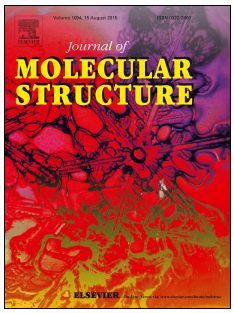

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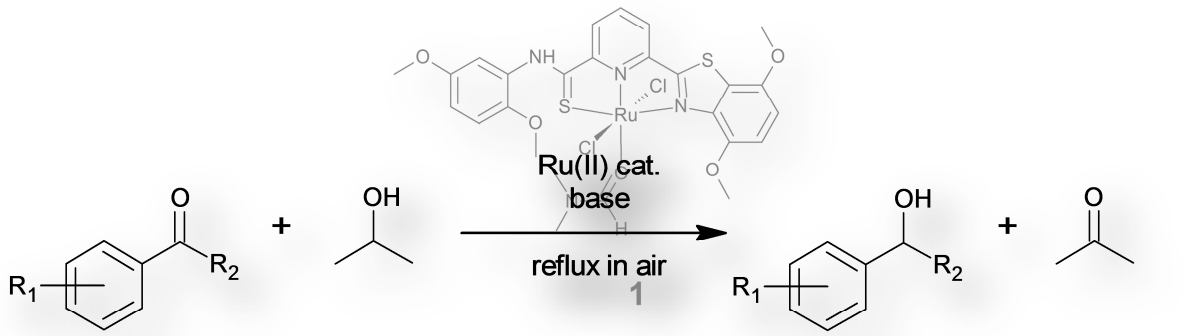

Electrochemical response of a Ru(II) benzothiazolyl-2-pyridinecarbothioamide pincer towards carbon dioxide and transfer hydrogenation of aryl ketones in air

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Abstract

A ruthenium(II) complex of 6-(4,7-dimethoxy-2-benzothiazolyl)-*N*-(2,5-dimethoxyphenyl)-2-pyridinecarbothioamide (*pbcta*), of the formula [Ru(pbcta)Cl_2(dmf)] (**1**, where DMF = dimethyl formamide) was prepared from $RuCl_3$•*x*H_2O and *pbcta* in DMF at reflux under argon atmosphere. The identity of **1** was confirmed from its elemental analysis, ESI MS, and a series of spectroscopic measurements. Voltammetric measurements on **1** in DMF and DFT studies on the structure optimized in the gas phase revealed predominantly ligand based electron transfer processes under argon. In the presence of a proton source, proton coupled electron transfer to the ligand occurs. Under a carbon dioxide atmosphere, voltammetric studies revealed that **1** is inactive for CO_2 reduction, and the redox responses observed in the presence of the proton source and/or CO_2 are ligand based leading to reactions with the coordinated *pbcta*. Transfer hydrogenation (TH) of aryl ketones was efficiently carried out in 2-propanol using **1** at reflux. TH of the aryl ketone substrates proceeded in air with almost quantitative conversions at 0.2–1.0 mol% catalyst.

Keywords: Ruthenium(II); NNS pincer ligand; Transfer hydrogenation; Aryl ketones

1 Introduction

The use of transition metal complexes as catalysts presents tremendous scope for performance optimization by tuning the ligands about the metal centre [1]. The metal often act as the catalytic site, and the ligands help to stabilize the metal in its various oxidation states throughout the catalytic cycle. In some cases, the ligand has been suggested to play a role in the catalytic process by acting as a proton or electron sink [2-4]. Consequently, non-innocent ligands i.e. ligands that can participate in acid base reactions whilst coordinated, and are also redox active at accessible potentials, may be useful in improving catalytic processes [5-10]. Although

many different types of complexes have shown significant activity, ruthenium polypyridyl complexes are particularly attractive due to their wide scope of applications [11-16]. For example, transfer hydrogenation (TH) is a useful protocol for the reduction of ketones and aldehydes to their corresponding alcohols [17]. Ruthenium(II) and iridium(III) complexes are usually applied as the most useful catalysts for the transfer hydrogenation of ketones [18-20]. Bifunctional catalysts containing ruthenium(II) complexes and (monotosylated) 1,2-diamines or aminoalcohols can offer high catalytic activity and selectivity due to the presence of a N–H functionality [21]. A great variety of related ligands and transition metal complex catalysts have been developed to mitigate the need for bifunctional systems. These include aminophosphines [22-25], N-heterocyclic carbenes (NHCs) [26, 27], pincer ligands of the κ^3-NNN type [28-30], to name a few. Catalytic TH involving transition metals are often performed in 2-propanol as the hydrogen donor, and under inert atmosphere to prevent oxidation of the catalyst, thus affording high conversion of the ketone to the desired alcohol [21]. Other systems employed include HCO_2H–Et_3N [31], or aqueous solution of HCO_2Na [32]. Nevertheless, the operational simplicity offered by the use of an inexpensive and non-toxic solvent such as 2-propanol, provides the additional advantage of the acetone by-product which can be easily removed. The reductive conditions enabled by the presence of a strong base such as KOH or K^{t}BuO, readily facilitates the reduction of C=O to C-OH bonds with good functional group tolerance. Despite the success of various systems, there is still a need to develop cheap, simple and effective systems, to improve the accessibility and scope of TH reaction.

