

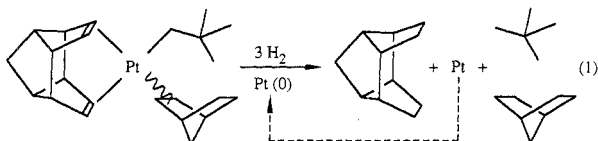
**The Reduction by Deuterium on Platinum Black of *exo*-2-Norbornyl- and *endo*-2-Norbornyl- to Norbornane-2-*d*<sub>1</sub> Occurs with Predominant Retention of Configuration<sup>1</sup>**

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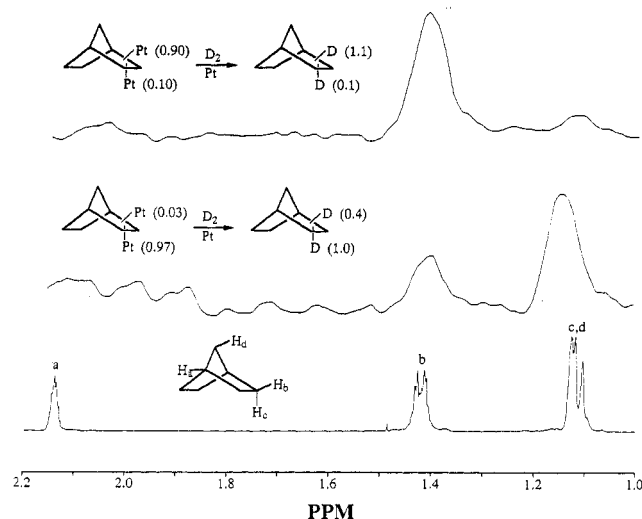
The heterogeneous, platinum-catalyzed hydrogenation of (diolefin)dialkylplatinum(II) complexes ((DO)PtR<sub>2</sub>) on platinum black produces alkanes by reduction of the diolefin and alkylplatinum moieties; the platinum(II) is reduced to platinum(0) and becomes part of the catalyst (eq 1).<sup>2-5</sup> This reaction involves (i)



adsorption of H<sub>2</sub> and (DO)PtR<sub>2</sub> on the surface of the catalyst, (ii) generation of platinum surface alkyls from the alkyl and diolefin moieties of the (DO)PtR<sub>2</sub> complex, and (iii) reaction of the surface alkyls with surface hydrides to produce alkanes.

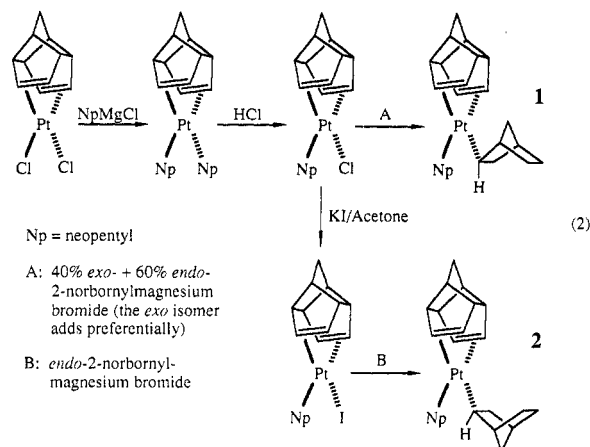
Although the stereochemical outcome of heterogeneous hydrogenations of olefins on noble metal catalysts is well studied,<sup>6</sup> the stereochemistry of reduction of the C\* bond has remained a matter of inference. Addition of H<sub>2</sub> occurs *cis*, on the less hindered face of the olefin.<sup>7-14</sup> Since it is assumed that olefins coordinate by presenting their less hindered face to the surface of the metal, and that H\* adds to this coordinated face, the inference from these results is that the reduction of the C\* bond occurs with retention of configuration. Inferring the stereochemistry of reduction of the C\* bond from the overall stereochemical course of the reduction of an olefin is, however, an uncertain process. We wished to determine directly the stereochemistry of the reaction C\* + D\* → CD.

This paper reports an investigation of the stereochemistry of the reduction of C\* bonds in heterogeneous hydrogenations, based on the adsorption of (DO)PtR<sub>2</sub> on platinum black to generate R\* groups. We synthesized samples containing predominantly (ho-



**Figure 1.** The <sup>1</sup>H NMR spectrum of norbornane-*d*<sub>0</sub> (bottom) and the <sup>2</sup>H NMR spectra of the norbornanes from the reductions by D<sub>2</sub> of a mixture of 97% **2** and 3% **1** (middle) and 90% **1** and 10% **2** (top).<sup>16</sup>

mohyostrophene)neopentyl(*exo*-2-norbornyl)platinum(II) (**1**) and samples containing predominantly (homohyostrophene)neopentyl(*endo*-2-norbornyl)platinum(II) (**2**) according to eq 2.



