The Reduction of C* Bonds Proceeds with Retention of Configuration: Stereochemical Investigation of the Heterogeneous Reduction by Dideuterium of (Homohypostrophene)neopentyl(2-norboryl)platinum(II) Complexes on Platinum Black

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Abstract: This paper reports an investigation of the heterogeneous, platinum(0)-catalyzed reductions by dideuterium of (homohypostrophene)neopentyl(exo-2-norboryl)platinum(II) (1) and (homohypostrophene)neopentyl(endo-2-norboryl)platinum(II) (2). The stereochemistries of bonding of the norbornyl groups to platinum are rigorously defined by crystal structures of 1 and 2. The reductions occur on the surface of the catalyst: the organic ligands are converted to alkene via reaction of surface alkyls with surface deuterides (D*): the platinum atom in the organometallic complex is reduced to platinum(0), and becomes part of the surface of the catalyst. Reduction of 1 with D$_2$ incorporates deuterium into the exo-2 position of norbornane; analogous reduction of 2 incorporates deuterium predominantly into the endo-2 position of norbornane. These results provide the most direct evidence now available that the stereochemistry of the reduction of C* bonds by H* (D*) proceeds with retention of configuration. Approximately 20% of the exo-2-norboryl* moieties undergo beta-H activation at rates competitive with reductive elimination as norbornanes-d$_2$, in contrast, approximately 35% of the endo-2-norboryl* moieties undergo alpha-H activation and epimerization to exo-2-norboryl* at rates competitive with reductive elimination as norbornanes-d$_4$. These results are rationalized on the basis of steric interactions between the norbornyl moieties and the surface of platinum. The reduction of homohypostrophene by D$_2$ incorporates deuterium exclusively into the exo positions of the product tetra cyclic[6,3,0]P$_5$P$_3$undecane (HOPH): analogous reductions of 1 and 2 incorporate deuterium predominantly into the endo positions of HOPH. These results provide further support that the reduction of (diolofin)diallylplatinum(II) complexes proceeds via initial adsorption of the platinum atom to the surface of the catalyst. Neopentane-d$_4$ is the major isomer of neopentane produced from the reductions of 1 and 2 by D$_2$.

Introduction
The stereoechemical outcome of heterogeneous hydrogenations of olefins on noble metal catalysts has been examined extensively. Despite these efforts and the continuing progress in understanding the structures of hydrocarbons on metal surfaces, the stereochemistry of reduction of the C* bond has been defined only by inference. Determining the stereochemistry of reduction of C* bonds is a challenge that remains to be met.

Scheme I. Proposed Analogy between Surface Alkyls Derived from Norborne (Left) and Those Derived from (Homohypostrophene)neopentyl(2-norboryl)platinum(II) (Right)

\[ \text{HOPH} \quad \text{Np} \]

Chemistry

\[ \text{H}^+ \quad \text{Np} \quad \text{H}^+ \quad \text{HOP-H}_4 \]

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bonds using the reduction of olefins requires a critical assumption since the initial stereochemistry of the C* bond is not known.\textsuperscript{25} Studies of the hydrogenation of olefins (that have no particular face selectivity) have demonstrated that, over most metals, H$_2$ adds predominantly cis to the double bond.\textsuperscript{26-32} In addition, "anchoring" at sites remote from the double bond increases the selectivity toward cis addition of H$_2$.\textsuperscript{23-34} Several studies showed that cis addition of H$_2$ occurs to the less hindered face of the olefin.\textsuperscript{42-49} These last reports constitute the most definitive, albeit indirect, characterization of the stereochemistry of reduction of C* bonds: the olefins probably coordinate by presenting their least hindered face to the surface of the metal; since H$_2$ adds to this face, the stereochemistry of the reduction of the C* bond proceeds with retention of configuration. We wanted to provide an independent and more direct determination of the stereochemistry of this reaction.

We have been studying the mechanisms of the heterogeneous hydrogenation of olefins and of organoplatinum compounds.\textsuperscript{50-56}

In this research, we showed that the heterogeneous, platinum-catalyzed hydrogenation of (dioxo)terpyridine(II) complexes (DO)PtR$_2$) on platinum black produces dioxo-H$_2$, 2 equiv of R-H, and platinum(0).\textsuperscript{50} The platinum(0) becomes part of the surface of the catalyst, and is catalytically active in subsequent hydrogencations (eq 1).\textsuperscript{54} This reaction involves (i) adsorption of dihydrogen and the components of (DO)PtR$_2$ on the surface of the catalyst, (ii) generation of platinum-surface alkyls (DO* and R*) from the alkyl and dioxo moieties originally present in the organometallic complex, and (iii) final reaction of the surface alkyls with surface hydrides to produce alkane by reductive elimination. This reaction can be used to generate R* of known initial structure.\textsuperscript{54,52} The intermediate surface alkyls generated from these reductions are related to those generated in heterogeneous hydrogenations of olefins (Scheme I).

