

## $\beta$ -Diimine Platinum Complexes for Alkane Dehydrogenation

Ulrich Fekl,<sup>†</sup> Werner Kaminsky, and Karen I. Goldberg\*

Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

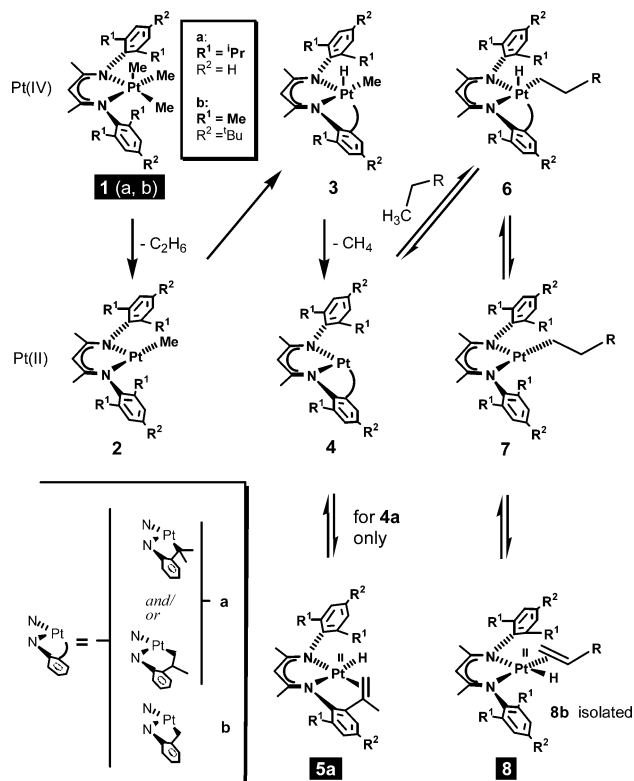
Received August 6, 2003; E-mail: goldberg@chem.washington.edu

Saturated hydrocarbons represent abundant and inexpensive chemical feedstocks, and the selective synthesis of valuable functionalized products directly from alkanes remains a prominent research goal. Significant progress has been made in this area during the last several years, particularly with late transition metal homogeneous catalysts.<sup>1,2</sup> Two very promising types of functionalization reactions are functionalizations which introduce heteroatoms, for example, conversions of alkanes to alcohols, and dehydrogenation reactions which produce olefins from alkanes. Generally, dehydrogenation reactions have been carried out with the metals rhodium<sup>3</sup> and iridium,<sup>4</sup> and heteroatom functionalizations mostly with the metal platinum.<sup>2</sup> This is perhaps somewhat accidental, because the difference in reactivity could be due to the ligands employed rather than to intrinsic properties of the metals.<sup>5</sup> Stoichiometric<sup>6</sup> and catalytic<sup>7</sup> alkane dehydrogenation reactions involving platinum in homogeneous solution are known but rare. In this contribution, the first significant steps toward using platinum complexes of  $\beta$ -diimine ligands for alkane dehydrogenations are presented.

Five-coordinate alkyl Pt(IV) species have been proposed as short-lived intermediates in platinum-catalyzed alkane functionalization cycles for many years. A  $\beta$ -diimine ligand was recently used to prepare the first example of a stable five-coordinate Pt(IV) alkyl complex (Scheme 1, **1a**).<sup>8,9</sup> Upon thermolysis, **1a** undergoes ethane reductive elimination, followed by C–H activation of the ligand, methane elimination, and  $\beta$ -hydrogen elimination (**1**  $\rightarrow$  **2**  $\rightarrow$  **3**  $\rightarrow$  **4**  $\rightarrow$  **5**) to form an olefin(hydrido) Pt(II) complex, where the olefin is part of the chelating ligand (**5a**).<sup>10</sup> Deuterium from deuterated alkane solvent is incorporated into **5a** selectively into the Pt–H, isopropyl, and isopropenyl positions, at elevated temperatures. It was proposed that this alkane activation occurs via the reversible sequence **5**  $\rightleftharpoons$  **4**  $\rightleftharpoons$  **6**  $\rightleftharpoons$  **7** (Scheme 1).<sup>11</sup> In this previous study using **1a** as a precursor, no alkane functionalization products, apart from deuterium/hydrogen exchange into the alkane, were observed. Although an olefin hydride **8a** might be formed reversibly, such a species was not detected. The intramolecular dehydrogenation product **5** is apparently the thermodynamic sink when alkyls which can undergo  $\beta$ -hydrogen elimination are present in *ortho*-positions on the arenes. Herein, we report on the generality of our synthetic approach to five-coordinate Pt(IV) alkyls of type **1** and on investigations of the chemistry of a five-coordinate Pt(IV) complex where the ligand cannot be dehydrogenated by  $\beta$ -hydrogen elimination.