Homohyostrophene was chosen to minimize generation of H\* by loss of hydrogen from the coordinating diolefin; 2-norbornyl is the best understood system with which to study the stereochemistry of carbon-metal bonds; the neopentyl group afforded selectivity toward *exo*-2-norbornylmagnesium bromide in the addition of a mixture of ca. 40% *exo*- and 60% *endo*-2-norbornylmagnesium bromide to (homohyostrophene)neopentylplatinum(II) chloride (step A of eq 2).

We reduced samples of **1** and **2** with D<sub>2</sub> over platinum black in *n*-pentane<sup>15</sup> and determined the location and number of the deuterium atoms in the resultant norbornanes using <sup>2</sup>H NMR and mass spectroscopy.<sup>16</sup> Analysis of the data is lengthy but straightforward and will be detailed separately; the conclusions are summarized in Figure 1. The top spectrum in Figure 1 refers, for example, to the reduction of a mixture of 90% **1** and 10% **2**. The resulting norbornanes contained, on average, 1.1 D in the *exo* position and 0.1 D in the *endo* position.

Interpretation of these results in terms of the stereochemistry of the reaction of 2-norbornyl\* moieties with D\* requires that we know the stereochemistry of formation of the 2-norbornyl\* moieties from **1** or **2**. We infer that this initial transformation proceeds with *retention* of configuration at carbon, based on the following data: (i) Stereochemical evidence suggests that the initial adsorption of the organoplatinum complex to the surface occurs at

(1) The National Science Foundation (Grant CHE-88-12709), the Office of Naval Research, and the Defense Advanced Research Projects Agency supported this work.

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(4) Miller, T. M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3164-3170.

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(15) Reductions were conducted at -20 °C under 2.4 atm of D<sub>2</sub>.

(16) The assignment of the resonances in the <sup>1</sup>H NMR spectrum of norbornane-*d*<sub>0</sub> is well established.<sup>12</sup>

the platinum center.<sup>3</sup> (ii) The reduction of (1,5-cyclooctadiene)Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> ((COD)PtPh<sub>2</sub>)—a complex in which transfer with inversion at carbon is not possible—proceeds at a rate comparable to that of the reductions of (COD)PtR<sub>2</sub> (R = Me, Et, *n*-Pr, *i*-Pr, *i*-Bu), complexes in which transfer with inversion at carbon is possible.<sup>2</sup> (iii) The reduction of (COD)PtNp<sub>2</sub>—a complex that generates neopentyl moieties<sup>17</sup>—also proceeds at a rate comparable to that of the reductions of the (COD)PtR<sub>2</sub> complexes.<sup>2</sup>

We conclude that the reduction of *exo*-2-norbornyl and *endo*-2-norbornyl moieties occurs with predominant retention of stereochemistry. The result from the reduction of *exo*-2-norbornyl appears to be stereochemically straightforward, with the only competing reaction being activation of ca. 20% of the *cis* C(3)-H (*exo*) bonds (probably by  $\beta$ -hydride elimination). The reduction of *endo*-2-norbornyl is more complicated. The observed results are accounted for by a model involving ca. 35% isomerization of *endo*-2-norbornyl to *exo*-2-norbornyl, but with the conversion of C to CD again occurring with retention of stereochemistry.

We have confirmed the structures of **1** and **2** using X-ray crystallography and have characterized (by MS and <sup>1</sup>H NMR) the alkane products of the reductions of **1** and **2**. These details, and their interpretations, will be described separately.

(17) Displacement with inversion at neopentyl centers is typically much slower than at other alkyl centers. See, for example: Ingold, C. K. *Q. Rev., Chem. Soc.* 1977, 11, 1-14.

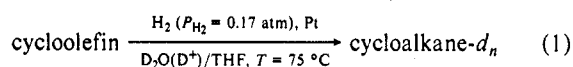
### The Extent of Incorporation of Excess Deuterium in the Platinum-Catalyzed Reduction of Unsubstituted Cycloolefins by H<sub>2</sub> in D<sub>2</sub>O/THF Increases with the Strain Energy of the Product Cycloalkanes<sup>1</sup>

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This paper describes the isotopic compositions of cycloalkanes produced by the catalytic reduction of cycloolefins (C<sub>n</sub>H<sub>2n-2</sub>) using H<sub>2</sub> and platinum black in 1:1 v:v THF/D<sub>2</sub>O<sub>pD=1</sub> (eq 1).<sup>2</sup> We



conducted the reductions under conditions in which the rate of mass transport of H<sub>2</sub> to the surface of the catalyst limited the rate of reaction.<sup>3,4</sup> Under these conditions, H<sub>2</sub> on the surface equilibrates essentially completely with D<sub>2</sub>O in solution. Figure 1 summarizes the isotopic compositions of the cycloalkanes.<sup>5</sup> The

(1) The National Science Foundation (Grant CHE-88-12709), the Office of Naval Research, and the Defense Advanced Research Projects Agency supported this work.

