

Facile, Thermoreversible Cycloaddition of Small Molecules to a Ruthenium(II) Arene β -Diketiminato

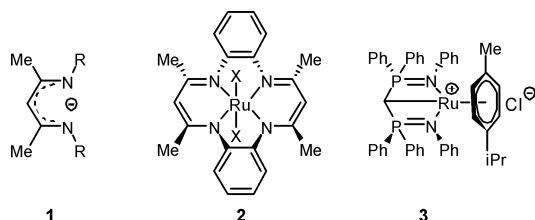
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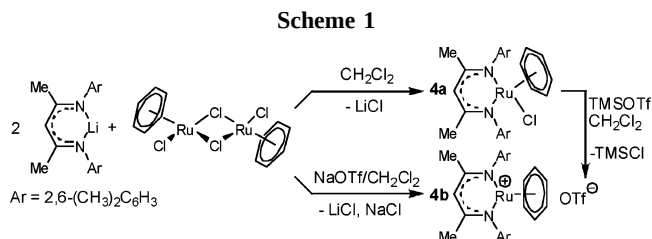
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Summary: Formation of a vacant coordination site on a Ru center permits an unusual binding of small molecules such as ethylene, acetylene, and dihydrogen, resulting in the transformation of the chelating β -diketiminato ligand to a β -diimine. These representative species are observed during the catalytic hydrogenation of styrene.

Identification of intermediates during a reaction cycle is fundamental to the understanding and improvement of basic catalytic processes. In general, a key step involves the generation of a coordinatively unsaturated metal center which receives and activates the incoming substrate.¹ Under typical conditions, these species are normally too reactive to be observed. Hence, in order to facilitate synthesis and comprehensive characterization, it is necessary to employ a ligand that can impart high thermodynamic and kinetic stability through means of strong electron donation and steric constraints. One class of ligand that satisfies these requirements are the β -diketiminates (**1**, abbreviated herein



as L), which have been utilized for the preparation of a number of interesting and application-oriented main-group- and transition-metal-centered compounds.² In particular, polymerization catalysts based on **1** in combination with Ti, Zr, Cr, Co, Ni, and Pd (ML) have been the focus of considerable attention.² Similar complexes with transition-metal centers are capable of activating H₂,³ N₂,⁴ and O₂.⁵ Examples of alkene and alkyne coordination by ML species are also known but generally are



η^2 -bound to the metal.⁶ Although numerous examples of iron β -diketiminato species are known,² analogous complexes of the heavier members of the group 8 triad, Ru and Os, have been notably absent.² This is surprising, considering that ruthenium complexes with smaller unsaturated diazo-coordinating ligands (i.e., (R)N(CH)_nN(R), $n = 1$ (anionic amidinates),⁷ 2 (neutral diazabutadienes)⁸) have been used for well over two decades, in addition to tetraazacyclotetradecine species⁹ (**2**) and acetylacetone¹⁰ chelating compounds. Furthermore, the unusual η^3 -(C,N,N')-bonded ruthenium bisphosphiniminomethanide complex **3** has also been recently reported.¹¹

Our investigations began with the synthesis and characterization of complexes based on the highly stable Ru(II)- η^6 -arene fragment. Using the lithiated version of **1**¹² in dichloromethane, combined with [(η^6 -C₆H₆)RuCl₂]₂, afforded clean reactions with LiCl and (η^6 -C₆H₆)RuCl(ArNCMe)₂CH (**4a**; Ar = 2,6-dimethylphenyl) as the only detectable products (Scheme 1). Removal of the chloride substituent is facilitated by the stoichiometric addition of Me₃SiOTf to **4a**, or more conveniently, a single-pot reaction is possible using the ruthenium dimer, **4a**, and sodium triflate in equal molar ratios. Compound **4b**, [(η^6 -C₆H₆)Ru((ArNCMe)₂CH)]OTf, is insoluble in Et₂O and hydrocarbon solvents but highly soluble in THF and chlorinated solvents. In the solid state, **4a** demonstrates moderate air sensitivity, and **4b** decomposes over several hours.