In alkane solvents at relatively low temperatures (ca. -20 °C) and high pressures of H$_2$ (ca. 2.5 atm), the rate-determining step in production of alkane is an unspecific reaction occurring on the surface.\textsuperscript{50} Under these conditions, the reduction by di-derivative of (1-cyclooctadiene)dipropylplatinum(II) produces 1-propane-d$_4$ as the major product, and that of (1-cyclooctadiene)dipropylplatinum(II) produces 2-propane-d$_4$ as the major product. These observations suggest that the regiochemistries of the propylplatinum moieties are preserved on transfer to the surface and on reduction.\textsuperscript{52}

In the work presented here, we used this system to characterize the stereochemistry of the reduction of C* bonds in heterogeneous hydrogenations. We synthesized (homohydroporphene)(neopentyl)(exo-2-norbornyl)platinum(II) (I) and (homohydroporphene)(neopentyl)(endo-2-norbornyl)platinum(II) (II), and confirmed their structures using X-ray crystallography. We selected homohydroporphene (HOP) as the dioxo for three reasons. First, we could examine the stereochemistry of the reduction of the HOP moiety in (HOP)PtR$_2$. Second, HOP cannot form surface π-alkyl groups, and is thus a relatively inert surface species that should not interfere in the reactions of coadsorbed alkyls. Third, we could readily obtain crystals of complexes containing HOP. We chose 2-norbornyl groups as ligands for two reasons. First, norbornyl groups substituted at C(2) exist as two epimers (exo and endo, each enantiomeric); we wanted to synthesize both epimers to simplify interpretation of the data from reductions of the platinum complexes.\textsuperscript{53} Second, the location of the deuterium atoms in the product norbornanes (exo vs endo) could be easily assigned.

(57) Selective synthesis of (DO)Pt(exo-2-norbornyl)R seemed possible because the exo Grignard reactant was shown to be more reactive in mixtures of ca. 40% exo-2- and 60% endo-2-norbornylmagnesium bromide.\textsuperscript{60} Synthesis of (DO)Pt(endo-2-norbornyl)R seemed possible because endo-2-norbornylmagnesium bromide can be produced selectively,\textsuperscript{59,60} and has a half-life of ca. 10 h at 0 °C. The data for these reactions were not included in the paper. (58) Jensen, F. R.; Nakamaye, K. L. J. Am. Chem. Soc. 1966, 88, 3437-3438.
(60) Rost, K. S.; Hill, C. L.; Whitesides, G. M. Unpublished results.
resolved by using $^1$H (or $^2$H) NMR spectroscopy. Neopentyl groups were chosen as ligands (rather than methyl groups) for two reasons. First, the reaction of mixtures of exo- and endo-2-norbornylmagnesium bromide (ca. 45% exo and 55% endo) with (HOP)PMeCl was selective (290% 1 produced), but analogous reaction with (HOP)PMeCl was not. Second, the substitution of neopentyl groups for methyl groups improved the crystallinity of (DO)Pir$_2$ complexes.

Reduction of these complexes with diiodacetylene over platinum black in alkaline solvents generated deuterated norbornanes via intermediate 2-norbornyl* moieties of known stereochemistry. We determined the location of the deuterium atoms in these norbornanes using $^1$H and $^2$H NMR spectroscopy, and analyzed the alkane products in these reductions by GC/MS. Finally, $^2$H NMR spectroscopy was used to locate the deuterium atoms in the homohyprostophanes produced in the reductions by D$_2$ of free homohyprostophane, and of samples containing 1 and 2.

**Experimental Section**

**General Procedure.** We purchased n-pentane (99.9%, anhydrous, sure-seal bottle) from Aldrich, and stored it under argon. n-Heptane (Aldrich, 99.9%, HPLC grade) was distilled from Na/K, and diethyl ether (Malinckrodt) was distilled from Na/benzophenone. We purchased toluene black (lot numbers 10410HT and 031910K, 99.6% n-propylen chloride (99%), exo-2-bromonorbornane (98%), norbornene (99%), benzophenone (99%), pentacyclo[5.4.0.0$^2$.0$^5$.0$^8$.0$^9$.0$^{11}$]deca-2,8-diene (98%), tert-butyl lithium (1 M in n-pentane), LiAlH$_4$ (1 M in diethyl ether), and 10% AgNO$_3$ on silica gel from Aldrich, and used them without further purification. Bis(n-chloro)dichlorobis(ethylenediyldiphenylphospine) (II) (Zeissman & Strem) and dideuterium (99.5 atom % D, Matheson) were used as received. Cyclopentadiene was distilled from dicyclopentadiene (Aldrich, 97%), and benzoinoquinone (Baker) was recrystallized from petroleum ether.

