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Synthesis and (spectro)electrochemical investigations of coordinatively-saturated (cyclopentadienyl)ruthenium–Hantzsch pyridinium/dihydropyridine conjugates

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ABSTRACT

Complexes with the $CpRu(PPh_3)$ fragment bound by iminopyridine ligands functionalised by a Hantzsch dihydropyridine donor of hydride ion or by a Hantzsch pyridinium acceptor of hydride ion have been prepared, and their redox chemistry studied by cyclic voltammetry and EPR and UV–Vis spectroelectrochemical investigations. These Ru(II) complexes have a coordinatively saturated, electronically precise (18-electron) ruthenium(II) centre with a non-labile ligand donor set, which suppresses complicating metal-centred reactivity and, thereby, allows the baseline physicochemical properties of the Hantzsch dihydropyridine/pyridinium-functionalised ligands to be investigated. In Ru(II) complexes, the iminopyridine chelate is linked to the Hantzsch pyridine groups by either an *ortho*-phenyl bridge (electronically delocalized) or by a *meta*-phenyl bridge (electronically isolated), which leads to notable differences in spectroscopic properties, even for ruthenium centre, and differences in redox reactions. Of note, the primary electrochemical reduction of the Ru(II) complexes with a Hantzsch pyridinium substituent is centred on this group, but did not afford the corresponding Ru(II) complexes with a 1,4-dihydropyridine substituent. Rather it was found that the reduction products were identical to the 1:1 hydroxide adducts formed upon addition of hydroxide ion to the starting Hantzsch pyridinium-substituted Ru(II) complexes. Based on these results and comparisons with data from the literature, the reduction products and hydroxide adducts are tentatively assigned as the corresponding hydroxy-dihydropyridine substituted Ru(II) complexes (during reduction, hydroxide ion was likely formed from the residual water present in the acetonitrile solvent). Implications for the electrochemical cycling of transition metal catalysts with Hantzsch pyridinium/dihydropyridine functional substituents are considered.

1. Introduction

Arthur Hantzsch first reported his route to the dihydropyridine which bears his name, Hantzsch's ester (Chart 1), over 130 years ago [1]. After languishing for well over a century, Hantzsch's ester has advanced over the last decade to the forefront of the synthetic chemists' armoury as an organic hydride reagent for asymmetric transfer hydrogenations of unsaturated organic substrates, reactions catalysed by chiral Brønsted and Lewis acids [2–9]. Although very useful, this reduction methodology suffers from the costly, atom inefficient, stoichiometric consumption of Hantzsch's ester. Several very recent studies have revealed that Ru- or Fe-catalysed hydrogenation at high pressure may regenerate Hantzsch's ester thereby allowing it to be employed in catalytic amounts [10–13].

Seeking a versatile catalytic methodology for transfer hydrogenation using Hantzsch's ester and other organic hydride donors under ambient conditions, we have followed a different line of attack. We recently introduced organic hydride-functionalised transition metal complexes as useful catalysts for the transfer hydrogenation of unsaturated substrates [14], and have reported several proof-of-concept demonstrations [15–18]. For example, Cp*Rh(diimine)Cl complexes were made where the diimines were the new pyridylimine (*pi*) ligands functionalised by Hantzsch dihydropyridine (*he*H) or Hantzsch pyridinium cation (he^+) moieties [16]. The complex $[Cp*Rh(pi\text{-}^2he)Cl]^{2+}$ (Chart 2) proved to be an excellent catalyst for transfer hydrogenation of imines by formate at room temperature in air. A catalytic cycle involving hydride transfer from a Rh-H species (formed by hydride transfer from

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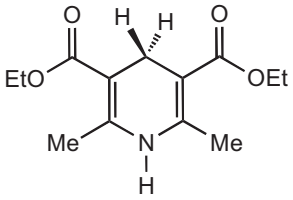
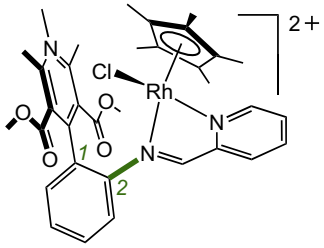


Chart 1. Hantzsch's ester.



[Cp*Rh(*pi*-^{2}*he*)Cl]$^{2+}$

Chart 2.

coordinated formate) to the pyridinium ring to afford the dihydropyridine and open a site at the Rh(III) centre was proposed. In this cycle, the imine substrate binds the electrophilic Rh(III) centre and is thus activated to back-transfer of hydride from the tethered dihydropyridine. The steps in the catalytic cycle mimick those involving substrate polarisation by metal binding and hydride transfer to/from substrate from/to NAD(P)H/NAD(P)$^+$ in the catalytic cycles of NAD(P)H/NAD(P)$^+$-dependent metallo-(de)hydrogenases [14].

