Communication

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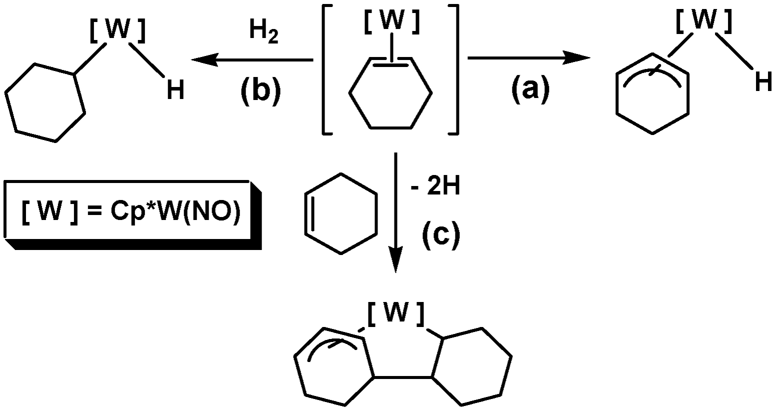

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Parallel Transformations of Cyclohexene Mediated by the Cp*W(NO) Fragment

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One of the principal uses of transition-metal organometallic complexes is as reagents and catalysts in organic syntheses.[1] Most of these applications exploit the fact that the chemistry of an organic molecule bound to a transition-metal center is markedly different from that exhibited by the molecule in its free state. In recent years, considerable attention has focused on simple hydrocarbons as the organic molecules to be transformed, primarily due to the potential for functionalization of these readily available materials into more desirable, higher-value products.[2] Our previous contributions to this area have included the development of 16-electron organometallic complexes of molybdenum and tungsten based on the Cp*M(NO) (Cp* = η^5-C_5Me_5; M = Mo, W) fragments for the sequential activation of hydrocarbon C−H bonds.[3] We now wish to report that the Cp*W(NO) fragment can also be used to mediate the three transformations of cyclohexene summarized in Scheme 1.

The three transformations are initiated by coordination of cyclohexene to the tungsten center and formally involve (a) intramolecular C−H activation of cyclohexene to form an η^3-cyclohexenyl hydrido complex,[4] (b) combination of cyclohexene and H_2 to form an η^1-cyclohexyl hydrido complex,[5] and (c) coupling of two molecules of cyclohexene with concomitant loss of two hydrogen atoms to form a novel η^1,η^3-(cyclohexyl)cyclohexenyl ligand.[6] The requisite 16e [Cp*W(NO)(η^2-cyclohexene)] intermediate can be generated by hydrogenolysis of an appropriate Cp*W(NO)(hydrocarbyl)$_2$ precursor in cyclohexene. The specific bis(neopentyl) system that we have examined in detail is illustrated in Scheme 2 along with our rationale that accounts for the formation of the isolated products **1**, **2**, and **3**. Thus, treatment of wine-red Cp*W(NO)(CH_2CMe_3)$_2$ with H_2 (1 atm) in neat cyclohexene in a 1:30:100 molar ratio under ambient conditions for 3 h results in the formation of a red-brown solution that contains **1**, **2**, and **3** as the main organometallic products in an approximate 6:1:2 ratio, respectively (as estimated by ^{1}H NMR spectroscopy). Extraction of the dried reaction residue with cold Et_2O and crystallization of the extracted material from THF at −30 °C affords red diamond-shaped crystals of **3**. The remaining material was purified by chromatography on silica with hexanes/Et_2O as eluant to eventually obtain **2**·Et_2O as dark red crystals and **1** as a yellow powder.[7]

The identity of complex **1** as an η^3-cyclohexenyl hydrido complex has been established by its characteristic spectroscopic properties, most notably its ^{1}H NMR spectrum (C_6D_6) that contains a distinctive hydride resonance at δ −0.57 ($^1J_{WH} = 131.7$ Hz) and its IR spectrum as a KBr pellet that exhibits a ν_{WH} at 1898 cm^{-1}. We have previously isolated **1** in 32% yield from the gentle thermolysis of Cp*W(NO)(CH_2CMe_3)(η^3-$H_2CCHCMe_2$) at 50 °C in neat cyclohexane.[8]

Bimetallic complex **2**·Et_2O is quite thermally sensitive, and its identity has been confirmed by a single-crystal X-ray diffraction analysis.[9] Its intramolecular metrical parameters resemble those previously established for related complexes containing $W_2(\mu$-$H)_2$ central cores.[10] Specifically, its W−W bond length of 3.0315(2) Å is indicative of a W═W double bond that enables each tungsten center to attain an 18-valence-electron configuration. As shown in Scheme 2, we believe that **2** arises via adduct formation between the transiently formed 16-electron hydrido complexes, Cp*W(NO)(H)(C_6H_{11}) and Cp*W(NO)(H)(CH_2CMe_3).