We collected the $^1$H NMR spectra on a Bruker WM 300 spectrometer operating at 46.03 MHz with broad-band 1 H decoupling, and referenced to tetramethylsilane. Melting points were obtained in capillaries sealed under vacuum. We used a Hewlett-Packard 592A GC/MS (70-eV electron impact ionization) to measure mass spectra, and collected these data using the software for selected ion monitoring from Hewlett-Packard. The UV absorbance spectra of a sample containing predominantly 1 and one containing predominantly 2 were obtained with a Perkin-Elmer 552 spectrophotometer, and are included as supplementary material. We measured the UV absorbances of aliquots of kinetic runs on a Cilford 240 single-beam spectrophotometer at 286 and 292 nm for reductions of samples containing predominantly 1 and 2, respectively (vide infra). The methods used to collect the X-ray structures of 1 and 2 are included as supplementary material. The lowest energy conformation and $^1$H NMR coupling constants of homohyprostophane (HOPPH) were calculated with Macromodel V2.0 using the MM2(85) parameter set.52 Oneida Research Co. performed the elemental analyses.

**Procedure for Reductions.** Each reaction was performed as follows. A 20-mL pressure-reactor bottle (purchased from Lab Glass, and silanized as described previously) was charged with 30 mg of platinum black and a 10 × 6 mm magnet stir bar. The vessel was capped with a neoprene septum, purged with argon, and immersed to within ~1 cm of its metal crown cap in a large bath of water/ethyleneglycol (1:1, v/v) regulated by a Neslab Cryocool at ~20 ± 1 °C. Solvent (1 mL) was added, and diethyl ether was added to the reactor to a syringe needle inserted into the septum. The vessel was purged for 15 s, and then pressurized to 2.4 atm (as monitored by inserting a syringe needle equipped with a pressure gauge through the septum of the reactor; these data were reproducible and probably accounted for). Stirring was started and maintained at 1800 rpm (the number of revolutions per minute of the magnetic stirring bar as measured by a calibrated strobe light). After 10 min, the stirrer was stopped, and the catalyst was allowed to settle to the bottom of the vessel. The solvent was then removed from the catalyst via cannula. A yellow solution of the platinum complex (ca. 25 mg dissolved in 4 mL of n-pentane or n-heptane) was cooled to ~20 °C and added to the catalytic cannula. Stirring was initiated and allowed to continue at 1800 rpm for 90 min. After this time, the solution was clear, and showed no UV absorbance.

For reductions in n-pentane, the hydrocarbon products (with the exception of neopentane) were separated from the solvent by preparative GC on a F&M 700 instrument. We used a 1/4 in. × 6 ft UCW-98 column operated at 150 °C with a helium flow of ca. 30 mL/min.

**Kinetics of Reductions.** Previous studies of the kinetics of reduction of (DO)Pir$_2$ in alkaline and protic solvents$^{15}$ under the conditions used here showed that, for a wide variety of diolfin and R groups (where R is alkyl), the kinetic features—rates of reduction and zero-order dependence on the concentration of substrate—were similar. On the basis of these observations, and because we had only limited quantities of 1 and 2, we did not perform an explicit investigation of the kinetics of reduction of these compounds. Nevertheless, since some platinum complexes, for example, (norbornadienide)dimethylplatinum(II), react autocatalytically with H$_2$,$^{49}$ we needed to establish whether an autocatalytic reaction was important in the reductions of 1 and 2.

In order to test for autocatalysis, we ran blank reductions of mixtures of 1 and 2 in n-pentane without any catalyst present. Immediately after addition of the dissolved platinum complexes, we removed an aliquot ($t = 0$) from the reactor. Stirring was resumed, and an aliquot was removed every 15 min until 90 min had elapsed. We diluted the aliquots under air by a factor of 100 by transferring 50 mL to a 5-mL volumetric flask. The diluted solution was transferred to a 3.0-mL quartz cuvette (10 × 10 × 30 mm) for analysis. The UV absorbances did not diminish for either substrate during the 90-min period; we conclude, therefore, that autocatalysis did not contribute to the reduction of these compounds under the conditions employed here.

**Synthesis of Tetracyclo[6.3.0.0$^3$.0$^6$.0$^9$.0$^{12}$]undeca-2,6-diene (Homohyprostophane).** We synthesized homohyprostophane (ca. 50-g scale) using the method of Smith and Barborak (Scheme III).$^{65}$ The details of this synthetic strategy are provided as supplementary material. Since we observed that homohyprostophane decomposes to an insoluble white material on storage at ~6 °C, we chose 6 as the immediate target of the large-scale synthesis, and converted this compound directly to homohyprostophane when desired.