(2) We chose D<sub>2</sub>O/THF (1:1 v:v; pD<sub>D<sub>2</sub>O</sub> = 1) because a survey of solvent systems indicated that this system yielded cyclooctanes having the highest content of deuterium in reductions of cyclooctene.

(3) We performed the reductions in a specially designed round-bottomed flask (volume = 225 mL): a small teat (volume ca. 10 mL) protruded from the bottom of the flask; a Swagelok valve and a rubber septum capped the flask. After charging the teat with a stir bar (3/8 × 3/16 in.) and 40 mg of Pt black, we purged the flask with Ar and added 0.5 mL of dry THF and 0.5 mL of D<sub>2</sub>O (adjusted to pD = 1 with D<sub>2</sub>SO<sub>4</sub>). The apparatus was purged with a mixture of 10% H<sub>2</sub> in Ar for 1 min with stirring; the rate of rotation of the stir bar was 1400 rpm. We pressurized the vessel to 10 psi (P<sub>H<sub>2</sub></sub> = 0.17 atm), stirred for 4 min, placed the flask in an oil bath (75 ± 3 °C), and stirred for 5 min. We removed the solvent via cannula and added the substrate (15–20 mg in 3 mL of D<sub>2</sub>O/THF) via syringe. Stirring was started and continued for 1 h. Analysis by GC/MS indicated that all reductions were complete.

(4) Miller, T. M.; Izumi, A. N.; Shih, Y.-S.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 3146–3156.

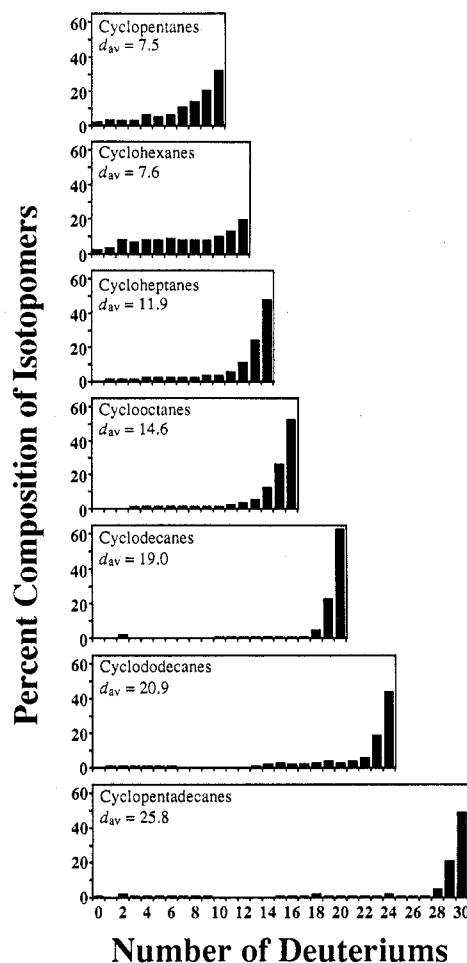


Figure 1. Isotopic distributions and values of  $d_{av}$  for the cycloalkanes from the reductions of the corresponding cycloolefins by H<sub>2</sub> and D<sub>2</sub>O/THF (1:1 v:v; pD<sub>D<sub>2</sub>O</sub> = 1) over platinum black.<sup>5</sup> The difference in values of  $d_{av}$  from duplicate runs was, in all cases,  $\leq 0.2$ .

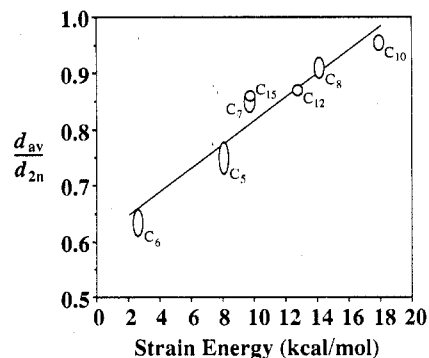


Figure 2. Values of  $d_{av}/d_{2n}$  vs strain energies of cycloalkanes (C<sub>n</sub>H<sub>2n</sub>).<sup>5,17</sup> For consistency, the strain energies are all calculated values, obtained using Macromodel V2.0.<sup>18,19</sup> The line drawn through the points was determined by linear regression.

important observations are as follows: (1) the isotope of hydrogen found in the cycloalkanes was predominantly that present in D<sub>2</sub>O rather than that present in H<sub>2</sub>; (2) the cycloalkanes contained deuterium in large excess of that required for stoichiometric

(5) Isotopic compositions were determined by GC/MS.<sup>6</sup> The average content of deuterium,  $d_{av}$ , describes the extent of incorporation of deuterium. Isotopic abundances were corrected for natural abundance of <sup>13</sup>C. Values of  $d_{av}$  are probably accurate to  $\pm 0.3$  D.

$$d_{av} = \sum_{n=1}^m n(\% \text{ alkane-}d_n)$$

(6) Miller, T. M.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 3156–3163.