried out using a modified procedure with benzimidazole as the NHC precursor.[14] Protonation of the benzimidazole moieties in PhP(bim)$_2$ followed by reaction with [Ru(Bz)(bpy)(OTf)](OTf) (Bz = benzene, bpy = 2,2′-bipyridine, OTf = trifluoromethanesulfonate) leads to a precursor where only the P atom binds to the Ru center (Figure S1 in the Supporting Information). This complex is then cleanly converted to [**1-OH$_2$**]$^{2+}$ at 175 °C in ethylene glycol (Figure S2 in the Supporting Information). Interestingly, the ^{1}H NMR and ^{31}P NMR spectra of [**1-OH$_2$**]$^{2+}$ in CD_2Cl_2 or DMSO-d_6 show multiple products with broad resonances (Figure S3 in the Supporting Information). However, addition of a Cl^- source to a solution of [**1-OH$_2$**]$^{2+}$ in either solvent leads immediately to clean and interpretable ^{1}H, ^{31}P, and ^{13}C NMR spectra (Figures S4 and S5 in the Supporting Information). Crystals suitable for X-ray diffraction were grown of [**1-Cl**]$^+$ by slow diffusion of Et_2O into an acetone solution (Figure 2). The Cl^- acts to lock the N–H protons into a symmetric geometry due to H-bonding interactions, which may also explain why the ^{1}H NMR spectrum of [**1-OH$_2$**]$^{2+}$ shows multiple resonances when H_2O is bound if a variety of H-bonding interactions cause multiple conformers to exist in solution. The ^{1}H NMR spectrum of [**1-OH$_2$**]$^{2+}$ is also sharp and well-defined in CD_3OD (Figure S6 in the Supporting Information), similar to the spectrum of [**1-Cl**]$^+$, although the N–H protons cannot be located in CD_3OD, likely due to H/D exchange.