Ruthenium complexes have also been implicated in the electro-catalytic reduction of carbon dioxide on various electrode surfaces and solvents in the presence of proton sources such as water and alcohols [8, 15, 33]. Electro-catalytic proton reduction is often coupled to carbon dioxide reduction, however Ru(II) is not associated with proton reduction, despite the accessibility of the Ru(IV/III/II) reduction couples in many ruthenium containing complexes [34, 35]. However, Sponholz et al [36] illustrated the homogenous catalytic hydrogen generation from ethanol. The homogeneously catalyzed hydrogenation of carbon dioxide (CO_2) to formic acid was first reported in 1976 [37]. In recent times, various authors [15, 38-40] have continued to illustrate the ability of ruthenium (and other metals) to directly hydrogenate CO_2 either with hydrogen gas (hydrogenation), or via transfer hydrogenation to produce species such as formate. Transfer hydrogenation is less explored than hydrogenation, but it is a safer and more

economical route as stated above. The direct reduction of CO_2 is not only of environmental importance [41], but it is also of industrial significance [42, 43] as species such as formate are useful synthons, and potential hydrogen store for the hydrogen economy. Other studies have also investigated the conversion of CO_2 to methanol, and an excellent review is given by Li et al [44].

In previous studies we reported on the development of pyridyl carbothioamide derivatives as pincer ligands [45, 46], as well as various coordination complexes for electro-catalytic proton reduction [46-49]. In those studies, it was shown the ligand framework possess accessible redox potentials, which may present an opportunity for them to act as electron shuttles. In this report, the synthesis of the ruthenium(II) complex of 6-(4,7-dimethoxy-2-benzothiazolyl)-*N*-(2,5-dimethoxyphenyl)-2-pyridinecarbothioamide (*pbcta*), its electrochemical behavior towards CO_2, and application to the transfer hydrogenation of some aryl ketones are outlined.

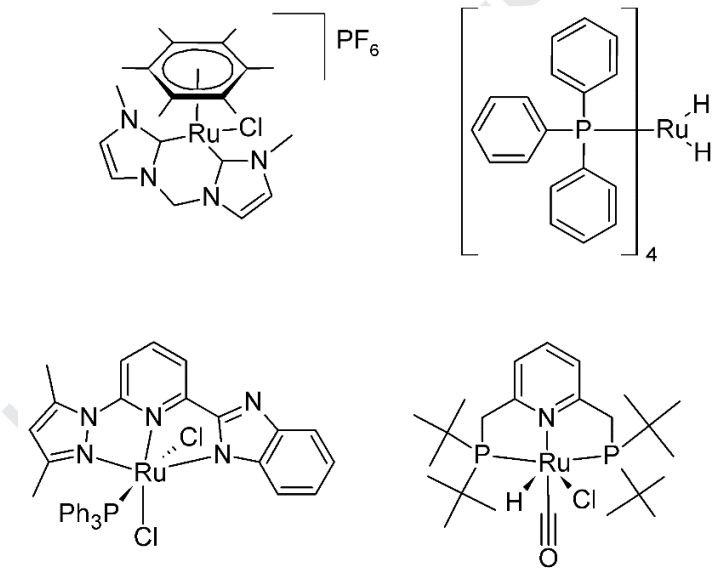

Figure 1. Examples of complexes employed in catalytic (transfer) hydrogenation.

2 Experimental

All reagents were purchased from commercial sources (BDH and Sigma-Aldrich) and solvents were purchased as HPLC grade and used without further purification. Absorbance measurements were performed on a HP 8453A diode array spectrophotometer. IR spectra were recorded as neat samples using an ATR accessory on a Bruker Vector 22 FTIR

spectrophotometer. High-resolution ESI MS spectra were acquired via positive electrospray ionization on a Bruker 12 Tesla APEX –Qe FTICR-MS with an Apollo II ion source. Samples were dissolved in acetonitrile or 1:1 dichloromethane/acetonitrile, followed by direct injection using a syringe pump with a flow rate of 2 μL s^{-1}. The data was processed using Bruker Daltonics Data Analysis Version 3.4. Solution ^{1}H NMR spectra were measured using a Bruker ACE 500-MHz Fourier transform spectrometer and were referenced internally to the residual protons of the incompletely deuterated solvent.

All electrochemical experiments were performed on a DigiIvy DY2312 potentiostat, under an argon atmosphere (unless otherwise stated) at room temperature. A standard three electrode cell setup was employed, using a glassy carbon working electrode (diameter = 3 mm), a silver wire quasi-reference electrode and a platinum wire as an auxiliary electrode. Ferrocene, which was used as an internal reference showed a reversible wave at +0.65 V in DMF. The ionic strength was maintained at 0.1 M $[^{n}Bu_4N]PF_6$. The solvents used in the electrochemical experiments were dried using standard procedures [50].

