

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

Emmanuel Puig,¹ Manel Kechaou-Perrot,¹ Lucía Menéndez-Rodríguez,² Pascale Crochet,² Victorio Cadierno,² Jean-Marc Sotiropoulos,³ Karinne Miquieu,³ Raphael Verron,⁴ Cedric Fischmeister,⁴ Pierre Sutra,¹ and Alain Igau,^{1*}

¹ CNRS; Laboratoire de Chimie de Coordination; 205 Route de Narbonne, F-31077 Toulouse, France; Université de Toulouse; UPS, LCC; F-31077 Toulouse; France.

E-mail address: alain.igau@lcc-toulouse.fr

² Laboratorio de Compuestos Organometálicos y Catálisis (Unidad Asociada al CSIC), Centro de Innovación en Química Avanzada, Universidad de Oviedo, Julián Clavería 8, E-33006 Oviedo, Spain.

³ Université de Pau & des Pays de l'Adour, UMR CNRS 5254, IPREM 2 avenue du Président P. Angot, 64053 Pau, Cedex 09, France.

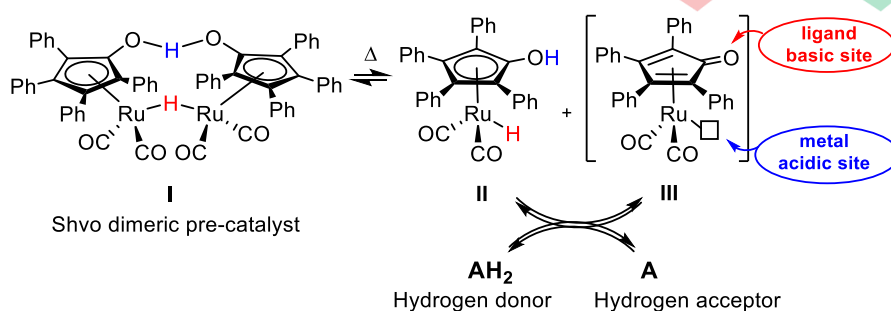
⁴ Université de Rennes, CNRS, Institut des Sciences Chimiques de Rennes, UMR6226, 263 Avenue Général Leclerc, 35000 Rennes, France.

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.

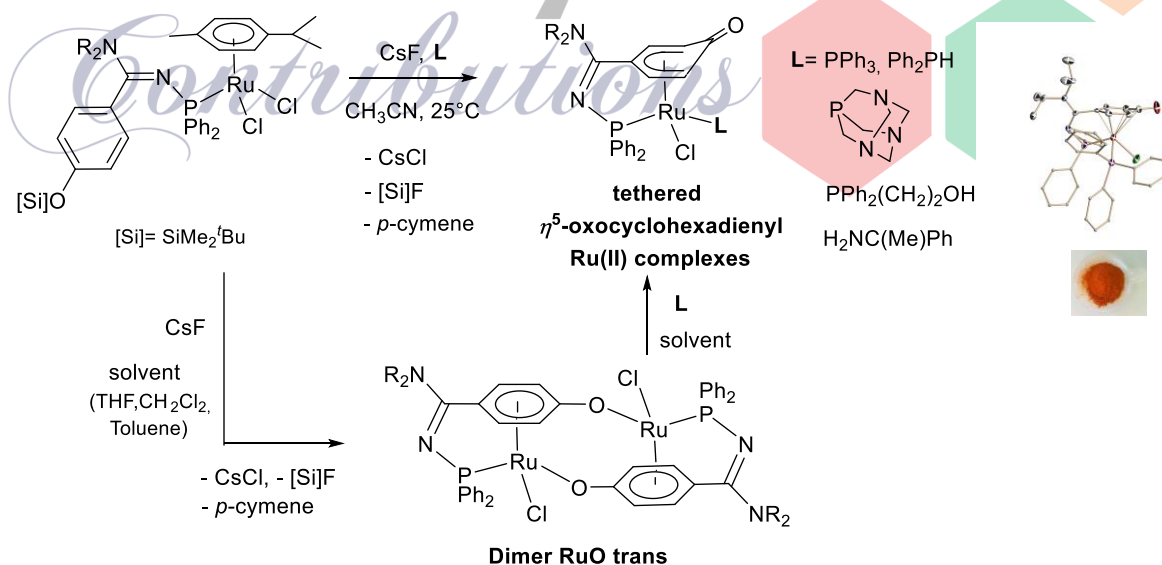
Following the Shvo-type molecular catalysts in which the cyclopentadienone cyclic ligand act as an internal pendant basic site, we developed a straightforward synthesis of tethered η^5 -oxocyclohexadienyl half-sandwich ruthenium(II) complexes [3]. Since the first η^5 -oxocyclohexadienyl metal complex 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 η^5 -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 ring in the region between 80 to 115 ppm. All proton and 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 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.