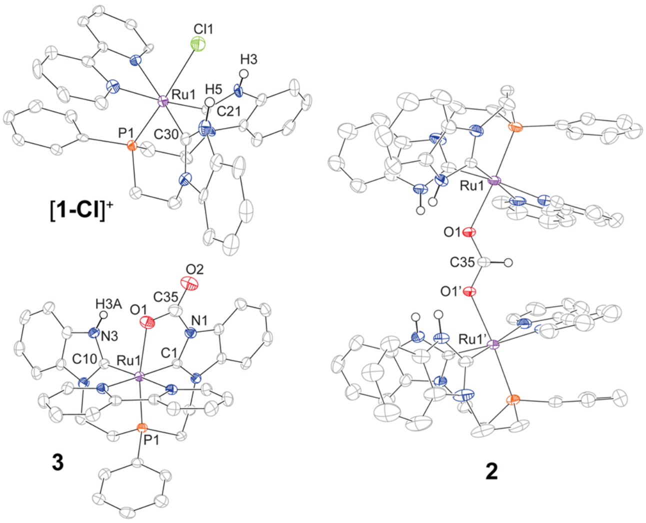


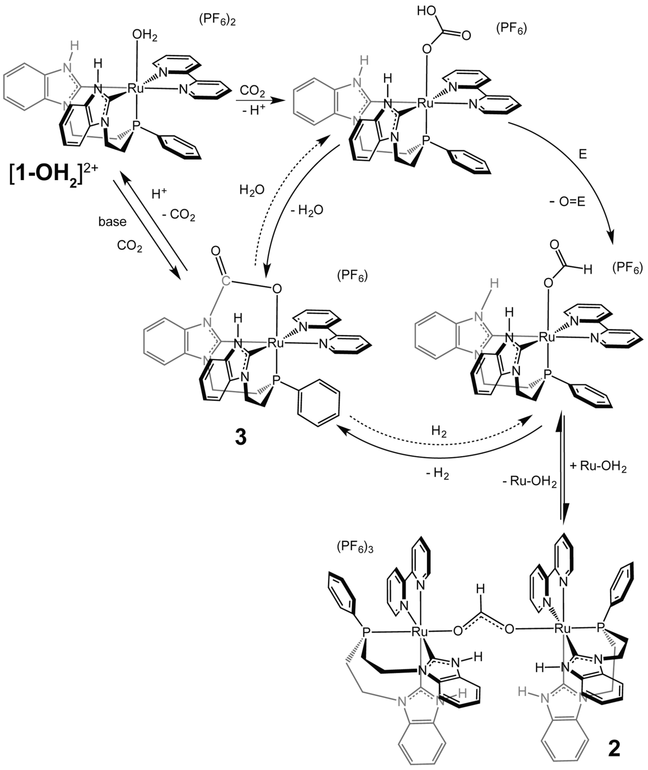
Figure 2. Molecular structures of [**1-Cl**]$^+$, **2**, and **3** with thermal ellipsoids shown at 50% probability. [**1-Cl**]$^+$ displays H-bonding interactions between N–H groups and bound Cl with one Cl^- counterion omitted for clarity. Complex **2** is a formate-bridged bimetallic Ru complex with three PF_6^- counterions removed for clarity. The same structure was determined for addition of CO_2, HCO_3^-, and HCO_2^- to **1**. The structure of **3** shows a carbamate with the O atom bound to the Ru center with one PF_6^- counterion removed for clarity. Selected interatomic distances (Å) and angles (deg): for [**1-Cl**]$^+$, Ru1–Cl1 2.534(2), Ru1–C21 2.011(6), Ru1–C30 2.024(6), H3–Cl1 2.475, H5–Cl1 2.509; for **2**, Ru1–O1 2.181, C35–O1 1.246, O1–C1–O1′ 125.3; for **3**, Ru1–O1 2.219, O1–C35 1.301, C35–O2 1.2229, C35–N1 1.457, H3A–O1 2.532, O1–C35–O2 127.29.

We studied the reaction of [**1-OH$_2$**]$^{2+}$ and CO_2 with the goal of exploring possible CO_2 reduction chemistry. Addition of CO_2 to solutions of [**1-OH$_2$**]$^{2+}$ in CH_2Cl_2 yielded orange crystals after standing at room temperature for several days. These crystals were analyzed by X-ray diffraction and were found to be a formate-bridged bimetallic complex (**2**, Figure 2). Complex **2** was also independently prepared by the addition of sodium formate to a solution of [**1-OH$_2$**]$^{2+}$ in CH_2Cl_2. The O–C–O bond angle in **2** is 125.3° with C–O bond lengths of 1.246 Å, consistent with reported formate-bridged metal complexes.[15] The IR spectrum of **2** displays a strong stretch at 1548 cm^{-1} (Figure S7 in the Supporting Information) and a peak in the ^{13}C NMR at 170 ppm, both suggestive of a metal formate species.[15] It should be noted that while the Ru–formate complex crystallizes in the bimetallic form in CH_2Cl_2, a solvent in which it is sparingly soluble, we believe that it readily converts to the monometallic form and 1 equiv of Ru–solvento complex in a coordinating solvent (Figures S8 and S9 in the Supporting Information). We hypothesized that the mechanism for reduction of CO_2 to formate proceeds via initial formation of a Ru–bicarbonate intermediate, as CO_2 can insert into M–OH and M–OH_2 bonds to equilibrate with bicarbonate.[16] This provides a plausible route for formation of a Ru–HCO_3^- species which could undergo deoxygenation to form the reduced Ru–formate. Direct addition of $NaHCO_3$ to solutions of [**1-OH$_2$**]$^{2+}$ in CH_2Cl_2 also leads to complex **2** in low yield, consistent with the intermediacy of a Ru–HCO_3^- species. Although other examples exist of reduction of HCO_3^- to formate, they require added energy by initial formation of a M–H bond,[17] the use of high pressures of H_2, or the use of an applied electrochemical potential.[18]

Importantly, the formation of **2** from CO_2 and HCO_3^- represents a formal reduction of the added carbon species. A plausible explanation is that HCO_3^- bound to the Ru center is deoxygenated by another species in solution, leading to the reduction of HCO_3^- to formate (Scheme 1). Deoxygenation of a bound carbonate has at least one precedent in the literature where an O atom was transferred to a phosphine with concomitant production of CO_2 mediated by a Rh^{III}–Rh^{I} cycle.[19] Addition of excess triphenylphosphine or trioctylphosphine, in the presence or absence of a nitrile, to [**1-OH$_2$**]$^{2+}$ and CO_2 or HCO_3^- also did not lead to the buildup of phosphine oxides, as evidenced by ^{31}P NMR spectroscopy. In reactions of complex [**1-OH$_2$**]$^{2+}$ with CO_2 and HCO_3^-, an oxidized product has not been identified; the fate of the O atom is the subject of continuing investigation.