**Synthesis of Tetracyclo[6.3.0.0$^3$.0$^6$.0$^9$.0$^{12}$]undeca-2,6-diene (Homohyprostophane).** Homohyprostophane (HOPPH) is the product from the reduction of homohyprostophane with H$_2$ over platinum black. Following the procedure for reductions outlined above, we hydrogenated 0.104 g (0.72 mmol) of homohyprostophane in n-pentane. The solution was separated from the catalyst by using a pipet, and the solvent was carefully removed by a flow of argon. Sublimation of the resulting white solid gave 0.077 g (52% of HOPPH) as a waxy white solid. Mp: sublimed. MS: m/z (rel intensity) 148 (38) M$^+$, 119 (49), 91 (35), 81 (31), 80 (64), 79 (76), 77 (40), 67 (100), 66 (95), 41 (76), 39 (94), 27 (68).$^{2}$H NMR (CDCl$_3$, 500 MHz, Figs. 1 and 2; $^3$J 2.05, $^3$J 1.98 (br) $^3$J 8 Hz, H$_2$), 1.58 (br d, 4 H, $^3$J = 8 Hz, H$_2$), 1.46 (s, 2 H, H$_2$), 1.45 (br d, 4 H, $^3$J = 8 Hz, H$_2$).$^{2}$C NMR (CDCl$_3$, 100.6 MHz): 48.1, 43.0, 30.4, 25.5. Anal. Caled for C$_{19}$H$_{22}$: C, 89.12; H, 10.88. Found: C, 88.85; H, 10.90.

**Synthesis of Grignard Reagents.** 2-Norbornylmagnesium Bromide. We synthesized this Grignard reagent several times using the following procedure. We placed 5.0 g (0.206 mol) of magnesium chips and a magnetic stir bar in a 200-mL round-bottomed flask. The flask was capped with a rubber septum, and flame-dried under argon. Diethyl ether (ca. 80

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63 Reductions of homohyprostophane and norbornene were performed similarly. (64) In ref 50, we described the procedure for removing aliquots. (65) Smith, E. C.; Barborak, J. C. J. Org. Chem. 1976, 41, 1433–1437.
66 These assignments are supported by 2D $^1$H NMR analysis (COXY), and coupling constants calculated by using Macromodel V2.05 for HOPPH. Macromodel V2.0 predicts that the coupling between H$_2$ and H$_2$ is 8 Hz, and that between H$_2$ and H$_2$ is 1 Hz; a 2D COSY spectrum confirms that, on the basis of our assignment, the coupling between H$_2$ and H$_2$ is greater than that between H$_2$ and H$_2$.
mL was added, stirring was started, and 10.0 mL (0.078 mol) of exo-2-bromonorbornane in ca. 20 mL of diethyl ether was added via cannula. A slow rate of addition was maintained so that the temperature of the flask was warm, but the solution was not refluxing. After the addition was complete, the solution was stirred for 1 h, and then allowed to sit overnight.

Titration of these solutions typically showed the solutions to be 0.6-0.7 M in 2-norbormynagnesium bromide (ca. 60-70% yield). According to prior reports, these solutions contained a mixture of ca. 40% exo- and 60% endo-2-norbormynagnesium bromide.36,38

**endo-2-Norbormynagnesium Bromide.** This Grignard reagent was synthesized using a variation on established procedures.6,60 We transferred under argon 50.0 mL (30.0 mmol) of a 0.6 M solution of 2-norbormynagnesium bromide to a flame-dried, 100-mL Schlenk flask capped with a rubber septum, and containing a magnetic stir bar. The flask was placed in an 80°C salt/ice-water bath, and stirring was initiated. We added via cannula solution of 3.28 g of benzophenone (18.0 mmol, 0.6 equiv) in 10 mL of diethyl ether. The solution rapidly turned dark pink; a white precipitate was observed. The solution was allowed to stir for 5 min at -10°C, after which the flask was placed in a dry ice/acetone bath at -78°C. We attached a medium glass frit having male ground-glass joints at both ends to a 100-mL Schlenk flask. This filtration apparatus was flame-dried under a purge of argon. After cooling, we attached the apparatus under a flow of argon to the Schlenk flask containing the dark pink solution. The solution was filtered quickly through the frit; the filtrate, presumably containing endo-2-norbormynagnesium bromide,6,60 was stored at -78°C, and used shortly thereafter.

