

Intramolecular C–H Activation Reactions of Molybdenacyclobutanes

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The formation of a metallacyclobutane is a key step during a number of important catalytic organometallic processes, including olefin metathesis,^{1–4} σ -bond metathesis, and olefin insertion into M–C linkages.⁴ Consequently, metal complexes capable of forming metallacyclobutanes have the potential to function as catalysts for the transformation of simple hydrocarbons into functionalized organic compounds. In this report, we describe unprecedented intramolecular C–H activations of molybdenacyclobutanes that eventually produce coupled organic products.

We have previously reported the activation of various substrates by the transient 16-electron neopentylidene complex, Cp*Mo(NO)(=CHCMe₃), which results from the spontaneous loss of neopentane from Cp*Mo(NO)(CH₂CMe₃)₂ (**1**) under ambient conditions.^{5,6} Even though the reactions of the neopentylidene complex with cyclic olefins result in metallacycles, these metallacycles have not exhibited any olefin metathesis reactivity. They favor instead the unprecedented C–H activation processes summarized in Scheme 1.

As shown in the box in Scheme 1, the extent of reactivity of a particular molybdenacyclobutane complex depends on the size of the cyclic olefin employed to generate it. For instance, dissolution of **1** in cyclopentene at 20 °C for 18 h results in the exclusive formation of orange **2A**, which can be isolated by crystallization from pentane/Et₂O. Key features of the ¹H NMR spectrum of **2A** in C₆D₆ include the upfield resonance (–0.05 ppm) assigned to the proton in the β -position of the metallacycle as well as a downfield resonance (7.94 ppm) attributed to the cyclopentane proton α to the metal. The molecular structure of **2A** has also been confirmed by a single-crystal X-ray diffraction analysis (Supporting Information). However, heating of **2A** in cyclopentene does not lead to any further reactivity of the metallacycle other than its eventual decomposition.

The reaction of **1** with cyclohexene is somewhat more complicated in that the ¹H NMR spectrum of the reaction mixture after 24 h indicates the presence of several organometallic complexes. These complexes, probably **3A**, **3B**, and **3C**, are difficult to separate. Nevertheless, yellow **3C** can be obtained analytically pure by chromatography on neutral alumina followed by crystallization from

Et₂O. The ¹³C NMR spectrum of **3C** in C₆D₆ shows downfield resonances at 115.8, 94.1, 85.9, and 76.9 ppm, indicating a metal interaction with four of the carbons in the product possibly in an η^4 -trans-diene structure (Scheme 1). However, structural data from single-crystal X-ray crystallography (Figure 1) suggest that the three carbons in the cyclohexane ring are best described as interacting with the metal in π fashion as an allyl group and that the remaining carbon is best described as having a simple σ -bond to the metal center. Thus, the X-ray data indicate an allyl–alkyl description for **3C** in the solid state, while ¹³C NMR data indicate at least some η^4 -diene character in solution.⁷

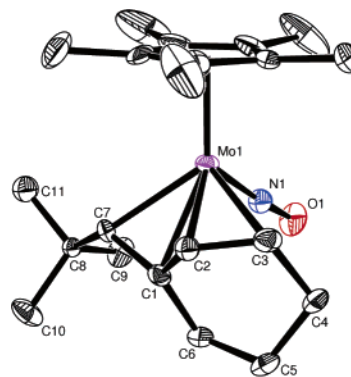
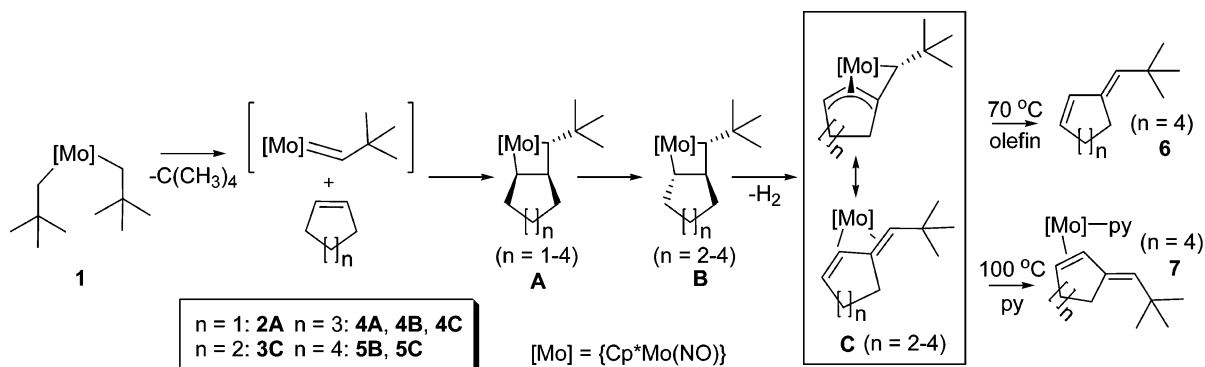


Figure 1. Solid-state molecular structure of **3C** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å): Mo(1)–C(7) = 2.299(4), Mo(1)–C(1) = 2.233(4), Mo(1)–C(2) = 2.115(9), Mo(1)–C(3) = 2.301(5).