Controlled-potential electrolysis (CPE) measurements for the production of hydrogen were conducted at –1.10 V (vs Ag), on stirred solutions for 20 min in a sealed two-chambered H-cell separated by a fine frit, where one chamber held the working and reference electrodes in 10 mL of 0.36 mM of complex in 0.1 M $[^{n}BuN_4]PF_6$ (supporting electrolyte) with 12 mM *p*-toluenesulfonic acid monohydrate (*p*-TSOH) (as a proton source) and the second chamber held the auxiliary electrode in 5 mL of the solvent with the supporting electrolyte. A glassy carbon plate (contact area ~2 cm × 1 cm × 3 mm) and Pt wire were used as the working and auxiliary electrodes, respectively, with Ag wire as the reference electrode. The solution was purged with Ar for 20 minutes and then sealed under an Ar atmosphere before the start of each electrolysis experiment.

Transfer hydrogenation experiments were performed under an inert atmosphere of dry argon or ambient air. The solvents were purified using standard procedures [51] and, where necessary, were distilled under argon or nitrogen atmosphere using the appropriate drying agent. The ketone substrates were obtained from commercial suppliers and used without further purification. GC analysis was carried out on a Hewlett-Packard 6890 gas chromatograph equipped with a 5973 MSD detector and β-DEX 120 chiral capillary column (30 m × 0.25 mm; Supelco, USA).

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2.1 Semi-Empirical and Density Functional Theory calculations

Density functional theory calculations were carried out using the GAMESS software package[1] [52, 53]. The structures were optimized (see supporting info) in the gas phase as indicated by the absence of imaginary frequencies in the Hessian, using PW91X/SBKJC [54, 55] with the common polarization and spherical coordinates. Solvent optimization in DMF using the SMD solvation method [56]. The GAMESS input file was generated using MacMolPlt 7.7[2] [57], and the output file viewed using the same. The SBKJC basis set results was initially compared to those obtained using the Sapporo core/valence relativistic basis sets (SPK) double zeta potentials (PW91X/SPKr-DZP) [58-60]. This basis set provided identical FMO, to the SBKJC basis set, albeit with different energies (as was expected, see supporting information). However, the family of SPK basis sets were more computationally demanding while not providing more useful information. Consequently only the calculations based SBKJC basis set are discussed.

2.2 Preparation of [Ru(pdcta)Cl_2(DMF)] (1)

The 6-(4,7-dimethoxy-2-benzothiazolyl)-*N*-(2,5-dimethoxyphenyl)-2-pyridinecarbothioamide ligand (*pbcta*) was prepared following literature protocol [45]. In a pressure tube, $RuCl_3$•*x*H_2O (23 mg, 0.11 mmol) and *pbcta* (49 mg, 0.10 mmol) were dissolved in DMF (20 mL) and Et_3N (0.5 mL). The mixture was then thoroughly sparged with Ar and then refluxed for 6 h, following which, the solution was almost completely distilled under reduced pressure. The residue was dissolved and transferred to a beaker using DCM (20 mL) and dried under a strong stream of air. The resulting solid was washed with copious amounts of water and diethyl ether, then air dried. A brown solid was isolated with yield 83% (59.4 mg). High-resolution ESI MS (positive mode) *m/z* = of 640.04567 for the [Ru(pdcta)Cl_2]-H^+ species (see supporting information). Elemental analysis: Found: C, 44.16; H, 3.22; N, 7.86. Calc. for $C_{23}H_{21}Cl_2N_3O_4RuS_2$•$C_3H_7NO$: C, 43.82; H, 3.96; N, 7.86%. Selected IR (ATR) / cm^{-1}: 3423

[1] GAMESS: an open-source general ab initio quantum chemistry package. https://www.msg.chem.iastate.edu/gamess/index.html

[2] MacMolPlt: an open-source molecular builder and visualization tool for GAMESS. http://brettbode.github.io/wxmacmolplt/

ν(NH), 2834 ν(CH_{DMF}), 1639 ν($C{=}O_{DMF}$) 1598–1500 ν($C{=}C_{aryl}$). λ_{max} (DMSO) / nm (ε ± 200 / M^{-1} cm^{-1}) 274 (18600), 320 (16100), broad shoulder from 460–1000. δ_H(dmso-d_6): 3.77 (3H, s), 3.99 (6H), 4.04 (3H) overlapping singlets, 6.56–6.74 (1H), 7.07 (3H), 7.96 (1 H), 8.14 (1H, CH_{DMF}), 8.26-8.54 (3H, m), 10.79 (1H, NH).

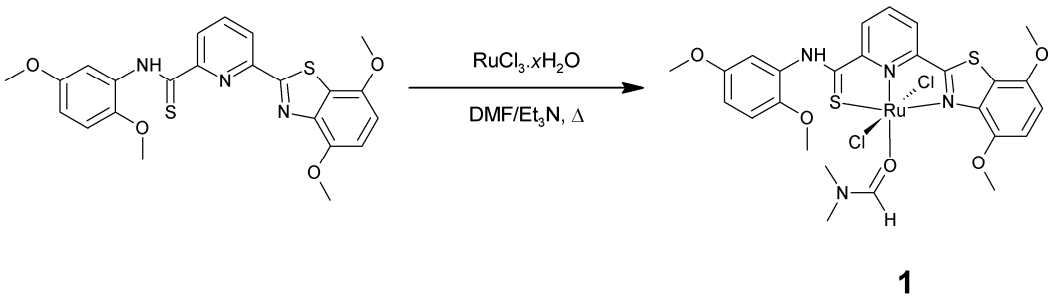
2.3 General procedure for transfer hydrogenation of ketones