In a series of NMR experiments, the potassium salts of various diimine ligands were allowed to react with the Pt(IV) precursor [Me<sub>3</sub>Pt(OTf)<sub>4</sub> (OTf = F<sub>3</sub>CSO<sub>3</sub>) in alkane solvent. In addition to **1a**, related five-coordinate complexes [{"(*o*-R<sup>1</sup><sub>2</sub>-*p*-R<sup>2</sup>C<sub>6</sub>H<sub>2</sub>)NC(R<sup>3</sup>)<sub>2</sub>CH]-PtMe<sub>3</sub> (**1**) were prepared: **1b** (R<sup>1</sup> = Me, R<sup>2</sup> = <sup>t</sup>Bu, R<sup>3</sup> = Me), **1c** (R<sup>1</sup> = Me, R<sup>2</sup> = H, R<sup>3</sup> = Me), and **1d** (R<sup>1</sup> = Et, R<sup>2</sup> = H, R<sup>3</sup> = <sup>t</sup>Bu). The room temperature <sup>1</sup>H NMR spectra for all compounds **1**

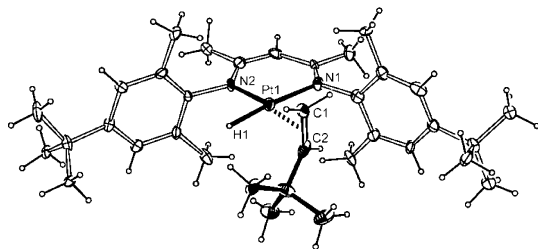
Scheme 1



exhibited a characteristic singlet (with <sup>2</sup>J<sub>PtH</sub> = 74 Hz) integrating to three methyls, showing that all Pt-bonded methyls are equivalent on the NMR time scale, as was previously observed for **1a**.<sup>8</sup> The Pt(IV) complex **1b** having a new chelate ligand (prepared by standard methods)<sup>12</sup> which bears methyl groups in the *ortho*-positions of the arenes is of particular interest.<sup>13</sup> If similar to the thermolysis of **1a**, a species **4** is generated upon thermolysis of **1b**, dehydrogenation of the ligand will not be possible. In this case, stoichiometric alkane activation and dehydrogenation (**4**  $\rightarrow$  **6**  $\rightarrow$  **7**  $\rightarrow$  **8**) may be feasible.

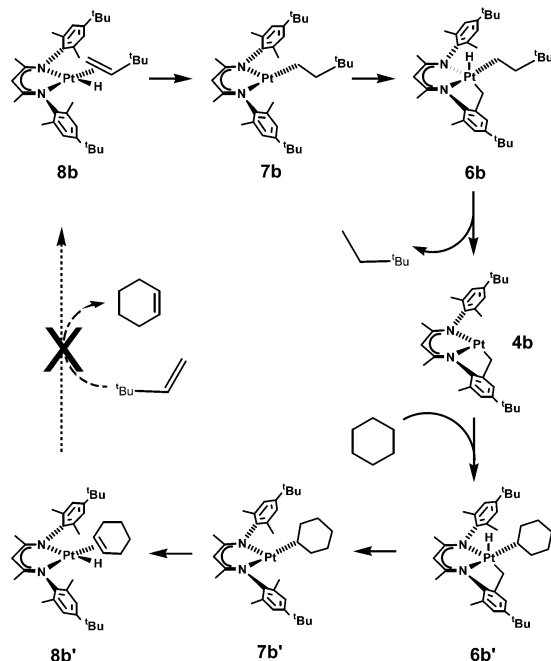
The major product of thermolysis of **1b** in the alkane solvent neohexane is indeed the Pt(II) olefin hydride complex **8b** (Scheme 1, R = <sup>t</sup>Bu). A hydride signal at  $\delta$  -21.5 in the <sup>1</sup>H NMR spectrum shows platinum coupling of <sup>1</sup>J<sub>Pt–H</sub> = 1185 Hz, suggestive of a Pt(II) hydride with a hard donor atom in the *trans* position.<sup>12,14</sup> The signals for the Pt-coordinated neohexene are also observed by NMR, as well as all other expected signals.<sup>12</sup> A single-crystal X-ray structure determination<sup>15</sup> of **8b** confirmed the molecular structure, shown in Figure 1 (selected parameters in the legend). In a similar thermolysis reaction, the use of cyclohexane as the solvent leads to the analogous cyclohexene hydride, unambiguously characterized by NMR spectroscopy.<sup>12</sup> These thermolysis reactions in alkane solvent are accompanied by some decomposition, and the highest yields of the olefin hydride products (40–50%) are obtained when

