1120 *Organometallics* **2007,** *26,* 1120−1122

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

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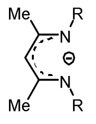
Received January 8, 2007

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-diketiminate 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 H_2,[3] N_2,[4] and O_2.[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-diketiminate 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)$_n$N(R), n = 1 (anionic amidinates),[7] 2 (neutral diazabutadienes)[8]) have been used for well over two decades, in addition to tetraazacyclotetradecine species[9] (**2**) and acetylacetone[10] chelating compounds. Furthermore, the unusual η^3-(C,N,N′)-bonded ruthenium bisphosphiniminomethanide complex **3** has also been recently reported.[11]



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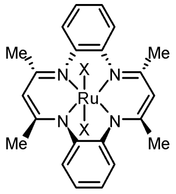

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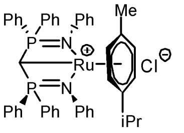

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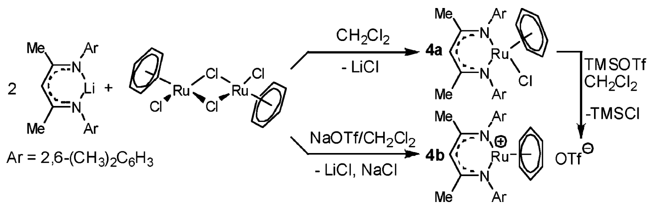
Scheme 1



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 $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, afforded clean reactions with LiCl and $(\eta^6\text{-}C_6H_6)RuCl((ArNCMe)_2CH)$ (**4a**; Ar = 2,6-dimethylphenyl) as the only detectable products (Scheme 1). Removal of the chloride substituent is facilitated by the stoichiometric addition of Me_3SiOTf 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**, $[(\eta^6\text{-}C_6H_6)Ru((ArNCMe)_2CH)]OTf$, is insoluble in Et_2O 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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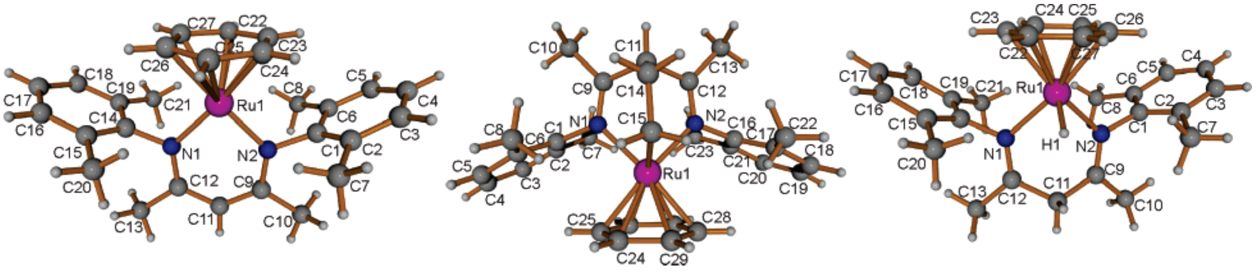
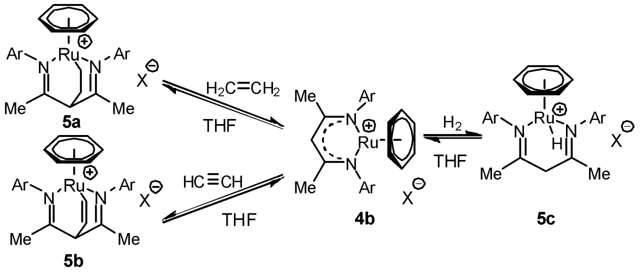


Figure 1. Ball and stick diagrams of complexes **4b** (left), **5a** (center), and **5c** (right). Solvates and anions have been omitted for clarity.

Scheme 2[a]



[a] X = OTf.

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 C_6H_6−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-$C_6Me_6Ru(N(^iPr))_2CPh]PF_6$, 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 $\epsilon = 5455$) in the UV−visible spectrum of **4b** dissolved in dichloromethane. Similar types of MLCT interactions have been observed for arene−Ru−diazabutadiene complexes.[8c]

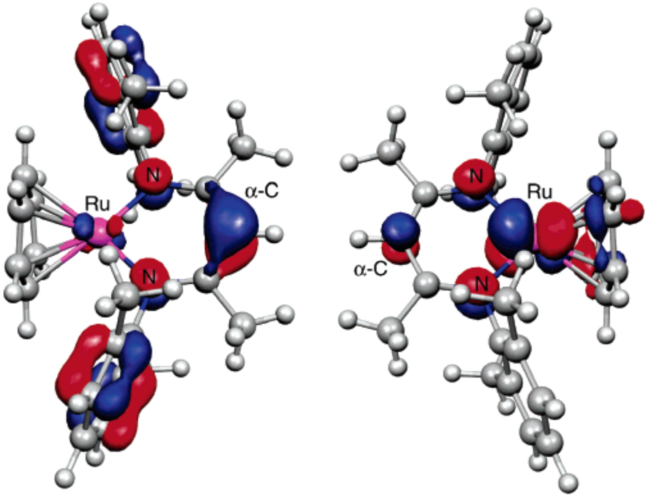


Figure 2. Graphical representation of the computationally modeled Kohn−Sham orbitals comprising the HOMO (left) and LUMO (right) levels in complex **4b**.

During evaluations of **4b** as a catalyst for styrene hydrogenation (vide infra), it was observed that the solutions rapidly 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 CH_2Cl_2. ^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 CH_2 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_3−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 N_2 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 diazoacetate[15] and methyl transfer within $Pt(CH_3)_5(ArNCMe)_2$-CH; Ar = 2,6-$^iPr_2C_6H_3$),[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 H_2 was also examined. Under 100 bar of H_2 pressure, solution NMR revealed instantaneous formation of a hydride species ($\delta(^1H)$ -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 ^{13}C NMR spectra of **5c** resemble those of **5a** and **5b**, including a low-field-shifted diastereotopic α-CH_2 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 H_2 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, H_2 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$-C_3-$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 H_2) 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 H_2, 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 H_2 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 systems[21] the identical dominant species $[(C_6H_5Et)Ru(ArNCMe)_2CH)]^+$ 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., $[(Ru(ArNCMe)_2CH))_2Cl_n]^+$, 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$-\beta$-diketiminate complexes readily activates H_2, 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$-\beta$-diketiminate complexes with different ligand substitution patterns.

Acknowledgment. This research was supported by a grant from the European Marie Curie Action (A.D.P., *CARCAS* Project Contract no. MEIF-CT-2005-025287) and the EPFL. We wish to thank Drs. Euro Solari and Christian G. Hartinger for their technical assistance.

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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