Tethered η^5-Oxocyclohexadienyl Piano-Stool Ruthenium(II) Complexes: A New Class of Catalysts?

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S *Supporting Information*

ABSTRACT: The straightforward synthesis of tethered η^5-oxocyclohexadienyl Ru(II) complexes is presented. Pioneering results in catalysis show that these original half-sandwich Ru(II) complexes allow the effective isomerization of allylic alcohols under mild conditions without further additives; η^5-oxocyclohexadienyl ruthenium complexes may be considered as a new class of catalysts.
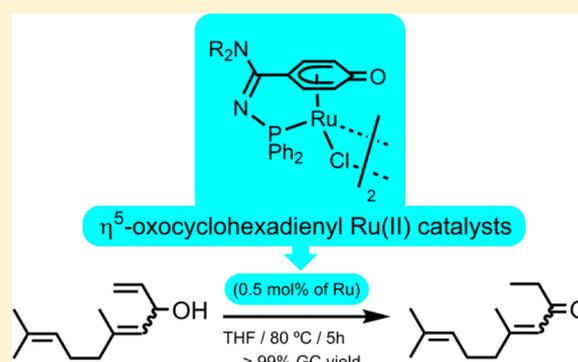
Ruthenium is one of the most intensively used metals in catalysis,[1] partly due to its lower price compared to other noble metals but also because a wide span of highly stable Ru-based catalysts can be prepared. A relevant example is Shvo's catalyst **I** (Figure 1),[2] a cyclopentadienone-ligated diruthenium
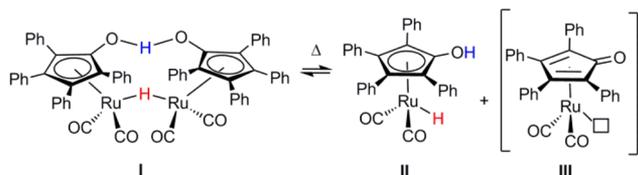

Figure 1. Shvo's catalyst **I** and its thermal dissociation products **II** and **III**.

complex that efficiently promotes a number of environmentally friendly and atom-economical chemical transformations.[3] Shvo et al. proposed that **I** thermally dissociates into two monoruthenium active species, the 18-electron **II** species and the remaining elusive 16-electron **III** complex (Figure 1).

Half-sandwich Ru(II) complexes with η^6-arene ligands **IV** (Figure 2) are also efficient catalysts or catalyst precursors for a wide range of reactions, and the scope of their applications has considerably increased in the past decades.[1] Especially, their corresponding configurationally stable piano-stool tethered complexes[4] have found great interest in asymmetric catalysis.[4a,5]
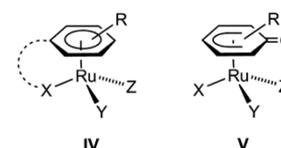

Figure 2. Half-sandwich-Ru(II) η^6-arene **IV** and η^5-oxocyclohexadienyl complexes **V**.

Within the family of six-membered rings coordinated in an η^n-hapto mode to a transition metal, η^5-oxocyclohexadienyl ligands have been relatively little studied.[6,7] To the best of our knowledge there is no example of a catalytically active half-sandwich ruthenium complex **V** with an η^5-oxocyclohexadienyl as ligand (Figure 2).[6] Indeed, half-sandwich Ru-based η^5-oxocyclohexadienyl complexes are very scarce, and their corresponding tethered complexes unknown.[8]

Herein, we describe the straightforward preparation of the first tethered η^5-oxocyclohexadienyl half-sandwich ruthenium(II) complexes. We furthermore probed the catalytic activity of this new class of Ru(II) complexes in the redox isomerization of allylic alcohols.

As shown in Scheme 1, complex **1**[9] reacted quantitatively (^{31}P NMR) with 1 equiv of CsF followed by the addition of

