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Ruthenium(0) complexes with triazolylidene spectator ligands: Oxidative activation for (de)hydrogenation catalysis☆

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ABSTRACT

Transmetallation of silver triazolylidene intermediates with the ruthenium(0) precursor [Ru(Cp=O)(CO)$_2$]$_2$ afforded low-valent ruthenium(0) complexes containing a triazole-derived NHC ligand (Cp=O = 3,4-di(4-methoxyphenyl)-2,5-diphenyl-cyclopentadienone). Protonation of the carbonyl group of the Cp=O ligand significantly reduces the π character of the Ru–CO bond as deduced from ν_{CO} analysis. The new triazolylidene ruthenium(0) complexes were evaluated as catalyst precursors in transfer hydrogenation of 4-fluoro-acetophenone and in the acceptorless dehydrogenation of benzyl alcohol. Low activities were noted, though in both reactions, catalytic performance is markedly increased when cerium(IV) was added. Electrochemical analysis indicates that activation of the catalyst precursor proceeds via cerium-mediated oxidation of the ruthenium center, which facilitates dissociation of a CO ligand to enter the catalytic cycle. Such oxidative activation of catalyst precursors may be of more general scope.

Introduction

N-Heterocyclic carbenes (NHCs) have become some of the most popular ligands in transition metal chemistry due to their efficiency as ancillary ligands to improve catalytic activity [1]. Their success is due to a combination of unique properties, such as their easily tunable electronic and steric properties that influence the metal center and which allow catalytic activity to be rationally optimized. The exploitation of such concepts is particularly appealing because the synthesis of NHC ligand precursors as well as NHC metal complexes is fairly simple and highly versatile [2].

Accordingly, a variety of catalytic reactions have strongly benefited from introduction of NHC ligands, such as ruthenium-catalyzed olefin metathesis [3], palladium-catalyzed cross-coupling reactions [4], iridium-catalyzed reductions and oxidations [5], and gold-catalyzed activation of π-bonds, to name but a few [6]. Apart from olefin metathesis, NHC ruthenium complexes have shown catalytic activity in various redox transformations [7], including: transfer hydrogenation [8], hydrogenation of olefins [9] and esters [10], asymmetric hydrogenation [11], amide synthesis from alcohols and nitriles [12], dehydrogenation of esters and imines from alcohols [13], racemization of chiral alcohols [14], oxidation of alcohols [15] and water oxidation [16]. Most of the literature on NHC ruthenium chemistry features ruthenium(II) complexes, while low-valent NHC ruthenium(0) systems are restricted to a few examples based on either [Ru$_3$(CO)$_{12}$] or [Ru(CO)$_2$(PPh$_3$)$_3$] as precursors [17]. Recently, a straightforward approach towards NHC ruthenium(0) complexes has been developed [18], which is based on a dimeric ruthenium(0) cyclopentadienone dicarbonyl dimer [19]. Cleavage of the dimer in the presence of a free carbene or a silver carbene precursor provided access to a new class of ruthenium complexes.

Here we have expanded this synthetic methodology to 1,2,3-triazolylidenes as strong donor NHC-type ligands [20]. Triazolylidenes offer a vast synthetic flexibility due to their convenient accessibility through [2 + 3] dipolar cycloaddition of alkynes and azides [21]. In addition, their enhanced donor properties as compared to more commonly utilized imidazolylidenes may further destabilize the ruthenium(0) oxidation state and hence facilitate substrate activation by metal/ligand cooperation in analogy to the reduced portion of Shvo's catalyst [22]. Thus, it will be of particular interest to evaluate the propensity of the new triazolylidene ruthenium(0) complexes to dehydrogenate substrates

☆ In memoriam A.E Shilov in recognition and admiration of his pioneering work on C–H bond activation.

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via formal H_2 transfer, as this process may lead to efficient catalysts for acceptorless oxidation (alcohol dehydrogenation) or transfer hydrogenation.

Results and discussion

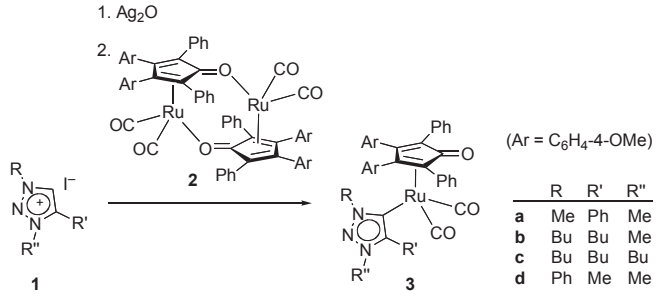
Synthesis of triazolylidene Ru complexes

The triazolium salts **1a**–**d**, readily accessible by "click" cycloaddition of the corresponding alkynes and azides and subsequent alkylation [21], were successfully transformed into the silver triazolylidene intermediates as reported previously [23]. Transmetalation with the low-valent ruthenium precursor afforded complexes **3a**–**d** in very high yields (Scheme 1). Complexes **3** constitute a class of ruthenium(0) complexes which contain exclusively carbon-donor ligands.

