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Hydrogenation of CO_2 to Formic Acid with Iridium^{III}(bisMETAMORPhos)(Hydride): the Role of a Dormant *fac*-Ir^{III}(trihydride) and an Active *trans*-Ir^{III}(dihydride) Species

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An Ir^{III}-monohydride species bearing a chemoresponsive ligand is active in catalytic CO_2 hydrogenation to formic acid with DBU as exogenous base. Spectroscopic and computational data reveal a *trans*-Ir^{III}-dihydride as essential catalytic intermediate and an Ir^{III}(H)$_3$ species as dormant off-cycle product. This insight will aid future design of improved CO_2 reduction catalysts.

Carbon dioxide utilization has attracted much interest in academia and industry, both from an environmental perspective as well as being an alternative C_1 carbon building block.[1] In particular the reduction toward formic acid (HCOOH) has been investigated intensively, as it has potential as a reversible hydrogen storage system, alongside other commercial applications in e.g. the rubber, agricultural and textile industry.[2] The hydrogenation of CO_2 to HCOOH is endergonic by 33 kJ·mol^{-1} mainly because of a large loss in entropy (Eq. 1). Temperature, pressure, solvent and additives can be used to influence the equilibrium of this reaction. The addition of an external base such as ammonia or NEt_3 results in a thermodynamically more stable formate-base ion-pair, is often added to drive the equilibrium toward HCOOH formation (Eq. 2).

$$H_2\,(g) + CO_2\,(g) \rightleftharpoons HCOOH\,(l) \qquad \Delta G^0 = 33\ \mathrm{kJ \cdot mol^{-1}} \qquad (1)$$

$$H_2\,(aq) + CO_2\,(aq) + NH_3\,(aq) \rightleftharpoons HCO_2^-\,(aq) + NH_4^+\,(aq) \qquad \Delta G^0 = -35\ \mathrm{kJ \cdot mol^{-1}} \qquad (2)$$

The most active homogeneous catalysts to date for CO_2 hydrogenation to HCOOH under basic conditions are based on either Ir or Ru (Figure 1; **A**-**C**).[3-5] Outer-sphere interactions such as hydrogen bonding and chemoresponsive ligand reactivity were found to play an essential role In these catalysts to ensure efficient turnover.[5-8] The importance of outer-sphere interactions has also been established for various systems specifically reported to catalyze the microscopic reverse, *i.e.* formic acid dehydrogenation.[2a,9,10] Similar outer-sphere interactions were reported for iridium-trihydride complex **D-CO_2**, bearing a chemoresponsive PNP ligand that engages in a stabilizing hydrogen bond interaction with CO_2.[11] DFT calculations have resulted in a postulated correlation between the Ir-H$_{axial}$ bond length and the relative free energy ΔG^0 of CO_2 insertion: a longer Ir-H$_{axial}$ bond length (*i.e.* weaker bond) enhances Ir-formate formation (*i.e.* facilitates CO_2 insertion). A related correlation between the hydricity of an Ir-H fragment and the rate of CO_2 insertion has recently been formulated, again based on a computational study.[12]

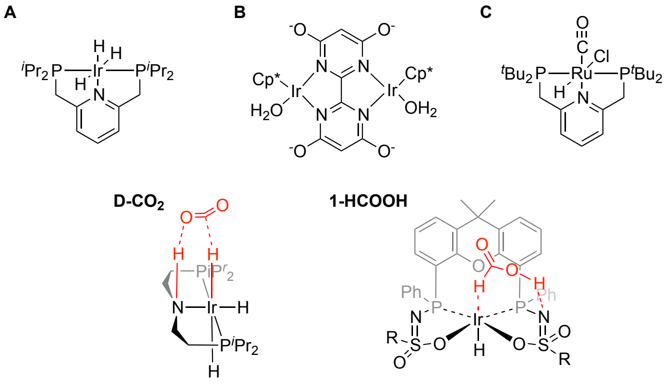

Figure 1. Catalysts **A**-**C** and **D-CO_2** for CO_2 hydrogenation to HCOOH and the formic acid adduct of Ir^{III}(H)(bisMETAMORPhos) complex **1** (**1-HCOOH**; R = 4-butylbenzene).