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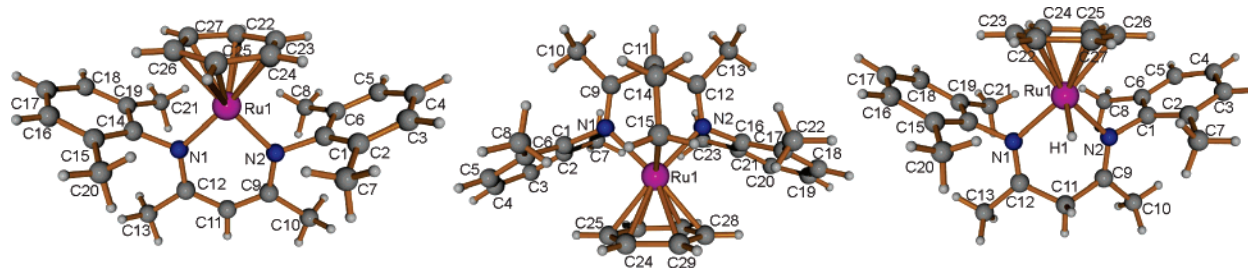
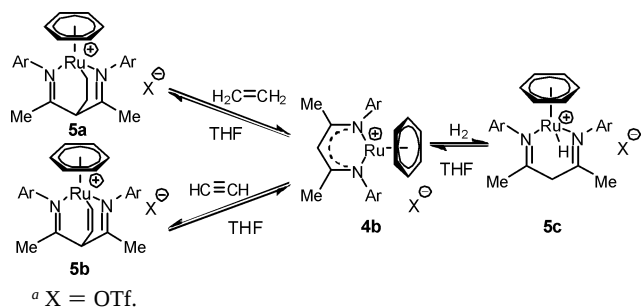


Figure 1. Ball and stick diagrams of complexes **4b** (left), **5a** (center), and **5c** (right). Solvates and anions have been omitted for clarity.

Scheme 2^a



A number of spectroscopic methods were used to characterize **4a** and **4b** (see the Supporting Information for a complete description). In particular, the structures (**4b** is shown in Figure 1; **4a** (Figure S1) and metric parameters are given in the Supporting Information) were determined from X-ray diffraction data. The structure of **4a** features a Ru–Cl bond (2.521(1) Å) that is within error equal to the longest distance for the Ru η^6 -arene subset,¹³ and in **4b**, the anion weakly interacts with the cation (the nearest H···O distance is 2.275 Å). The general geometric arrangement of **4a** and **4b** consists of flanking ligand aryl groups parallel to the metal–arene group, perpendicular to the plane of the metal–nitrogen heterocycle. In the case of **4a**, the C₆H₆–Ru fragment is tilted out of the plane Ru–N_{centroid}–C(11) by 154.79°, but not to the extent as in **3**, 73.8°. The effect of chloride removal and formation of a coordinatively unsaturated metal center is readily apparent in the Ru–N bond distances (**4b**, 1.997(5), 1.994(5) Å; **4a**, 2.099(2) Å). The N–Ru–N bite angle (**4a**, 86.7(1)°; **4b**, 88.5(2)°) is also significantly less than that observed for the series 2 of tetraazo species (average 97.4°).¹² The arene centroid to Ru distance (**4a**, 1.688 Å; **4b**, 1.670 Å) is typical of species with five- or four-membered diaza-coordinating ligands. In contrast to arene-ruthenium chelated amidinates or bisphosphiniminomethanide species, where the α -carbon forms a direct Ru–C bond (η^6 -C₆Me₆Ru(NⁱPr)₂CPh]PF₆, 2.431(5) Å;¹⁴ **3**, 2.224(3) Å),^{11a} in complexes **4a** and **4b** this feature is absent, the separation distance being significantly greater (3.384 and 3.386 Å, respectively). Another interesting aspect upon removal of the chloride from **4a** is the change in color. Normally, unsaturated 16-electron ruthenium complexes are dark red or purple; however, **4b** is dark orange. This difference can be attributed to a strong metal-to-ligand charge transfer, as indicated by a broad adsorption at 434 nm (with ϵ = 5455) in the UV–visible spectrum of **4b** dissolved in dichloromethane. Similar types of MLCT interactions have been observed for arene–Ru–diazabutadiene complexes.^{8c}

