An Air and Moisture Stable Boat Shaped Hydroxo-Bridged Ruthenium(II) Binuclear Complex for the Catalytic Hydrogenation of CO$_2$

Uttam K. Das,[a] Graham J. Tizzard,[b] Simon J. Coles,[b] and Gareth R. Owen*[a]

A new hydroxo-bridged ruthenium (II) complex [{Ru(η^6-p-cymene)(^{i}Pr$_2$P—O)}$_2$(μ-OH)]Cl (**2**) has fortuitously been isolated from the reaction between the known ruthenium(II) complex [RuCl$_2$(η^6-p-cymene)(^{i}Pr$_2$P-OH)] (**1**) in either CDCl$_3$ or CHCl$_3$ solutions in the presence of excess DBU (1,8-diazabicyclo(5.4.0)undec-7-ene) at room temperature. Complex **2** is only formed under specific conditions as an orange-colored air and moisture stable binuclear complex. It is formed via the deprotonation of the P—OH unit in [RuCl$_2$(η^6-p-cymene)(^{i}Pr$_2$P-OH)]. Complex **2** has been fully characterized by spectroscopic and analytical methods. Its structure was determined by single crystal X-ray diffraction which reveals a boat-shaped motif containing a bridging hydroxide unit which undergoes hydrogen bonding with a chloride counterion. Complex **2** was utilized as a catalyst for the hydrogenation of CO$_2$ to formic acid salt using molecular hydrogen. The catalytic reactions were performed at 100 °C in THF in the presence of DBU as a base to isolate [DBU + H][OC(O)H] salt as the final product. Using catalyst loadings down to 0.01 mol%, it was possible to hydrogenate gaseous CO$_2$ with TONs up to 9900.

Introduction

There has been great interest in the synthesis and investigations of bi- and multi-nuclear transition metal complexes which contain bridging ligands between the metal centers.[1] The interplay and potential cooperativity between the metal centers, facilitated by the ligand bridge, can provide some rather interesting properties, and thus, valuable transformations. For example, there have been a number of sophisticated examples in the design of magnetic materials containing unusual metal oxidation states.[2] Furthermore, such systems have been studied as a means of correlating the relationship between the bridging structural motif and its role within the active sites in biological systems.[3] As such, binuclear ligand-bridged transition metal complexes represent an interesting

class of coordination compounds in terms of their unique structure, bonding, and potential chemical properties (Figure 1).

The first examples of binuclear ruthenium arene complexes were reported by Winkhaus and Singer in 1967.[4] In 1972, Zelonka and Baird further developed on this by reporting the synthesis of phosphine coordinated monomeric complexes from these binuclear chloride-bridged ruthenium arene complexes.[5] Since then, the synthesis and structure of a wide range of ligand bridged ruthenium complexes have been reported.[6–9] Hirano reported a triply hydroxo-bridged ruthenium complex, formed via the accidental incorporation of water into the reaction mixture. Interestingly, this binuclear complex was found to be an active catalyst in the transfer hydrogenation of carbonyl compounds (ketones and aldehydes) and hydration of nitriles.[10] The Yi group reported a tetranuclear ruthenium μ-hydroxo,μ-oxo-hydride complex and demonstrated it to be a highly cooperative catalyst.[11] In 2005, Onishi prepared the

[a] Dr. U. K. Das, Prof. G. R. Owen
Chemical and Environmental Sciences, and Sustainable Environment Research Centre
University of South Wales,
Pontypridd
UK, CF37 4AT
E-mail: gareth.owen@southwales.ac.uk

[b] Dr. G. J. Tizzard, Prof. S. J. Coles
National Crystallography Service, School of Chemistry
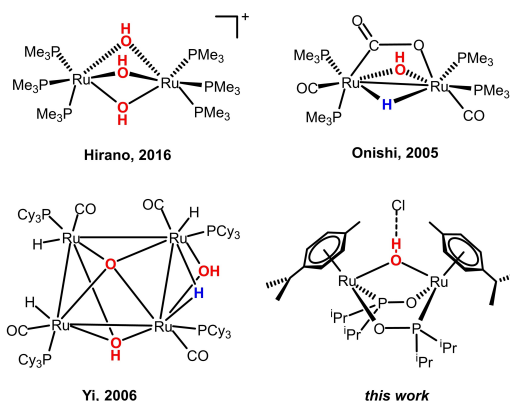University of Southampton
Highfield
Southampton
UK, SO17 1BJ

Figure 1. Selected bi- and multi-nuclear ruthenium complexes containing hydroxo-, hydrido- and oxo-bridging units.

