Room Temperature Hydrogenation of CO_2 Utilizing a Cooperative Phosphorus Pyridone-Based Iridium Complex

Shepherd Siangwata,[a] Alex Hamilton,[b] Graham J. Tizzard,[c] Simon J. Coles,[c] and Gareth R. Owen*[a]

The synthesis, characterization and application of a new complex, [Ir(κ^2-*P,N*-**6-D^{Cy}Pon***)(COD)] (**1**), where **6-D^{Cy}Pon*** is the anionic species, 6-dicyclohexylphosphino-2-oxo-pyridinide, is reported herein. Complex **1** was found to be an active catalyst in the hydrogenation of CO_2 at room temperature. The ligand, **6-D^{Cy}Pon***, is derived *via* deprotonation of a novel pro-ligand,

6-D^{Cy}Pon (6-dicyclohexylphosphino-2-pyridone) during the synthesis of **1**. The ligand is shown to participate within the reversible hydrogenation of **1**, via a cooperative process, in which the species, [IrH$_3$(κ^2-*P,N*-**6-D^{Cy}Pon**)(COD)] (**2**), was spectroscopically characterized, where **1** reacts with two equivalents of H$_2$.

There has been ongoing interest over many decades surrounding the transformation of CO_2 into new molecules. Much focus has been on the hydrogenation of CO_2 into formate species with a wide range of transition metal complexes which have been reported to be highly active in this transformation.[1] On the other hand, there are only a very limited number of systems which demonstrate any catalytic activity at room temperature. More specifically, iridium systems tend to give very low TONs in the absence of heating. One key aspect which features across those room temperature examples involves metal-ligand cooperation (MLC)[2] and/or secondary coordination sphere interactions.[3] These are particularly important in facilitating the hydrogen activation step. One recent example, involving an amide NHC-based iridium catalyst, reported TONs up to 93 (in 1 h) when the catalysis was performed at 30 °C.[4] Similarly, a series of iridium complexes containing bidentate bis-nitrogen or mixed nitrogen carbon-based ligands have been reported with TONs ranging from 92 to 2230 at 25 °C, over periods up to

70 h.[3,5–9] In 2020, Fujita and Himada reported further stand out iridium complexes containing picolinamide ligands which exhibited significantly higher activities reaching in the region of 5500 at 50 h.[10]

We recently reported the synthesis of a new ligand **6-D^{i}PPon** (6-diisopropylphosphino-2-pyridone) as the second edition of what we envisaged would be a family of ligands of this type (Figure 1, top).[11] These ligand systems are of interest due to their potential to tautomerize, between the 2-pyridone (**Pon**) and 2-hydroxypyridine (**Pin**) forms. In addition to this, we have shown that they undergo deprotonation to form the anionic 2-oxo-pyridinide (**Pon***) (Figure 1, middle). Furthermore, Breit and Meuwly demonstrated the potential for these ligands to form pseudo chelates or form ligand bridging motifs via hydrogen bonding between two 2-pyridone units (Figure 1, bottom).[12,13] Related ligand systems where metal-ligand coop-

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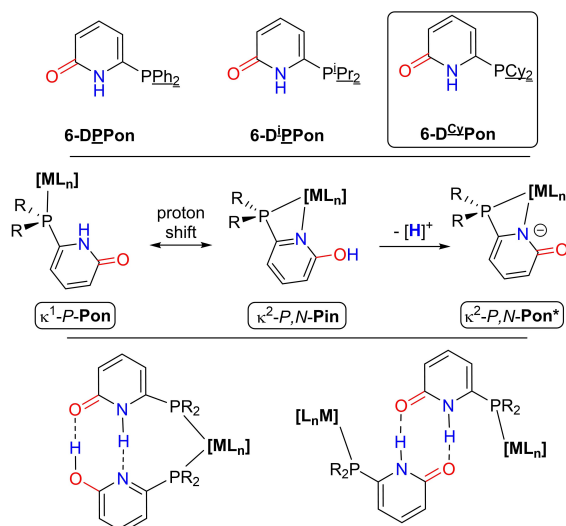
Figure 1. Ligands containing a phosphino-2-pyridone unit (top), proton responsive transformations and coordination modes observed (middle), and pseudo chelates and bridging motifs formed as additional secondary hydrogen bonding components within the κ^1-*P*-**Pon** coordination mode (bottom).