During evaluations of **4b** as a catalyst for styrene hydrogenation (vide infra), it was observed that the solutions rapidly

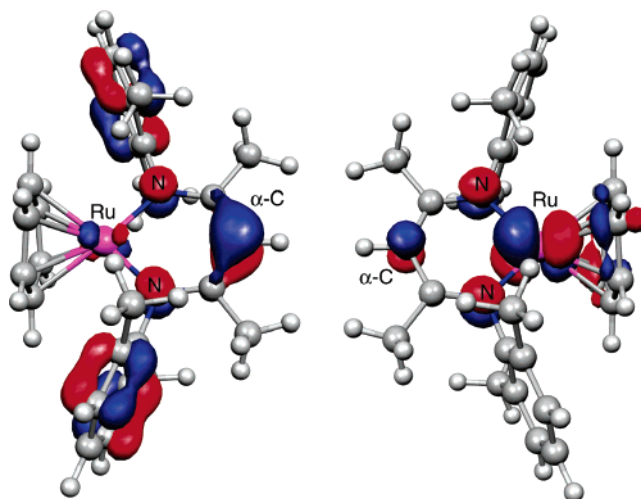


Figure 2. Graphical representation of the computationally modeled Kohn–Sham orbitals comprising the HOMO (left) and LUMO (right) levels in complex **4b**.

changed color upon the addition of the substrate. Hence, investigations into prototypical reactions were conducted by combining **4b** with ethylene or acetylene under atmospheric pressure (Scheme 2). Immediately, solutions of **4b** in THF yielded pale yellow precipitates (**5a** and **5b**), which are highly soluble in CH₂Cl₂. ¹H COSY spectroscopy revealed that the ethylene and acetylene had inserted between the Ru and central α -position carbon of the β -diketiminate ligand. Additionally, the frequency of the α -proton is significantly shifted to a higher field than in **4b**. Crystals suitable for X-ray diffraction analyses were obtained in both cases (Figure 1). The structures reveal a three-legged piano-stool configuration with a Ru σ -bonded CH₂ or CH group forming alkanyl (**5a**) and alkenyl (**5b**) complexes. Additionally, the entire β -diketiminate ligand has undergone modification, including a shortening of the C β –N bonds and, more significantly, the Ru and α -carbon centers being folded out of the original metal–ligand plane, thus breaking the electronic π -delocalization along the N–C β –N chain. The most striking difference between **5a** and **5b** is the C–C distance of the inserted substrate, which is primarily manifested as a shorter Ru–C distance in the alkenyl complex: **5b**, 2.065(2) Å; **5a**, 2.159(3) Å. Surprisingly, both types of cycloaddition reactions are reversible, with **5b** quantitatively reverting back to **4b** at room temperature, in solution, over a period of 1 day under a N₂ atmosphere. Similarly, **5a** loses ethylene, but only at elevated temperatures (>50 °C). Other examples of transition-metal β -diketiminate species that undergo ligand insertion reactions at the α -carbon position are known (e.g., FeCl(ArNCMe)₂CH) with diazoacetate¹⁵ and methyl transfer within Pt(CH₃)₅(ArNCMe)₂CH; Ar = 2,6-*i*-Pr₂C₆H₃),¹⁶ but none of the above are reported