ChemCatChem

Research Article
doi.org/10.1002/cctc.202400362

Chemistry Europe
European Chemical
Societies Publishing

ruthenium dimeric complex, [{Ru(PMe$_3$)$_2$CO}$_2$(μ-H)(μ-OH)(κ^2-*O,C*–CO$_2$)] which was found to undergo multiple transformations.[12] Bera and co-workers focused on hydroxycarbonyl-bridged binuclear ruthenium compounds with their relevance to water-gas shift chemistry and transformations involving CO$_2$.[13] More recently, a catalytic reaction involving the hydrogenation of CO$_2$ to formate was published using μ-hydrido and DMSO-bridged diruthenium complex as catalyst, albeit with moderate TONs.[14]

As part of our ongoing interest in developing novel non-innocent ligand systems for the transformation of CO$_2$, we recently reported a set of mononuclear ruthenium complexes capable of catalyzing the hydrogenation of CO$_2$ to formate-salts based on a [RuCl$_2$(η^6-*p*-cymene)(PR$_3$)] structure using a new ligand, 6-diisopropylphosphino-2-pyridone (**6-D^{i}PPon**).[15] We have also very recently reported an iridium system containing the derivative ligand, 6-dicyclohexylphosphino-2-pyridone (**6-D^{Cy}Pon**), which was found to be highly active at room temperatures.[16] To explore this further, we expanded our focus towards related ruthenium complexes containing phosphinous acid ligands. During these investigations, we isolated a novel binuclear complex bridged by a hydroxyl unit under fortuitous reaction conditions. Herein, we wish to report the synthesis, characterization, and solid-state structure of this complex. We also wish to report the successful application of the complex for the catalytic hydrogenation of CO$_2$ into formic acid, isolated as a formate-salt in the presence of DBU base.

Results and Discussion

The synthesis of the complex, [RuCl$_2$(η^6-*p*-cymene)(^{i}Pr$_2$P-OH)] (**1**) was accomplished by using a modified version of a previous report.[17] This complex contains an acidic P–OH unit and so its reactivity with DBU as base was investigated. A CDCl$_3$ solution of the complex was prepared in an inert atmosphere glove box (H$_2$O < 0.1%) in an NMR tube and a drop of DBU was added. The ^{31}P{^{1}H} NMR spectrum of the resulting reaction mixture showed the full consumption of complex **1** and the formation of three new phosphorous containing species with signals at 101.9 ppm, 97.1 ppm and 96.3 ppm, in a ratio of 1:1:8 (see Figure S10b in the supporting information).[18] These three signals are shifted upfield with respect to the starting complex, **1** (134.5 ppm in CDCl$_3$, Figure S10a). Monitoring the reaction mixture over time did not result in any significant changes to

the ratio of three species in solution. Exposure of the reaction mixture to an open atmosphere or adding a small drop of water, however, led to the rapid conversion to a new single resonance at 140.6 ppm in the ^{31}P{^{1}H} NMR spectrum.[19]

In a separate reaction, a solution of **1** was prepared in CDCl$_3$ solvent in the open air and an excess of DBU was added. Again, the ^{31}P{^{1}H} NMR spectrum of the reaction mixture showed the full consumption of **1** and the formation of two new phosphorus containing products with signals at 140.0 ppm and 105.1 ppm in a ratio of 98:2 after 1 h. An orange solid was obtained via extracted from a H$_2$O/DCM mixture in 85% isolated yield. The identify of the product was confirmed as [{Ru(η^6-*p*-cymene)(^{i}Pr$_2$P–O)}$_2$(μ-OH)]Cl (**2**) via a range of spectroscopic and analytical techniques as outlined in the following sections. On the basis of the experimental data, we propose that the reaction from **1** to **2** proceeds as shown in Scheme 1.

Characterization of the isolated complex **2** was carried out. The ^{31}P{^{1}H} NMR spectrum (in CDCl$_3$) confirmed the expected resonance as a singlet at 140.6 ppm. The corresponding ^{1}H NMR spectrum confirmed the presence of both *p*-cymene and ^{i}Pr$_2$P–O ligands in a ratio of 1:1 via integration. Furthermore, one additional broadened signal was located at 4.45 ppm which had an integration of 0.5 H compared to the aforementioned ligands. Thus, it was rationalized that **2** was a binuclear complex which contained a bridging hydroxide unit between the ruthenium centers. In **1**, the signals corresponding to the *p*-cymene protons are located as two doublet resonances at 5.63 and 5.59 ppm, in a 2:2 ratio. Interestingly, the corresponding chemical environments in **2** were located as three doublet resonances at 6.70, 5.37, and 4.69 ppm and one triplet resonance at 5.09 ppm; the four signals in a 1:1:1:1 ratio. More significantly, the downfield chemical shift of one of these proton environments (6.70 ppm) and the presence of a triplet resonance suggested that the coordination of *p*-cymene ligand was atypical in solution. A ^{1}H{^{31}P} NMR experiment confirmed that the triplet resonance, at 5.09 ppm in the standard experiment, involves coupling to the phosphorus center since it is observed as a doublet resonance in the decoupled experiment. The ^{13}C{^{1}H} NMR spectrum was of interest. Two of the carbon nuclei within the cymene ring were observed as doublets, 88.9 ppm (^{2}J$_{PC}$ = 13.6 Hz) and 95.5 ppm (^{2}J$_{PC}$ = 8.7 Hz) whilst the other carbons within the ring were singlets. Finally, the MS spectrum of **2** gave the expected isotopic pattern (m/z) for the
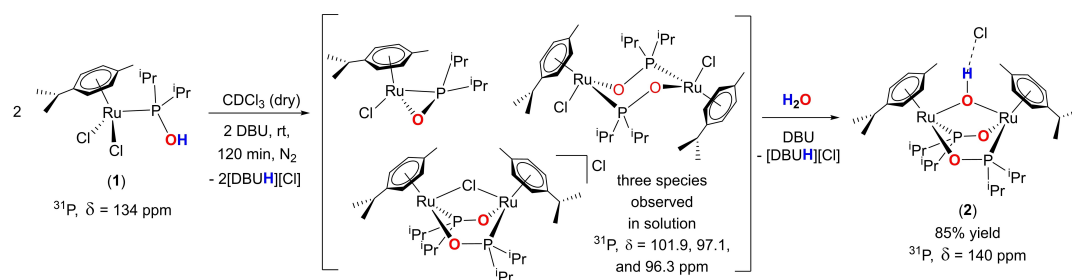
Scheme 1. Synthesis of [{Ru(η^6-*p*-cymene)(^{i}Pr$_2$P–O)}$_2$(μ-OH)]Cl (**2**) via three deprotonation steps from **1**. Possible intermediate species observed under dry conditions shown.