In a typical catalytic run, a mixture of **1** (2.1 mg, 0.003 mmol, 1 equiv) and the base (0.03 mmol, 10 equiv.) were stirred in 2-propanol (3 mL) in a pressure tube (Radley tube^{TM}) under air or inert atmosphere for 15-20 min. To this mixture, the ketone (1.5 mmol, 500 equiv.) was added and the resulting mixture stirred at the desired temperature. At the end of the reaction, the mixture was filtered through a short pad of silica gel, transferred and made up in a volumetric flask prior to dilution and injection on the GC column. This was followed by vacuum distillation and the product isolated as a pale yellow oil after purification by silica gel chromatography with hexane: ethyl acetate (5:1) as the eluent.

3 Results and discussion

3.1 Synthesis and characterization

The 6-(4,7-dimethoxy-2-benzothiazolyl)-*N*-(2,5-dimethoxyphenyl)-2-pyridinecarbothioamide ligand (*pbcta*) was prepared according to a protocol reported in an earlier study [45]. The preparation of the ruthenium(II) complex [Ru(pbcta)Cl_2(DMF)] (**1**) from $RuCl_3$•xH_2O followed a similar protocol to that of [Ru(pbt)$_2Cl_2$]•0.25CH_3COCH_3 (where pbt = 2-(2'-pyridyl)benzothiazole) [61]. In the IR and NMR spectra of the [$RuCl_2$(pdcta)(DMF)] complex, the amide NH is retained, suggesting that the ligand is in a neutral form [62, 63], unlike its Pd(II) analogue [45, 46]. The elemental analysis, the mass spectrum and other spectroscopic data (see electronic supporting information) are consistent with the proposed formulation.



1

Scheme 1. Preparation of [Ru(pbcta)Cl_2(DMF)] (**1**).

3.2 DFT and Electrochemical studies

In the gas phase optimized structure, the $\nu(C{=}O_{DMF})$ is calculated at 1637 cm^{-1} and observed at 1639 cm^{-1}. The bond length of the C=S in **1** is predicted to be 1.787 Å compared to 1.666 Å in the crystal structure of *pbcta* [45], and the C-S bonds in the benzothiazole ring are predicted at 1.810 and 1.840 Å compared to 1.723 and 1.747 Å observed. On average, bond lengths of the C-S are predicted at ca 5% greater than those observed in the free ligand, whereas, the C=S bond in **1** is predicted to be ca 7% longer than the free C=S bond. This extra bond lengthening is suggesting a strong interaction between the Ru and coordinated sulfur, and the LUMO and LUMO+1 are mixed $\pi^*/\sigma^*/d\text{-}\pi$ orbitals consistent with the π-back-bonding characteristics of sulfur of the thioamide and the nitrogen of the benzothiazole [64]. However, the retention of N-H stretching frequency in the experimental IR spectrum is clearly indicating that the thioamide functionality is retained, and thus the *pbcta* ligand remains neutral. Density functional theory calculations in the gas phase (and in DMF using the SMD solvation method [56]) analyzing the molecular orbitals of **1** (Fig. 2), revealed that the LUMO and LUMO+1 largely involves the coordinated *pbcta* moiety. Specifically the LUMO heavily populated by the thioamide group and LUMO+1 is delocalized across the pyridothiazole portion of the coordinated *pbcta*. On the other hand, the HOMO is centered on Ru-Cl moiety and HOMO-1 and -2 are fairly mixed with metal center and the thioamide moieties.

