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Tethered oxocyclohexadienyl piano-stool Ru(II) complexes : a new class of metal-ligand bifunctional catalysts

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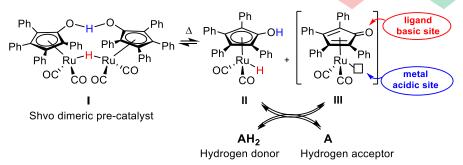
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ABSTRACT

The straightforward synthesis of tethered η^5 -oxocyclohexadienyl metal complexes is presented. Preliminary studies in catalysis demonstrate that these tethered half-sandwich Ru(II) complexes behave as bifunctional catalysts with metal-ligand cooperativity and are promising candidates for the development of hydrogen-based energies and chemical storage (i.e. dissociated hydrogen).

1. INTRODUCTION

In current hot topics related to sustainable energy, catalysts displaying metal-ligand cooperation are among the most efficient. Bifunctional complexes featuring metal acidic and ligand basic sites are associated to highly efficient (de)hydrogenation processes [1]. A relevant example of piano-stool bifunctional complex via metal-ligand cooperation is the archetypical Shvo's pre-catalyst (Scheme 1) [2], a η^4 -cyclopentadienone-ligated diruthenium complex.



Scheme 1. Thermal decomposition of the Shvo dimeric pre-catalyst.

Following the Shvo-type molecular catalysts in which the cyclopentadienone cyclic ligand act as an internal pendant basic site, we developped a straightforward synthesis of tethered η^{5} oxocyclohexadienyl half-sandwich ruthenium(II) complexes [3]. Since the first η^{5} -oxocyclohexadienyl metal complex published in 1976 by Cole-Hamilton, Young and Wilkinson [4], half-sandwich related complexes are very scarce [5]. Previous to our studies, none of η^{5} -oxocyclohexadienyl metal complexes were tested in catalysis.

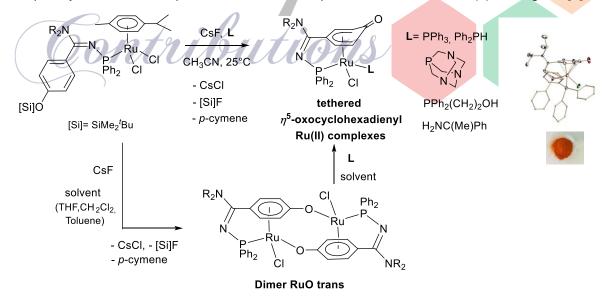


The synthesis of **tethered** η^5 -oxocyclohexadienyl half-sandwich ruthenium(II) complexes is presented as well as selected catalytic activities including the redox isomerization of allylic alcohols and (transfer)hydrogenation reactions. Preliminary theoretical studies on these η^5 -oxocyclohexadienyl complexes have also been investigated.

2. SYNTHESIS OF TETHERED η⁵-OXOCYCLOHEXADIENYL Ru(II) COMPLEXES

Herein, we describe the straightforward preparation of the first examples of tethered η^5 -oxocyclohexadienyl half-sandwich transition metal complexes.

As shown in Scheme 2, the starting *p*-cymene complex reacted quantitatively in a one pot procedure with 1 equiv. of CsF at 25°C followed by the addition of L type ligands to form the corresponding **tethered** η^5 -oxocyclohexadienyl Ru(II) complexes in an isolated good yield (>70%). The complexes have been spectroscopically fully characterized by elemental analysis, mass spectrometry, IR and multinuclear NMR spectroscopy. The protons of the η^5 -C₆H₄O ring are observed at low frequency shift from 3.5 to 6.0 ppm; this observation is comparable to that previously reported for untethered η^5 -oxocyclohexadienyl complexes [5]. In the ¹³C NMR spectrum, six resonances were observed for the η^5 -C₆H₄O unit, one deshielded singlet signal in the area of 155-160 ppm corresponding to the carbon linked to the oxygen atom and five shielded signals corresponding to the other carbon atoms of the η^5 -oxocyclohexadienyl ligand have been identified and display different resonances in accord with the stereogenic nature of the metal center. The tethered η^5 -oxocyclohexadienyl complexes [5]. complexes display also a strong broad IR ν (C=O) absorption at around 1540 cm⁻¹, a frequency value that compares well with that of previous untethered Ru(II) analogues [5].



Scheme 2. Synthesis of tethered η^5 -oxocyclohexadienyl ruthenium(II) complexes.

