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Hydrogenation of CO₂ to formic acid with iridium (bisMETAMORPhos) (hydride): the role of a dormant fac-Ir (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 CO2 hydrogenation to formic acid with DBU as the exogenous base. Spectroscopic and computational data reveal a trans-Ir^{III}-dihydride as the essential catalytic intermediate and an Ir^{III}(H)₃ 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. In particular, its reduction to formic acid (HCOOH) has been investigated intensively, given its potential as a reversible hydrogen storage system, alongside 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)).

$$H_2(g) + CO_2(g) \rightleftharpoons HCOOH(1) \Delta G^0 = 33 \text{ kJmol}^{-1}$$
 (1)

$$H_2(aq) + CO_2(aq) + NH_3(aq) \longrightarrow HCO_2^-(aq) + NH_4^+(aq)$$

 $\Delta G^0 = -35 \text{ kJmol}^{-1}$

(2)

The most active homogeneous catalysts to date for CO₂ hydrogenation to HCOOH under basic conditions are based

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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. 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. 9,10 Similar outersphere 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-Haxial 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 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 Ir^{III}(H)(bisMETAMORPhos) complex 1 to form 1-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 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 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

A
$$Pr_{2} \stackrel{H}{\longrightarrow} \stackrel{H}{\longrightarrow} \stackrel{P}{\longrightarrow} pr_{2}$$

$$D-CO_{2}$$

$$Pr_{2} \stackrel{H}{\longrightarrow} \stackrel{H}{\longrightarrow} pr_{2}$$

$$Pr_{2} \stackrel{H}{\longrightarrow} \stackrel{H}{\longrightarrow} pr_{2}$$

$$Pr_{2} \stackrel{H}{\longrightarrow} \stackrel{H}{\longrightarrow} pr_{2}$$

$$Pr_{2} \stackrel{H}{\longrightarrow} pr_{2}$$

$$Pr_{2} \stackrel{H}{\longrightarrow} pr_{2}$$

$$Pr_{2} \stackrel{H}{\longrightarrow} pr_{2}$$

$$Pr_{3} \stackrel{H}{\longrightarrow} pr_{4}$$

$$Pr_{4} \stackrel{H}{\longrightarrow} pr_{5}$$

$$Pr_{5} \stackrel{H}{\longrightarrow} pr_{5}$$

Fig. 1 Catalysts A-C and D-CO₂ for CO₂ hydrogenation to HCOOH and the formic acid adduct of Ir^{III}(H)(bisMETAMORPhos) complex 1 (1-HCOOH; R = 4-butylbenzene).

frequency (TOF) of 18 h⁻¹ in the first 30 minutes of the reaction and a turnover number (TON) of 30 after 90 minutes (Fig. 2, green curve). The conversion did not increase significantly between 90 and 180 minutes and a final concentration of 0.015 M HCOOH was obtained.

When catalysis was performed under the same catalytic conditions but in the presence of 1.0 mmol (0.5 M) of NEt₃, only a slight increase in activity was observed (Fig. 2, red curve). In contrast to this negligible effect of NEt3 on the catalytic performance, the addition of 1.0 mmol of DBU (1,8diazabicyclo[5.4.0]undec-7-ene) led to a significant improvement in the catalytic activity, with a TOF of 636 h⁻¹ between 0-30 minutes and a TON of 685 after 180 minutes (Fig. 2, blue curve), 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: pK_a 12.0; NEt₃: pK_a 9.0). Similar differences in the catalytic performance of NEt₃ and DBU were observed in system C.⁵ The

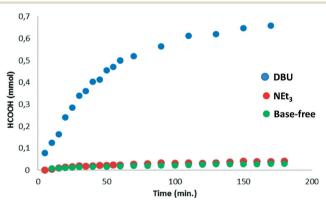


Fig. 2 Catalytic CO₂ hydrogenation with 1 (0.5 mM) under base-free conditions (green) and with the addition of 1000 equiv. (0.5 M) of NEt₃ (red) or DBU (blue). Solvent: DMSO- d_6 , T = 373 K, total reaction volume = 2 mL. The absolute amount of HCOOH produced in mmol is plotted vs. time in minutes.

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 $1, \P$ (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)

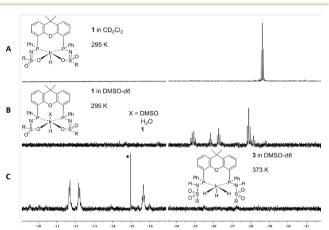


Fig. 3 ¹H NMR spectra of (A) 1 dissolved in CD₂Cl₂, (B) 1 dissolved in DMSO- d_6 , and (C) formation of 3 from 1 with H₂/CO₂ (25/25 bar) at 373 K in DMSO- d_6 , R = 4-butylbenzene. * indicates a minor impurity.§

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

[§] 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: κ^1 -O, κ^1 -S, and κ^2 -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 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-doublets at δ -11.9 ppm $(^2J_{\rm P-H}$ of 154.3 and 14.9 Hz) and a triplet at δ –15.7 ppm $(^2J_{\rm P-H}$ 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 ³¹P-¹H coupling (14.9 Hz), while the triplet originates from coupling of a hydride to two cis-positioned phosphorus nuclei. In the corresponding phosphorusdecoupled ¹H 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 fivefac-Ir^{III}(H)₃coordinate trihydride complex 3, (bisMETAMORPhos) (see Scheme 1). Related fac-Ir^{III}(H)₃ complexes with Xantphos show similar spin systems. 15 The 2/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 1H NMR spectroscopy, as they tend to overlap with aromatic signals. 13,16 After releasing the CO₂/ H₂ 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 H₂, 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. 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 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 CO₂ for complexes 2 and 3 by DFT calculations (BP86, def2-TZVP), using R = phenyl on the sulfone group for computational simplicity (Fig. 4). Complex

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

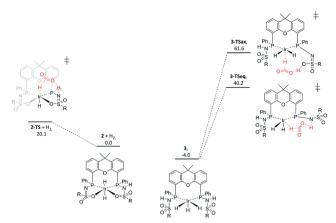
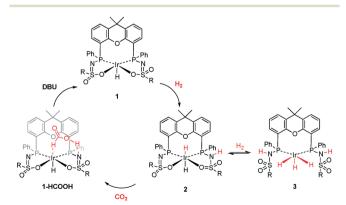


Fig. 4 DFT-calculated potential energy diagram of hydride transfer to CO_2 from complexes **2** and **3**. ΔG_{298K}^0 in kcal mol^{-1} , R = phenyl (Turbomole, ¹⁷ BP86, def2-TZVP).

3 is lower in energy than 2 ($\Delta\Delta G_{298\mathrm{K}}^0$ = -4 kcal mol $^{-1}$), which is in agreement with the observation of 3 by $^1\mathrm{H}$ 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: $\Delta G_{298\mathrm{K}}^0$ = 65.6 kcal mol $^{-1}$) or one of the equatorial hydrides (3TS-eq: $\Delta G_{298\mathrm{K}}^0$ = 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 CO₂ 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 CO₂ 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_{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 CO₂ insertion in 2 (20.1 kcal mol⁻¹) relative



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.

Fig. 5 Comparison of Ir-H bond lengths in the DFT-calculated optimized structures of complexes 2 and 3 (Turbomole, 18 BP86, def2-TZVP). The values are in Å, R = phenyl.

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 trans-dihydride configurations allow for catalytically accessible energy barriers for CO₂ 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 CO2. 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

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 CO₂/H₂ (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 CO₂/H₂ 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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