Scheme 1. Synthesis of η^5-Oxocyclohexadienyl Complexes 2 and 3
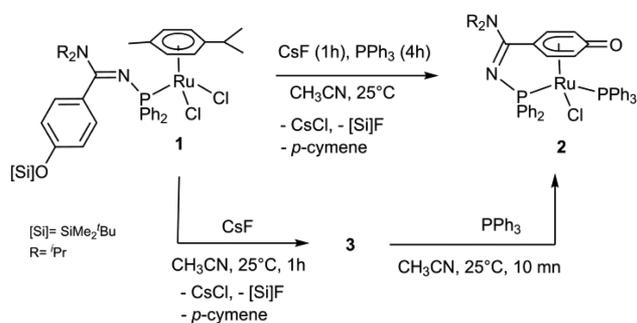
PPh$_3$ to form the tethered η^5-oxocyclohexadienyl complex **2** (80% yield) in a one-pot synthesis. This compound exhibits two doublet resonances at 73.2 (PN) and 38.2 (PPh$_3$) ppm in the ^{31}P{^{1}H} NMR spectrum ($^2J_{PP}$ = 44 Hz). The protons of the η^5-C$_6$H$_4$O ring are observed at 6.03, 5.10, 4.29, and 3.88 ppm; the low-frequency shift of these protons is comparable to that previously reported for untethered η^5-oxocyclohexadienyl complexes.[6] In the ^{13}C NMR spectrum, six resonances were observed for the η^5-C$_6$H$_4$O unit, one deshielded singlet signal at 159.1 ppm corresponding to the carbon linked to the oxygen atom and five shielded signals corresponding to the other carbon atoms of the ring at 79.1 (J_{CP} = 5.1 Hz), 85.3 (J_{CP} = 6.2 Hz), 88.2 (s), 101.1 (J_{CP} = 6.7 Hz), and 112.0 (J_{CP} = 5.1 Hz) 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. Complex **2** displays a strong broad IR ν(C=O) absorption at around 1542 cm^{-1}, a frequency value that compares well with that of previous untethered Ru(II) analogues.[6]

The solid-state structure of **2** was determined by single-crystal X-ray diffraction analysis (Figure 3). The pentadienyl
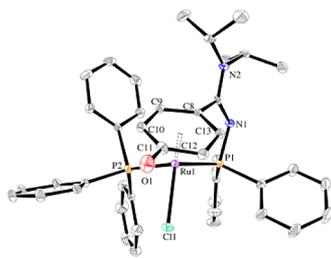

Figure 3. Molecular structure of complex **2** (H atoms omitted for clarity).

binding mode of the η^5-C$_6$H$_4$O ligand is indicated by the long C—C bonds to C11 (C11—C10 1.439(4) and C11—C12 1.468(4) Å) relative to the rest of C—C distances within the six-membered ring (1.381(4)−1.421(4) Å). The O—C11 length of 1.246(3) Å is consistent with double-bond character and comparable to analogous distances previously reported for its untethered counterparts (e.g., 1.277 Å for [RuH(η^5-C$_6$H$_5$O)-(PPh$_3$)$_2$]·MeOH).[6a] The phenyl ring is slightly folded such that the *ipso* carbon C11 is bent away from the Ru center, as indicated by examination of the least-squares planes. The C11 and O atoms lie 0.158 and 0.300 Å, respectively, out of the plane defined by the pentadienyl carbon atoms (C8−C10, C12, C13). The angle between the pentadienyl plane and that defined by C10−C12 and O is 8.78°, which confirms the

puckering of the C$_6$H$_4$O ligand. The bond lengths and angles in the *N*-phosphino amidine backbone ^{i}Pr$_2$N−C=N−PPh$_2$ are comparable to those recorded for the corresponding tethered η^6-arene-κ^1-*P*-ruthenium complexes previously described by us.[4f] Complex **2** can be stored in air at room temperature for days without any decomposition. The stability of **2** was further investigated by thermogravimetric analysis, which revealed a decomposition temperature at about 250 °C under a nitrogen atmosphere (see the Supporting Information for more details).