molecular ion $[M-Cl+H]^+$ at 755.26 amu and elemental analysis was also consistent with the formation of **2**.

Single crystals suitable for X-ray crystallography were obtained for **2** (Figure 2). Orange-coloured plates were grown by layering a concentrated DCM solution of **2** with diethyl ether. The crystal structure was solved in a monoclinic, $I2/_a$ space group. The structure consists of two independent half complexes within the unit cell where the dimeric complexes possess a mirror plane cutting through the OH bonds. The molecular structure of **2** revealed a unique boat shaped binuclear complex involving a bridged RuO(H)Ru motif to form a bicyclic complex. The complex is cationic where the chloride anion undergoes hydrogen bonding with the bridging hydroxide, where the O1–Cl1 distances are 3.072(5) and 3.032(5) Å, in the two independent structures. Structural
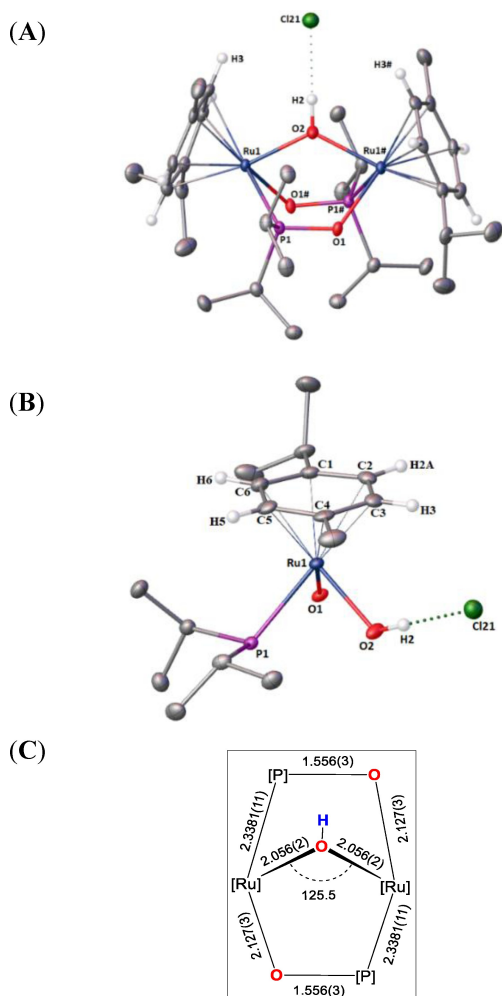

(A)

(B)

(C)

Figure 2. X-ray crystal structure of **2**. (A) Only one of the two independent complexes in the unit cell is presented in this figure, (B) half structure of **2** is presented, and (C) angles and distances of the boat shaped unit of **2**. Thermal ellipsoids at 50% ellipsoid level, (# denotes the symmetrically equivalent atom). Selected angles for this complex (°), O1–Ru1–P1 78.15(8), O1#–P1–Ru1 111.17(12), P1#–O1–Ru1 123.43(17), O2–Ru1–O1 83.06(12), O2–Ru1–P1 80.16(9). See supporting information for further details. All hydrogen atoms, apart from H1 and the CH protons of *p*-cymene units been omitted for clarity. The hydroxide bridged boat shaped core highlighted in (C) where all other substituents and ligands at the phosphorus and ruthenium centres have also been removed for clarity.