To probe the deoxygenation reaction pathway further, 1,1,3,3-tetramethyldisiloxane (TMDS) was added to a solution of [**1-OH$_2$**]$^{2+}$ and ^{13}C-labeled $NaHCO_3$ in DMSO-d_6. Since an oxygen atom must be removed from HCO_3^- in order to make formate, it was hypothesized that the added silane reagent would offer an attractive acceptor for the O atom. After reacting at 50 °C overnight, the only observable species by ^{13}C NMR is a new ^{13}C-containing species, **3** (^{13}C 155 ppm), in near 100% yield as determined by ^{1}H NMR spectroscopy (Figures S10–S13 in the Supporting Information). Running the same reaction with 10 equiv of $NaH^{13}CO_3$ in the absence of TMDS, however, also leads to clean conversion to **3** (Figure S14 in the Supporting Information), albeit in lower (64%) yield. These experiments taken together suggest that the new species **3** may

Scheme 1. Proposed Overall Transformation of Reduction of H_2O to H_2



form independently of the formate-bridged bimetallic complex **2**.

To determine if **2** was relevant to the formation of **3**, the conversion of [**1-Cl**]$^+$ in the presence of 1 equiv of $NaH^{13}CO_2$ in DMSO-d_6 was monitored by ^{31}P, ^{13}C, and ^1H NMR spectroscopy. Over the course of days at 68 °C, [**1-Cl**]$^+$ cleanly converts to the formate species, which goes on to give **3** with concomitant formation of H_2 (4.61 ppm in the ^1H NMR, Figure 3). The new species **3** shows a shift in the ^{31}P NMR from 52 ppm in **2** to 47 ppm and a shift in the ^{13}C NMR from 170 ppm for **2** to 155 ppm for **3** (Figure S15 in the Supporting Information). The IR spectrum of **3** is also distinct from that of **2** with two C–O stretches at 1634 and 1602 cm^{-1} (Figure S16 in the Supporting Information). These data suggest that the formate C atom remains bound to the Ru complex in some fashion and is not released as CO_2 gas (^{13}C NMR 124 ppm). Reaction of [**1-OH$_2$**]$^{2+}$ with $NaH^{13}CO_2$ in acetone also leads to **3**, with a ^{13}C signal at 155 ppm and release of H_2, as confirmed by GC analysis (Figure S17 in the Supporting Information).

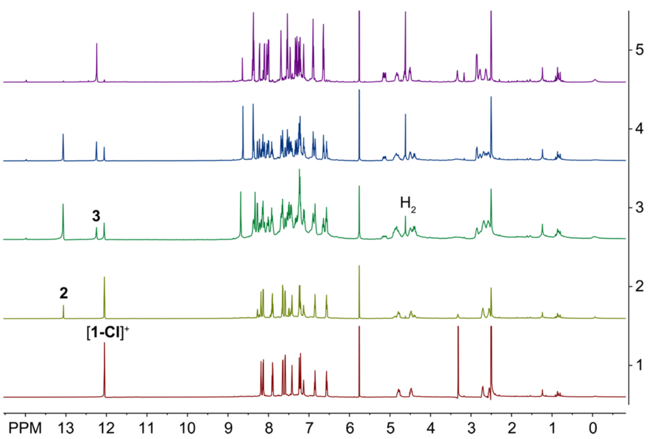
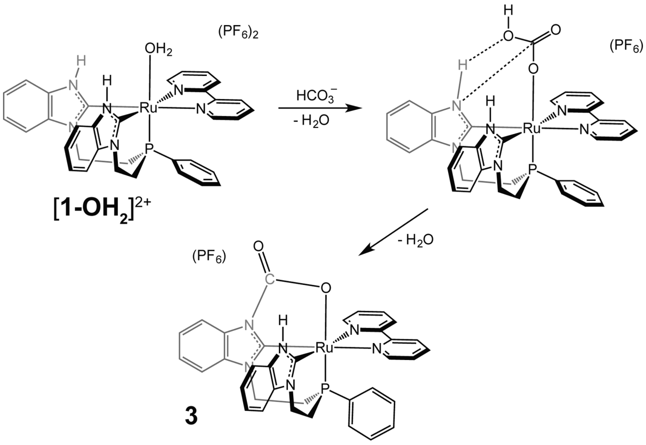