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eration has been observed within a hydroxypyridine based unit have been reported.[14,15] In our previous work,[11] we outlined the successful application of a ruthenium *p*-cymene complex containing the isopropyl analogue of these ligands in the hydrogenation of CO_2 in the presence of DBU (Figure 2). We reported moderate activities with TONs up to 2550 at 100 °C in THF over the course of 48 h. It is believed that 2-oxo-pyridinide unit of the ligand plays a role in the heterocyclic cleavage of molecular hydrogen (Figure 2). During the course of our subsequent investigations, we prepared an additional ligand within this family, **6-D^{Cy}Pon** (6-dicyclohexylphosphino-2-pyridone) (Figure 1, top). To our surprise, an iridium complex containing this ligand exhibited very high catalytic activities at room temperature. Herein, we wish to report the synthesis and characterization of [Ir(κ²-*P,N*-6-D^{Cy}Pon*)(COD)] (**1**) (where **6-D^{Cy}Pon***) is the anionic species, 6-dicyclohexylphosphino-2-oxo-pyridinide). Also reported are the results of our preliminary room temperature catalytic investigations for the hydrogenation of CO_2 utilizing this complex.

The new complex, **1**, was synthesized via the addition of one equivalent of **6-D^{Cy}Pon** (see details of the synthesis in the supporting information) to one half of an equivalent of the binuclear complex, [Ir(OMe)(COD)]$_2$ (where COD = 1,5-cycloocta-diene) in dichloromethane (Scheme 1). The protic ligand was deprotonated *in situ* due to the presence of the methoxide unit in the precursor. This acts as an internal base leading to methanol as by-product. A standard workup procedure afforded **1** as an orange solid product in excellent yield (91%).

Complex **1** was fully characterized by spectroscopic and analytical methods (see supporting information). The ^{1}H NMR spectrum of **1** (in CDCl$_3$) was consistent with the formation of the expected product. The spectrum was notable for the absence of a signal for the NH proton, previously observed as a broad signal at 9.40 ppm for the free ligand (*c.f.* Figure S8 with Figure S13 in the supporting information). The three proton environments on the pyridyl ring were observed as three

multiplet resonances at 7.10 ppm (ddd), 6.38 ppm (dd) and 5.73 ppm (ddd). The corresponding ^{1}H{^{31}P} NMR spectrum was used to aid assignment by comparing the two spectra and identifying the reduction in the multiplicity of the signals (see Figure S13). There were a number of overlapping signals in the region between 1.03 and 2.22 ppm, corresponding to the protons of the cyclohexyl substituents and the CH$_2$ units of the COD moiety. The two alkene units of the COD ligand were located at 5.90 and 3.78 ppm, in which the significantly down-field chemical shift of the two is assigned to the one *trans* to the phosphorus donor [the carbon signal for this environment shows as a doublet resonance at 88.0 ppm ($J_{PC} = 10.6$ Hz) in the corresponding ^{13}C{^{1}H} spectrum]. The ^{31}P{^{1}H} NMR spectrum of **1** showed one single sharp resonance at −31.5 ppm. This is a large upfield shift with respect to the chemical shift observed for the free ligand **6-D^{Cy}Pon** at 3.0 ppm. This is consistent with a κ²-*P,N* coordination mode in **1**, where the ligand is in the anionic **6-D^{Cy}Pon*** form, as found in the related **6-D^{i}PPon** ligand systems.[11] The infrared spectrum of **1** exhibited a CO stretching band at 1622 cm^{-1}. Furthermore, the mass spectrum (ESI$^+$) correlated with the proposed structure by giving a clear peak at 592.23 a.m.u. corresponding to the [M+H]$^+$ cation.

Single orange block-shaped crystals suitable for X-ray crystallography were obtained via recrystallisation of a concen-trated solution of **1** in THF. The molecular structure shows an iridium metal center containing the anionic **6-D^{Cy}Pon*** ligand coordinated in a κ²-*P,N* mode with an additional η²:η² coordinated COD ligand (Figure 3). The P,N ligand forms a tight four-membered chelate where the corresponding P–Ir–N angle is 69.13(3)°. The COD moiety has been modelled as partially disordered where one of the double bonds is positioned over two locations in a ratio 56:44 (Figure S23). The iridium center exhibits a distorted square planar geometry, where the smallest *cis* angle involves the **6-D^{Cy}Pon*** ligand. Focusing on the 2-oxo-pyridinide unit within the structure, the C–C and C–N bond distances within the ring (shown in Figure 4) suggest some
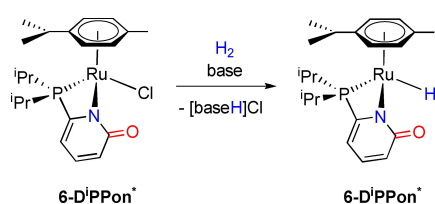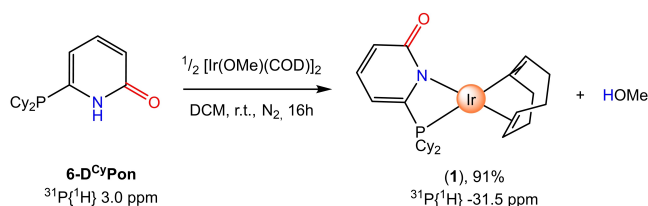