The reaction of **1** with cyclooctene at 20 °C for 18 h produces metallacycle **5B**, which at first glance is quite similar to the cyclopentene cis metallacycle **2A**. The metal-bound carbons of **5B** show similar ¹³C NMR resonances, and the signals attributable to the protons attached to those carbons also have similar chemical shifts. Single-crystal X-ray diffraction, however, reveals a metallacycle with a trans orientation of the protons at the bridgehead positions (H1 and H2, Figure 2). Unfortunately, ¹H–¹H coupling constants for the cis and trans metallacycles are not sufficiently

Scheme 1



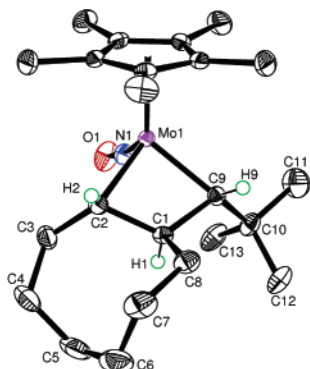


Figure 2. Solid-state molecular structure of **5B** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å): Mo(1)–C(2) = 2.071(2), Mo(1)–C(9) = 2.070(2), C(1)–C(2) = 1.608(3).

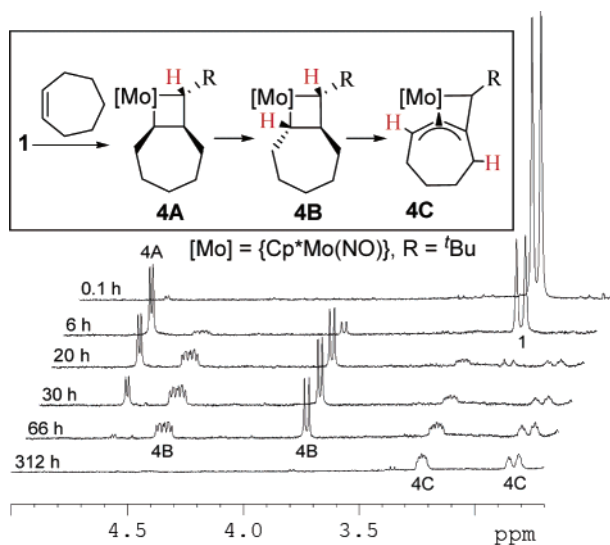


Figure 3. A portion of the ^1H NMR spectra of the reaction of **1** with cycloheptene in cyclohexane- d_{12} .

different to definitively determine cis and trans orientations spectroscopically. Monitoring of the cyclooctene reaction by ^1H NMR spectroscopy also does not result in observation of a cis metallacycle intermediate.

Heating of **5B** in cyclohexane at 50 °C for 24 h gives rise to a new species that can be isolated by column chromatography. Spectroscopic properties of this yellow product (**5C**) identify it as an allyl–alkyl complex analogous to **3C**. Furthermore, monitoring of this transformation in C_6D_6 by ^1H NMR spectroscopy reveals the growth of a small singlet at 4.56 ppm indicative of the production of H_2 during the course of the reaction.

Monitoring of the reaction of **1** with cycloheptene in cyclohexane- d_{12} by ^1H NMR spectroscopy (Figure 3) indicates the presence of three products which grow in sequentially during the reaction that ultimately leads to the exclusive formation of the single product **4C**. This product can be isolated and purified by column chromatography, and its ^1H and ^{13}C NMR spectra indicate an allyl–alkyl structure analogous to **3C**. The other two species observed

are not amenable to column chromatography, but **4B** can be crystallized from the final reaction mixture. Spectral data (Figure 3) are most consistent with **4B** being the trans metallacycle. **4A** has not yet been isolated except in combination with **4B**, but ^1H and ^{13}C NMR spectra support its assignment as the cis metallacycle.

By simply varying the ring size of the cyclic olefin, we have thus gained some insight into the general mechanism for the reaction of cyclic olefins with the neopentylidene complex. A cis metallacycle forms initially. Next, rearrangement to the trans species occurs rapidly, perhaps via C–H activation of the β -hydrogen, except in the case of the cyclopentene, whose small ring size precludes access to a trans orientation. The trans species is then converted to the allyl–alkyl structure via intramolecular allylic C–H activation and loss of H_2 . In the case of cyclooctene, this step requires heat, presumably due to the enhanced stability of the trans octane species.

In an effort to probe the subsequent reactivity of the allyl–alkyl complexes, **5C** has been exposed to pyridine at 100 °C for 18 h. The reaction mixture changes from yellow to orange, and new complex **7** can be isolated by column chromatography. The ^1H NMR spectrum of **7** in C_6D_6 shows four downfield resonances, three of which are attributable to a metal-bound pyridine ligand. The fourth, a singlet, is assigned to the exocyclic alkene which has been displaced from the metal's coordination sphere by the pyridine.

Finally, the functionalized cyclooctene **6** can be completely liberated from the metal by simply heating **5C** in various olefins (Scheme 1). In terms of the organic product, the overall reaction couples a cyclic olefin with a neopentylidene group, thereby creating a newly conjugated system of two double bonds.

In summary, we have prepared molybdenacyclobutanes capable of unprecedented intramolecular C–H activations leading to the loss of H_2 and formation of new allyl–alkyl complexes that can then be compelled to release the cyclic olefin coupled to the neopentyl fragment. These complexes differ from previously reported metallacyclobutanes in that they show no propensity for metathesis processes, favoring instead C–H activation routes.

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Supporting Information Available: Experimental procedures and complete characterization data for compounds **2–7** (PDF) and full details of the crystal structure analyses of **2A**, **3C**, and **5B**, including associated tables (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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