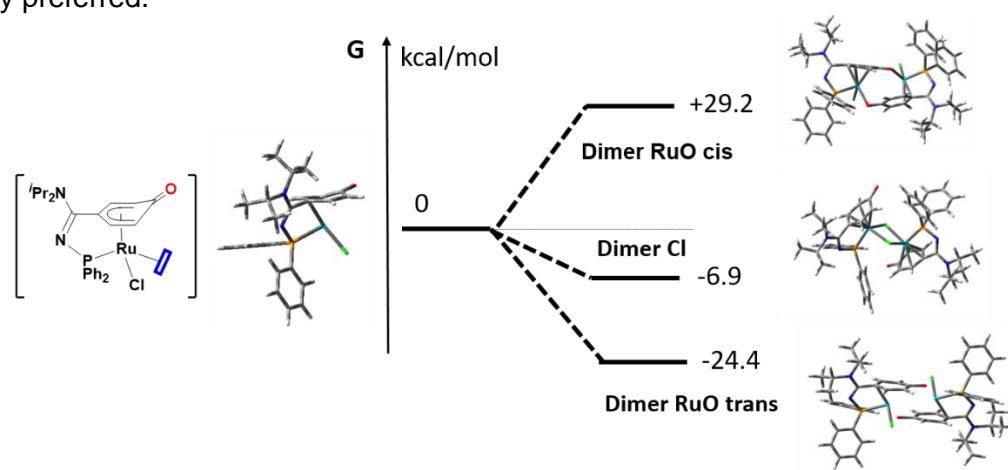
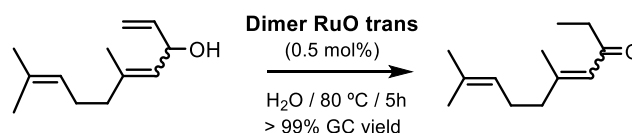


Figure 1. DFT calculations of the Gibbs free energy minima for **Dimer RuO cis/trans** and **Dimer Cl** isomers.

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 η^5 -OXOCYCLOHEXADIENYL Ru(II) COMPLEXES

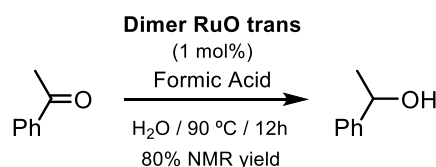
Herein we report pioneering evidence for catalytic activity of η^5 -oxocyclohexadienyl metal complexes. The dimer complex is particularly active in mild experimental conditions in the catalytic redox isomerization of allylic alcohols, a synthetically useful and atom-economic transformation. The **Dimer 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 $[\text{RuH}(\eta^5\text{-C}_6\text{H}_5\text{O})(\text{PPh}_3)_2]$ [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.

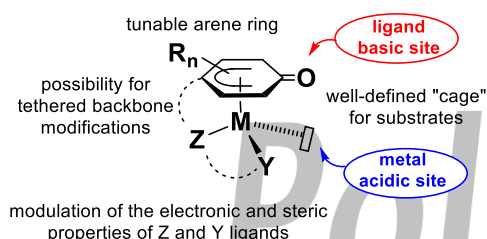


Figure 2 Schematic representation of the general structure of piano-stool η^5 -oxocyclohexadienyl bifunctional transition metal catalysts.

Our pioneering experimental and theoretical results obtained so far with η^5 -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.

References

- [1] K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy *Chem. Rev.* **2018**, 1187, 372-433. P. A. Dub, J. C. Gordon *ACS Catal.* **2017**, 7, 6635-6655 and references cited therein.
- [2] Y. Shvo, D. Czarkie, D.F. Chodosh *J. Am. Chem. Soc.* **1986**, 108, 7400.
- [3] M. Kechaou-Perrot, L. Vendier, S. Bastin, J.-M. Sotiropoulos, K. Miqueu, L. Menéndez-Rodríguez, P. Crochet, V. Cadierno, A. Igau *Organometallics* **2014**, 33, 6294.
- [4] D. Cole-Hamilton, R. J. Young, G. Wilkinson, *J.C.S. Dalton* **1976**, 1995.
- [5] A. Igau *Coord. Chem. Rev.* **2017**, 344, 299.
- [6] R. H. Morris, *Chem. Rev.* **2016**, 116, 8588. P. A. Dub, J. C. Gordon *Dalton Trans.* **2016**, 45, 6756.

Acknowledgements

C. Fischmeister, P. Sutra and A. Igau acknowledge l'Agence Nationale de Recherche (ANR) for financial support (ANR-18-CE07-0006-01 *Catalysts with Metal-Ligand Cooperation for Sustainable Energy - CatEngy*). E. Puig and R. Verron thank ANR for a post-doctoral and a PhD grant. M. Kechaou-Perrot is grateful to MESR for a PhD grant. L. Menéndez-Rodríguez, P. Crochet, and V. Cadierno thank the MINECO for financial support (projects CTQ2010-14796 and CTQ2013-40591). K. Miqueu and J.-M. Sotiropoulos thank the Université de Pau et des Pays de l'Adour for access to their computer cluster. L. Vendier and H. Gornitzka are greatly acknowledged for X-ray analysis.