Figure 2. Transformation of [RuCl(*p*-cymene)(κ²-*P,N*-**6-D^{i}PPon***)] to the corre-sponding hydride complex via base-assisted heterolytic cleavage of molec-ular hydrogen.

Scheme 1. Synthesis of [Ir(κ²-*P,N*-**6-D^{Cy}Pon***)(COD)] (**1**) via addition of **6-D^{Cy}Pon** to one half an equivalent of [Ir(OMe)(COD)]$_2$ in DCM.
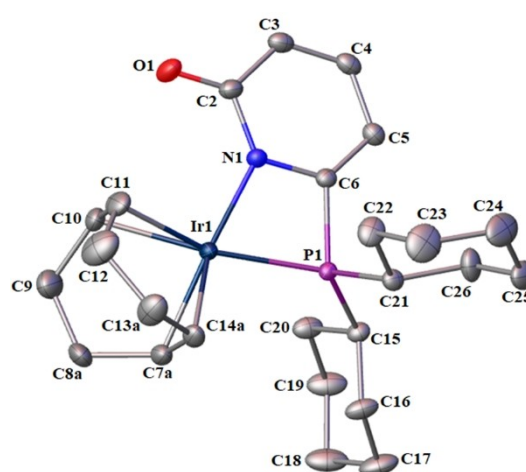

Figure 3. Crystal structure of complex **1** (thermal ellipsoids at 50% ellipsoid level). The structure contains disorder within the COD moiety (see supporting information for details) only the major component shown in this figure. Selected bond distances (Å) and angle (°): Ir1–P1 2.2975(3), Ir1–N1 2.0768(12), N1–Ir1–P1 69.13(3) (see Figure 4 for further details).
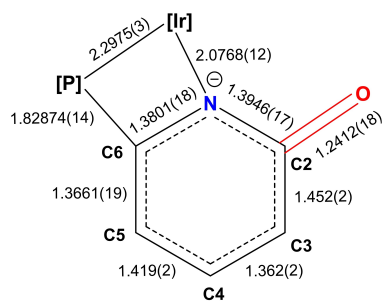
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Figure 4. Highlighting the bond distances (Å) within the 2-oxo-pyridinide unit in the crystal structure of **1**.

Table 1. Hydrogenation of CO_2 catalyzed by **1**.[a]

$$H_2 \text{ (30 bar)} + CO_2 \text{ (20 bar)} \xrightarrow[\text{THF / r.t.}]{\text{Complex 1} \atop \text{DBU (500 - 10,000 equiv.)}} [DBU + H]^+ [OC(O)H]^-$$

Conversions up to 97% TON's up to 4000 at room temperature

Entry	Time	DBU (equiv.)[b]	Conversion (%)[c]	TON[d]
1	0.5 h	500	52	260
2	1 h	500	85	425
3	2 h	500	97	485
4[e]	2 h	0	trace	n/a
5	24 h	5000	53	2650
6	24 h	10000	31	3100
7	48 h	10000	40	4000

[a] Reactions carried out using H_2 and CO_2 at 30 and 20 bar, respectively, in THF (5 mL) with catalyst **1** (5.9×10^{-3} g, 0.01 mmol) at room temperature and varying quantities of DBU as base; [b] the number of equivalents of DBU is relative to the catalyst **1**; [c] Conversions were determined using ^{1}H NMR spectroscopy; [d] TONs were calculated using the formula TON = (number of mmol formate-salt product formed / number of mmol catalyst used); [e] Reaction carried out in the absence of DBU base.

degree of delocalization with clear double bond character between C(2) and O(1) atoms. This C=O unit within the complex is positioned in close proximity to the hydrogen atoms on one of the double bonds of the coordinated COD unit with O(1)—H(10) and O(1)—H(11) distances of approximately 2.475(2) Å and 2.617(2) Å, respectively. These short distances may account for the larger than expected downfield shift for the one coordinated alkene environment in the ^{1}H NMR spectrum for this compound.

