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CO₂ hydrogenation by phosphorus–nitrogen PN³P-pincer iridium hydride complexes: elucidation of the deactivation pathway†

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PN³P–Ir pincer hydride complexes were synthesized and characterized as catalysts and key intermediates in the direct hydrogenation of CO₂ to formate under mild conditions. The formation of a dearomatized PN³P*–Ir(I)–CO species was identified as a plausible key process accountable for the loss of catalytic activity in the CO₂ hydrogenation.

Carbon capture and sequestration (CCS) has been the subject of extensive research and commercial efforts.^{1–5} The selective hydrogenation of carbon dioxide (CO₂) under mild conditions represents an economical and sustainable method of preparing valuable products and fuels from CO_2 .^{6,7} In this regard, significant achievements have been made using single-site homogeneous catalysts in CO₂ transformation, especially in the selective conversion of CO_2 and H_2 to formic acid or formate.^{8,9} While the hydrogenation of CO_2 to HCOOH is thermodynamically favored in the aqueous phase, the energy barrier is high. As a result, high reaction pressures and temperatures are generally needed. A number of transition-metal complexes, such as rhodium,^{10–15} ruthenium^{16–27} and iridium,^{28–37} have been investigated for the hydrogenation of CO_2 . Among these metals, iridium complexes appear very promising.

In recent years, highly efficient and selective hydrogen transfer reactions and dehydrogenation reactions mediated by pincer-ligated complexes have been reported.^{38,39} In addition, the catalytic conversion of *n*-alkanes to alkylaromatics using pincer supported iridium complexes⁴⁰⁻⁴⁴ and of glycerol to lactic acid⁴⁵⁻⁴⁷ have been well developed. For the reduction of



We recently demonstrated that $PN^{3}(P)$ -pincer complexes show unique properties in various challenging transformations in organic synthesis and catalytic studies,^{52–57} showing diverse catalytic activities and different thermodynamic and kinetic properties.^{58,59} Driven by the potential advantages of employing more electron-rich pincer complexes, herein, we present our development on $PN^{3}P$ –Ir(m) trihydride complexes in CO₂ hydrogenation to formate. A probable catalyst-deactivation step in the formation of a dearomatized $PN^{3}P^{*}Ir$ –CO complex is also discussed.

As has been suggested that Ir(III) trihydride complexes serve as effective catalysts in the hydrogenation of CO_2 ,²⁹ we devel-



Fig. 1 Examples of $PN^{X}P$ pincer Ir(III) trihydride catalysts for CO_2 hydrogenation.



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Scheme 1 Synthesis of PN³P-Ir(III) trihydride complexes.

oped a general route for the synthesis of the Ir(III) complexes based on PN³P ligands (Scheme 1). Cationic iridium(1) complexes 1a and 1b were synthesized by coordinating the PN³PR ligands (R = cyclopentyl (cPe) and *t*-butyl (^{*t*}Bu)) with a stoichiometric amount of [Ir(coe)₂Cl]₂, similar to the procedure provided in the literature.⁶⁰ We then introduced H₂ to eliminate the coordinating coe moiety resulting in the formation of cationic iridium(III) complexes 2a and 2b after the oxidative addition of one equivalent of H2. The NMR data of 2b collected in CDCl₃ at room temperature showed only one N-H (2H, δ 9.27 ppm) signal and one Ir-H (2H, δ -26.87 ppm) signal in the ¹H NMR spectrum and a signal at δ 126.2 ppm in the ³¹P NMR spectrum, suggesting a symmetric conformation enforced by the PN³P pincer ligand. In addition, the solid state molecular structure of 2b was consistent with the NMR details where two hydrides are equivalent (Fig. 2). The structure shows a square pyramidal configuration with a chloride as a dissociated counter anion.

The neutral dearomatized complexes **3a** and **3b** were obtained by employing one equivalent of KO^{*t*}Bu to deprotonate one of the NH arms in the PN³P pincer ligand.^{61,62} Unlike their $-CH_2$ analogs,⁶² these dearomatized PN³P* complexes were stable enough to be isolated at room temperature. The ¹H NMR spectrum of **3b** in C₆D₆ shows three sets of sp² C-H signals at δ 5.21 (d), 6.85 (d), and 6.92 (t) ppm, in agreement



Fig. 2 X-ray structure of complex 2b with 40% probability of thermal ellipsoids. The solvent and hydrogen atoms, except N–H and hydrides, were omitted for clarity. Selected bond lengths (Å): Ir1-N3 2.110(6), Ir1-P1 2.284(2), and Ir1-P2 2.279(2). Selected bond angles (°): (2b) P1–Ir1–P2 163.64(7).

with the dearomatization of the central pyridine ring. As expected, two sets of doublet phosphorus signals were observed in the ³¹P NMR spectrum (${}^{2}J_{P-P} = 299$ Hz), with an apparent triplet for a hydride (${}^{2}J_{P-H} = 12.0$ Hz) at δ –24.93 ppm in the ¹H NMR spectrum.^{38,52–56,58,59} The solid-state molecular structure of **3b** was obtained with two peaks in the Fourier map, indicative of two hydrides forming a distorted trigonal bipyramidal configuration (Fig. 3).