We previously reported on secondary interactions between formic acid and Ir^{III}(H)(bisMETAMORPhos) complex **1** to form **1-HCOOH** (Figure 1) as being relevant for the dehydrogenation of HCOOH.[13] The reactive bis(sulfonamidophophine) ligand in complex **1-HCOOH** functions both as an internal base to deprotonate of HCOOH and as a hydrogen bond donor/acceptor to pre-assemble HCOOH and stabilize catalytically relevant transition states. Herein, we report initial data on catalytic CO_2 hydrogenation with Ir^{III}(H)(bisMETAMORPhos) complex **1** and discuss the role of a relatively unreactive *fac*-Ir^{III}(H)$_3$ species, which is formed under the applied reaction conditions, based on *in situ* NMR experiments and DFT calculations. This insight may aid future catalyst design for metal-ligand bifunctional CO_2 hydrogenation.

To monitor the catalytic activity of complex **1** in CO_2 hydrogenation, high-pressure NMR experiments were performed at 373 K and 50 bars of CO_2 and H_2 (1:1 ratio) in DMSO-d_6, using DMF (0.5 M) as

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Electronic Supplementary Information (ESI) available: experimental and computational details. See DOI: 10.1039/x0xx00000x internal standard and in absence of external base.[14] Moderate catalytic activity for CO_2 hydrogenation was observed, with a turnover frequency (TOF) of 18 h^{-1} in the first 30 minutes of the reaction and a turnover number (TON) of 30 after 90 minutes (Figure 2, green curve). The conversion did not increase significantly between 90 to 180 minutes and a final concentration of 0.015 M HCOOH was obtained.

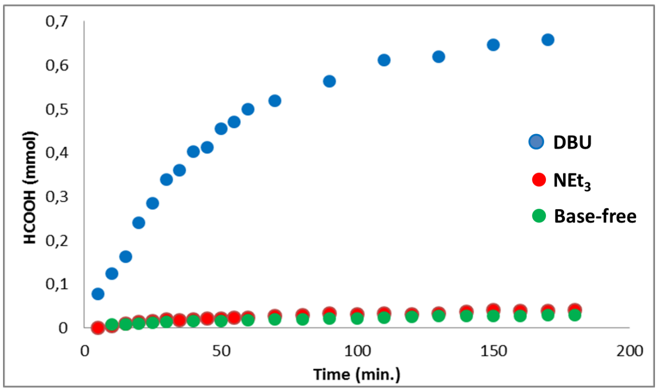


Figure 2. Catalytic CO_2 hydrogenation with **1** (0.5 mM) under base-free conditions (green) and with the addition of 1000 equiv (0.5 M) of NEt_3 (red) or DBU (blue). Solvent: DMSO-d_6, T = 373 K, total reaction volume 2 mL. Absolute amount of HCOOH produced in mmol is plotted *vs*. time in minutes.

When catalysis was performed under the same catalytic conditions but in the presence of 1.0 mmol (0.5 M) NEt_3, only a slight increase in activity was observed (Figure 2, red). In contrast to this negligible effect of NEt_3 on the catalyst performance, the addition of 1.0 mmol DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) led to a significant improvement of the catalytic activity, with a TOF of 636 h^{-1} between 0-30 minutes and a TON of 685 after 180 minutes (Figure 2, blue), corresponding to a base conversion of 0.685.[‡] The remarkable effect of the base on the catalytic activity can be explained by the difference in basicity in DMSO (DBU: pKa 12.0; NEt_3: pKa 9.0). Similar differences in catalytic performance with NEt_3 and DBU were observed with system **C**.[5] The formation of $HDBU^+ \cdot HCOO^-$ was monitored in time by the appearance of the $\underline{H}COO^-$ formate signal at 8.60 ppm in consecutive ^1H NMR spectra (see ESI). The concentration of H_2 increases over time, but is barely detectable in the first 30 minutes of reaction. The determined initial rates are therefore likely limited by mass transfer. Various solvents were used as reaction medium but this did not lead to enhanced catalytic activities. In dioxane a slight decrease in TOF was observed (588 h^{-1}) while in ethylene glycol the catalytic activity decreased significantly (TOF: 38 h^{-1}). To obtain more insight in the mechanism of CO_2 hydrogenation, complex **1** was studied by ^1H NMR spectroscopy under combined H_2 and CO_2 pressure in the absence of base. When **1** was dissolved in CD_2Cl_2, a well-defined triplet was observed in the ^1H NMR spectrum at δ -28.7 ppm (Figure 3A) as previously reported.[13] However, when **1** was dissolved in DMSO-d_6, six different hydride signals were detected in the region from δ -24.0 to -29.0 ppm (Figure 3B).