With **1** fully analyzed, and based on our previous investigations utilizing [RuCl(*p*-cymene)(κ^2-*P,N*-**6-D^{i}PPon***)] as catalyst,[11] we set out to explore the potential of **1** within the hydrogenation of CO_2 in the presence of a base. We based our initial investigation on the conditions that we previously utilised. As outlined in the introduction, there are limited examples of iridium based catalysts which are active for this transformation at room temperature.[1,4–10] One of the most active room temperature catalyst was reported by Fujita and Himada containing picolinamidate ligands which gave a TON in the region of 5500 at 50 h.[10] We were fortunate to discover that **1** was indeed an active catalyst for the transformation of CO_2 into formate-salt in the presence of H_2 and DBU. Moreover, it demonstrated activity at room temperature. The H_2 and CO_2 gases are in excess and so the number of equivalents of DBU provides the limiting factor in the transformation. A selection of the results obtained has been outlined in Table 1 to highlight its activity. Complex **1** showed a conversion of 52% within 30 min of pressurizing the reactor with H_2 and CO_2 (Table 1, entry 1). This equates to a TOF of 520 h^{-1} which exceeds or is commensurate with the most active catalysts for this transformation.[1] It should be noted that there is no standardized catalytic methodology that is utilised across the literature to enable direct comparisons. The conversion is increased to almost completion within 2 h (97%; TON = 485, entry 3). These results demonstrate the activity of this catalyst at room temperature within a short period of time. In order to challenge the catalyst further, the number of equivalents of DBU was increased, initially to 5,000 equivalents (entry 5) and finally to 10,000 equivalents (entry 6). In these cases, TONs of 2,650 and 3,100 were obtained after a 24 h period. For the latter case, the TON was found to increase further to 4,000 when the reaction was left for 48 h (entry 7). It should be noted that only a trace amount of a formate species (presumably formic acid)

was observed when the reaction was carried out in the absence of the base under room temperature conditions (entry 4). This is as expected since the formation of formic acid is thermodynamically unfavorable and requires the presence of a base.[16]

To gain a better understanding of the reasons for the high activities of **1** at room temperature, reactivity studies were carried out with H_2. The generation of an iridium—hydride species is almost certainly involved within the catalytic transformation cycle. In our previous report involving [RuCl(*p*-cymene)(κ^2-*P,N*-**6-D^{i}PPon***)], we suspected that the 2-oxo-pyridinide unit was involved within the activation of hydrogen, via a ligand cooperation mode, leading to the observed product, [RuH(*p*-cymene)(κ^2-*P,N*-**6-D^{i}PPon***)] (Figure 2).[11] In this case, however, no intermediate species, where the ligand was protonated, were observed. Furthermore, the activation of this ruthenium complex required heating to 85 °C. In the case of **1**, an instantaneous reaction leading to **2** was observed when an NMR tube containing a benzene-d_6 solution of **1** was pressurized with H_2 (Scheme 2). Here, a color change from orange to yellow was observed, highlighting that the activation of hydrogen was very facile. Examination of the ^{31}P{^{1}H} NMR spectrum of the resulting reaction mixture indicated full conversion to a single observable product as shown by a single
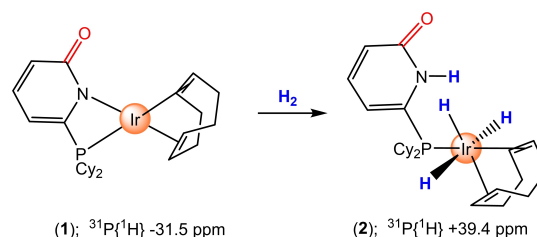
Scheme 2. Reaction of [Ir(κ^2-*P,N*-**6-D^{Cy}Pon***)(COD)] (**1**) with H_2.

