

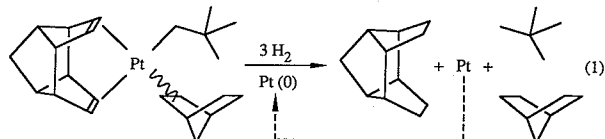
The Reduction by Deuterium on Platinum Black of *exo*-2-Norbornyl- and *endo*-2-Norbornyl- to Norbornane-2-*d*₁ Occurs with Predominant Retention of Configuration¹

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The heterogeneous, platinum-catalyzed hydrogenation of (diolefin)dialkylplatinum(II) complexes ((DO)PtR₂) 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).²⁻⁵ This reaction involves (i)



adsorption of H₂ and (DO)PtR₂ on the surface of the catalyst, (ii) generation of platinum surface alkyls from the alkyl and diolefin moieties of the (DO)PtR₂ 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,⁶ the stereochemistry of reduction of the C* bond has remained a matter of inference. Addition of H₂ occurs *cis*, on the less hindered face of the olefin.⁷⁻¹⁴ 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)PtR₂ on platinum black to generate R* groups. We synthesized samples containing predominantly (ho-

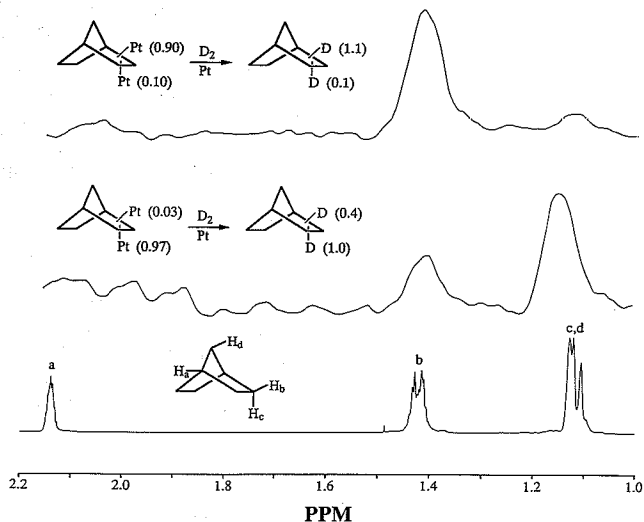
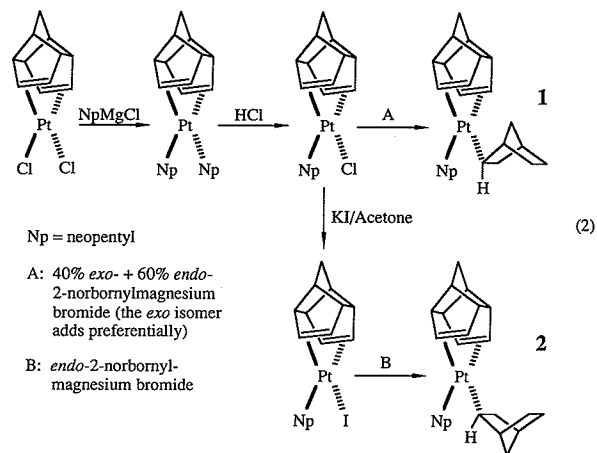


Figure 1. The ¹H NMR spectrum of norbornane-*d*₀ (bottom) and the ²H NMR spectra of the norbornanes from the reductions by D₂ of a mixture of 97% **2** and 3% **1** (middle) and 90% **1** and 10% **2** (top).¹⁶

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 D₂ over platinum black in *n*-pentane¹⁵ and determined the location and number of the deuterium atoms in the resultant norbornanes using ²H NMR and mass spectroscopy.¹⁶ 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

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

(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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(15) Reductions were conducted at -20 °C under 2.4 atm of D₂.

the platinum center.³ (ii) The reduction of (1,5-cyclo-octadiene)Pt(C₆H₅)₂((COD)PtPh₂)—a complex in which transfer with inversion at carbon is not possible—proceeds at a rate comparable to that of the reductions of (COD)PtR₂ (R = Me, Et, *n*-Pr, *i*-Pr, *i*-Bu), complexes in which transfer with inversion at carbon is possible.² (iii) The reduction of (COD)PtNp₂—a complex that generates neopentyl moieties¹⁷—also proceeds at a rate comparable to that of the reductions of the (COD)PtR₂ complexes.²

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 β -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 ¹H 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.