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to be reversible. A product analogous to **5b** resulting from ethylene insertion into an Al β -diketiminate has been characterized in solution, but the reaction is only reversible following the addition of a strong nucleophile.¹⁷

In the interest of identifying possible intermediates formed during the catalytic hydrogenation process, the reaction between **4b** and H₂ was also examined. Under 100 bar of H₂ pressure, solution NMR revealed instantaneous formation of a hydride species ($\delta(^1\text{H})$ –5.10 ppm, t_1 = 1.392 s), which is also formed, albeit more slowly, under 5 bar of pressure. In general, the ¹H and ¹³C NMR spectra of **5c** resemble those of **5a** and **5b**, including a low-field-shifted diastereotopic α -CH₂ group. Product **5c** can be isolated on a larger scale in an autoclave. However, the isolated highly reactive solid readily reverts back to **4b** in the absence of a H₂ atmosphere at room temperature, but its lifetime is prolonged if kept below –25 °C. Nevertheless, a solid-state ATR-IR spectrum was obtained, revealing a diagnostic Ru–H stretch at 1883 cm^{–1}. Crystals were obtained for X-ray diffraction studies by exploiting the insoluble nature of **5c** in THF. The structure is analogous with those of **5a** and **5b**, featuring an identical folding pattern of the β -diimine ligand.¹⁸ Hence, this reaction represents a rare example of reversible heterolytic cleavage of dihydrogen by a nucleophilic carbon center, whereas for the majority of cases, H₂ cleavage is facilitated by electronegative elements such as N, O, S, and Cl.¹⁹ A DFT-optimized model of **4b**²⁰ reveals that the α -carbon center has the greatest (–0.48) negative charge within the Ru–N–C₃–N ring. This, combined with the positively charged

ruthenium (+0.05), creates a 1,4-metal-based dipole within the complex. Moreover, both the HOMO and LUMO are mainly comprised of contributions from the d_{yz} orbital of Ru and the p_y orbital associated with the α -carbon of the chelating β -diketamine (Figure 2). Both results suggest that substrate activation by complex **4b** involves a concerted mechanism, whereby the HOMO of the complex interacts with the LUMO of the substrate (the π^* -MO of the olefin or the σ^* -MO of H₂) and simultaneously the LUMO of the complex combines with the substrate HOMO. A number of other metal β -diketiminate complexes are known to react with H₂, including those containing Rh,^{3a} Ir,^{3b} and Pt,^{3c} yielding terminal hydrides, while Fe^{3d} and Cr^{3e} form dimeric species with bridging hydrides. However, none of these systems involve the interaction and reversible transformation of the β -diketiminate ligand.

Our preliminary evaluation of styrene hydrogenation with **4a** and **4b** (1:1000 catalyst to substrate ratio) in THF at 80 °C and 40 bar of H₂ reveals turnover frequencies of 1000 and 838 mol mol^{–1} h^{–1}, respectively. ESI-MS of nanoelectrosprayed aliquots from the catalytic reactions reveal for both systems²¹ the identical dominant species [(C₆H₅Et)Ru(ArNCMe)₂CH]⁺ at m/z 515, while for **4b**, a styrene-coordinated analogue of **5b** is present (m/z 617), and for **4a** several dimeric chloro-bridged species, i.e., [(Ru(ArNCMe)₂CH)]₂Cl₂⁺, are observed. Related halogen-bridged Ru complexes with phosphine ligands have been characterized and shown to be efficient hydrogenation catalysts.^{22,23}

In conclusion, we have demonstrated that facile generation of a vacant coordination site in arene–Ru– β -diketiminate complexes readily activates H₂, alkenes, and alkynes, resulting in thermally reversible cycloaddition with ligand participation. A future report will examine the hydrogenation ability of a series of arene–Ru– and arene–Os– β -diketiminate complexes with different ligand substitution patterns.

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Supporting Information Available: Text, tables, figures, and CIF files giving experimental procedures with characterization data and crystallographic details for **4a,b** and **5a–c** and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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