resonance at 39.4 ppm (shifted from −32.9 ppm; see Figure S22 in supporting information). This is suggestive of a change in coordination mode and re-protonation of the phosphorus ligand, *i.e.* a change from κ²-*P*,*N*-**6-D^{Cy}Pon***** to κ¹-*P*-**6-D^{Cy}Pon**. The large change in chemical shift being consistent with the phosphorus ligand changing from being in a four membered chelate to a monodentate coordination mode. The corresponding ¹H NMR spectrum, recorded 10 min following addition of H₂, was also consistent with the clean conversion to this new product as the only spectroscopically observed species (Figure S21, top). Most notable was the presence of two broadened signals at −9.82 ppm and −14.05 ppm integrating for 2H and 1H, respectively. Furthermore, a broad resonance at 11.23 ppm was also observed, corresponding to the NH unit on the coordinated **6-D^{Cy}Pon** ligand. Based on the spectroscopic evidence, the new complex **2** has been assigned as [Ir(H)₃(κ¹-*P*-**6-D^{Cy}Pon**)(COD)], the product resulting from the reaction of two H₂ molecules with **1**. In this transformation, one molecule of hydrogen is activated directly at the iridium center, whilst the other is added across the iridium-nitrogen bond, *via* a ligand cooperation type reaction.

DFT predictions of the ¹H NMR signals for the proposed complex **2** (with Me substituents in place of the Cy groups on the **6-D^{Cy}Pon** ligand) were in good agreement with experimental observations. The optimized structure (Figure 5) shows a distorted octahedral geometry with the hydride ligands in a *mer* configuration. The predicted hydride signals showed a similar difference of 4.5 ppm, with the single *cis* hydride being further upfield compared to the two *trans* hydrides, in agreement with experimental integration pattern. The NH proton signal was calculated at 10.45 ppm; see supporting information for computational details.

The reaction with H₂ was demonstrated to be reversible. When a solution containing **2** was placed under vacuum (to remove the H₂ atmosphere in the NMR tube) the mixture slowly converted back to **1** over the course of 16 h [see Figures S19c-S19f)]. It should be noted, however, that this reversibility was not a fully clean transformation. As can be seen in Figures S19 and S20, there is a reduction in peak intensities which indicate the possible formation of NMR inactive species within the mixture. In addition, multiple low intensity signals in the
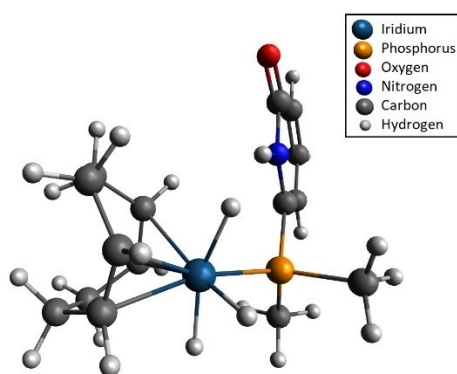
hydride region of the ¹H NMR spectrum are also observed. Furthermore, small amounts of cyclooctane are observed when **2** is left standing in solution. These grow over time and result from the hydrogenation of COD. The loss of COD from the coordination sphere of **2** is likely to be one of the decomposition pathways. These observations highlight the rather reactive nature of **2**. Overall, it is likely that the facile multiple activation of H₂ is responsible for the exceptional catalytic activity of **1** at room temperature. Further experimental studies to better understand the overall reactivity of **1** are being carried out alongside computational investigations.

In summary, the synthesis of a novel iridium complex containing the new ligand **6-D^{Cy}Pon** has been reported. This complex has been shown to react with H₂ rapidly at room temperature where the pyridone based ligand is involved within the H–H bond cleavage. Thus, we have demonstrated that this family of ligands offers a novel mode to the ligand cooperation toolbox. Moreover, we have shown that the complex possesses excellent catalytic activity for the hydrogenation of CO₂ at room temperature. This is atypical of most homogeneous systems which typically require elevated temperatures for this transformation.

Supporting Information

Acknowledgements

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Figure 5. DFT calculated structure for complex **2**. Protons on COD moiety and methyl groups are omitted for clarity.

Legend: Iridium, Phosphorus, Oxygen, Nitrogen, Carbon, Hydrogen

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RESEARCH ARTICLE

A new ligand system has been developed which is shown to activate H_2 via a novel ligand cooperation mode. In this case, H_2 adds across an iridium-nitrogen bond. The process has been shown to be reversible. This process has been utilised in the hydrogenation of CO_2 where, the catalyst demonstrates activity at room temperature.
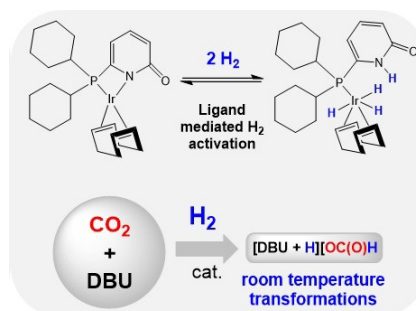
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