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Hydrogenation of CO₂ to formic acid with iridium³⁺(bisMETAMORPhos)(hydride): the role of a dormant fac-Ir³⁺(trihydride) and an active trans-Ir³⁺(dihydride) species†

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An Ir³⁺-monohydride species bearing a chemoresponsive ligand is active in catalytic CO₂ hydrogenation to formic acid with DBU as the exogenous base. Spectroscopic and computational data reveal a trans-Ir³⁺-dihydride as the essential catalytic intermediate and an Ir³⁺[H₂] species as the dormant off-cycle product. This insight will aid future design of improved CO₂ reduction catalysts.

Carbon dioxide utilization has attracted much interest in academia and industry. This relates to renewable energy applications and as an alternative C₁ carbon building block in synthesis.¹ In particular, its reduction to formic acid (HCOOH) has been investigated intensively, given its potential as a reversible hydrogen storage system, alongside other commercial applications in e.g. the rubber, agricultural and textile industries.² The hydrogenation of CO₂ to HCOOH is endergonic by 33 kJ mol⁻¹ mainly because of a large loss in entropy (eqn (1)). Temperature, pressure, solvent and additives can be used to influence the equilibrium of this reaction. CO₂ hydrogenation is often performed with addition of an external base such as ammonia or NEt₃, as this results in a thermodynamically more stable formate-base ion pair, which drives the equilibrium toward HCOOH formation (eqn (2)).

\[
\begin{align*}
\text{H}_2(g) + \text{CO}_2(g) & \rightleftharpoons \text{HCOOH}(l) \quad \Delta G^\circ = +33 \text{ kJmol}^{-1} \quad (1) \\
\text{H}_2(\text{aq}) + \text{CO}_2(\text{aq}) + \text{NH}_3(\text{aq}) & \rightleftharpoons \text{HCOO}^- (\text{aq}) + \text{NH}_4^+ (\text{aq}) \\
& \Delta G^\circ = -35 \text{ kJmol}^{-1} \quad (2)
\end{align*}
\]

The most active homogeneous catalysts to date for CO₂ hydrogenation to HCOOH under basic conditions are based on either Ir or Ru (Fig. 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.⁶–⁸ The importance of outer-sphere interactions has also been established for various systems specifically reported to catalyze the microscopic reverse process, i.e. formic acid dehydrogenation.⁹,¹⁰ Similar outer-sphere interactions were reported for an iridium-trihydride complex D-CO₂ bearing a chemoresponsive PNP ligand that engages in a stabilizing hydrogen bond interaction with CO₂.¹¹ DFT calculations have been used to postulate a correlation between the Ir-H₆ axial bond length and the relative free energy ΔG°ₘ of CO₂ insertion: a longer Ir-H₆ axial bond length (i.e. weaker bond) enhances Ir formate formation (i.e. facilitates CO₂ insertion). A related correlation between the hydricity of an Ir–H fragment and the rate of CO₂ insertion has recently been formulated, again based on a computational study.¹²

We previously reported the secondary interactions between formic acid and Ir³⁺[H₆(bisMETAMORPhos)] complex 1 to form HCOOH (Fig. 1) as being relevant for the dehydrogenation of HCOOH.¹³ The reactive bis(sulfonamidophosphine) ligand in complex 1-HCOOH functions both as an internal base to deprotonate HCOOH and as a hydrogen bond donor/acceptor to pre-assemble HCOOH and stabilize catalytically relevant transition states. Herein, we report initial data for catalytic CO₂ hydrogenation with Ir³⁺[H₆(bisMETAMORPhos)] complex 1 and discuss the role of a relatively unreactive fac-Ir³⁺[H₆] 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 CO₂ hydrogenation.

To monitor the catalytic activity of complex 1 in CO₂ hydrogenation, high-pressure NMR experiments were performed at 373 K and 50 bar of CO₂ and H₂ (1:1 ratio) in DMSO-d₆, using DMF (0.5 M) as the internal standard and in the absence of an external base.¹⁴ Moderate catalytic activity for CO₂ hydrogenation was observed, with a turnover...
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Fig. 1 Catalysts A–C and D-CO₂ for CO₂ hydrogenation to HCOOH and the formic acid adduct of IrIII(H)(bisMETAMORPhos) complex 1 (1-HCOOH; R = 4-butylbenzene).

Fig. 2 Catalytic CO₂ hydrogenation with 1 (0.5 mM) under base-free conditions (green) and with the addition of 1000 equiv. (0.5 M) of NEt₃ (red) or DBU (blue). Solvent: DMSO-d₆, T = 373 K, total reaction volume = 2 mL. The absolute amount of HCOOH produced in mmol is plotted vs. time in minutes.