analysis shows that two 'Ru(*p*-cymene)' units are held together by two anionic ligands connected via a phosphorus donor (L-type) and an oxide donor (X-type), one to each of the two ruthenium centres. The P–O bond lengths, 1.556(3) and 1.559(3), confirm this form over a possible deprotonated secondary phosphine oxide [P(V)] form where there is a double bond between the phosphorus and oxygen atoms. In this latter scenario, the phosphorus would have been X-type and an oxygen L-type (*i.e.* [(iPr₂)P(−)=O].[20] As a comparison, the phosphorus-oxygen double bond in the uncoordinated secondary phosphine oxide ligand, Ph₂P(=O)H, is 1.4881(11) Å,[21] whilst the corresponding single bonds in the reported crystal structure of [RuCl₂(*p*-cymene){PPh₂(−OH)}], range between 1.600(3) Å and 1.612(3) Å.[17] These secondary phosphine oxide ligands have some interesting coordination chemistry.[22] These bridging units within the structure form a six membered ring motif involving the atoms RuPORuPO with a boat structure. The ruthenium(II) centers are further linked by a hydroxo-bridging ligand. The bonding parameters of the resulting bicyclic core are shown in Figure 2(C). The Ru–O–Ru angles in the two independent structures are both 125.5(2)°. This is similar to other reported hydroxide- and oxo-bridged ruthenium complexes. This also highlights the C₂ symmetry through the OH bond.

Closer inspection of the structure reveals short contact distances between the aryl CH proton *ortho* to the methyl group on each *p*-cymene and the chloride anion. Furthermore, this proton is also close to both the oxygen and hydrogen atoms within the hydroxide ligand [Figure 2(B)]. The corresponding distances are H3–Cl21 2.8877(6), H3–O2 3.176(3) and H3–H2 2.76(1). The corresponding distances in the independent structure are 2.9776(6), 3.258(2) and 2.859(9), respectively. These short contact distances are likely to be the reason for the downfield chemical shift of 6.69 ppm, in the ¹H NMR spectrum, for the proton environment corresponding to the ones labelled H3 in Figure 2. The structure also reveals that the phosphorus atom (P1) is close to being *trans* to two carbons within the cymene ring. The P1–Ru1–C2 and P1–Ru1–C3 angles are 170.55(12)° and 148.41(12)°, respectively. The former angle is much closer to being *trans* [see Figure 2(B)]. The corresponding values in the independent structure with the asymmetric unit are 168.79(11)° and 149.48(11)°. This explains the observations within the ¹³C{¹H} NMR spectrum where carbons C2 and C3 within the cymene ring are coupling to the NMR active phosphorus nuclei.

We were interested in exploring the application of **2** towards the hydrogenation of CO_2 to formate salts.[23] Inspired by our recent report of ruthenium catalysed hydrogenation of CO_2,[15] both **1** or **2** were investigated for comparison. The results of our investigations are outlined in Table 1. In accordance with typically utilized reaction conditions, DBU was chosen as the base to provide [DBU+H][OC(O)H] as the reaction product (Table 1 graphic). Several conditions were investigated, including different pressures and ratios of H₂ and CO_2, different molar equivalents of DBU. In the first instance we carried out some preliminary high pressure NMR investigations by dissolving **2** in a solvent and pressurising the tubes with one

Table 1. Catalytic results for the hydrogenation of CO_2 to formate-salt, in the presence of DBU, catalysed by **1** or **2**.[a]

$$CO_2 + H_2 \xrightarrow[\text{THF, DBU, }\Delta]{\text{Cat (0.01 mmol)}} \left[DBU + H \right]^{\oplus} \left[\begin{array}{c} O \\ C \\ H \quad O \end{array} \right]^{\ominus}$$

Entry	Catalyst	Pressure of H_2:CO_2 (bar)	DBU (equiv)[b]	Temp (°C)	Time (h)	No of mmols of formate[c]	Yield of formate[d]	TON[e]
1	**1**	20:20	–	rt[f]	48	–	–	–
2	**1 or 2**	20:20	–	100	48	–	7–12 equiv. of HC(O)OH [g]	–
3	**1**	30:20	500	100	24	3.5	71%	350
4	**2**	30:20	500	100	24	4.3	86%	430
5	**2**	30:20	500	100	48	4.9	98%	490
6	**2**	30:20	1000	100	24	8.1	81%	810
7	**2**	30:20	1000	100	48	9.9	99%	990
8 [h]	**2**	30:20	1000	100	48	8.0	80%	800
9	**2**	30:20	5000	100	24	30.0	60%	3000
10	**2**	30:20	5000	100	48	49.5	99%	4950
11	**2**	30:20	10000	100	24	59.0	59%	5900
12	**2**	30:20	10000	100	48	99.0	99%	9900
13	**1**	30:20	10000	100	48	60.0	60%	6000

[a] For entries 1–13, these were carried out in a high-pressure reactor with 20 mL THF; [b] Amount of DBU with respect to catalyst loading; [c] No of mmols of [DBU + H][O$_2$CH] formed as determined by ^{1}H NMR spectroscopy using DMF as internal standard; [d] Corresponding yields of [DBU + H][O$_2$CH] formed; [e] TON = (mole of formate-salt formed / mole of catalyst used); [f] Reaction carried out at room temperature, approximately 23 °C; [g] when the reaction was carried out in the absence of base, small quantities of HC(O)OH were formed in the mixture. [h] Reaction carried out in presence of mercury (0.05 mmol).

or both of the gases, H_2 and CO_2 to 2 bar. In all cases, no changes to the starting complex were observed within their corresponding ^{1}H and ^{31}P{^{1}H} NMR spectra over time with temperatures up to 100 °C.