**Synthesis of Platinum Complexes. (Homolyphotrophosphate)platinum(II) Diiodide (HOP)PtCl2.** Under argon, we added 3.51 g of a 3:1 mixture of homolyphotrophosphate/triaiobocane (ca. 18 mmol of homolyphotrophosphate) in 25 mL of benzene to an orange suspension of 5.0 g (8.5 mmol) of Zeise's dimer in 100 mL of benzene in a 250-mL round-bottomed flask equipped with a magnetic stir bar. Stirring for 24 h at room temperature produced a precipitate of white needles in a dark brown solution. We collected the precipitate by filtration through a medium glass frit, and washed it with benzene. Recrystallization of the precipitate from hot chloroform yielded 3.68 g (8.97 mmol) of (HOP)PtCl2 as white needles (53% yield based on phosphorus). Mp: 250-260°C dec.1 H NMR (CDCl3, 400 MHz): δ 6.38 (t, J = 7.1 Hz, 4 H), 3.24 (q, J = 7.1 Hz, 4 H), 2.36 (m, 2 H), 1.85 (s, 2 H). Anal. Calcld. for C51H52PtCl2: C, 62.25; H, 2.92. Found: C, 62.72; H, 3.00.

**Homolyphotrophosphate)platinum(II) Diiodide, (HOP)PtCl2.** The diiodide was obtained in quantitative yield from (HOP)PtCl2 by suspending the dichloride in diiodomethane, saturating the solution with KI (the solution turned from clear to yellow immediately upon addition of KI), and stirring for 3 days. Aqueous workup and extraction with chloroform followed by recrystallization from hot chloroform yielded (HOP)PtCl2, white needles. Mp: 247-258°C dec.1 H NMR (CDCl3, 500 MHz): δ 6.47 (t, J = 7.1 Hz, 4 PtCl2) with Pt satelltes, JPt = 79 Hz, 4 H), 3.30 (sep, J = 1.9 Hz, 2 H), 1.73 (t, J = 7.1 Hz, 4 H), 1.93 (q, J = 7.1 Hz, 2 H). Anal. Calcld. for C51H52PtCl2: C, 62.25; H, 2.04. Found: C, 62.25; H, 2.02.

**Homolyphotrophosphate)dineopentylplatinum(II), (HOP)PnPtNP.** This compound could be prepared from either of the corresponding dichloride or diiodide; we present here a representative example. In a flame-dried, 100-mL Schlenk flask equipped with a magnetic stir bar, a suspension of 0.902 g (1.88 mmol) of (HOP)PtCl2 in diethyl ether (50 mL) was cooled to -78°C under an atmosphere of argon. We added 0.6 M solution of npeptidephosphine chloride (7.2 ml, 4.3 mmol) dropwise via cannula. The solution was stirred, and allowed to warm slowly to 0°C. Analysis by TLC (1:1 n-pentane/diethyl ether) showed the reaction to be complete. We added excess H2O slowly to quench excess Grignard reagent. The aqueous phase was extracted with diethyl ether and the extracts dried over magnesium sulfate. Decolorizing carbon (Norit) was added, and the solution was filtered into a 250-mL round-bottomed flask. We concentrated the solution to dryness on a rotary evaporator, and obtained a yellow-green solid. This solid was chromatographed on silica gel with n-pentane as the eluant. The first fraction collected (the column, yellow, absorb in the UV) contained the product. Removal of solvent followed by recrystallization from diethyl ether/methanol yielded 0.683 g (1.42 mmol; 76% yield) of (HOP)PnPtNP. Mp: 106-107°C.1 H NMR (CDCl3, 400 MHz): δ 5.30 (t, J = 7.1 Hz, 4 PnPtNP), 3.30 (sep, J = 1.9 Hz, 2 H), 1.85 (t, J = 7.1 Hz, 4 H), 1.40 (m, 1 H), 1.35 (s, 9 H), 1.28 (m, 1 H), 1.09 (s, 2 H).1 H NMR (CDCl3, 400 MHz): 108.0, 107.3, 106.9, 105.8, 69.23, 69.18, 54.6, 54.0, 53.9, 53.8, 53.5, 46.4, 43.4, 42.4, 41.5, 41.9, 41.8, 37.9, 38.8, 37.5, 38.3, 36.1, 33.6, 35.9, 29.9. Anal. Calcld. for C30H26PnPtCl4: C, 54.64; H, 6.78. Found: C, 54.59; H, 6.56.

A similar synthesis on somewhat larger scale (0.256 g, 0.574 mmol (HOP)PnPtNP) produced 0.163 g (0.322 mmol, 58% yield) of a mixture of 1 (90%) and 2 (10%).6 We used this mixture for the isotopic reductions.