This paper is not about catalysis. Rather, in order to advance understanding of transition metal complexes functionalised by Hantzsch dihydropyridine/pyridinium substituents in general, we have made the new complexes with a CpRu(PPh_3) centre bound by dihydropyridine or pyridinium-functionalised pyridylimine ligands that are depicted in Chart 3. Detailed spectro-electrochemical studies have been undertaken and are reported herein. The non-labile ligand donor set combined with the coordinative and electronic (18-electron) saturation at the ruthenium(II) centre was deliberately targetted to suppress metal-centred reactivity (including all possibility of catalytic reactions) thereby allowing the baseline electrochemical properties of the non-innocent Hantzsch dihydropyridine or pyridinium cation-substituted pyridylimine ligands to be examined. The work addresses the important question of whether direct electrochemical regeneration of a Hantzsch dihydropyridine substituent, as is proposed for the active species formed from catalyst [Cp∗Rh(*pi*-^{2}*he*)Cl]$^{2+}$ (Chart 2) [16], is possible. Also, interesting effects resulting from the presence or absence electronic communication between the metal and dihydropyridine/pyridinium cation centres are revealed.

2. Experimental

2.1. General methods

NMR spectra were obtained on Bruker Avance DPX-300, 400, 500 and 600 spectrometers at 298 K operating at 300, 400, 500 and 600 MHz frequency for ^{1}H NMR experiments and at 75.5, 100.6, 125.7 and 150.9 MHz for ^{13}C NMR experiments, respectively. ^{1}H and ^{13}C chemical shifts were calibrated against solvent signals; spin–spin couplings are given in Hz. EPR spectra were recorded using a Bruker EMX EPR spectrometer at 298 K. FT-IR spectra were recorded on KBr discs using a Nicolet Avatar 360 FT-IR spectrometer at 2 cm^{-1} resolution. Mass spectra were run on a Thermo Fisher Scientific Orbitrap LTQ XL ion trap mass spectrometer using a nanospray ionisation source. UV–Vis spectra were recorded using a Varian Cary 50 Bio UV–Vis spectrophotometer. Elemental analyses were obtained at the Microanalytical Unit of the Research School of Chemistry, Australian National University.

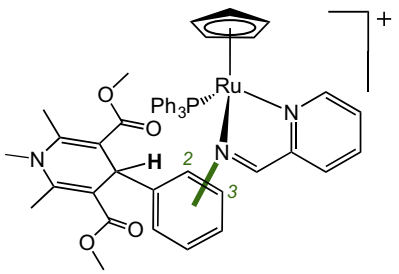
2.2. Materials

Solvents were dried and obtained under dinitrogen from a PureSolv MD solvent purification system. The ligands, *pi*-^{2}*he*H and *pi*-^{3}*he*H, were available from a previous study [16]. [CpRuCl(PPh_3)$_2$] was synthesised according to a literature procedure [19]. 4-Methyl-*N*-(4-methylbenzylidene)aniline was synthesised heating equimolar amounts of *p*-tolylaldehyde and *p*-toluidine at reflux in ethanol for 30 min, cooling and collecting the resulting crystalline solid by filtration. Tetra(n-butyl)ammonium hexafluorophosphate was recrystallised from acetone and dried under vacuum before use. All other chemicals were commercial and were used as obtained (Chart 4).

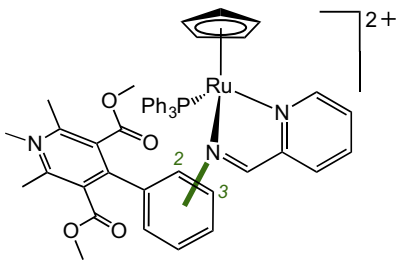
2.3. Syntheses of complexes

2.3.1. [CpRu^{II}(*pi*-^{2}*he*H)(PPh_3)][PF_6] (**1**)

Ligand *pi*-^{2}*he*H (30 mg, 0.072 mmol), [CpRu(PPh_3)$_2$Cl] (52 mg, 0.072 mmol) and K[PF_6] (100 mg, 0.54 mmol) were suspended in de-aerated methanol/THF (1:4, 30 mL) and stirred at reflux under dinitrogen overnight. The solvent was removed *in vacuo*, the resulting residue diluted with water and extracted with several portions of dichloromethane. The combined organic extracts were dried over sodium sulfate, filtered and the solvent was removed *in vacuo*. The crude mixture was purified using flash column chro-



1: [CpRu(PPh_3)(*pi*-^{2}*he*H)]$^+$
2: [CpRu(PPh_3)(*pi*-^{3}*he*H)]$^+$



3: [CpRu(PPh_3)(*pi*-^{2}*he*)]$^{2+}$
4: [CpRu(PPh_3)(*pi*-^{3}*he*)]$^{2+}$

Chart 3.