Despite this, we proceeded to explore both **1** and **2** under catalytic conditions since these would be at much higher pressures (a total of 40 bar). To our surprise, we did indeed observe catalytic conversion. Initially, it was found that trace amounts of HC(O)OH were formed as the product in the absence of DBU. It is generally accepted that a base is required for the hydrogenation of CO_2 to formate species due to the thermodynamics of the reaction.[24,25] Under the conditions tested, however, between 7 and 12 equivalents of a formic acid were observed under the catalytic conditions used (Table 1, entry 2). The conversion did not increase beyond this, however. The rationale behind this was due to the stability of the catalyst with increasing concentrations of formic acid. It was noted that black particles were observed within the reaction mixtures when they were performed in the absence of base. Furthermore, under such conditions the presence of free *p*-cymene is also observed within the corresponding ^{1}H NMR spectra.

On the other hand, excellent conversions were observed in the presence of the base. DBU-formate salt was obtained from the reaction of gas mixtures of H_2 and CO_2 up to 50 bar (H_2 and CO_2; 30:20) in THF at 100 °C in the presence of 500 equiv. of DBU with catalytic amounts of **1** (Table 1, entry 3). Here, a conversion of 71% of the DBU was observed after a 24 h period. Under the same conditions, the performance of **2** was

improved, providing a conversion of 86% (Table 1, entry 4). This represents a TON of 430. This improved to 98% (TON of 490) when the catalytic reaction was carried out for 48 h (entry 5). When the number of equivalents of DBU was increased further to 1000 excellent conversions were observed with a TON of 990 after 48 h (entries 6 and 7). Again, increasing the number of equivalents of DBU further to 5000, the conversion was 99% after 48 h with a TON of 4950 (entry 10). We found the highest TON 9900 using catalyst **2** and 10000 equivalent of DBU at 100 °C, a total pressure of 50 bar (H_2 and CO_2; 30:20) in 48 h (Table 1, entry 12). In all cases, the conversion of the DBU to the corresponding formate salt went to completion after a 48 h period suggesting that complex **2** is a robust catalyst.

Under these optimized conditions, a comparative study utilising **1** as the catalyst precursor was carried out. In this case, although it performed well, a conversion of only 60% of the DBU-formate salt was formed (entry 13) after the 48 h period. Furthermore, NMR studies revealed only uncoordinated phosphorus products in the mixtures after the catalytic runs. A possible explanation for the better overall performance of **2** due to its stability as a result of its binuclear structure. In order to provide further insight on the stability of **2** during the catalytic testing, we also performed a mercury drop test. The conditions from entry 7 were repeated in the presence of small quantity of mercury. The conversion was reduced from 99% to 80% showing that the mercury had a minor impact on the catalyst performance. It did not reduce substantially and there was no evidence of ruthenium nanoparticle absorption. It was

ChemCatChem

Research Article
doi.org/10.1002/cctc.202400362

Chemistry
Europe
European Chemical
Societies Publishing

concluded that the transformations are largely homogeneous with either minor decomposition of the catalyst over time or that the presence of mercury within the reaction has a minor negative impact on the catalyst performance.[26]

These results demonstrate that **1** and **2** are both high performing catalysts for the hydrogenation of CO_2. Complex **2** is a more robust catalyst. To the best of our knowledge, the maximum TON of 9900 achieved for this transformation is better performing than most other reported ruthenium catalyst operating at temperatures of 100 °C or under.[23,27–29] There are two examples where higher TONs are recorded.[30,31] It should be noted that, with the large variance in the conditions used for this transformation across the literature, it is challenging to make direct comparisons. One of the reasons for the high performance of the catalyst could be due to the cooperation between the two ruthenium centers, involving binuclear reaction pathways.[32] These reaction pathways are currently being explored to understand the modes of activation of H_2 and CO_2.