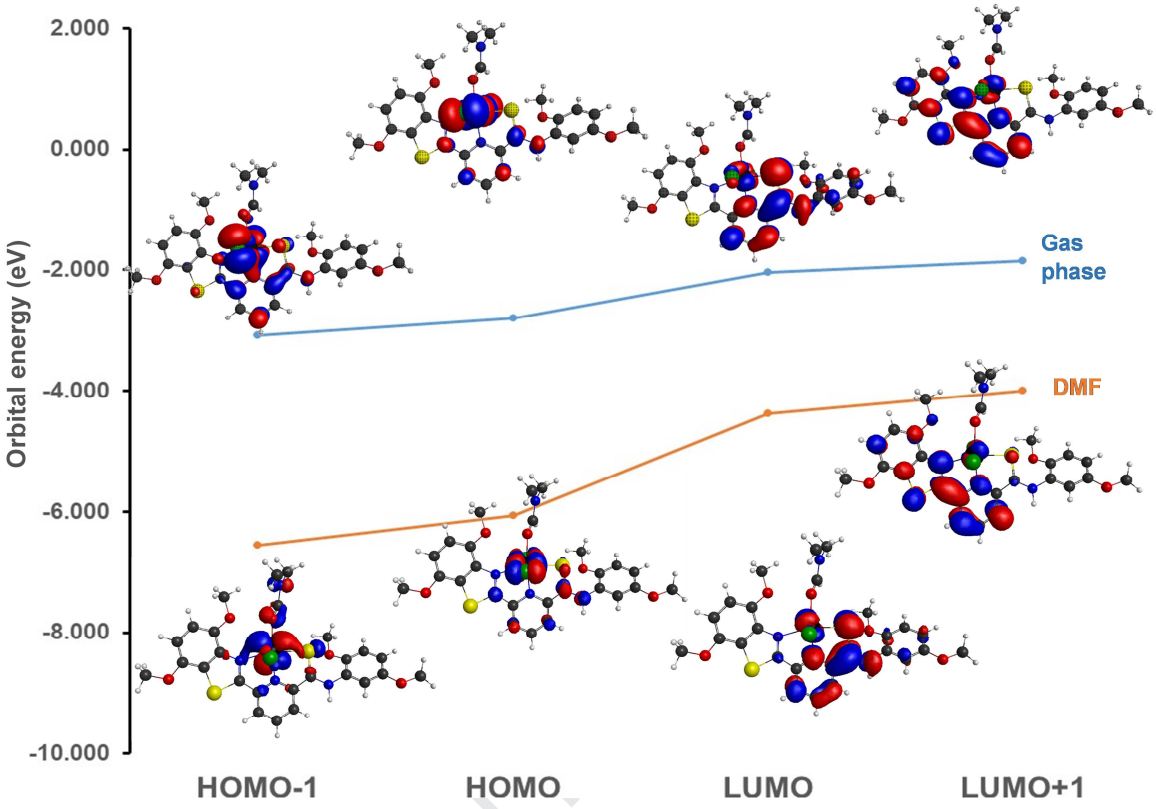


Figure 2. DFT optimized structures in the gas phase (PW91X/SBKJC) and in DMF (PW91X/SBKJC/SMD) for **1**.

Cyclic and square wave voltammograms of **1** compared to *pbcta*, revealed a series of predominantly ligand based redox processes. In the voltammograms of *pbcta*, there are two reversible reductions, one electron each, between –1.1 → –1.7 V versus Ag [46] (Fig. 3 and Fig. S4). In **1**, the first of these reduction waves observed in *pbcta* is absent; however the first reduction wave of **1** which is also a reversible wave observed at $E_{½}$ = –1.48 V (see Fig. S5), coincides with the second reduction wave of *pbcta*. When compared to *pbcta* this first wave in **1** appears to be a two electron reduction (Fig. 3). There is second reduction which was observed at E_{pc} = –1.93 V (two electrons) and a third at E_{pc} = –2.10 V versus Ag, both of which are nearly identical to those observed in *pbcta*. The coordination of *pbcta* to the Ru(II) metal centre removes the initial reduction of the thioamide that leads to a thioamide radical anion in uncoordinated *pbcta*. This behavior is suggesting a significant change about the sulfur of the C=S moiety upon coordination to the Ru metal centre, and is also consistent with the intense p-π/d-π mixing and the lowering of the energies of its orbitals due to bonding. The second

reduction wave in **1** is a two electron wave resulting reduction of the benzothiazole ring of the *pbcta* ligand. At anodic potentials, the Ru(II/III) oxidation was observed at +1.20 V followed by ligand oxidation (thioamide) at +1.52 V. The redox potentials are comparable to similar Ru(II) containing species [8, 63, 65], and are consistent with the locations of the MOs as discussed above.

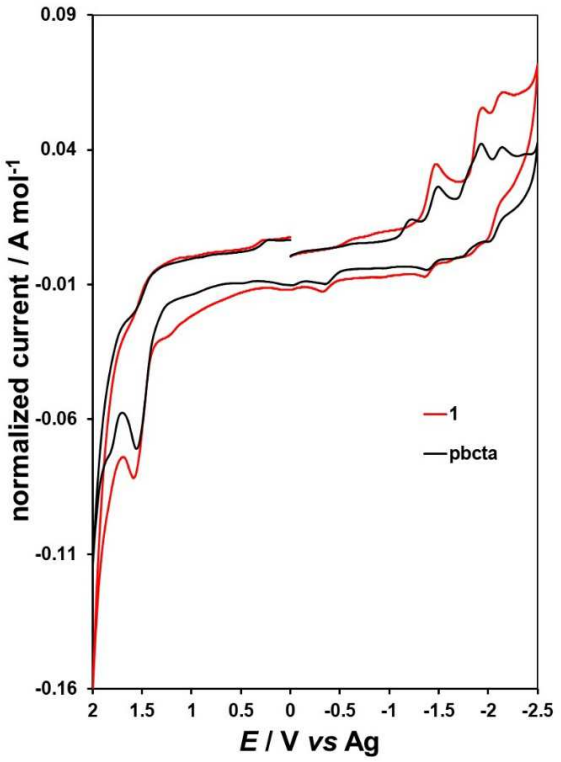


Figure 3. Normalized cyclic voltammograms of **1** and *pbcta* in DMF on a glassy carbon electrode. [**1**] = 0.84 mM, *pbcta* = 1.63 mM, supporting electrolyte = 0.1 M ($^{n}Bu_4N]PF_6$).

