The Reduction by Deuterium on Platinum Black of exo-2-Norboryl- and endo-2-Norboryl- to Norborne-2-d1 Occurs with Predominant Retention of Configuration

T. Randall Lee and George M. Whitesides*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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The heterogeneous, platinum-catalyzed hydrogenation of diphenylene)dialkylplatinum(II) complexes ((DO)PtR2) on platinum black produces alkyl by reduction of the diphenylene and alkylplatinum moieties; the platinum(II) is reduced to platinum(0) and becomes part of the catalyst (eq 1).3-5 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 diphenylene moieties of the (DO)PtR2 complex, and (iii) reaction of the surface alkyls with surface hydrides to produce alkyls.

Although the stereochemical outcome of heterogeneous hydrogenations of olefins on noble metal catalysts is well studied, the stereochemistry of reduction of the C=C bond has remained a matter of addition. Addition of H2 occurs cis, on the less hindered face of the olefin.6,14 Since it is assumed that olefins coordinate by presenting their less hindered face to the surface of the metal, and that H2 adds to this coordinated face, the inference from these results is that the reduction of the C=C bond occurs with retention of configuration. Inferring the stereochemistry of reduction of the C=C bond from the overall stereoselective course of the reduction of an olefin is, however, an uncertain process. We wished to determine directly the stereochemistry of the reaction C=C + D2 → CD.

This paper reports an investigation of the stereochemistry of the reduction of C=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-

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Homohypostrophe was chosen to minimize generation of H2 by loss of hydrogen from the coordinating diphenylene; 2-norboryl is the best understood system with which to study the stereochemistry of carbon–metal bonds; the neopentyl group affords selectivity toward exo-2-norborylmagnesium bromide in the addition of a mixture of ca. 40% exo- and 60% endo-2-norborylmagnesium bromide to (homohypostrophe)neopentylplatinum(II) chloride (step A of eq 2)

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(16) The assignment of the resonances in the 1H NMR spectrum of norborne-d4 is well established.
the platinum center. The reduction of \((1,5\text{-cyclooctadiene})\text{Pt(C}_6\text{H}_5\text{)}_2((\text{COD})\text{PtPh}_2)\) —a complex in which transfer with inversion at carbon is not possible—proceeds at a rate comparable to that of the reductions of \((\text{COD})\text{PtR}_2\) (\(R = \text{Me, Et, n-Pr, i-Pr, i-Bu}\)), complexes in which transfer with inversion at carbon is possible. \(^3\) (iii) The reduction of \((\text{COD})\text{PtNp}_2\) —a complex that generates neopentyl moieties\(^{17}\) —also proceeds at a rate comparable to that of the reductions of the \((\text{COD})\text{PtR}_2\) complexes.\(^2\)

We conclude that the reduction of \(\text{exo-2-norbornyl}\), and \(\text{endo-2-norbornyl}\) moieties occurs with predominant retention of stereochemistry. The result from the reduction of \(\text{exo-2-norbornyl}\) appears to be stereochemically straightforward, with the only competing reaction being activation of ca. 20% of the cis \(\text{C}(3)\text{–H}\) (exo) bonds (probably by \(\beta\)-hydride elimination). The reduction of \(\text{endo-2-norbornyl}\) is more complicated. The observed results are accounted for by a model involving ca. 35% isomerization of \(\text{endo-2-norbornyl}\) to \(\text{exo-2-norbornyl}\), but with the conversion of \(\text{C}_2\) to \(\text{CD}\) 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 \(^1\text{H}\) 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. \(\text{Q. Reu.},\) \textit{Chem. Soc.} \textbf{1977}, \textit{11}, 1–14.