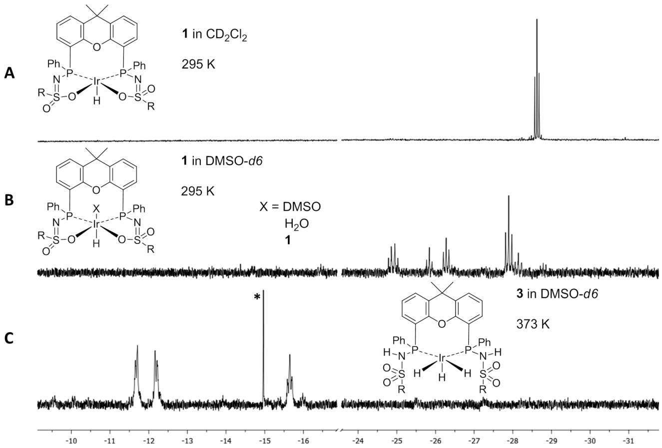
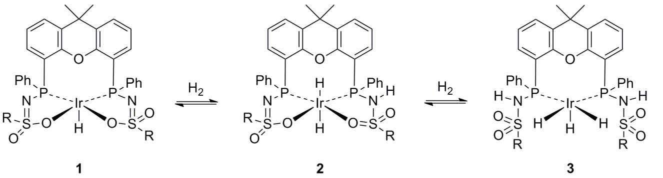


Figure 3. A) **1** dissolved in CD_2Cl_2; B) **1** dissolved in DMSO-d_6; C) formation of **3** from **1** with H_2/CO_2 (25/25 bar) at 373 K in DMSO-d_6, R = 4-butylbenzene. * Indicates minor impurity.[#]

The generation of these species may result from: 1) coordination of either DMSO, H_2O or the oxygen of the xanthene backbone to the vacant axial site of complex **1**,[φ] 2) dimer formation to give {(**1**)$_2$} as previously observed in solid state[13] or 3) the formation of different diastereomers by rotation of the sulfone group. Molecular structures of both a dimer and an axial H_2O adduct of complex **1** have been reported.[13] Upon pressurizing a DMSO-d_6 solution of **1** in a high-pressure sapphire NMR tube with 50 bar CO_2/H_2 (1:1) at room temperature, no changes were observed in the ^1H NMR spectrum after one hour. Heating the sample to 373 K led to the formation of a new species that displayed two broad hydride signals: a doublet-of-doublet at δ –11.9 ppm ($^2J_{P\text{-}H}$ of 154.3 and 14.9 Hz) and a triplet at δ –15.7 ppm ($^2J_{P\text{-}H}$ 17.7 Hz) in a 2:1 ratio (Figure 3C). The coupling constants observed for the doublet-of-doublet are distinctive for *trans* (154.3 Hz) and *cis* $^{31}P\text{-}^1H$ coupling (14.9 Hz), while the triplet originates from coupling of a hydride to two *cis*-positioned phosphorus nuclei. In the corresponding phosphorus-decoupled ^1H NMR spectrum, two singlets were observed. The ratio of the two hydride signals proved independent of temperature, suggesting that they belong to a single species. Together, this suggests the formation of five-coordinate trihydride complex **3**, *fac*-$Ir^{III}(H)_3$(bisMETAMORPhos), see Scheme 1. Related *fac*-$Ir^{III}(H)_3$ complexes with Xantphos show similar spin-systems.[15] The $^2J_{H\text{-}H}$ couplings, which are typically in the range of 2.6-7.4 Hz, could not be resolved due to broadening of the spectrum at 373 K. The N-H resonances of the protonated ligand arms could not be identified by ^1H NMR spectroscopy, as they tend to overlap with aromatic signals.[13,16] After releasing the CO_2/H_2 pressure, **3** remained stable for at least one hour at room temperature. Upon re-heating the depressurized solution to 373 K, the hydride signals corresponding to **3** disappeared and complex **1** was regenerated, concomitant with the formation of H_2, showing that the formation of **3** from **1** is reversible (Scheme 1).