Conclusions

In summary, the synthesis and characterization of a new binuclear ruthenium complex has been reported herein. A new μ-hydroxo-bridged (η^6-p-cymene) ruthenium (II) complex [{Ru-(η^6-p-cymene)(^{i}Pr$_2$P–O)}$_2$(μ-OH)]Cl has been isolated from the reactions between a known ruthenium (II) complex [RuCl$_2$(η^6-p-cymene)(^{i}Pr$_2$P–OH)] in wet CDCl$_3$/CHCl$_3$ in presence of DBU at room-temperature. The deprotonation of the hydroxyl functional group of [RuCl$_2$(η^6-p-cymene)(^{i}Pr$_2$P–OH)] followed by nucleophilic chloride substitution reaction forms a novel orange-colored air and moisture stable binuclear ruthenium (II) complex. [{Ru(η^6-p-cymene)(^{i}Pr$_2$P–O)}$_2$(μ-OH)]Cl has been fully characterized by elemental and spectral analysis (IR, NMR and mass spectrometry). The molecular structures of Ru complexes [{Ru(η^6-p-cymene)(^{i}Pr$_2$P–O)}$_2$(μ-OH)]Cl was determined by single-crystal X-ray diffraction as boat-shaped μ-hydroxo-bridge molecule with a chloride anion. This [{Ru(η^6-p-cymene)(^{i}Pr$_2$P–O)}$_2$(μ-OH)]Cl complex was used as catalyst for the hydrogenation of CO_2 to formic acid using molecular hydrogen. The catalytic reactions were performed at 100 °C temperature in THF in presence of DBU as a base to isolate DBU-formate as final product. Using 0.01 % Ru catalyst in THF was possible to hydrogenate gaseous CO_2 to solid DBU-formate salt in excellent conversions with a TON up to 9900.

Experimental Section

(i) Synthesis and characterisation of complex 2: In air, a suspension of [RuCl$_2$(p-cymene)(^{i}Pr$_2$POH)][17,33] (110 mg, 0.25 mmol) was stirred in standard CHCl$_3$ (5 mL) and a solution of DBU (115 mg, 0.75 mmol) in 5 mL of CHCl$_3$ was added dropwise into it. This reaction mixture was stirred at ambient temperature for 1.5 h. After evaporation of solvent the mass was extracted with 15 mL of n-hexane/CH$_2$Cl$_2$ mixture (90:10), filtered and evaporated. The extra DBU and DBU-salt were separated using H$_2$O/CH$_2$Cl$_2$ mixture in a separating funnel. The CH$_2$Cl$_2$ part was dried over anhydrous MgSO$_4$. Evaporation of CH$_2$Cl$_2$ solution in vacuo yielded pure complex **2** (85 mg, 0.11 mmol, 85 %) as an orange solid. Single crystals suitable for X-ray diffraction were obtained by layering a dilute solution of CH$_2$Cl$_2$ over Et$_2$O at 298 K. ^{1}H NMR (CDCl$_3$, 298 K, 400.13 MHz): δ 6.70 (d, $^3J_{HH}$ = 6.4 Hz, 2H, H3), 5.37 (d, $^3J_{HH}$ = 6.4 Hz, 2H, H2a), 5.09 (t, $^3J_{HP}$ = 4.4 Hz, 2H, H5), 4.69 (d, $^3J_{HH}$ = 5.2 Hz, 2H, H6), 4.45 (s, 1H, OH), 2.53-2.46 (m, 2H, ^{i}Pr–CH), 2.24–2.08 (m, 4H, ^{i}Pr–CH), 2.10 (s, 6H, cym-CH_3), 1.31–1.26 (dd, $^3J_{HH}$ = 7.2 Hz, 6H, cym-^{i}Pr-CH_3), 1.20–1.13 (m, 18H, cym-CH_3 + P^{i}Pr–CH_3), 1.07–102 (m, 12H, P^{i}Pr–CH_3). ^{31}P{^{1}H} (CDCl$_3$, 298 K, 161.98 MHz): 140.62 (s). ^{13}C{^{1}H} (CDCl$_3$, 298 K, 100.62 MHz): δ 108.58 (s, C1), 95.46 (d, $^2J_{PC}$ = 5.4 Hz, C3), 88.96 (d, $^2J_{PC}$ = 13.6 Hz, C2), 84.37 (s, C4), 81.48 (s, C5), 68.45 (s, C6), 34.43 (d, $^1J_{PC}$ = 23.5 Hz, P^{i}Pr-CH), 31.26 (d, $^1J_{PC}$ = 27.8 Hz, P^{i}Pr-CH), 31.07 (s), 24.10 (s), 19.60 (s), 18.99 (s), 18.59 (d, $^2J_{PC}$ = 6.6 Hz, P^{i}Pr-CH), 18.50 (s), 17.75 (d, $^2J_{PC}$ = 5.5 Hz, P^{i}Pr-CH$_3$), 16.73 (d, $^2J_{PC}$ = 3.1 Hz, P^{i}Pr-CH$_3$). IR (ν, cm^{-1}): 3110 (OH), 3034, 2954, 2919, 2867 (CH). MS: 755.26 [M–I+H]$^+$. Elemental analysis: Expected (%) C; 48.69, H; 7.28, found (%) C; 48.47, H; 6.97.