**Homolyphotrophosphate)neopentyl-end2-norbormynagnesium bromide, (HOP)NPb.** A flame-dried, septum-capped, 500-mL round-bottomed flask was charged with a magnetic stir bar was charged with 0.253 g (0.471 mmol) of (HOP)NPb in a minimum amount of diethyl ether, and cooled under argon to -10°C in a salt/ice-water bath. To this stirred solution, we added via cannula the solution containing the endo-2-norbormynagnesium bromide (ca. 18 mmol; vide supra). Over the course of 1 h at -10°C, the solution turned from yellow to brown. Analysis by TLC (1:1 n-pentane/diethyl ether) showed the presence of starting material (Rf ~0.5) and, possible product (Rf ~0.9). Elution with n-pentane showed that the spot at Rf ~0.9 had several components. We quenched the reaction by adding H2O. The aqueous phase was extracted with diethyl ether; the extracts were combined and dried with magnesium sulfate. We added decolorizing carbon (Norit), and filtered the solution into a round-bottomed flask. Rotary evaporation yielded a yellow solid that was chromatographed on silica gel with n-pentane as the eluant. The first yellow fractions showed absorbance in the UV, and contained the desired...
product. Recrystallization from diethyl ether/methanol yielded 30 mg (0.059 mmol, 13% yield) of 2 as yellow needles. Mp: 111–118 °C dec.

1H NMR (CDCl3, 500 MHz): δ 3.79 (t of "t" with Pt satellites, J = 4.5, JPt-H = 52 Hz, 2 H), 5.62 (t of "t" with Pt satellites, J = 4.5, JPt-H = 48 Hz, 1 H), 5.55 (t of "t" with Pt satellites, J = 4.5, JPt-H = 52 Hz, 1 H), 3.03 (br s, 1 H), 2.80 ("t" with Pt satellites, JPt-H = 96 Hz, 1 H), 2.66 (m, 2 H), 2.47 (m, 2 H), 2.42 (m, 2 H), 2.37 (m, 1 H), 1.99 and 1.84 (AB = 11 Hz, 2 H), 1.92 (complex m, 3 H), 1.70 (m, 2 H), 1.35–1.53 (complex m, 4 H), 1.33 (s, 2 H), 1.09 (s, 2 H). Anal. Calcd for C20H20Pt: C, 54.64; H, 6.78. Found: C, 54.58; H, 6.60.

Two subsequent syntheses produced 0.091 g (0.18 mmol, 39% yield) of a mixture of 2 (98%) and 1 (2%), and 0.062 g (0.12 mmol, 26% yield) of a mixture of 2 (97%) and 1 (3%). We used the latter mixture for the isotopic reductions.

Isotopic Analysis of Alkanes-d4. For analyses by GC/MS, we used the average content of deuterium, dav, (eq 2), to describe the isotopic compositions of the alkanes produced in the reductions. In analyses by NMR, the values of dav simply reflect the content of deuterium derived from integrations (vide infra). We believe that all values of dav are accurate to ±5% absolute.

Isotopic analyses by GC/MS were conducted using procedures analogous to those described earlier.10-25 The relevant mass spectral data (m/e (rel intens)) are the following: for norbornane, 96 (100.0) M+, 95 (29.7), 97 (7.2); for HOPH, 148 (100.0) M*, 149 (6.7). Distribution of the ions from norbornane were corrected for (M-1)* by iteratively subtracting from the (n-1)th peak the (M-1)* percentage of the corrected value for the n-th peak, and normalizing the resulting distribution. Distributions of ions for both molecules were corrected for natural abundance of 13C by iteratively subtracting from the n-th peak the (M+1)* percentage of the corrected value for the (n-1)th peak, and normalizing the resulting distribution.69 No other fragment ions with relative abundances >1.0 fell within the range of relevant m/z.

In analyses by 1H NMR, standard integration techniques using Bruker software were used to determine the isotopic content of norbornane-d4 and HOPH-d4. For analyses of norbornane-d4, we integrated H4 and (H2 + H2) relative to H4 (see Figure 3) for analyses of HOPH-d4, we integrated (H4 + H2) and H2 relative to H4 and H2 (see Figure 6). We used a 10-s relaxation delay (relaxation + acquisition time totalled 13 s) to acquire the spectrum.

We used an acquisition time of 2 s to collect the 1H spectra of the norbornanes. No relaxation delay was employed. The resonances at δ 1.12 and 1.42 were integrated relative to each other by enlarging the printed spectra, cutting out the peak areas, and weighing them. Triplicate analyses of each spectrum differed by no more than 0.7%.

Results and Discussion

X-Ray Crystal Structures. Figure 1 and 2 are ORTEP plots of the structures of 1 and 2. These structures are described in detail in the supplementary material to this paper. Each compound clearly possesses a unique stereochemistry of bonding of the norbornyl group to platinum (exo vs endo). The observation that the thermal ellipsoids in Figure 1 are larger than those in Figure 2 might reflect the fact that we collected the structure of 1 at 0 °C, and the structure of 2 at −58 °C.