Ruthenium(II) systems are well known for their ability to reduce carbonyl compounds in a variety of reactions such as hydrogenation, transfer hydrogenation, and as electrocatalysis to name a few, whereas Ru(III) polypyridyls are well known for the water oxidation reaction. To this end, complex **1** was investigated in the electrocatalytic reduction of CO_2 in the presence and absence of proton sources, by voltammetric techniques. Other systems based on the ligand framework demonstrated electro-catalytic response on the presence of a proton source [46, 66]. Ruthenium is not known for this reaction, and it was confirmed by controlled potential electrolysis experiments of **1** in the presence and absence of *p*-toluene sulfonic acid (see Fig. S6). The proton coupled reduction of CO_2 is more energetically favorable than generating the $CO_2^{\bullet-}$

[67, 68]. In the presence of weak proton donors such as 2-propanol (^{i}PrOH) or ethanol, the current at the first reduction wave approximately doubles (Fig. 4). A similar behavior is observed in *pbcta* in the potential range at which **1** is reduced. Further studies indicate that under a CO_2 atmosphere, the current at the first reduction potential is doubled and the voltammogram of **1** was restored upon sparging with Ar, suggesting that the interaction with CO_2 was a non-covalent interaction. Voltammograms in a CO_2 atmosphere with the proton source resulted in negligible increase in the peak current compared to CO_2 or ^{i}PrOH only (Fig. 4). Several radical anions are known to reduce carbon dioxide to oxalate [69]. However, the nature of reactions with CO_2 is suggesting that the thiolate generated from the reduction of the thioamide most likely reacts with CO_2 to generate a thiocarbonate species. Though not desired for this reaction, thiocarbonates can be used as a carrier for CO_2, as these are readily oxidized to release CO_2 and produce a disulfide [70]. These data indicate that **1** is inactive for the direct CO_2 reduction, and the redox responses observed in the presence of the proton source and/or CO_2 are ligand based leading to reactions with the coordinated *pbcta* (Scheme 2). In this scheme, the coordination complex is suggested to undergo a net $4e^-$, $4H^+$, however it is expected to proceed via two sequential $2e^-$, $2H^+$ reductions. In the presence of CO_2, the thiolate anion from the initial $2e^-$ process is a potent nucleophile that readily attacks the electrophilic carbon of CO_2 to generate the thiocarbonate species. Though not shown in the scheme, the free ligand is also expected to first form a thienyl radical which will be readily protonated in the presence of a proton source, followed by additional reductions and protonation.

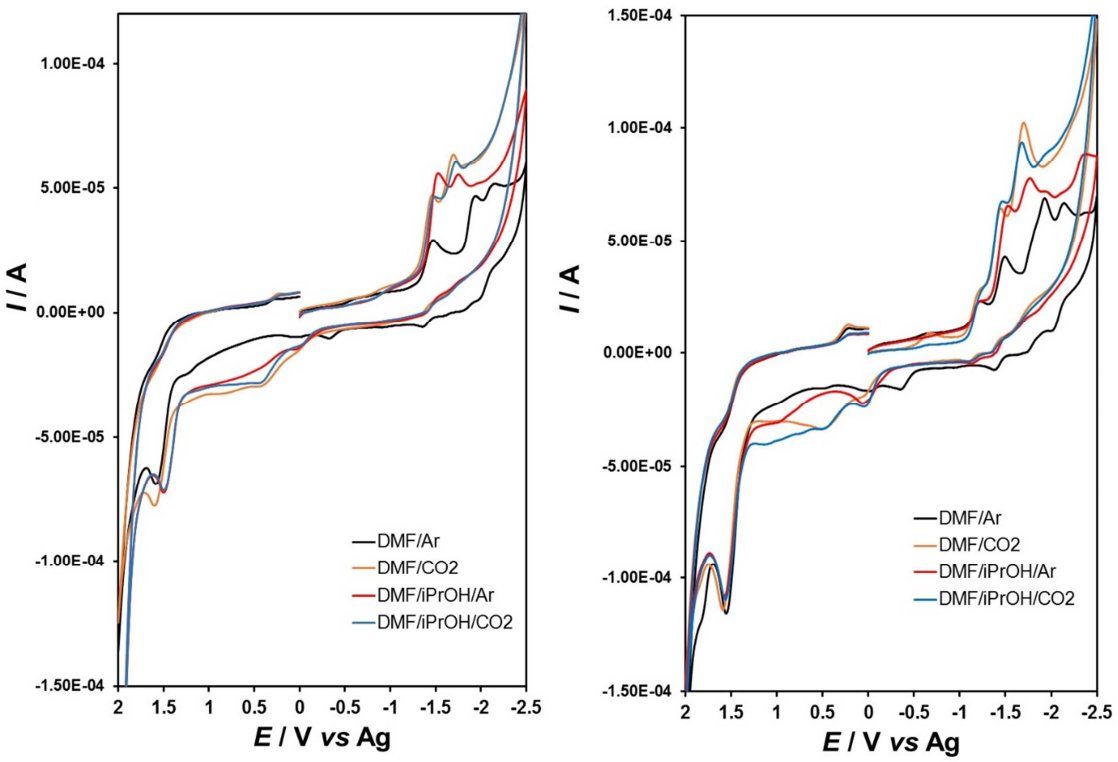
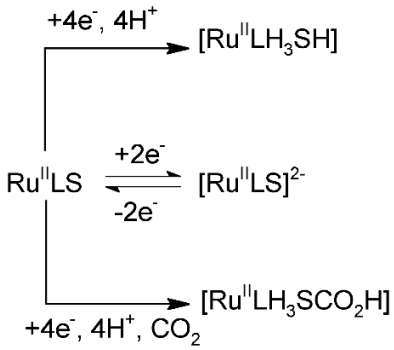


Figure 4. Cyclic voltammograms of **1** (left) and *pbcta* (right) with and without ^{i}PrOH under Ar and CO_2 atmospheres on a glassy carbon electrode. Conditions: [**1**] = 0.84 mM, [*pbcta*] = 1.63 mM, CE = Pt wire, supporting electrolyte = 0.1 M ($^{n}Bu_4N$]PF_6).