<sup>†</sup> Current address: University of Toronto, UTM, Mississauga, ON, Canada L5L 1C6.



**Figure 1.** Thermal ellipsoid representation (30% probability, except hydrogens) for **8b** ( $R = t\text{-Bu}$ ). Selected distances and angles ( $\text{\AA}$ , deg; centroid  $X$  defined halfway between  $C1$  and  $C2$ ):  $\text{Pt1-N1}$ , 2.12(1);  $\text{Pt1-N2}$ , 1.99(1);  $\text{Pt1-C1}$ , 2.10(1);  $\text{Pt1-C2}$ , 2.17(2);  $\text{Pt-X}$ , 2.02(2);  $\text{Pt1-H1}$ , 1.6;  $C1-C2$ , 1.40(2);  $\text{N1-Pt1-N2}$ , 90.3(4).

### Scheme 2



the reactions are performed at only slightly elevated temperature ( $35\text{ }^{\circ}\text{C}$ , 110–200 h).

The above experiments show that intermolecular dehydrogenation is possible using a five-coordinate  $\text{Pt(IV)}$  precursor complex with a suitably designed  $\beta$ -diimine ligand. In addition, if the  $\text{Pt(II)}$  olefin hydride product **8b** reacts in a fashion analogous to that of the cyclometalated olefin hydride **5a**, this complex should be able to undergo reversible olefin insertion into the  $\text{Pt-H}$  bond, creating an open site for further alkane activation. Indeed, heating the neohexene hydride complex **8b** ( $R = t\text{-Bu}$ , Scheme 1) in cyclohexane ( $78\text{ }^{\circ}\text{C}$ , 1 h) leads to the corresponding cyclohexene hydride **8b'**. The most reasonable mechanism for this stoichiometric transfer dehydrogenation reaction is depicted in Scheme 2. Following olefin insertion to generate an open coordination site (**8b**  $\rightarrow$  **7b**), cyclometalation (**7b**  $\rightarrow$  **6b**) and successive reductive elimination and oxidative addition reactions lead to a three-coordinate  $\text{Pt(II)}$  cyclohexyl complex (**7b'**) which undergoes  $\beta$ -hydrogen elimination to form **8b'**. The involvement of cyclometalation is supported by deuterium labeling.<sup>16</sup>

Also shown in Scheme 2 is that *catalytic* transfer dehydrogenation should be possible if the olefin substitution reaction to regenerate the neohexene hydride (**8b'**  $\rightarrow$  **8b**) was facile. This is interesting because in this proposed cycle, unlike in virtually all currently known transfer dehydrogenation systems, neither dihydrogen complexes nor dihydrides would be involved. However, no

catalytic turnovers were observed with the **8b** (or **8b'**) system and cyclohexane with neohexene as a potential hydrogen acceptor.