(ii) Catalytic hydrogenation of CO$_2$ to formate-salt: In a nitrogen-filled glovebox, catalyst (0.01 mmol), DBU (quantities as indicated in Table 1) were dissolved in 10 mL THF. The mixture transferred to high-pressure autoclave reactor (250 mL) under nitrogen and equipped with a magnetic stir bar. After pressurizing the reactor with CO$_2$ gas, the reactor was pressurized with H$_2$ gas then heated and stirred on a preheated oil bath for indicated time. Then, the reactor was cooled to room temperature, and the pressure was carefully released. DMF (in equivalent molar quantity to DBU) was then added as an internal standard into the reaction mixture. The reaction mixture was then analysed by ^{1}H NMR with a few drops of D$_2$O to lock the signals.

Supporting Information

Full experimental details in addition to selected analytical and spectroscopic data for complex **2** are provided in the Supporting Information. Crystallographic parameters and catalytic results are also provided. Deposition Number **2330580** (for **2**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service. The authors have cited additional references within the Supporting Information.[34–36]

Acknowledgements

spectrometry data collection and Elemental analysis service at London Metropolitan University.

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.

[1] S. Tanaka, H. Tsurugi, K. Mashima, *Coord. Chem. Rev.* **2014**, *265*, 38–51. https://doi.org/10.1016/j.ccr.2014.01.012.

[2] D. M. D'Alessandro, F. R. Keene, *Chem. Rev.* **2006**, *106*, 2270–2298. https://doi.org/10.1021/cr050010o.

[3] P. Štarha, *Coord. Chem. Rev.* **2021**, *431*, 213690. https://doi.org/10.1016/j.ccr.2020.213690.

[4] G. Winkhaus, H. Singer, *J. Organomet. Chem.* **1967**, *7*, 487–491. https://doi.org/10.1016/S0022-328X(00)85370-X.

[5] R. A. Zelonka, M. C. Baird, *J. Organomet. Chem.* **1972**, *35*, C43–C46. https://doi.org/10.1016/S0022-328X(00)86874-6.

[6] B. Therrien, *Coord. Chem. Rev.* **2009**, *253*, 493–519. https://doi.org/10.1016/j.ccr.2008.04.014.

[7] K. J. Hurst, *Coord. Chem. Rev.* **2005**, *249*, 313–328. https://doi.org/10.1016/j.ccr.2004.06.017.

[8] D. Carmona, A. Mendoza, J. Ferrer, J. F. Lahoz, L. O. Oro, *J. Organomet. Chem.* **1992**, *431*, 87–102. https://doi.org/10.1016/0022-328X(92)83288-S.

[9] M. Yuki, K. Sakata, Y. Hirao, N. Nonoyama, K. Nakajima, Y. Nishibayashi, *J. Am. Chem. Soc.* **2015**, *137*, 4173–4182. https://doi.org/10.1021/jacs.5b00584.

[10] S. Kiyota, T. Kobori, H. Soeta, Y.-I. Ichikawa, N. Komine, S. Komiya, M. Hirano, *Polyhedron* **2016**, *120*, 3–10. https://doi.org/10.1016/j.poly.2016.04.006.

[11] C. S. Yi, T. N. Zeczycki, I. A. Guzei, *Organometallics* **2006**, *25*, 1047–1051. https://doi.org/10.1021/om0510674.

[12] Y. Arikawa, S. Nagae, J.-I. Morishita, K. Hiraki, M. Onishi, *Angew. Chem. Int. Ed.* **2005**, *44*, 5509–5513. https://doi.org/10.1002/anie.200501335.

[13] M. Majumdar, A. Sinha, T. Ghatak, S. K. Patra, N. Sadhukhan, S. M. Wahidur Rahaman, J. K. Bera, *Chem. Eur. J.* **2010**, *16*, 2574–2585. https://doi.org/10.1002/chem.200902797.

[14] X.-F. Mo, C.-F. Xiong, T. Cheng, C. Liu, G. Chen, P. He, X.-Y. Yi, *Inorg. Chim. Acta* **2023**, *552*, 121510. https://doi.org/10.1016/j.ica.2023.121510.

[15] R. Ayyappan, U. K. Das, I. Abdalghani, R. C. Da Costa, G. J. Tizzard, S. J. Coles, G. R. Owen, *Inorg. Chem.* **2023**, *62*, 6704–6710. https://doi.org/10.1021/acs.inorgchem.3c00287.

[16] S. Siangwata, A. Hamilton, G. J. Tizzard, S. J. Coles, G. R. Owen, *ChemCatChem* **2024**, e202301627. https://doi.org/10.1002/cctc.202301627.

[17] L. V. Graux, M. Giorgi, G. Buonoa, H. Clavier, *Dalton Trans.* **2016**, *45*, 6491–6501. https://doi.org/10.1039/c5dt04683a.

[18] Similar reactions were performed under different conditions including different solvents and stoichiometries of DBU as base. The distribution of species varied in each case as determined by ^{31}P NMR spectroscopy. Attempts to isolate any species from these mixtures were unsuccessful.

[19] It was observed that more than one molar equivalent of DBU was needed to ensure conversion to **2**.