Figure 3. ^1H NMR (500 MHz, DMSO-d_6) spectra over time of the reaction of [**1-Cl**]$^+$ with $NaH^{13}CO_2$ in DMSO at 60 °C, showing conversion to **2** followed by formation of **3** along with release of H_2, evidenced by the singlet at 4.6 ppm.

Complex **3** can also be formed via deprotonation of a N–H moiety of [**1-OH$_2$**]$^{2+}$, followed by reaction with $^{13}CO_2$, as confirmed by ^1H and ^{13}C NMR (^{13}C 155 ppm, Figures S18 and S19 in the Supporting Information). We hypothesized **3** to be a carbamate that formed through reaction of the C atom of CO_2 with the deprotonated N atom of the benzimidazole ligand backbone. This would be consistent with both the deprotonation followed by reaction with CO_2 and the dehydrogenation of formate where a proton from an N–H and a hydride from formate could form H_2 with simultaneous formation of the N–C bond to make a carbamate (Scheme 1). Additionally, the carbamate may form directly from reaction with bicarbonate via acid/base chemistry and formation of a N–C bond (Scheme 2). This pathway is consistent with observation of the facile formation of **3** when [**1-OH$_2$**]$^{2+}$ or [**1-Cl**]$^+$ was heated in DMSO in the presence of $NaH^{13}CO_3$.

Scheme 2. Alternative Mechanism of Formation of 3 from [1-OH$_2$]$^{2+}$



The ^{13}C NMR chemical shift of **3** and IR stretches are also consistent with those of other reported carbamates with an O atom bound to an adjacent metal center.[20] Crystals suitable for X-ray diffraction were grown from slow evaporation of a solution of **3** in CH_2Cl_2 (Figure 2). The structure displays a carbamate moiety where the O atom is bound to the Ru center, which also removes a plane of symmetry in the molecule, making the benzimidazole arms of the PhP(Etbim)$_2$ ligand chemically distinct. This is reflected in the ^1H and ^{13}C NMR spectra, where the N–H (12.2 ppm) integrates for one proton, the diastereotopic – CH_2– protons of the PhP(Etbim)$_2$ split into distinct resonances (Figure S20 in the Supporting Information), and the ^{13}C resonances for the C1 carbon atoms of the carbene ligands show up as distinct with chemical shifts of 202.9 ppm (s) and 193.6 (d, $^2J_{CC}$ = 15 Hz; Figure S21 in the Supporting Information).

In conclusion, we have synthesized and characterized a new Ru complex that interacts with CO_2 via a unique pathway where HCO_3^- is initially formed and then deoxygenated to give the $2e^-/2H^+$ reduced formate. Dehydrogenation of formate, generating H_2 gas, then occurs spontaneously without loss of CO_2 from the complex. Further, HCO_3^- can directly react with $[\mathbf{1\text{-}OH_2}]^{2+}$ through a dehydration reaction to give an "activated" CO_2 in the form of a carbamate moiety. These results are significant, as they represent a spontaneous reduction of CO_2 without high-pressure H_2, electrochemical potential, or strong reducing agents. We are continuing to study the initial reduction reaction to better understand this mechanism and its potential to operate catalytically for reduced carbon products. Scheme 2 may also suggest a pathway to store H_2 if formal addition of H_2O to **3** can generate a Ru−bicarbonate complex. This overall scheme simplifies to a water-splitting reaction that is catalytic in $[\mathbf{1\text{-}OH_2}]^{2+}$ and CO_2 ($H_2O + E \rightarrow O = E + H_2$) and provides a unique method of H_2 production from water. Initial results indicate that addition of strong acids remove the CO_2 from **3**, although studies remain ongoing in this area.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00595.

Experimental details, NMR spectra, IR spectra, and crystal structure data. (PDF)
Crystallographic data (CIF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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