Hydrogenation of CO2 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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Hydrogenation of CO2 to formic acid with iridium\textsuperscript{III}(bisMETAMORPhos)(hydride): the role of a dormant \textit{fac}-Ir\textsuperscript{III}(trihydride) and an active \textit{trans}-Ir\textsuperscript{III}(dihydride) species\textsuperscript{†}

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Carbon dioxide utilization has attracted much interest in academia and industry. This relates to renewable energy applications and as an alternative C\textsubscript{1} carbon building block in synthesis.\textsuperscript{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.\textsuperscript{2} The hydrogenation of CO\textsubscript{2} to HCOOH is endergonic by 33 kJ mol\textsuperscript{-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. CO\textsubscript{2} hydrogenation is often performed with addition of an external base such as ammonia or NEt\textsubscript{3}, 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(\text{g}) + \text{CO}_2(\text{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}) \quad \Delta G^\circ = -35 \text{kJmol}^{-1} \quad (2)
\end{align}

The most active homogeneous catalysts to date for CO\textsubscript{2} hydrogenation to HCOOH under basic conditions are based on either Ir or Ru (Fig. 1; A–C).\textsuperscript{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.\textsuperscript{5–8} 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.\textsuperscript{9,10} Similar outer-sphere interactions were reported for an iridium-trihydride complex D-CO\textsubscript{2} bearing a chemoresponsive PNP ligand that engages in a stabilizing hydrogen bond interaction with CO\textsubscript{2}.\textsuperscript{11} DFT calculations have been used to postulate a correlation between the Ir-H\textsubscript{axial} bond length and the relative free energy $\Delta G^\circ$ of CO\textsubscript{2} insertion: a longer Ir-H\textsubscript{axial} bond length (i.e. weaker bond) enhances Ir formate formation (i.e. facilitates CO\textsubscript{2} insertion). A related correlation between the hydricity of an Ir–H fragment and the rate of CO\textsubscript{2} insertion has recently been formulated, again based on a computational study.\textsuperscript{12}

We previously reported the secondary interactions between formic acid and Ir\textsuperscript{III}[H(bisMETAMORPhos)] complex 1 to form 1-HCOOH (Fig. 1) as being relevant for the dehydrogenation of HCOOH.\textsuperscript{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 CO\textsubscript{2} hydrogenation with Ir\textsuperscript{III}[H(bisMETAMORPhos)] complex 1 and discuss the role of a relatively unreactive \textit{fac}-Ir\textsuperscript{III}(H\textsubscript{3})\textsubscript{a} species, which is formed under the applied reaction conditions, based on \textit{in situ} NMR experiments and DFT calculations. This insight may aid future catalyst design for metal-ligand bifunctional CO\textsubscript{2} hydrogenation.

To monitor the catalytic activity of complex 1 in CO\textsubscript{2} hydrogenation, high-pressure NMR experiments were performed at 373 K and 50 bar of CO\textsubscript{2} and H\textsubscript{2} (1:1 ratio) in DMSO-\textsubscript{d6}, using DMF (0.5 M) as the internal standard and in the absence of an external base.\textsuperscript{14} Moderate catalytic activity for CO\textsubscript{2} hydrogenation was observed, with a turnover...
The remarkable effect of the base on the catalytic activity can be explained by the difference in basicity in DMSO (DBU: $pK_a$ 12.0; NEt$_3$: $pK_a$ 9.0). Similar differences in the catalytic performance of NEt$_3$ and DBU were observed in system C. The formation of HDBU$^+\cdot$HCOO$^-$ was monitored over time by the appearance of the HCOO$^-$ formate signal at 8.60 ppm in consecutive $^1$H NMR spectra (see the 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 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 CO$_2$ hydrogenation, complex 1 was studied by $^1$H NMR spectroscopy under combined H$_2$ and CO$_2$ pressure in the absence of a base. When 1 was dissolved in CD$_2$Cl$_2$, a well-defined triplet was observed in the $^1$H NMR spectrum at $\delta$ = 28.7 ppm (Fig. 3A) as previously reported. However, when 1 was dissolved in DMSO-d$_6$, six different hydride signals were detected in the region from $\delta$ = 24.0 to 29.0 ppm (Fig. 3B).

The generation of these species may result from: (1) the coordination of either DMSO, H$_2$O 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 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$_2$O 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)

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The formation of 3 is accompanied by a species ‘A’ displaying a sharp singlet at $\sim$15.0 ppm ($\dagger$). The ratio of 3 to ‘A’ remains unchanged over time. This complex is thus likely not a derivative of 1, nor does it match previously described deactivation products.$^{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 the synthesis of 1). This unidentified complex is a poor CO$_2$ hydrogenation catalyst (TON of 159 after 90 minutes at 373 K).

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

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¶ DMSO is known to have several coordination modes: χ$^3$-O, χ$^4$-S, and χ$^5$-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 δ −11.9 ppm ($^2$J_{P-H} of 154.3 and 14.9 Hz) and a triplet at δ −15.7 ppm ($^3$J_{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 ($^2$J_{P-H} 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$^{	ext{III}}$(H)$_3$-bisMETAMORPhos (Scheme 1). Related fac-Ir$^{	ext{III}}$(H)$_3$ complexes with Xantphos show similar spin systems.

3 is lower in energy than 2 ($\Delta G^0_{298K} = -4$ 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 ($3$TS-ax; $\Delta G^0_{298K} = 65.6$ kcal mol$^{-1}$) or one of the equatorial hydrides ($3$TS-eq; $\Delta G^0_{298K} = 44.2$ kcal mol$^{-1}$) is considered too endergonic to be catalytically relevant (see the ESIf 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$_{ax}$ 1.631 and 1.632 Å; Ir–H$_{eq}$ 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. This 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.

3


Scheme 2 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.

Scheme 1 Conversion to 3 from 1 upon addition of two equivalents of H$_2$.
Fig. 5 Comparison of Ir-H bond lengths in the DFT-calculated optimized structures of complexes 2 and 3 (Turbomole, BP86, def2-TZVP). The values are 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 the added base on the catalytic 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-tri-hydride 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