[20] L. V. Graux, M. Giorgi, G. Buono, H. Clavier, *Organometallics* **2015**, *34*, 1864–1871. https://doi.org/10.1021/om501300p.

[21] S. Härling, J. Greiser, T. M. A. Al-Shboul, H. Görls, S. Krieck, M. Westerhausen, *Aust. J. Chem.* **2013**, *66*, 1264–1273. https://doi.org/10.1071/CH13259.

[22] A. Gallen, A. Riera, X. Verdaguer, A. Grabulosa, *Catal. Sci. Technol.* **2019**, *9*, 5504–5561. https://doi.org/10.1039/C9CY01501A.

[23] S. Kushwaha, J. Parthiban, S. K. Singh, *ACS Omega* **2023**, *8*, 38773–38793 https://pubs.acs.org/doi/10.1021/acsomega.3c05286.

[24] S.-T. Bai, G. De Smet, Y. Liao, R. Sun, C. Zhou, M. Beller, B. U. W. Maes, B. F. Sels, *Chem. Soc. Rev.* **2021**, *50*, 4259–4298. https://pubs.rsc.org/en/content/articlelanding/2021/cs/d0cs01331e.

[25] T. Singh, S. Jalwal, S. Chakraborty, *Asian J. Org. Chem.* **2022**, *11*, e202200330. https://doi.org/10.1002/ajoc.202200330.

[26] I. C. Chagunda, T. Fisher, M. Schierling, J. S. McIndoe, *Organometallics* **2023**, *42*, 2938–2945. https://doi.org/10.1021/acs.organomet.3c00340.

[27] R. Ayyappan, R. C. Da Costa, G. R. Owen, *Recent developments in homogeneous catalysis for the functionalisation of CO_2, in Organometallic Chemistry* RSC, Ed. N. Patmore, I. P. Elliot **2023**, *Ch 2*, 23–67. https://books.rsc.org/books/edited-volume/2034/chapter/4650656/Recent-developments-in-homogeneous-catalysis-for.

[28] K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.* **2018**, *118*, 372–433. https://doi.org/10.1021/acs.chemrev.7b00182.

[29] S. Kushwaha, J. Parthiban, S. K. Singh, *Organometallics* **2023**, *42*, 3066–3076. https://doi.org/10.1021/acs.organomet.3c00286.

[30] P. Munshi, A. D. Main, J. C. Linehan, C.-C. Tai, P. G. Jessop, *J. Am. Chem. Soc.* **2002**, *124*, 7963–7971. https://pubs.acs.org/doi/10.1021/ja0167856.

[31] M. Scott, B. B. Molinos, C. Westhues, G. Franciò, W. Leitner, *ChemSusChem* **2017**, *10*, 1085–1093. https://doi.org/10.1002/cssc.201601814.

[32] S. Sinhababu, Y. Lakliang, N. P. Mankad, *Dalton Trans.* **2022**, *51*, 6129–6147. https://pubs.rsc.org/en/content/articlelanding/2022/dt/d2dt00210h.

[33] D. Zell, S. Warratz, D. Gelman, J. S. Garden, L. Ackermann, *Chem. Eur. J.* **2016**, *22*, 1248–1252. https://doi.org/10.1002/chem.201504851.

[34] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71* 3–8. https://doi.org/10.1107/S2053273314026370.

[35] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341. https://doi.org/10.1107/S0021889808042726.

[36] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8. https://doi.org/10.1107/S2053229614024218.

RESEARCH ARTICLE

Dr. U. K. Das, Dr. G. J. Tizzard, Prof. S. J. Coles, Prof. G. R. Owen*

1 – 7

An Air and Moisture Stable Boat Shaped Hydroxo-Bridged Ruthenium(II) Binuclear Complex for the Catalytic Hydrogenation of CO_2
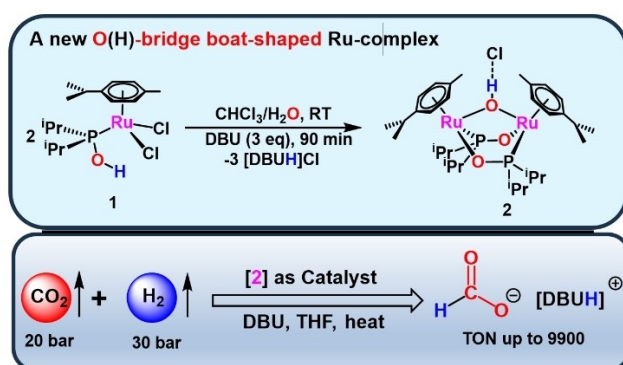
The deprotonation of a coordinated phosphinous acid ligand on a ruthenium p-cymene complex provides a two atom P–O bridging unit leading to a binuclear ruthenium complex featuring a bridging hydroxide ligand. The resulting complex was found to be highly active in the catalytic hydrogenation of CO_2 to formate salts with TONs up to 9900.