Finally, the trihydride complexes **4a** and **4b** were obtained by treating **3a** and **3b** in the presence of H_2 in THF. The ¹H NMR spectrum of complex **4a** in C_6D_6 shows two sets of hydride signals, at δ –18.15 ppm and –11.76 ppm with an integral intensity ratio of 2:1, and two sets of signals for three protons in the sp² region (5.60 (d) and 6.81 (t) ppm), indicating the rearomatization of the central pyridine ring. Complex **4a** was confirmed by the X-ray diffraction analysis (Fig. 4). The solid-state molecular structure of **4a** was consistent with the NMR details. Trihydride **4a** has an octahedral geometry with three peaks in the Fourier map assigned to hydrides on the Ir center, consistent with the reported ¹Pr–PNP–Ir trihydride compound.²⁹



Fig. 3 X-ray structure of complex 3b with 40% probability of thermal ellipsoids. The solvent and hydrogen atoms, except N–H and hydrides, were omitted for clarity. Selected bond lengths (Å): (3b) Ir1–N3 2.063(6), Ir1–P1 2.2725(8), and Ir1–P2 2.2955(8). Selected bond angles (°): (3b) P1–Ir1–P2 162.79(3).



Fig. 4 X-ray structures of complex **4a** with 40% probability of thermal ellipsoids. The solvent and hydrogen atoms, except N–H and hydrides, were omitted for clarity. Selected bond lengths (Å): **(4a)** Ir1–N3 2.117(3). Selected bond angles (°): **(4a)** P1–Ir1–P2 164.07(3).

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Several pincer-ligated iridium hydride complexes^{29,30} are well known to catalyze CO₂ hydrogenation. Therefore, the catalytic activity of complexes 4a and 4b was examined accordingly in THF/H₂O solution (Table 1). According to the results of entries 1 and 2, the performance of 4b (yield 17.6%) is better than that of 4a (vield 6.3%) under the same conditions. 4b was thus chosen to evaluate the influence of the reaction conditions, such as temperature and reaction time, for the CO₂ hydrogenation reaction. The results of entries 2-4 show that the yield increases (17.6% to 49.6%) in the beginning with increasing temperature (120-130 °C), but then decreases with temperature increasing continually (130-140 °C). These observations suggest that 4b is not stable at high temperature. Prolonging the reaction time to 18 hours did not improve the yield of formate (49.6% to 51.0%, entry 5), indicating that 4b is likely to be deactivated within 12 hours.

To gain more insight into the catalyst deactivation, additional experiments were carried out. The treatment of 4b with H₂ and CO₂ (1:1, 120 psi) at 140 °C for 24 hours afforded 5b in 78% yield after recrystallization (Scheme 2), and in this process, the water should be generated as a by-product (Scheme 2). Furthermore, the hydrogenation of CO_2 which is catalyzed by complex 5b showed no activity (Table 1, entry 6). The ³¹P NMR spectrum of 5b indicated the presence of two nonequivalent P atoms. In the ¹H NMR spectrum, three sets of sp^2 C-H signals at 5.11(d), 6.74 (d), and 6.83 (t) ppm were observed, indicating the dearomatization of the central pyridine ring. The molecular structure of 5b shows a slightly distorted square-planar coordination geometry (Fig. 5). The metal-carbon bond distance is 1.837(6) Å, just slightly longer than that in the PNP-Ir-CO complex (Ir-CO: 1.818(2) Å).⁶² The Ir-N bond distance of 5b (2.076(4) Å) and that in the PNP-Ir-CO

Table 1 Hydrogenation of CO2 catalyzed by Ir(III)-pincer complexes

Entry	Cat.	T (°C)	P(psi)	Time (h)	Yield ^a (%)	TON	$TOF (h^{-1})$	
1	4a	120	120	12	6.3	630	53	
2	4b	120	120	12	17.6	1760	147	
3	4b	130	120	12	49.6	4960	413	
4	4b	140	120	12	30.6	3060	255	
5	4b	130	120	18	51.0	5100	283	
6	5b	130	120	18	_	_	_	

^{*a*} Total pressure at room temperature: 120 psi ($H_2:CO_2 = 1:1$). Yields: Calculated by ¹H NMR analysis using sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard, based on the added KOH base (1.0×10^{-3} mol). Catalyst loading: 1.0×10^{-7} mol. [THF]/[H_2O] = 1/4 (ratio by volume).



Scheme 2 Production complex 5b from complex 4b in the presence of CO_2/H_2 .



Fig. 5 X-ray structure of 5b with 40% probability of thermal ellipsoids. The solvent and hydrogen atoms, except N–H, were omitted for clarity. Selected bond lengths (Å): (5b) Ir1–N3 2.076(4), Ir1–C22 1.837(6), Ir1–P1 2.3000(14), and Ir1–P2 2.3008(13). Selected bond angles (°): (5b) P1–Ir1–P2 163.33(5) and C(22)–Ir(1)–N(1) 179.3(2).

complex (2.083(2) Å) were practically identical. Consistent with our results, **5b** was unable to catalyze the CO_2 hydrogenation under the same conditions shown in Table 1. The formation of the CO ligand implies that the reverse water gas shift (RWGS) reaction also takes place in the presence of the PN³P–Ir complex,^{62–66} and this process is likely responsible for the loss of catalytic activity.

In summary, we have developed a general method for synthesizing $PN^{3}P$ pincer Ir(m) trihydride complexes and obtained several key structures involved in the CO_2 hydrogenation process. While the Ir complexes showed favorable activity (a turnover number up to 5100), the formation of a dearomatized $PN^{3}P^*$ -Ir(n)-CO species was identified as a plausible key pathway for the catalyst deactivation. Our work reveals that the RWGS should be taken into account for future catalyst design to avoid this unfavorable process to maximize the catalyst activity and lifetime.

Conflicts of interest

There are no conflicts to declare.

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