

## Parallel Modes of C–H Bond Activation Initiated by $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)$ at Ambient Temperatures<sup>1</sup>

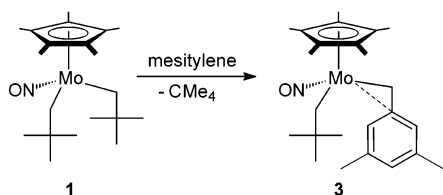
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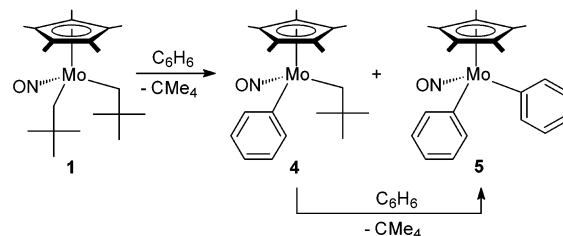
The functionalization of hydrocarbon C–H bonds by soluble transition-metal complexes is of increasing practical interest.<sup>2,3</sup> Previously, reports from this group have described the thermal conversion of  $\text{Cp}^*\text{W}(\text{NO})(\text{hydrocarbonyl})_2$  complexes into transient tungsten alkylidene,<sup>4,5</sup> acetylene,<sup>6</sup> or allene<sup>7</sup> species that can subsequently activate the C–H bonds of hydrocarbon solvents in a variety of ways. The reactive tungsten species are typically formed by thermolysis of suitable organometallic precursors at temperatures ranging from 50 to 80 °C. However, under these conditions some of the C–H activation processes are not clean, thereby leading us to surmise that some of the operative chemistry might be obscured by the thermal instability of the organometallic complexes involved. Consequently, we decided to extend our studies to encompass the congeneric molybdenum precursors. We began our investigations with  $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$  (**1**)<sup>8</sup> since we knew from previous work that the related  $\text{CpMo}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$  complex forms a dimeric molybdenum alkylidene complex in  $\text{CH}_2\text{Cl}_2$  below room temperature.<sup>9</sup> We now report the preliminary results of our investigations of the thermal chemistry of this molybdenum complex which reveal parallel C–H bond activation chemistry mediated not only by transient alkylidene complexes but also by transient benzyne complexes under unusually mild conditions.

At first glance, the thermal reactivity of **1** resembles that reported previously for its isostructural<sup>10</sup> tungsten analogue. For example, the reactions of **1** with tetramethylsilane or mesitylene for 30 h at ambient temperatures result in the clean formation of free neopentane and  $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)$  (**2**) or  $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{CMe}_3)(\eta^2\text{-CH}_2\text{C}_6\text{H}_3\text{-3,5-Me}_2)$  (**3**), respectively. Neither product

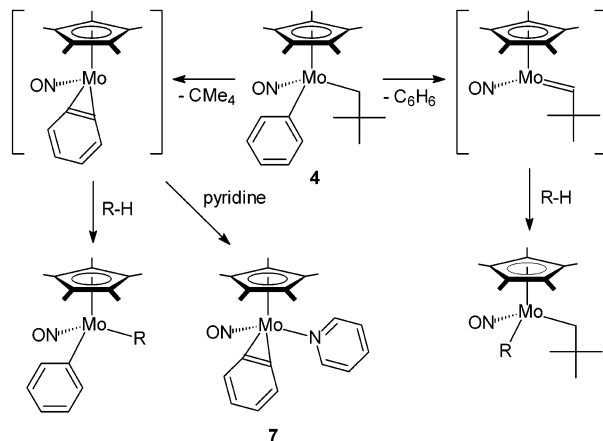


undergoes further reactivity under these mild reaction conditions. Similarly, the reaction of **1** with  $\text{C}_6\text{D}_6$  generates predominantly  $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{D}_5)$  (**4-d<sub>6</sub>**) and neopentane, with stereospecific deuterium incorporation at the synclinal methylene position of the neopentyl ligand. A kinetic analysis of this reaction in the temperature range 26–40 °C (monitored by <sup>1</sup>H NMR spectroscopy) reveals a first-order loss of **1**, and a linear Eyring plot affords  $\Delta H^\ddagger = 99(1) \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -11(4) \text{ J mol}^{-1} \text{ K}^{-1}$ . These parameters are very similar to those determined previously at higher temperatures for the analogous tungsten