Formation of complexes **3a**–**d** was established by ^{1}H NMR, ^{13}C{^{1}H} NMR, and IR spectroscopy as well as ESI–MS and for representative examples, by single crystal X-ray diffraction analysis. IR spectroscopy provided a particularly convenient methodology for monitoring the progress of the transmetalation reaction, as the Ru–CO vibrations of the precursor complex shifted distinctly by 20 cm^{-1} to lower energy upon triazolylidene coordination (ν_{CO} = 2018, 1967 cm^{-1} in **2**, and 1999, 1938 cm^{-1} in **3b**, Table 1). The bathochromic shift is slightly but consistently more pronounced when the triazolylidene ligand contained only alkyl substituents, and less strong when phenyl substituents are present, irrespective of the connectivity pattern. The carbene ligand in **3a** with the phenyl group attached to the carbon induced the same shift as the analogous carbene with the phenyl group attached to nitrogen (**3d**). These data suggest that the CO stretch vibration may be used as a probe for the qualitative assessment of the carbene donor properties [23,24]. In line with this notion, coordination of 2-imidazolylidenes induces a slightly smaller bathochromic shift ($\Delta\nu$ = 4 cm^{-1}), which reflects their weaker donor properties when compared to triazolylidenes [20a,b]. Potentially, backbonding from the electron-rich ruthenium(0) center to the carbene ligand may affect the CO stretch vibration and may thus complicate a simple linear correlation between IR frequencies and donor properties.

Further evidence of the formation of complexes **3a**–**d** was obtained from NMR data, in particular the disappearance of the low field signal of the triazolium precursor in the ^{1}H NMR spectrum and the downfield shift of the carbenic resonance in the ^{13}C NMR spectra. This nucleus resonates in the 154–158 ppm range and hence some 20 ppm higher field than in ruthenium(II) complexes, indicative for a low valent and electron-rich metal center.

Unambiguous structural evidence was obtained by X-ray diffraction analysis of single crystals of complexes **3a** and **3d**. The molecular structure reveals the expected piano-stool geometry with the cyclopentadienone ligand occupying one face and the two



Scheme 1. Synthesis of cyclopentadienone triazolylidene ruthenium(0) complexes **3a**–**d**.

Table 1
Relevant carbonyl stretch vibrations (cm^{-1}) of the complexes.

Complex	Ru–CO	Cp=O
2	2018, 1967	–
3a	2004, 1945	1577
3b	1999, 1938	1583
3c	1998, 1937	1584
3d	2003, 1944	1578
3a + HBF_4	2036, 1979	–

CO ligands and the triazolylidene forming the three legs (Fig. 1). Bond lengths and angles (Table 2) are very similar in both complexes, suggesting only marginal steric consequences upon swapping the methyl and phenyl wingtip groups in the triazolylidene ligand. As expected, the Ru–C_{trz} bond is longer in complexes **3a** and **3d** than in analogues featuring a higher-valent ruthenium(II) metal center (Δd = 0.06 Å) [15].

Catalytic alcohol oxidation

The triazolylidene Ru(0) complex **3a** was evaluated as catalyst precursor for the oxidation of alcohols using benzyl alcohol (BnOH) as model substrate. While ruthenium(II) systems with a cymene spectator ligand gave attractive conversions even in the absence of oxidants or base [15], runs performed with **3a** in the absence of such additives were essentially non-productive with <5% conversion (Table 3, entry 1). Better results were obtained upon adding $[Ce(NH_3)_6](NO_3)_2$ (CAN) as oxidizing agent to activate the catalyst precursor **3a** [25].

Initial background measurements indicated that in the absence of a ruthenium complex, CAN catalyzes the oxidation of BnOH to benzaldehyde on its own under the applied reaction conditions. Background conversions reached 80% when 10 mol% CAN was used, and dropped to 40% and 30% approximately, if the CAN loading was reduced to 5 and 2.5 mol%, respectively (entries 2–4, Figs. S1–S3). Addition of complex **2**, *i.e.* the carbene-free ruthenium(0) precursor, had no notable effect and yields and conversions mirrored those of CAN only (entry 8). Possibly, the lack of a stabilizing ligand for ruthenium(II) induces rapid decomposition, supported also by the brown color that rapidly developed upon heating the mixture. In contrast, complex **3a** induced a considerable acceleration (entries 5–7). For example, with 5 mol% **3a** and 2.5 mol% CAN, 84% conversion was accomplished within 24 h (*cf.* 31% conversion in the background reaction). At higher CAN loading (10 mol%), the catalytic competence of **3a** is evident in particular at early stages of the oxidation. After 2 h, 57% conversion was observed with the Ru^0/Ce^{IV} couple (25% with Ce^{IV} only, 0% with Ru^0 only), and oxidation was essentially complete after less than 8 h. While the selectivity is typically high and conversion occurs selectively to the desired aldehyde, further improvement of the catalytic performance of **3a** may need a focus on an oxidant for ruthenium that is less catalytically active than CAN.

Catalytic transfer hydrogenation

In addition to alcohol dehydrogenation, we were also interested to see whether complexes **3** are active in transfer hydrogenation. A model reaction employed complex **3a** as catalyst precursor and 4-fluoroacetophenone as substrate under standard transfer hydrogenation conditions [26], *i.e.* refluxing *i*PrOH as hydrogen source (Table 4).

Catalytic runs were performed in particular for comparing the catalytic activity of the triazolylidene ruthenium(0) complex **3a** and the triazolylidene-free dimeric precursor **2** under various