To investigate the reason for the lack of catalysis, the cyclohexene hydride **8b'** was heated with an excess of neohexene in  $\text{C}_6\text{D}_6$ . No reaction in the presence of 4 equiv of neohexene (0.05 M) was observed over a period of 20 h at  $50\text{ }^{\circ}\text{C}$ . Under more forcing conditions, 440 equiv of neohexene (5 M) at  $90\text{ }^{\circ}\text{C}$  for 1 h, starting material was recovered along with unidentified decomposition products, but no olefin substitution product **8b** ( $R = t\text{-Bu}$ ) was detected. The reluctance of **8b'** to undergo olefin substitution is likely due to the sterically demanding groups on the olefin and on the ligand. Olefin substitution at  $\text{Pt(II)}$  is normally associative in nature and thus hindered by steric bulk.<sup>17</sup>

In conclusion, we have shown that novel five-coordinate platinum(IV) alkyl complexes can be made with a variety of  $\beta$ -diimine ligands and that they are useful precursors to unsaturated  $\text{Pt(II)}$  species for alkane activation. Stoichiometric alkane dehydrogenation was observed using either a five-coordinate  $\text{Pt(IV)}$  precursor or an olefin hydride complex of  $\text{Pt(II)}$ . Although alkane functionalization with this system has not been made catalytic as yet, such catalysis may be feasible if the olefin substitution rate at these  $\text{Pt(II)}$  complexes can be substantially increased.

**Acknowledgment.** We thank the National Science Foundation for support of this work, Deutscher Akademischer Austauschdienst for a fellowship award to U.F., and Prof. G. W. Coates and Scott Allen (Cornell) for a sample of the ligand used to prepare **1d**.

**Supporting Information Available:** Synthetic details for the compounds discussed (PDF) and crystallographic data for **8b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

### References

- Recent general reviews on C–H bond activation and functionalization: (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (b) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437.
- Recent reviews on C–H bond activation and functionalization emphasizing platinum catalysts: (a) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259. (b) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer: Boston, 2000. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180.
- Wang, K.; Goldman, M. E.; Emge, T. J.; Goldman, A. S. *J. Organomet. Chem.* **1996**, *518*, 55.
- (a) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086. (b) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025.
- Eisenstein, O.; Crabtree, R. H. *New J. Chem.* **2001**, 25, 665.
- (a) Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467. (b) Vedernikov, A. N.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **2003**, 27, 665.
- Yamakawa, T.; Fujita, T.; Shinoda, S. *Chem. Lett.* **1992**, 905.
- Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423.
- Simultaneously, a five-coordinate dihydrido(silyl)  $\text{Pt(IV)}$  complex was reported: Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 6425.
- Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804.
- “Three-coordinate” intermediates (**2**, **4**, and **7**) could be stabilized by agostic C–H bond interactions with the open site. A nickel analogue of **7**: Wiencko, H. L.; Kogut, E.; Warren, T. H. *Inorg. Chim. Acta* **2003**, *345*, 199.
- See Supporting Information.
- Complex **1b** has an advantage over **1c** in that the *tert*-butyl groups in the *para*-positions of **1b** impart an increased solubility in alkane solvents.
- Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219–221*, 157.
- $\text{C}_{35}\text{H}_{54}\text{N}_2\text{Pt}$ , MW = 697.9, clear prism, triclinic, space group =  $P\bar{1}$ ,  $T = 130(2)\text{ K}$ ,  $a = 9.6220(8)\text{ \AA}$ ,  $b = 9.9680(11)\text{ \AA}$ ,  $c = 18.557(3)\text{ \AA}$ ,  $\alpha = 81.019(8)^\circ$ ,  $\beta = 81.772(8)^\circ$ ,  $\gamma = 69.642(6)^\circ$ ,  $Z = 2$ ,  $R_1$  ( $I > 2\sigma(I)$ ) = 0.0597,  $wR_2$  (all data) = 0.1415, GOF( $F^2$ ) = 1.01.
- Reaction of **8b** ( $R = t\text{-Bu}$ ) with  $\text{C}_6\text{D}_{12}$  to form the cyclohexene- $d_{10}$  deuteride (52% yield by  $^1\text{H}$  NMR) liberates all-protio neohexane, supporting that cyclometalation occurs as an intermediate step.
- Saito, K.; Kashiwabara, K. *J. Organomet. Chem.* **1987**, *330*, 291.

JA037781Z