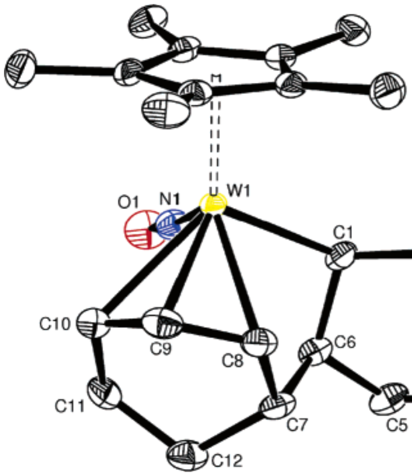
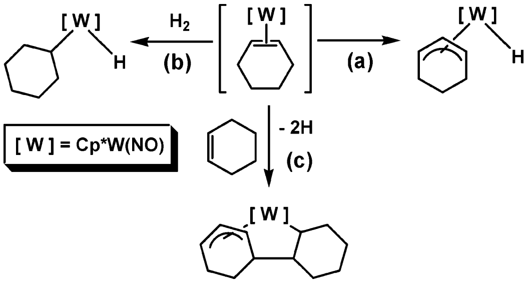


Figure 1. Solid-state molecular structure of **3** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)−N(1) = 1.780(2), N(1)−O(1) = 1.225(3), W(1)−C(1) = 2.273(2), W(1)−C(8) = 2.284(2), W(1)−C(9) = 2.268(2), W(1)−C(10) = 2.434(2), C(8)−C(9) = 1.413(3), C(9)−C(10) = 1.401(3), W(1)−N(1)−O(1) = 174.8(2), C(1)−W(1)−C(8) = 70.62(9), C(8)−W(1)−C(10) = 61.68(8), C(8)−C(9)−C(10) = 118.8(2).

Scheme 1



Finally, monometallic complex **3** has been characterized by conventional spectroscopic methods, and its solid-state molecular structure (Figure 1) has been established by an X-ray crystallographic analysis.[11] Its most interesting structural feature is the η^1,η^3-(cyclohexyl)cyclohexenyl ligand, which again results in the metal center attaining an 18-electron configuration. The unsymmetrical η^1,η^3 (as opposed to an η^2,η^2) mode of attachment of this coupled ligand to the metal center is probably reflective of electronic factors. We have previously seen manifestations of similar factors in Cp′M(NO)(η^4-*trans*-diene) complexes (Cp′ = Cp (η^5-C_5H_5) or Cp*) of both molybdenum[12] and tungsten.[6]

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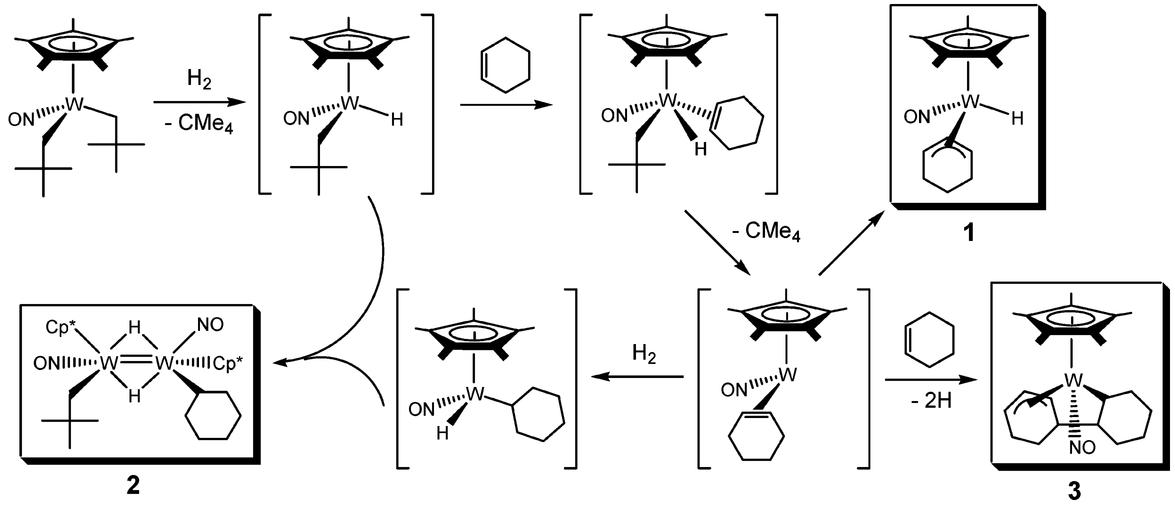
Scheme 2