NMR Spectra of the Norbornanes. Figure 3 shows the 1H and 13C NMR spectra of the norbornanes resulting from the reductions by D2 of samples containing 90% 1 and 10% 2, and 97% 2 and 3% 1. These data show that the reduction of 1 incorporates deuterium into the exo position of norbornane, and the reduction of 2 incorporates deuterium predominantly into the endo position of norbornane. Assuming that the stereochemistry of bonding of the norbornyl moieties to platinum is maintained upon transfer to the surface (vide infra), these results argue that the reduction of C* bonds proceeds with predominant retention of configuration.

Formation of 2-Norbornyl+ Occurs Without Loss of the Stereochemistry of Bonding between the 2-Norbornyl Moieties and Platinum(II). Stereochemical69 and kinetic68 data provide support.
for this contention: the stereochemistry of reduction of the dieolefin moieties of (DO)PtR₂ complexes indicate that the mechanism for reduction of these complexes occurs by initial adsorption at platinum (vide infra). Adsorption at platinum should not invert the stereochemistry of the norbornyl–Pt bond.

The rate-determining step in the heterogeneous hydrogenations of (DO)PtR₂ complexes has not been unambiguously identified, but the activation energy for the reduction of (1,5-cyclooctadiene)dimethylplatinum(II) [(COD)PtMe₂] over platinum black in n-heptane is 15 ± 2 kcal/mol.⁷⁰ and that for inversion at a methyl carbon (e.g., S₃₂₂ displacement on Me₁ and MeBr₂) is typically 15–20 kcal/mol.⁷¹ The similar magnitude of these activation energies suggests that if inversion at carbon occurs in the reductions of (DO)PtR₂ complexes, the rates of these reductions should be influenced by structure in ways similar to those well established for S₃₂₂ reactions. In fact, the reductions of (COD)PtR₂ complexes and S₃₂₂ displacements on alkyl iodides (taken as a representative set) follow very different patterns of relative rates. For the former reaction, the relative rates of reduction are (COD)PtMe₂ (1.0), (COD)PtEt₂ (1.0), (COD)Pt-tBu₂ (0.35), (COD)Pt-iPr₂ (0.40), (COD)Pt(Ph₂)(0.60), and (COD)PtPh₂ (0.60).⁷² For the latter, the relative rates of displacement by Cl⁻ with inversion at carbon are Me₁ (1.0), EtI (0.90), iso-PrI (0.0029), iso-BuI (0.0034), NpI (0.0000013), and PhI (0.0).⁷³ The absence of a correlation between the rates of reduction of (DO)PtR₂ complexes and the rates of inversion at carbon in S₃₂₂ reactions is compatible with the hypothesis that the mechanism for the reduction of the platinum complexes involves retention at C₁ of the R group in the reaction RPt → R*. 

Mass Spectral Analysis of the Norbornanes. Figure 4 provides the mass spectral data for the norbornanes produced in the reductions by D₂ of norbornene, and samples containing 90% 1 and 10% 2, and 97% 2 and 3% 1. Norbornane-d₄ is the major product from reductions of the platinum complexes, and norbornane-d₄ is the major product from the reduction of norbornene.

Table I gives the values of d₄ determined from the mass spectral and ¹H NMR analyses of these norbornanes, and shows that the results from both analytical methods are in good agreement. The fact that these numbers agree indicates that activation of H₄ and H₅ (more correctly, incorporation of deuterium into these positions)

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**Table I. Isotopic Compositions (d₄) of the Alkanes-d₄ from the Reductions by D₂ of 1, 2, Homohyprostophene, and Norbornene**

<table>
<thead>
<tr>
<th>Alkane-d₄</th>
<th>Substrate</th>
<th>d₄ (MS)</th>
<th>d₄ (¹H NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>homohyprostophene</td>
<td>1 (90%) + 2 (10%)</td>
<td>5.22</td>
<td>5.26</td>
</tr>
<tr>
<td></td>
<td>2 (97%) + 1 (3%)</td>
<td>5.24</td>
<td>5.30</td>
</tr>
<tr>
<td>homohyprostophene</td>
<td></td>
<td>3.88</td>
<td>3.84</td>
</tr>
<tr>
<td>norbornane</td>
<td>1 (90%) + 2 (10%)</td>
<td>1.25</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>2 (97%) + 1 (3%)</td>
<td>1.44</td>
<td>1.35</td>
</tr>
<tr>
<td>norbornene</td>
<td></td>
<td>1.98</td>
<td>b</td>
</tr>
</tbody>
</table>

*The values of d₄ are probably accurate to ±5% absolute. The content of deuterium was not determined by ¹H NMR for this substrate.