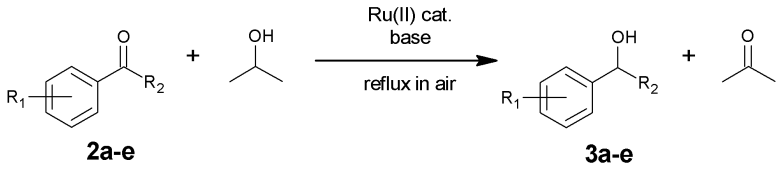
Scheme 2. Proposed mechanism for reduction of **1** in DMF, where L = ligand framework and S = sulfur of the thioamide.

3.3 Transfer hydrogenation of aryl ketones

Whilst there have been a few reports of SNS [71] and NNS [72-74] ligand systems in (asymmetric) hydrogenation of C=X bonds, reports of these systems in transfer hydrogenation is sparse. Transfer hydrogenation (TH) of carbonyl compounds under mild conditions such as room temperature and/or in air, require stable yet highly active transition metal catalysts. To this end, a number of pincer ligands of the NNN type has been reported to generate efficient Ru(II) (pre-)catalyst for the TH of carbonyl compounds in refluxing 2-propanol [1, 27-29]. Many of the systems explored with (asymmetric) TH require inert atmosphere at fairly low (0.05-1.0%) catalyst loading. The excellent catalytic performance of several planar tridentate ligands and their ruthenium(II) complexes in TH prompted us to investigate the catalytic activity of a substituted pyridylbenzothiazole (*pbcta*) NNS pincer ligand system and its ruthenium(II) complex in these transformations.

In our initial TH studies, acetophenone (**2a**) was selected as the model substrate, with K^{t}BuO as base, to screen the reaction conditions (Scheme 3). With 0.4 mol % of **1** as (pre-)catalyst, >99% conversion to 1-phenylethanol (**3a**) was observed under inert atmosphere, and 89% conversion in air (Table 1, entry 1). GC-MS analysis indicated that a racemic mixture of 1-phenylethanol was isolated as the only product. Complex **1** displayed both air and moisture-stability which allowed for the TH reactions to be conducted under inert atmosphere or in the presence of air. Further attempts to improve the enantioselectivity and activity of the system were investigated using a 5:2 mixture of trimethylamine/formic acid or sodium formate. However, **1** appeared to be incompatible with the TEAF mixture or sodium formate, since little to no conversion was observed (Table 1, entries 2 and 3).

Lowering the catalyst loading to 0.2 mol%, gave conversions of 88% and 89% within 24 h under inert atmosphere and aerobic conditions, respectively (entry 4). After 48 hours, the conversions had improved to 96% and >99% under inert atmosphere and aerobic conditions, respectively (entry 5). Evidently, TH could only be effected at reflux since no conversion was observed under ambient conditions (entry 6). Under similar conditions, the relatively cheaper base KOH, gave similar conversions to K^{t}BuO (Table 1, entry 7). With either base, the reductions under aerobic conditions gave slightly better conversions after 48 h.



Scheme 3. Transfer hydrogenation of aryl ketones.

Table 1. Transfer hydrogenation of acetophenone catalysed by **1**.

Entry	Base	S/C ratio	Temp (^{o}C)	Time (h)	Yield[a] (%)	
					inert	Air
1	K^{t}BuO	250	reflux	24	>99	89
2	TEAF	250	50	24	6	--
3	$NaHCO_2$	250	50	24	0	--
4	K^{t}BuO	500	reflux	24	88	89
5	K^{t}BuO	500	reflux	48	96	>99
6	K^{t}BuO	500	r.t.	48	0	--
7	KOH	500	reflux	48	95	97
8	none	500	reflux	24	0	--
9[b]	KOH	500	reflux	48	--	0
10[c]	KOH	500	r.t.	48	--	0
11[c]	KOH	500	reflux	48	--	61
12[d]	KOH	500	reflux	48	--	54

[a] By GC-MS analysis; [b] cat = $RuCl_3$•xH_2O/*pbcta* (1:1); [c] cat = **1**/PPh_3 (1:1); d cat = **1**/*bpy* (1:1)

