PN\textsuperscript{3}P-Ir pincer hydride complexes were synthesized and characterized as catalysts and key intermediates in the direct hydrogenation of CO\textsubscript{2} to formate under mild conditions. The formation of a dearomatized PN\textsuperscript{3}PP'-Ir(0)-CO species was identified as a plausible key process accountable for the loss of catalytic activity in the CO\textsubscript{2} hydrogenation.

Carbon capture and sequestration (CCS) has been the subject of extensive research and commercial efforts.\textsuperscript{1-5} The selective hydrogenation of carbon dioxide (CO\textsubscript{2}) under mild conditions represents an economical and sustainable method of preparing valuable products and fuels from CO\textsubscript{2}.\textsuperscript{6,7} In this regard, significant achievements have been made using single-site homogeneous catalysts in CO\textsubscript{2} transformation, especially in the selective conversion of CO\textsubscript{2} and H\textsubscript{2} to formic acid or formate.\textsuperscript{8,9} While the hydrogenation of CO\textsubscript{2} to HCOOH is a desirable reaction, the activation barrier is high. As a result, high reaction pressures and temperatures are generally needed. A number of transition-metal complexes, such as rhodium,\textsuperscript{10-13} ruthenium,\textsuperscript{14-16} palladium,\textsuperscript{17-19} and iridium,\textsuperscript{20-27} have been investigated for the hydrogenation of CO\textsubscript{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.\textsuperscript{38,39} In addition, the catalytic conversion of n-alkanes to alkylaromatics using iridium supported iridium complexes\textsuperscript{40-44} and of glycerol to lactic acid\textsuperscript{45-47} have been well developed. For the reduction of CO\textsubscript{2}, Himeda and Fujita \textit{et al.} used a dinuclear proton-switchable iridium catalyst bearing an N,N'-type ligand, 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine, as a bridging group, to afford an average TOF of 53 800 h\textsuperscript{-1} in the presence of KHCO\textsubscript{3} at 80 °C under 50 bar.\textsuperscript{52} When a strong electron-donating PNP ligand was introduced into the CO\textsubscript{2} hydrogenation, high activities of Ir(III) complexes towards CO\textsubscript{2} hydrogenation were demonstrated by the Nozaki group (Fig. 1), and an unprecedentedly high TON of 3 500 000 was achieved.\textsuperscript{29} Analogous “saturated” systems by Hazari \textit{et al.} also showed a high TON of 348 000,\textsuperscript{30} although a much higher temperature and pressure were necessary. Recent mechanistic studies on homogeneous iridium catalytic systems in CO\textsubscript{2} hydrogenation suggested that the CO\textsubscript{2} activation pathways are dependent on the nature of the Ir catalysts and that a hydrido ligand on an Ir(III) center is essential.\textsuperscript{48-51}

We recently demonstrated that PN\textsuperscript{3}(P)-pincer complexes show unique properties in various challenging transformations in organic synthesis and catalytic studies,\textsuperscript{52-57} showing diverse catalytic activities and different thermodynamic and kinetic properties.\textsuperscript{58,59} Driven by the potential advantages of employing more electron-rich pincer complexes, herein, we present our development on PN\textsuperscript{3}P-Ir(III) trihydride complexes in CO\textsubscript{2} hydrogenation to formate. A probable catalyst-deactivation step in the formation of a dearomatized PN\textsuperscript{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\textsubscript{2},\textsuperscript{29} we devel-
Dissociated counter anion. shows a square pyramidal configuration with a chloride as a where two hydrides are equivalent (Fig. 2). The structure obtained by employing one equivalent of KO\textsubscript{Bu} with 40% probability of thermal 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 \textsuperscript{19}Pr-PNP-Ir trihydride compound.\textsuperscript{29}

Finally, the trihydride complexes 4a and 4b were obtained by treating 3a and 3b in the presence of \textsubscript{2}H\textsubscript{2} in THF. The \textsuperscript{1}H NMR spectrum of complex 4a in C\textsubscript{6}D\textsubscript{6} shows two sets of hydride signals, at $\delta$ $\approx$ 18.15 ppm and $\approx$ 11.76 ppm with an integral intensity ratio of 2:1, and two sets of signals for three protons in the sp\textsuperscript{2} 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 \textsuperscript{19}Pr-PNP-Ir trihydride compound.\textsuperscript{29}