### Scheme 1



### Scheme 2

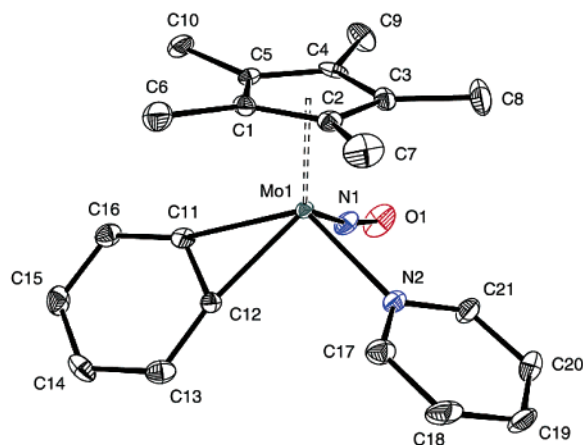


complex,  $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ ,<sup>4b</sup> and they are consistent with rate-determining  $\alpha$ -hydrogen abstraction from a neopentyl methylene group and formation of the reactive alkylidene species,  $\text{Cp}^*\text{Mo}(\text{NO})(=\text{CHCMe}_3)$ , probably as its hydrocarbon solvate.<sup>11</sup>

Remarkably, the reaction of **1** with  $\text{C}_6\text{H}_6$  at room temperature leads to the sequential activation of two molecules of benzene. Thus, a  $\text{C}_6\text{H}_6$  solution of **1** reacts at ambient temperatures to yield  $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)$  (**4**) along with the diphenyl complex,  $\text{Cp}^*\text{Mo}(\text{NO})(\text{C}_6\text{H}_5)_2$  (**5**) (Scheme 1). As shown, the reaction of **4** with  $\text{C}_6\text{H}_6$  at room temperature also cleanly generates **5**. Of note, the analogous reaction of **4** with  $\text{C}_6\text{D}_6$  affords primarily **4-d<sub>6</sub>** (27%) and **5-d<sub>6</sub>** (68%), along with traces of  $\text{Cp}^*\text{Mo}(\text{NO})(\text{C}_6\text{D}_5)_2$  (**5-d<sub>10</sub>**). In addition, solutions of **5** in  $\text{C}_6\text{D}_6$  are converted to **5-d<sub>6</sub>** at room temperature, and **5-d<sub>10</sub>** is fully formed after 48 h at 40 °C. The intermediacy of a transient benzyne complex in this chemistry (see Scheme 2) is suggested by the following observations. First, when the conversion of **4-d<sub>6</sub>** to **5-d<sub>10</sub>** in  $\text{C}_6\text{D}_6$  is monitored by <sup>2</sup>H{<sup>1</sup>H} NMR spectroscopy, no incorporation of deuterium into the  $\text{Cp}^*$  methyl substituents is observed. Mechanisms involving intramolecular oxidative addition of a  $\text{Cp}^*$  C–H bond to a metal center and formation of intermediate “tucked-in” complexes are known to result in such deuterium scrambling.<sup>12</sup> Second, the thermolysis of **4** in pyridine-*d*<sub>5</sub> at room temperature for 30 h affords a mixture

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**Figure 1.** ORTEP diagram of  $\text{Cp}^*\text{Mo}(\text{NO})(\eta^2\text{-C}_6\text{H}_4)(\text{NC}_5\text{H}_5)$  (**7**) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Mo(1)–C(11) 2.124(4), Mo(1)–C(12) 2.153(4), C(11)–C(12) 1.356(6), Mo(1)–N(1) 1.774(4), Mo(1)–N(2) 2.223(3); Mo(1)–N(1)–O(1) 169.2(4).

of the trapped alkylidene complex,  $\text{Cp}^*\text{Mo}(\text{NO})(=\text{CHCMe}_3)(\text{NC}_5\text{D}_5)$  (**6-d<sub>5</sub>**, 75%) and the trapped  $\eta^2$ -benzynes complex,  $\text{Cp}^*\text{Mo}(\text{NO})(\eta^2\text{-C}_6\text{H}_4)(\text{NC}_5\text{D}_5)$  (**7-d<sub>5</sub>**, 25%). The benzyne proton resonances of **7-d<sub>5</sub>** are inequivalent, occurring as overlapping multiplets at  $\delta$  7.48 (2H), 7.78 (1H), and 7.89 (1H). The line shapes of these signals are invariant from 20 to 85 °C in pyridine-*d*<sub>5</sub>, thereby indicating that **7** is stereochemically rigid in this solution and that the Mo- $\eta^2$ -C<sub>6</sub>H<sub>4</sub> linkage is static.

Complexes **6** and **7**, prepared by thermolysis of **4** in pyridine, can be readily separated by fractional crystallization. Compound **7** as its benzene solvate has been subjected to a single-crystal X-ray crystallographic analysis, and the resulting ORTEP diagram of **7** is shown in Figure 1.<sup>13</sup> The length of the benzyne C–C bond coordinated to the molybdenum center is 1.356(6) Å, and the other C–C distances in this ligand range from 1.374(6) to 1.394(6) Å with an average value of 1.383 Å. The two Mo–C(benzyne) distances of 2.124(4) and 2.153(4) Å are unequal and larger than those extant in the molybdenum toluene complex,  $\text{Mo}(\eta^2\text{-2-MeC}_6\text{H}_3)(2\text{-MeC}_6\text{H}_4)_2(\text{PMe}_2\text{Ph})_2$  (2.011 and 2.056 Å).<sup>14</sup> The infrared spectrum of **7** in KBr exhibits strong absorptions at 1537 and 1583  $\text{cm}^{-1}$ , which are assigned to  $\nu_{\text{NO}}$  and  $\nu_{\text{C}=\text{C}}$  stretching frequencies, respectively.

The neopentylidene and benzyne intermediates derived from **4** react readily with the aliphatic C–H bonds of various substrates to generate mixtures of products. For example, thermolysis of **4** in tetramethylsilane at room temperature for 48 h results in the formation of **2** (29%) and  $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\text{C}_6\text{H}_5)$  (**8**, 41%).<sup>15</sup> Similarly, **4** reacts with mesitylene to yield **3** and  $\text{Cp}^*\text{Mo}(\text{NO})(\eta^2\text{-CH}_2\text{C}_6\text{H}_3\text{-3,5-Me}_2)(\text{C}_6\text{H}_5)$  (**9**). Although the insertion of unsaturated small molecules into a metal–carbon bond of a benzyne complex is a well-established phenomenon, only a relatively few benzyne complexes (either isolated or invoked) have been reported to undergo intermolecular C–H bond activation processes, and then usually at temperatures in excess of 100 °C.<sup>16–19</sup> The distribution of products resulting from the reactions of hydrocarbons with **4** (Scheme 2) appears to be dependent on the nature of the hydrocarbon substrate, possibly due to the presence of  $\sigma$ -hydrocarbon complexes on the reaction coordinates of the alkylidene and

the benzyne intermediates.<sup>11,20</sup> More detailed mechanistic studies and DFT calculations of these facile and parallel C–H bond activation systems are currently in progress, with a view to developing new avenues of hydrocarbon activation chemistry. The results of these investigations will be reported in due course.

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**Supporting Information Available:** Experimental procedures and characterization data for the new compounds described (PDF) and X-ray crystallographic data for **7**·C<sub>6</sub>H<sub>6</sub> (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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