Species **1** is stable under pure CO_2, but NMR signals that indicate the slow formation of **3** appear under pure H_2 atmosphere. The formation of **3** is suggested to proceed via formation of intermediate **2** through heterolytic splitting of H_2 by **1**, as previously described.[13] Subsequently, another equivalent of H_2 is activated, presumably also in a heterolytic fashion, by decoordination of the neutral ligand arm to generate a vacant site and with the anionic ligand arm acting as an internal base, resulting in the square pyramidal *fac*-$Ir^{III}(H)_3$(bisMETAMORPhos) species **3**.



Scheme 1. Conversion of **3** from **1** upon addition of two equivalents H_2.

Interestingly, prior to the formation of **3**, the generation of 14 equivalents of HCOOH was evidenced by ^1H NMR spectroscopy. Upon complete conversion to **3**, no further HCOOH generation was observed. This suggests that **3** may be a catalytically dormant species and that **2** is the active species. This hypothesis was further investigated by studying the energetics of the hydride transfer to CO_2 for complexes **2** and **3** by DFT calculations (BP86, def2-TZVP), using R = phenyl on the sulfone group for computational simplicity (Figure 4). Complex **3** is lower in energy than **2** ($\Delta\Delta G^{\circ}_{298K}$ –4 kcal mol^{-1}), which is in agreement with the observation of **3** by ^1H NMR spectroscopy. For species **2**, hydride transfer to CO_2 via transition state **2-TS** has a reasonable activation barrier of 20.1 kcal mol^{-1}, given the applied catalytic conditions. In complex **3**, hydride transfer to CO_2 could theoretically also occur. However, transfer of either the axial hydride (**3TS-ax**: ΔG°_{298K} 65.6 kcal mol^{-1}), or one of the equatorial hydrides (**3TS-eq**: ΔG°_{298K} 44.2 kcal mol^{-1}) is likely too endergonic to be catalytically relevant (see ESI for details).

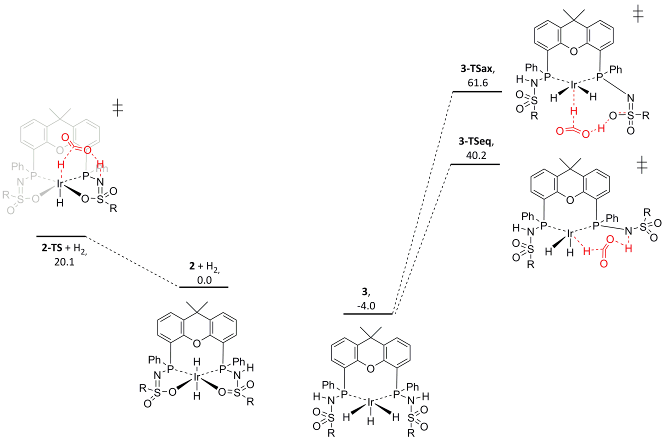
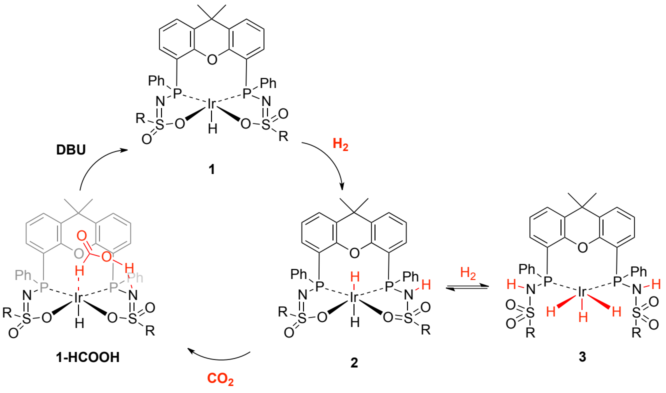


Figure 4. DFT calculated potential energy diagram for hydride transfer to CO_2 from complexes **2** and **3**. ΔG°_{298K} in kcal mol^{-1}, R = phenyl (Turbomole,[17] BP86, def2-TZVP).