The literature has illustrated the importance of the base, even though its true role remains unclear. To this end, TH reactions with **1** was investigated in the absence of base, and no conversion to the desired 1-phenylethanol was obtained (Table 1, entry 8). Evidently, for effective TH, a base was required for the generation of the active catalytic species. The TH of acetophenone was also examined in situ with the (pre-)catalyst precursors, $RuCl_3$•xH_2O/pbcta (1:1) (Table 1, entry 9). There was no conversion to the desired alcohol. This suggests that Ru(III) is not the active (pre-)catalyst nor is Ru(II) likely generated from Ru(III) under the reaction conditions. Even though the activity of **1** under aerobic conditions was quite pleasing, the absence of chiral induction remained a major concern. In a previous study, it was demonstrated that co-ligands, triphenylphoshine (PPh_3) or 2,2'-bipyridine (bpy) when added to complexes of with a similar ligand frame work to *pbcta* resulted in enhanced Faradaic efficiencies of the Co(II) compounds in electrocatalytic proton reduction [66]. To this end, the addition of PPh_3 (1 equiv.) as a co-ligand to the reaction mixtures was investigated. PPh_3 is

expected to add steric bulk at the metal centre and also potentially offer additional stability to the transition state(s), thereby enhancing the enantioselectivity [75]. The addition of PPh_3 resulted in the decreased activity of **1** (entries 10-11), and the chiral induction remained unimproved. Evidently, the bulkiness of the **1**/PPh_3 system hindered the reaction progress rather than accelerate it. A similar conclusion can be made of co-ligand *bpy* (entry 12), which is suggesting that the co-ligands are reducing the sites available for substrate binding.

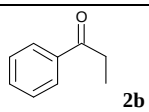
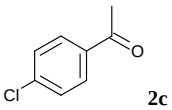
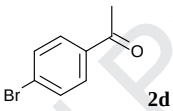
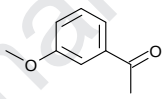
The catalytic reductions with complex **1** as a (pre-)catalyst were extended to other aryl ketone substrates **2b**-**e**. Increasing the steric congestion at the ketone group as in the case of propiophenone, **2b** (Table 2, entries 1-3) required an increased loading of 1 mol% to achieve 97% conversions after 48 h (entry 3). The *p*-halosubstituted substrates, 4-chloroacetophenone (**2c**), and 4-bromoacetophenone (**2d**), gave 82 and 14% conversions, respectively, at 0.2 mol% catalyst loading after 48 h (entries 4 and 5). Interestingly, 4-bromoacetophenone required 1 mol% of the (pre-)catalyst to achieve quantitative conversion after 48 h (>99%, entry 7). The reason for this discrepancy is not immediately understood. Increasing the catalyst loading from 0.2 to 0.5 mol% (Table 2, entry 9) resulted in 98% conversion of 3-methoxyacetophenone (**2e**) to 1-(3-methoxyphenyl)ethanol, which is an important synthon for the synthesis of 3-methoxy-2,6-dimethylphenethyl alcohol [76], and one of its enantiomer for rivastigmine hydrogen tartrate [77-79].

It is plausible that the present transfer hydrogenation may follow an inner-sphere mechanism wherein generation of a Ru(II) hydride is the catalytically active species [28, 80]. The TH of the ketone is presumably initiated from the in situ generation of a ruthenium(II) alkoxide species, by abstracting a proton from the alcohol to extrude 1 equivalent of hydrogen chloride. The resulting alkoxide species undergoes β-hydride elimination to give the true catalytic species, a Ru–H intermediate, and the concomitant release of acetone. Coordination of the ketone substrate to the Ru–H species followed by hydride transfer from the metal to the coordinated substrate carbonyl gives another Ru(II)-alkoxide. The hydrogenated product is released upon the transfer of hydrogen from 2-propanol to the substrate and regeneration of the ruthenium(II) alkoxide species.

In summary, an active Ru(II) complex was developed on the NNS pincer ligand as (pre-)catalyst for the TH of ketones to the corresponding alcohols in air. The system appears to

tolerate a variety of functional groups, however it does not facilitate enantio-differentiation. Efforts are underway to optimize the reaction times, and to enhance the enantioselectivity of the ligand system.

Table 2. Transfer hydrogenation of aryl ketones catalysed by **1** in air.

Entry	Substrate	S:C	Yield[a] (%)
1	 **2b**	500	19
2		200	69
3		100	97
4	 **2c**	500	82
5	 **2d**	500	14
6		200	56
7		100	>99
8	 **2e**	500	87
9		200	98

[a] By GC-MS analysis; reaction conditions: base = KOH, reaction time = 48 h, temp. = reflux.

Conclusions

A novel Ru(II) pincer compound was synthesized and voltammetric studies indicated that it redox properties are ligand centred. The compound was inactive towards the electrocatalytic reduction of CO_2, however it showed good activity towards the transfer hydrogenation of aryl ketones under aerobic conditions.

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Highlights:

- Ru(II) κ^3-SNN pincer ligands is reported for transfer hydrogenation in air
- The frontier molecular orbitals are assessed using DFT methods
- Voltammetric studies revealed that compound is inactive for CO_2 reduction
- TH of the aryl ketones proceeded in air with almost quantitative conversions

Author Statement

Shannen C. Lorraine: Conceptualization, Methodology, Experimentation and Data processing, Reviewing, Editing.

Mark A.W. Lawrence: Conceptualization, Methodology, Experimentation and Data processing, Initial draft preparation, Graphical Preparation, Reviewing, Editing.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: