

A Beneficial Kinetic Effect of an  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>H Ligand

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**Abstract:** C–H activation of benzene at 26 °C by ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)W(NO)(CH<sub>2</sub>CMe<sub>3</sub>)( $\eta^3$ -CH<sub>2</sub>CHCHMe) results after 4 h in the production of five new organometallic complexes, only two of which are isomers of the desired ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)W(NO)(C<sub>6</sub>H<sub>5</sub>)( $\eta^3$ -CH<sub>2</sub>CHCHMe) compound. In contrast, the identical reaction involving the  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>H analogue affords only the phenyl complexes during the first 24 h, thereby facilitating their isolation in good yields. This striking difference in reactivity can be attributed to the lesser steric demands of the  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>H ligand that result in its complexes reacting at a significantly slower rate.

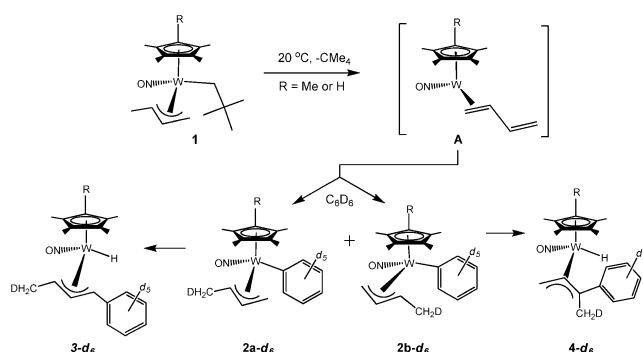
Pentahapto-cyclopentadienyl groups such as  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> (Cp) and  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> (Cp\*) are ubiquitous in transition-metal organometallic chemistry and have been utilized as nonreactive, stabilizing ligands in a wide variety of complexes that undergo all the fundamental organometallic reactions.<sup>1</sup> On occasion, however, the particular cyclopentadienyl ligand employed can control the characteristic chemical properties of a particular compound. A striking illustration of this fact is provided by the observation by Chirik and co-workers that replacement of Cp\* ligands in zirconocenes by the less sterically demanding  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>H (Cp') groups alters how N<sub>2</sub> coordinates to the metal centers and how it subsequently reacts with H<sub>2</sub> and CO.<sup>2</sup> In a similar vein Evans and co-workers recently utilized Cp' instead of Cp\* ligands to prepare the first dinitrogen complex of scandium, [Cp'ZrSc]<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -N<sub>2</sub>).<sup>3</sup> We now wish to report that a similar replacement in one of our C–H activating “piano-stool” nitrosyl complexes results in cleaner chemical transformations that afford the desired products in significantly better isolated yields. This useful outcome is a manifestation of the less crowded Cp' complex undergoing reactions that are primarily dissociative in nature at a significantly slower rate than its Cp\* analogue.

We have established previously that thermolysis of Cp\*W(NO)-(CH<sub>2</sub>CMe<sub>3</sub>)( $\eta^3$ -CH<sub>2</sub>CHCHMe) (**1**\*)<sup>4</sup> at ambient temperatures results in the loss of neopentane and the formation of the 16e  $\eta^2$ -diene intermediate complex, Cp\*W(NO)( $\eta^2$ -CH<sub>2</sub>=CH=CH=CH<sub>2</sub>) (**A**\*).<sup>5</sup> In the presence of linear alkanes, **A**\* effects single C–H activations of the hydrocarbons exclusively at their terminal carbons and cleanly forms 18e Cp\*W(NO)(*n*-alkyl)( $\eta^3$ -CH<sub>2</sub>CHCHMe) complexes.<sup>5</sup> In contrast, treatment of **1**\* with benzene at room temperature affords “a complex mixture of organometallic compounds”.<sup>5</sup> Fortunately, replacement of the Cp\* group in **1**\* [ $\nu_{\text{NO}}$  (Nujol) = 1594 cm<sup>-1</sup>] by the Cp' ligand to form **1**' [ $\nu_{\text{NO}}$  (Nujol) = 1595 cm<sup>-1</sup>] has enabled us to establish that the initial activation of benzene does indeed produce the expected phenyl derivatives for both complexes (Scheme 1 with C<sub>6</sub>D<sub>6</sub> as the reactive substrate). However, these phenyl complexes are thermodynamically unstable and eventually isomerize to a mixture of  $\eta^3$ -phenylallyl hydrido complexes, the isomerizations occurring more rapidly in the Cp\* system.