When **1** was reacted with CsF at room temperature in CH$_3$CN, in the absence of PPh$_3$ (Scheme 1), the solution turned immediately from light to dark orange, and after 1 h, the ^{31}P NMR spectrum showed the disappearance of the resonance at 45.0 ppm from compound **1** at the expense of complex **3**, which exhibits a singlet signal at 76.9 ppm. Strong evidence for the proposed formulation as a dinuclear complex is provided by mass spectrometric analysis. From the peak-for-peak correspondence found between the simulated and recorded isotope patterns of the intense molecular ion peak at m/z 1080.1, we propose for **3** a dimeric structure with the general composition [Ru(OC$_6$H$_4$-C(N^{i}Pr$_2$)=N-PPh$_2$)Cl]$_2$. The low-frequency shift of the four C$_6$H$_4$O-ring protons in complex **3** compared to **1** indicates π-coordination to the ruthenium center. In the ^{13}C NMR spectrum, six resonances were observed for the η^5-oxocyclohexadienyl unit, one deshielded singlet at 159.9 ppm corresponding to the carbon linked to the oxygen atom and five shielded signals corresponding to the other carbon atoms of the ligand in the range of those found for **2**. Complex **3** displays a strong broad IR ν(C=O) absorption around 1540 cm^{-1}, in the same range as for **2**. Overall, the spectral parameters of the η^5-oxocyclohexadienyl ligand in **3** are very similar to those observed for **2**. Moreover, dimer **3** reacts rapidly and cleanly with PPh$_3$ to generate the mononuclear complex **2** (Scheme 1). Even though we cannot totally exclude the κ^1-O-bonded dimeric structure **3'** (Figure 4), all the recorded experimental
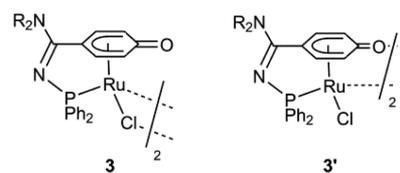

**Figure 4.** Proposed dimeric structures **3** and **3'**.

data are strongly in favor of the chloride-bridged structure **3** (Figure 4). Unfortunately, all attempts to obtain good-quality crystals for X-ray diffraction studies have been unsuccessful so far.

Therefore, computational studies have been carried out for the two isomers **3** and **3'**. DFT calculations found two minima on the surface energy potential corresponding to the proposed **3** and **3'** structures (see the Supporting Information for more details). The geometrical parameters of the monometallic fragment [Ru(OC$_6$H$_4$-C(N^{i}Pr$_2$)=N-PPh$_2$)Cl] in both isomers are very similar to those recorded for **2**. The calculations clearly indicated that the structure **3** shown in Scheme 1 is strongly preferred with a stabilization of 13 kcal·mol^{-1} compared to the energy of **3'**.

First experiments show the catalytic potential of complexes **2** and **3**. We chose to investigate the redox isomerization of allylic alcohols, a synthetically useful and atom-economic transformation, for which Ru complexes have shown to be especially

active.[10,11] Pleasantly, we found that dimer **3** is active in the isomerization of the model substrate 1-octen-3-ol (Table 1).

**Table 1. Catalytic Isomerization of 1-Octen-3-ol to Octan-3-one Using 3**[a]
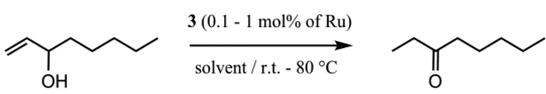
entry[a]	% Ru	solvent	temp	time	yield[b]
1	1 mol %	THF	80 °C	5 min	>99%
2	0.5 mol %	THF	80 °C	10 min	>99%[c]
3	0.1 mol %	THF	80 °C	1 h	>99%
4	0.5 mol %	THF	40 °C	4 h	>99%
5	0.5 mol %	THF	rt	72 h	96%
6	0.5 mol %	H$_2$O	80 °C	40 min	>99%

[a]Reactions performed under a N$_2$ atmosphere using 2 mmol of 1-octen-3-ol (0.5 M solutions). [b]Yields of octan-3-one determined by GC. [c]90% isolated yield after workup.

Thus, performing the catalytic reaction in THF at 80 °C with a metal loading of 1 mol % of Ru (0.5 mol % of **3**), selective and quantitative formation of octan-3-one was observed by GC after only 5 min of heating (entry 1 in Table 1; TOF = 1200 h^{-1}).[12] Note that, contrary to the vast majority of ruthenium catalysts known for this transformation,[10] compound **3** is able to operate under base-free conditions.[13,14] A possible cooperative effect of the C=O unit of the η^5-oxocyclohexadienyl ligand or the pendant N^{i}Pr$_2$ group, which could facilitate the generation of the more coordinating oxo-allyl anion by deprotonation of the allylic alcohol, may explain this fact. As shown in entries 2 and 3, lower metal loadings were tolerated without a drastic increase in the reaction times. A wide range of temperatures and solvents in which **3** is able to operate is tolerated (full details in the Supporting Information). For example, at 40 °C, complete conversion of 1-octen-3-ol into octan-3-one was reached within 4 h using a metal loading of 0.5 mol % (entry 4). At rt, a longer time is required to attain a good conversion (entry 5).[15] Especially noteworthy is the possibility of using water as solvent (entry 6).[16] Other allylic alcohols were subjected to the action of complex **3**, and efficient and selective formation of the desired carbonyl compounds was in all cases observed (full details in the Supporting Information). As a representative example, the chemoselective and quantitative isomerization of the citral-derived alcohol **4** (1:1 mixture of *E/Z* isomers) into the ketone **5** is shown in Scheme 2.[17]