The neutral dearomatized complexes 3a and 3b were obtained by employing one equivalent of KO\textsubscript{Bu} to deprotonate one of the NH arms in the PN\textsuperscript{3}P pincer ligand.\textsuperscript{61,62} Unlike their -CH\textsubscript{3} analogs,\textsuperscript{63} these dearomatized PN\textsuperscript{3}P complexes were stable enough to be isolated at room temperature. The \textsuperscript{1}H NMR spectrum of 3b in C\textsubscript{6}D\textsubscript{6} shows three sets of sp\textsuperscript{2} C–H signals at $\delta$ 5.21 (d), 6.85 (d), and 6.92 (t) ppm, in agreement with the dearomatization of the central pyridine ring. As expected, two sets of doublet phosphorus signals were observed in the \textsuperscript{31}P NMR spectrum ($J_{P-P}$ = 299 Hz), with an apparent triplet for a hydride ($J_{P-H}$ = 12.0 Hz) at $\delta$ $\approx$ 24.93 ppm in the \textsuperscript{1}H NMR spectrum.\textsuperscript{18,52-58,59} 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).

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Several pincer-ligated iridium hydride complexes\textsuperscript{29,30} are well known to catalyze CO\textsubscript{2} hydrogenation. Therefore, the catalytic activity of complexes \textit{4a} and \textit{4b} was examined accordingly in THF/H\textsubscript{2}O solution (Table 1). According to the results of entries 1 and 2, the performance of \textit{4b} (yield 17.6\%) is better than that of \textit{4a} (yield 6.3\%) under the same conditions. \textit{4b} was thus chosen to evaluate the influence of the reaction conditions, such as temperature and reaction time, for the CO\textsubscript{2} 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 \textit{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 \textit{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 \textit{4b} with H\textsubscript{2} and CO\textsubscript{2} (1:1, 120 psi) at 140 °C for 24 hours afforded \textit{5b} in 78\% yield after recrystallization (Scheme 2). Furthermore, the hydrogenation of CO\textsubscript{2} which is catalyzed by \textit{4b} showed no activity (Table 1, entry 6). The \textsuperscript{31}P NMR spectrum of \textit{5b} indicated the presence of two nonequivalent P atoms. In the \textsuperscript{1}H NMR spectrum, three sets of sp\textsuperscript{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 \textit{5b} shows a slightly distorted square-planar coordination geometry (Fig. 5). The metal–carbon bond distance is 1.838(6) Å, just slightly longer than that in the PNP-Ir-CO complex (1.818(2) Å).\textsuperscript{62} The Ir–N bond distance of \textit{5b} (2.076(4) Å) and that in the PNP-Ir–CO complex (2.083(2) Å) were practically identical. Consistent with our results, \textit{5b} was unable to catalyze the CO\textsubscript{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 PN\textsuperscript{3}P–Ir complex,\textsuperscript{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\textsuperscript{3}P pincer Ir(III) trihydride complexes and obtained several key structures involved in the CO\textsubscript{2} hydrogenation process. While the Ir complexes showed favorable activity (a turnover number up to 5100), the formation of a dearomatized PN\textsuperscript{3}P–Ir(iii)–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.

### Table 1 Hydrogenation of CO\textsubscript{2} catalyzed by Ir(III)-pincer complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>T (°C)</th>
<th>P (psi)</th>
<th>Time (h)</th>
<th>Yield(^{a}) (%)</th>
<th>TON</th>
<th>TOF (h(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>\textit{4a}</td>
<td>120</td>
<td>120</td>
<td>12</td>
<td>6.3</td>
<td>630</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>\textit{4b}</td>
<td>120</td>
<td>120</td>
<td>12</td>
<td>17.6</td>
<td>1760</td>
<td>147</td>
</tr>
<tr>
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<td>\textit{4b}</td>
<td>130</td>
<td>120</td>
<td>12</td>
<td>49.6</td>
<td>4960</td>
<td>413</td>
</tr>
<tr>
<td>4</td>
<td>\textit{4b}</td>
<td>130</td>
<td>120</td>
<td>18</td>
<td>51.0</td>
<td>5100</td>
<td>283</td>
</tr>
<tr>
<td>5</td>
<td>\textit{5b}</td>
<td>130</td>
<td>120</td>
<td>18</td>
<td>—</td>
<td>5100</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>\textit{5b}</td>
<td>150</td>
<td>120</td>
<td>18</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^{a}\)Total pressure at room temperature: 120 psi (H\textsubscript{2}: CO\textsubscript{2} = 1:1). Yields: Calculated by \textsuperscript{1}H NMR analysis using sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard, based on the added KOH base (1.0 × 10\textsuperscript{-3} mol). Catalyst loading: 1.0 × 10\textsuperscript{-2} mol. [THF]/[H\textsubscript{2}O] = 1/4 (ratio by volume).

### Scheme 2 Production complex 5b from complex 4b in the presence of CO\textsubscript{2}/H\textsubscript{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).

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

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### Notes and references