As shown in Scheme 1, the  $\eta^2$ -diene intermediate complexes **A** (i.e., either **A**\* or **A'**\*) activate C<sub>6</sub>D<sub>6</sub> in the anticipated manner to

form the corresponding phenyl derivatives as the two isomers **2a-d**<sub>6</sub> and **2b-d**<sub>6</sub>. However, **2a-d**<sub>6</sub> and **2b-d**<sub>6</sub> ultimately convert to the hydrido complexes **3-d**<sub>6</sub> and **4-d**<sub>6</sub>, respectively, by intramolecular exchange of the newly formed phenyl ligand with a terminal hydrogen atom on the allyl ligand. To the best of our knowledge, this type of isomerization, which is probably mediated by the metal center, is without precedent in the chemical literature.

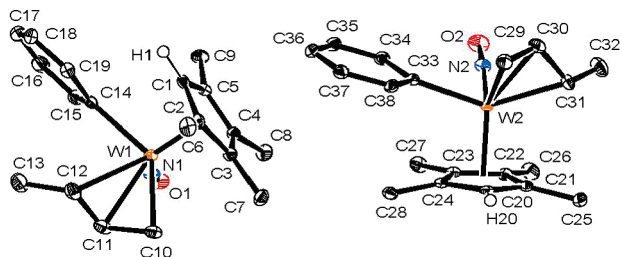
Scheme 1



The conversions depicted in Scheme 1 have been monitored by <sup>1</sup>H NMR spectroscopy, and they have been effected on a preparative scale with C<sub>6</sub>H<sub>6</sub> as the substrate. All nondeuterated new complexes have been isolated and characterized by conventional spectroscopic methods, including single-crystal X-ray crystallographic analyses of representative compounds.<sup>6</sup> Crystallization of **2'** from pentane affords crystals that contain both **2a'** and **2b'** in the lattice (Figure 1), but similar treatment of **2\*** produces crystals that contain only **2a\*** whose intramolecular dimensions are essentially identical to those of **2a'**.<sup>6</sup> As in Cp\*W(NO)(alkyl)( $\eta^3$ -allyl) complexes,<sup>7</sup> the allyl ligands of complexes **2** are in *endo* orientations with the *meso* protons pointing away from the cyclopentadienyl rings. Furthermore, there is a  $\sigma$ – $\pi$  distortion of the allyl ligands brought about by the electronic asymmetry at the metal centers.<sup>8</sup> The spectroscopic properties of complexes **2** indicate that they retain their “piano-stool” molecular structures in solutions. Interestingly, dissolution of crystals of **2a\*** in C<sub>6</sub>D<sub>6</sub> immediately results in a solution whose <sup>1</sup>H NMR spectrum exhibits signals attributable to both **2a\*** and **2b\*** thereby indicating that the two isomers are in rapid equilibrium with each other.

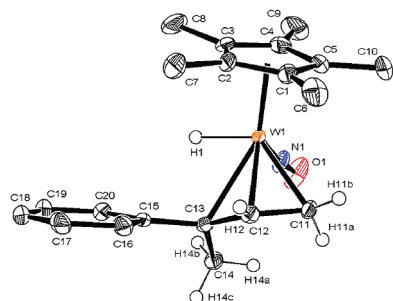
The synthesis of isomeric complexes **3\*** (minor) and **4\*** (major) is facilitated by warming of the reaction mixture to 45 °C for 24 h. Their molecular structures have been deduced from their diagnostic <sup>1</sup>H and <sup>13</sup>C-APT NMR spectra, and the structure of **4\*** has been confirmed by an X-ray crystallographic analysis (Figure 2). The signals due to the hydride ligands in **3\*** and **4\*** occur at  $\delta$  –0.63 ppm (<sup>1</sup>J<sub>WH</sub> = 124 Hz) and –0.05 ppm (<sup>1</sup>J<sub>WH</sub> = 127 Hz), respectively, and the intramolecular metrical parameters of **4\*** are similar to those of the other new complexes isolated during this work. Interestingly, the allyl ligand in **4\*** is in an *exo* orientation,

probably because of the two substituents on C(13) (Figure 2).<sup>9</sup> The final <sup>1</sup>H NMR spectrum of the mixture of **3\*** and **4\*** in C<sub>6</sub>D<sub>6</sub> also exhibits resonances that may be assigned to the minor coordination isomer of **3\*** in which the phenyl substituent on the allyl ligand is situated at the opposite end adjacent to the nitrosyl group.