Scheme 2. Isomerization of a Citral-Derived Allylic Alcohol
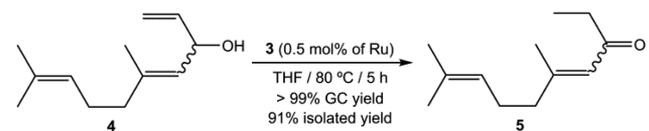
In conclusion, we developed a straightforward synthesis of original tethered piano-stool η^5-oxocyclohexadienyl Ru(II) complexes and provided pioneering evidence for catalytic activity of a metal complex incorporating an η^5-oxocyclohexadienyl ligand. The dimeric Ru(II) complex presented herein is effective in the base-free redox isomerization of allylic alcohols and able to operate under mild conditions.[18] It is noteworthy that the monomeric ruthenium fragment of the η^5-oxocyclohexadienyl-Ru(II) dimer **3** is structurally related to the 16-electron monoruthenium active species **III** formed after thermal dissociation of the Shvo catalysts. More challenging organic transformations with related complexes in catalysis is currently under investigation in our laboratory.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental section, full characterization data for all new compounds, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(8) Note that tethered complexes incorporating the bidentate
aryloxide O-MOP ligand with a κ^1:η^6 coordination mode were
spectroscopically identified; see ref 6e.

(9) The κ^1-P ruthenium(II) complex **1** was prepared in an analogous
experimental procedure to those reported in ref 4f (characterization is
included in the Supporting Information).

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(12) (a) The mononuclear complex **2** is also active but much less
effective than **3** (see Supporting Information). The marked difference
in reactivity is most probably related to the higher facility of **3** to
generate vacant coordination sites by cleavage of the chloride bridges.
(b) The activity of dimer **3** was not affected when the catalytic
reaction was performed under aerobic conditions.

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usually required to facilitate its coordination to the active metal center.
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described for the Shvo complex **I** (TOF of 990 h^{-1} for the
isomerization of 1-octen-3-ol at 65 °C under base-free conditions):
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complexes containing tethered cyclopentadienyl-NHC ligands active
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workers, but their performances were also lower than that shown by
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activity of **3** remains unaltered in the presence of free *p*-cymene (50
equiv per Ru). This fact suggests that decoordination of the
oxocyclohexadienyl moiety does not take place during catalysis.

(15) Though other ruthenium catalysts are able to work at such low
temperature regimes, to the best of our knowledge, all of them need
the help of an external base: (a) Martín-Matute, B.; Bogár, K.; Edin,
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Rh(I) catalyst active at rt in the absence of base has been described:
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(16) See, for example: *Metal-Catalyzed Reactions in Water*; Dixneuf,
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(17) Isomerization of **4** to **5** was previously performed with the
arene-ruthenium(II) catalyst [RuCl$_2$(η^6-benzene)(PTA-Me)] (PTA-
Me = 1-methyl-3,5-diaza-1-azonia-7-phosphaadamantane chloride).
Ketone **5** was generated in 82% yield after 24 h of heating in THF
with 2.5 mol % of [RuCl$_2$(η^6-benzene)(PTA-Me)] and 6.25 mol % of
K$_2$CO$_3$, a result that is clearly inferior to that obtained with dimer **3**:
Menéndez-Rodríguez, L.; Crochet, P.; Cadierno, V. *J. Mol. Catal. A:
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(18) The untethered derivative [RuH(η^5-C$_6$H$_5$O)(PPh$_3$)$_2$] (synthe-
sized from ref 6a proved to be also active in the isomerization of the
model substrate 1-octen-3-ol, showing a catalytic performance similar
to that of dimer **3**. This fact is yet another proof of the considerable
potential in homogeneous catalysis of η^5-oxocyclohexadienyl-metal
derivatives, fully supporting further studies in the field.