Consistent with the reaction sequences contained in Scheme 2 are the following facts. Dihydrogen is an essential reactant since Cp*W(NO)(CH_2CMe_3)$_2$ simply does not react with cyclohexene alone under ambient conditions. Furthermore, the use of D_2 in place of H_2 does not result in any incorporation of deuterium into **1** or **3**. Finally, **1** does not convert to **3** when exposed to cyclohexene under the reaction conditions employed. Interestingly, when effected in a 1:10 mixture of cyclohexene/hexanes, the reaction of Cp*W(NO)(CH_2CMe_3)$_2$ with H_2 affords only bimetallic **2**, which can be isolated by crystallization from the final reaction mixture at −30 °C. The preliminary results of DFT calculations on these systems are generally consistent with the transformations depicted in Scheme 2 being operative in neat cyclohexene. However, they also suggest that 16-electron Cp*W(NO)H_2 plays a pivotal role as a reactive intermediate in a 1:10 cyclohexene/hexanes mixture.[13]

In summary, we have succeeded in isolating and characterizing three different types of organometallic products resulting from the transformations of cyclohexene effected at the Cp*W(NO) fragment. Current studies with this system are directed at establishing which other unsaturated substrates will undergo these types of conversions and at delineating the characteristic chemistry of the product complexes. The results of these investigations will be reported in due course.

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Supporting Information Available: Experimental procedures and complete characterization data for complexes **1**, **2**, and **3** (PDF), and full details of the crystal structure analyses of **2** and **3** including associated tables (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Evidence for the occurrence of acyclic alkene to π-allyl hydride rearrangements during the thermal reactions of W(CO)$_4$(alkene)$_2$ complexes has been presented previously. See: Szymańska-Buzar, T.; Jaroszewski, M.; Wilgocki, M.; Ziółkowski, J. J. *J. Mol. Catal. A: Chem.* **1996**, *112*, 203.

(5) The insertion of coordinated alkenes into M−H bonds is a fundamental transformation in transition-metal organometallic chemistry; see ref 1.

(6) For comparison, the dimerization of 1,3-cyclooctadiene mediated by the Cp*M(NO) [M = Mo, W] fragments affords a complex in which the coupled ligand is attached to the metal centers in a bis-η^2 fashion. See: Debad, J. D.; Legzdins, P.; Young, M. A.; Batchelor, R. J.; Einstein, F. W. B. *J. Am. Chem. Soc.* **1993**, *115*, 2051.

(7) Complete experimental details are provided in the Supporting Information.

(8) Ng, S. H. K.; Adams, C. S.; Hayton, T. W.; Legzdins, P.; Patrick, B. O. *J. Am. Chem. Soc.* **2003**, *125*, 15210.

(9) (9) Crystal data for **2**·Et_2O: triclinic, space group $P\bar{1}$, $a = 9.3217(1)$ Å, $b = 11.5165(2)$ Å, $c = 17.5796(3)$ Å, $\alpha = 85.575(1)°$, $\beta = 89.308(1)°$, $\gamma = 89.733(1)°$, $V = 1863.29(5)$ Å^3, $Z = 2$, $R_1 = 0.0210$, w$R_2 = 0.0461$, and GOF(F^2) = 1.138 for 8657 reflections and 402 variables.

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(11) Crystal data for **3**: monoclinic, space group $C2/c$, $a = 22.1618(3)$ Å, $b = 13.0316(2)$ Å, $c = 17.9373(3)$ Å, $\beta = 131.682(2)°$, $V = 3868.93(10)$ Å^3, $Z = 8$, $R_1 = 0.0168$, w$R_2 = 0.0379$, and GOF(F^2) = 1.068 for 4813 reflections and 231 variables.

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