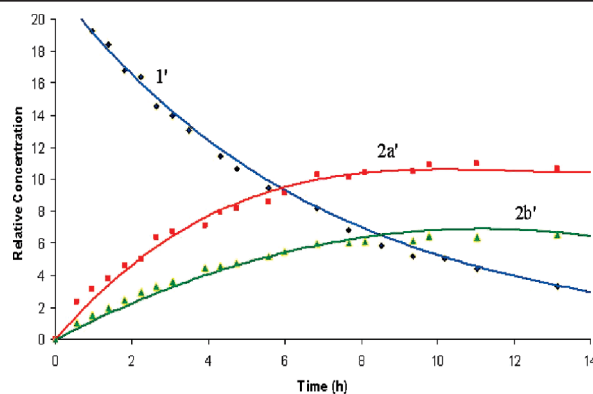


**Figure 1.** Solid-state molecular structures of **2a'** (right) and **2b'** (left) as they occur in the asymmetric unit with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): **2a'**: W(2)–C(29) = 2.360(3), W(2)–C(30) = 2.331(3), W(2)–C(31) = 2.291(3), W(1)–C(33) = 2.214(3), W(2)–N(2) = 1.775(3), N(2)–O(2) = 1.223(4), C(29)–C(30) = 1.378(5), C(30)–C(31) = 1.423(5), C(31)–C(32) = 1.512(5), C(29)–C(30)–C(31) = 118.2(3), W(2)–N(2)–O(2) = 172.1(3). **2b'**: W(1)–C(10) = 2.232(3), W(1)–C(11) = 2.357(3), W(1)–C(12) = 2.506(3), W(1)–C(14) = 2.210(3), W(1)–N(1) = 1.773(3), N(1)–O(1) = 1.225(4), C(10)–C(11) = 1.424(5), C(11)–C(12) = 1.367(5), C(12)–C(13) = 1.501(5), C(10)–C(11)–C(12) = 119.2(3), W(1)–N(1)–O(1) = 169.0(3).

Kinetic analyses of the benzene-activation reactions yield pseudo-first-order rate constants (s<sup>−1</sup>), Arrhenius activation energies (kJ mol<sup>−1</sup>) of  $(8.5 \pm 0.2) \times 10^{-5}$  and  $79.1 \pm 1.9$  and  $(3.6 \pm 0.1) \times 10^{-5}$  and  $93.2 \pm 6.6$  for **1\*** and **1'**, respectively. The corresponding Eyring parameters  $\Delta H^\ddagger$  (kJ mol<sup>−1</sup>) and  $\Delta S^\ddagger$  (J K<sup>−1</sup> mol<sup>−1</sup>) are  $90.6 \pm 6.6$  and  $-27.4 \pm 3.4$  and  $76.5 \pm 1.9$  and  $-66.6 \pm 3.0$ , respectively. The subsequent isomerizations of **2a** and **2b** to the hydrido complexes **3** and **4** also occur more rapidly for the Cp\* complexes. Thus, signals due to **3\*** and **4\*** begin to appear in the <sup>1</sup>H NMR spectrum of the benzene reaction mixture after 4 h at 26 °C when only 75% of **1\*** has been consumed. In contrast, hydride resonances attributable to **3'** and **4'** only begin to appear after 24 h at 26 °C when 96% of **1'** has reacted. In other words, for the first 24 h the Cp' reaction mixture contains only three organometallic complexes (cf. Figure 3) whereas the Cp\* reaction mixture after



**Figure 2.** Solid-state molecular structure of **4\*** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)–C(11) = 2.279(3), W(1)–C(12) = 2.279(3), W(1)–C(13) = 2.461(3), W(1)–H(1) = 1.68(4), W(1)–N(1) = 1.774(2), N(1)–O(1) = 1.222(3), C(15)–C(13) = 1.499(4), C(13)–C(12) = 1.400(4), C(12)–C(11) = 1.417(4), C(15)–C(13)–C(12) = 119.4(2), C(13)–C(12)–C(11) = 124.2(3), W(1)–N(1)–O(1) = 175.4(2).



**Figure 3.** Distribution of organometallic complexes during the C–H activation of benzene by **1'** at 26 °C.

4 h under identical conditions contains at least six such compounds, i.e. “a complex mixture”.<sup>5</sup> Clearly, the isolation of the desired products resulting from the C–H activation of benzene is easiest for the Cp' system.

It has been previously reported that Cp\* complexes can undergo rapid intramolecular rearrangements.<sup>10</sup> This work has demonstrated that the less sterically demanding Cp' group becomes the ligand of choice when the desired initial products undergo such subsequent rearrangements. Studies are currently in progress to establish the mechanisms of the rearrangements that result in the hydrido compounds **3** and **4** and to determine why the alkyl ligands in the related Cp\*W(NO)(*n*-alkyl)( $\eta^3$ -CH<sub>2</sub>CHCHMe) complexes evidently do not undergo such rearrangements.

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**Supporting Information Available:** A PDF file providing full details of experimental procedures and characterization data for all new complexes and a CIF file containing details of the crystallographic analyses of complexes **2a'** and **2b'**, **2a\***, and **4\***. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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