This observation is in line with the hypothesis that complex **3** is an off-cycle dormant species that is not directly involved in catalytic CO_2 hydrogenation (Scheme 2). Upon inspection of the computed structures for **2** and **3**, a correlation between the Ir-H bond length and the energy required for CO_2 insertion could be deduced (Figure 5). The Ir-H bonds in species **2** (1.674 and 1.692 Å) are longer than in **3** (Ir-H_{eq} 1.631 and 1.632 Å; Ir-H_{ax} 1.557 Å). The elongation in **2**, which results in weaker Ir-H bonds, likely originates from a mutual *trans* effect of the two hydride ligands. These bond length differences correlate nicely with the lower activation energy found for CO_2 insertion in **2** (20.1 kcal mol^{-1}) relative to **3** (44.2 and 65.6 kcal mol^{-1} for H_{eq} and H_{ax}, respectively). Our results are thus in agreement with the computational findings related to system **D**, demonstrating that *trans*-dihydride configurations allow for catalytically accessible energy barriers for CO_2 insertion.[11,12] Also, all transition states (**2-TS**, **3TS-ax** and **3TS-eq**) involve a stabilizing hydrogen bond interaction between the ligand backbone and CO_2. Improved catalyst design should focus on favoring the formation of **2** or analogues thereof. Research in this direction is currently ongoing in our laboratories.



Scheme 2. Potential catalytic cycle for CO_2 hydrogenation from **1** with the active dihydride intermediate **2** and the dormant species **3** as proposed off-cycle species.

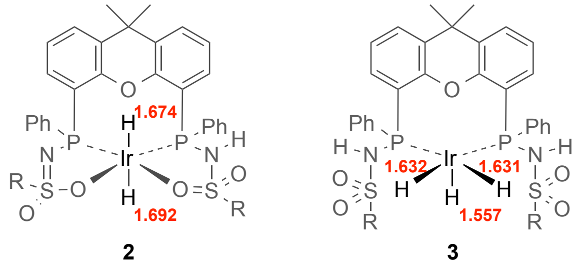


Figure 5. Comparison of Ir-H bond lengths in the DFT calculated optimized structures of complexes **2** and **3** (Turbomole,[18] BP86, def2-TZVP). Values in Å, R = phenyl.

Conclusions

Ir^{III}(H)(METAMORPhos) species **1** is able to catalytically hydrogenate CO_2 with a TOF of 18 h^{-1} in DMSO-d_6 at 373 K under 50 bar of CO_2/H_2 (1:1). A strong effect of added base on the catalyst activity was observed: triethylamine led to minor improvement, but DBU gave a significant enhancement of the reaction rate (TOF of 636 h^{-1}). The formation of a tight ion-pair between formic acid and DBU ($HDBU^{+}\cdot HCOO^{-}$) is suggested to provide the thermodynamic driving force. In situ NMR studies reveal that complex **1** is converted to *fac*-trihydride complex (**3**) under CO_2/H_2 atmosphere (50 bar, 1:1) upon heating to 373 K. DFT calculations suggest that complex **3** is a dormant species in the catalytic cycle and that *trans*-dihydride **2**, which is an intermediate in the conversion of **1** to **3**, is catalytically relevant. The formation of **3** is reversible, as complex **1** was regenerated upon release of pressure and heating to 373 K. Further studies to tune the reaction conditions for optimal catalytic activity and to design an optimized system should focus on the integration of a *trans*-dihydride arrangement.

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Notes and references

[‡] Significant loss of catalytic activity is observed over time, likely due to a pressure drop in the NMR tube during turnover; see ESI.

[¶] Hydrogenation experiments were also performed at different partial pressures of CO_2 and H_2 in the presence of DBU, see ESI.

[φ] DMSO is known to have several coordination modes: κ^1-*O*, κ^1-*S*, η^2-*S*,*O*. Species with the xanthene oxygen coordinating to Ir were all found to be close in energy based on DFT calculations [BP86, SV(P)].

[#] Formation of **3** is accompanied by a species 'A' displaying a sharp singlet at -15.0 ppm (*). The ratio of **3** to 'A' remains unchanged over time. This complex is thus likely not a derivative of **1**, nor does it match previously described deactivation products.[18] Stirring Ir(acac)(cod) in DMSO-d_6 under 50 bar CO_2/H_2 1:1 at 373 K resulted in identical spectral features (Ir(acac)(cod) is added in slight excess (5%) during synthesis of **1**). This unidentified complex is a poor CO_2 hydrogenation catalyst (TON of 1.9 after 90 minutes at 373 K).

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Catalytic hydrogenation of CO_2 to formate with an Ir^{III}(METAMORPhos) complex in the presence of DBU requires a *trans*-dihydride for catalytic turnover, with an off-cycle trihydride as dormant species.

Graphical Abstract