The solid-state structure determined by single-crystal X-ray diffraction analysis of the tethered η^5 -oxocyclohexadienyl ruthenium complex with the PPh₃ ligand confirmed the pentadienyl binding mode of the six membered η^5 -C₆H₄O cyclic ligand and the slight puckering of the ring. Note that this tethered η^5 -oxocyclohexadienyl- κ^1 -*P*-ruthenium complex can be prepared as an orange-red powder in grams scale and stored at air at room



temperature for days without any decomposition. A dimer structure has been identified after addition of CsF on the starting *p*-cymene complex (Scheme 1). Computational studies have been carried out on the different possible isomers for the dimeric structure. The calculations clearly indicated that the trans-dimeric structure with Ru-O interaction, **Dimer RuO trans**, is strongly preferred.

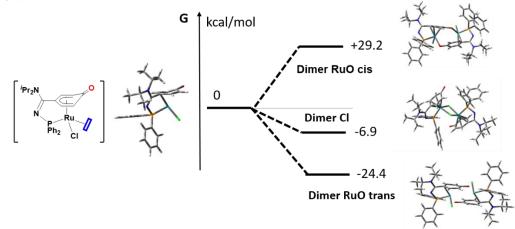
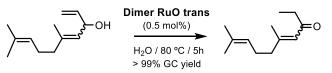


Figure 1. DFT calculations of the Gibbs free energy minima for Dimer RuO cis/trans and Dimer Cl isomers.

Note that the monomeric ruthenium fragment (Figure 1) of the **Dimer RuO trans** complex is structurally related to the 16-electron monoruthenium active species formed after thermal dissociation of the Shvo catalysts (Scheme 1).

3. CATALYTIC INVESTIGATIONS WITH TETHERED η⁵-OXOCYCLOHEXADIENYL Ru(II) COMPLEXES

Herein we report pioneering evidence for catalytic activity of η^5 -oxocyclohexadienyl metal complexes. The dimer complex is particularly active in mild experimental conditions in the catalytic redox isomerization of allylic alcohols, a synthetically useful and atom-economic transformation. The **Dimer RuO trans** is able to operate with low metal loadings, a wide range of temperatures and solvents including water and with a high degree of chemoselectivity (Scheme 3). Note that, contrary to the vast majority of ruthenium catalysts known for this transformation, **Dimer RuO trans** is working under base-free conditions. Interestingly, preliminary catalytic tests with the first reported η^5 -oxocyclohexadienyl transition metal complex [RuH(η^5 -C₆H₅O)(PPh₃)₂] [4] showed also remarkable activities and proved to be active in the isomerization of the model substrate 1-octen-3-ol under base-free conditions.

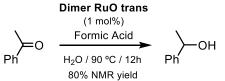


Scheme 3. Isomerization of a citral-derived allylic alcohol with Dimer RuO trans.

A possible cooperative effect of the CO unit of the η^5 -oxocyclohexadienyl ligand which could facilitate the generation of the more coordinating oxo-allyl anion by deprotonation of the allylic alcohol, may explain this fact.

Catalytic transfer hydrogenation of acetophenone with isopropanol and formic acid as hydrogen sources have been tested with **Dimer RuO trans**. All of these catalytic reactions are working under base free conditions with the best results (80% NMR conversion) recorded in water at 90°C with formic acid.





Scheme 4. Isomerization of a citral-derived allylic alcohol with Dimer RuO trans

Again, a cooperative of the oxocyclohexadienyl ligand may be envisaged to explain that this new class of catalysts operate under base-free conditions.

We lately recorded promising preliminary results recorded in the hydration reaction of nitriles and in the synthesis of γ -valerolactone by hydrogenation of biomass-derived levulinic acid with tethered η^5 -oxocyclohexadienyl ruthenium complexes.

4. CONCLUSION AND PERSPECTIVES

In conclusion, we developed a straightforward synthesis of the first examples of tethered piano-stool η^5 -oxocyclohexadienyl metal complexes and provided evidences for catalytic activity involving metal-ligand cooperativity.

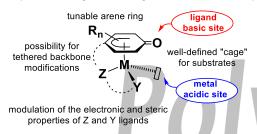


Figure 2 Schematic representation of the general structure of piano-stool η^5 oxocyclohexadienyl bifunctional transition metal catalysts.

pioneering experimental and theoretical results obtained so far with n^{5} -Our oxocyclohexadienyl ruthenium metal complexes point out the great potential of these new class of bifunctional catalysts [6], and pave the way for future investigations in challenging catalytic chemical transformations which will be reported soon. In contrast to the Shvo type catalysts, η^5 -oxocyclohexadienyl transition metal complexes are both sterically and electronically tunable on the metal center and on the π -coordinated cyclic ligand. It will be then possible to optimize the metal- η^5 -oxocyclohexadienyl ligand cooperativity for catalysis but also to look into asymmetric chemical transformations. For the above-mentioned reasons, we can expect that η^5 -oxocyclohexadienyl transition metal complexes have a long way to go in coordination chemistry extending their domain of applications.

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