Fig. 3 ¹H NMR spectra of (A) 1 dissolved in CD₂Cl₂, (B) 1 dissolved in DMSO-d₆, and (C) formation of 3 from 1 with H₂/CO₂ (25/25 bar) at 373 K in DMSO-d₆. R = 4-butylbenzene. * indicates a minor impurity. §

The remarkable effect of the base on the catalytic activity can be explained by the difference in basicity in DMSO (DBU: pKₐ 12.0; NEt₃: pKₐ 9.0). Similar differences in the catalytic performance of NEt₃ and DBU were observed in system C.⁵ The formation of HDBU⁺·HCOO⁻ was monitored over time by the appearance of the HCOO⁻ formate signal at 8.60 ppm in consecutive ¹H NMR spectra (see the ESI†). The concentration of H₂ 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 media 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 into the mechanism of CO₂ hydrogenation, complex 1 was studied by ¹H NMR spectroscopy under combined H₂ and CO₂ pressure in the absence of a base. When 1 was dissolved in CD₂Cl₂, a well-defined triplet was observed in the ¹H NMR spectrum at δ = –28.7 ppm (Fig. 3A) as previously reported.¹³ However, when 1 was dissolved in DMSO-d₆, six different hydride signals were detected in the region from δ = –24.0 to –29.0 ppm (Fig. 3B).

The generation of these species may result from: (1) the coordination of either DMSO, H₂O or the oxygen of the xanthene backbone to the vacant axial site of complex 1,§ (2) the dimer formation to give [(1)₂] as previously observed in the solid state¹³ or (3) the formation of different diastereomers by rotation of the sulfone group. Molecular structures of both a dimer and an axial H₂O adduct of complex 1 have been reported.¹³ Upon pressurizing a DMSO-d₆ solution of 1 in a high-pressure sapphire NMR tube with 50 bar CO₂/H₂ (1:1) pressure drop in the NMR tube during turnover; see the ESI.⁷

† Significant loss of catalytic activity is observed over time, likely due to a pressure drop in the NMR tube during turnover; see the ESI.⁷

§ The 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-d₆ under 50 bar CO₂/H₂ (1:1) at 373 K resulted in identical spectral features (Ir(acac)(cod) is added in slight excess (5%) during the synthesis of 1). This unidentified complex is a poor CO₂ hydrogenation catalyst [TON of 1.9 after 90 minutes at 373 K]. * DMSO is known to have several coordination modes: x⁴-O, x⁵-S, and x⁶-S-O. Species with the xanthene oxygen coordinated to Ir were all found to be close in energy based on DFT calculations [BP86, SV(P)].
at room temperature, no changes were observed in the $^1$H 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-doublets at $\delta -11.9$ ppm ($J_{\text{P-H}}$ of 154.3 and 14.9 Hz) and a triplet at $\delta -15.7$ ppm ($J_{\text{P-H}}$ of 17.7 Hz) in a $2:1$ ratio (Fig. 3C). The coupling constants observed for the doublet-of-doublets are indicative of trans ($154.3$ Hz) and cis $^3$P-$^1$H coupling ($14.9$ Hz), while the triplet originates from coupling of a hydride to two cis-positioned phosphorus nuclei. In the corresponding phosphorus-decoupled $^1$H NMR spectrum, two singlets were observed. The ratio of the two hydride signals proved to be 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.$^{13}$ The $J_{\text{H-H}}$ 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 $^1$H 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$_3$, 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 the formation of intermediate 2 through heterolytic splitting of H$_2$ by 1, as previously described.$^{13,16}$ 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.

Interestingly, prior to the formation of 3, the generation of 14 equivalents of HCOOH was evidenced by $^1$H 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 (Fig. 4). Complex 3 is lower in energy than 2 ($\Delta\Delta G^0_{298K} = -4$ kcal mol$^{-1}$), which is in agreement with the observation of 3 by $^1$H 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, the transfer of either the axial hydride (3TS-ax: $\Delta\Delta G^0_{298K}$ = 65.6 kcal mol$^{-1}$) or one of the equatorial hydrides (3TS-eq: $\Delta\Delta G^0_{298K}$ = 44.2 kcal mol$^{-1}$) is considered too endergonic to be catalytically relevant (see the ESI for details).

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 of 2 and 3, a correlation between the Ir-H bond length and the energy required for CO$_2$ insertion could be deduced (Fig. 5). The Ir-H bonds in species 2 (1.674 and 1.692 Å) are longer than those in 3 (Ir-H$_{\text{eq}}$, 1.631 and 1.632 Å; Ir-H$_{\text{ax}}$, 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

![Scheme 1](image1.png) Conversion to 3 from 1 upon addition of two equivalents of H$_2$.

![Scheme 2](image2.png) Potential catalytic cycle of CO$_2$ hydrogenation from 1 with the active dihydride intermediate 2 and the dormant species 3 as the proposed off-cycle species.
to 3 (44.2 and 65.6 kcal mol\(^{-1}\) for \(H_{\text{eq}}\) and \(H_{\text{ax}}\), 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 (TS) 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.

Conclusions

\(\text{Ir}^{3+}(\text{H})(\text{METAMORPhos})\) 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 the added base on the catalyst activity was observed: triethylamine led to a 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\(^+\)-HCOO\(^{-}\)) is suggested to provide the thermodynamic driving force. In situ NMR studies reveal that complex 1 is converted to a 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 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