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**Scheme III. Proposed Reactions of the Norbornyl* Moieties Generated in the Reduction by D₂ of a Mixture of 90% 1 and 10% 2 (Hydrogen Atoms Omitted for Clarity)**

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endo position, and 0.4 D in the exo position. Since the incorporation of deuterium into the endo position does not exceed 1.0 D, the excess deuterium probably does not result from β incorporation of deuterium into the endo* moieties. Scheme IV summarizes the proposed reactions occurring in the reduction of endo*. The incorporation of excess deuterium into endo* moieties probably occurs via α incorporation72,73 and epimerization of ca. 35% of the endo* moieties to exo* moieties followed by β incorporation of deuterium into ca. 20% of these exo* moieties.74 The reactions shown in Scheme IV rationalize the incorporation of excess deuterium, and are in qualitative agreement with the isotopic distributions shown in Figure 4 (ca. 60% norbornane-d1, 20% norbornane-d3, and 10% norbornane-d4) for the reduction of 79% 2 and 3% 1.

In summary, the reduction of exo* moieties occurs via (1) simple reductive elimination (major pathway, ca. 70%), and (2) β incorporation of deuterium prior to reductive elimination (minor pathway, ca. 20%). Since α incorporation into exo* does not occur, α-H activation of exo* probably does not occur; hence, epimerization from exo* to endo* does not occur. The reduction of endo* moieties occurs via (1) simple reductive elimination (major pathway, ca. 65%), and (2) α-H activation and epimerization to exo* followed by reduction of exo* as described above (minor pathway, ca. 35%). Since β incorporation into endo* does not occur, β-H activation (β-H elimination) of endo* probably does not occur.

The reasons for the differences in reactivity between exo* and endo* cannot be determined from the experimental data. In the following two paragraphs, we provide largely speculative rationalizations75 for the apparent differences in reactivity between these surface moieties assuming that the rate-limiting step for production of norbornane is reductive elimination from the surface.30-33

The observation of α-H activation/epimerization of endo* to exo* but not of exo* to endo* can be rationalized on the usual basis of a steric preference for exo by large substituents (here, the surface of platinum). The following argument assumes that the barriers to reductive elimination as norbornane are similar for exo* and endo*. A norbornyl group bonded endo to Pt* is probably energetically destabilized (relative to exo*) due to the unfavorable steric interactions between the distal endo hydrogen and the surface of platinum; consequently, the barrier to conversion of endo* to exo* is relatively low, and the rate of conversion of endo* to exo* is competitive with the rate of reductive elimination of endo-2-norboryl groups from the surface. The transition states for conversion of endo* to exo* and exo* to endo* are probably the same. Since exo* is a more stable surface species than endo*, the barrier to conversion of exo* to endo* is relatively high, and the rate of conversion of exo* to endo* is negligible in comparison to the rate of reductive elimination of exo-2-norboryl groups from the surface.

The observation of β-H elimination in exo* moieties, but not in endo* moieties can also be rationalized assuming that the barriers to reductive elimination as norbornane are similar for exo* and endo*. The formation of endo-norbornene* from endo* is disfavor because endo-norbornene* is destabilized relative to endo* due to increased steric repulsions between the distal endo hydrogens and the surface of platinum. Consequently, the energy of the transition state for β-H elimination in endo* is high relative to that for reductive elimination of this moiety; the rate of β-H elimination is, therefore, negligible compared to the rate of reductive elimination. Formation of exo-norbornene* from exo*
is probably less stericly demanding than formation of endo-nobornene* from endo*. As a consequence, the transition state for β-H elimination in exo* is comparable in energy to that for reductive elimination of this species; hence, the rate of β-H elimination is competitive with that for reductive elimination.

**Mass Spectra of the Neopentanes.** Figure 5 shows the mass spectral data for neopentane-d1 and the neopentanes produced in the reductions by D2 of mixtures of I and 2. No M* ion is observed in the mass spectrum of neopentane: the base peak is the M-CH3* ion. We are reluctant to infer the isotopic compositions of the neopentanes from these data since we do not know isotope effects for loss of, for example, CH2 relative to CH2D; we can, however, infer qualitatively that the neopentanes from the reduction of I and 2 are predominantly composed of neopentane-d1, and that the same isotopic species is (are) produced from both I and 2.

**1H NMR Spectra of the Homohypostrophanes.** Figure 6 compares the 1H NMR spectra of the homohypostrophanes (HOPH-d6) produced in the reduction by H2 of homohypostrophene, and the reductions by D2 of homohypostrophene and samples containing I and 2. The assignments of the 1H resonances are described in the Experimental Section.56,76 In the reduction of homohypostrophene by D2, the loss of the resonance attributed to the exo protons of HOPH indicates that deuterium adds exclusively at the exo positions of HOPH. Analogous reductions of samples containing predominantly 1 or 2 are indistinguishable from one another, and less isotopically cleanly than the reduction of homohypostrophene. In the reductions of I and 2, the loss of the resonance attributed to the endo protons of HOPH predominates: ca. 3.1 H are lost from the endo positions, and 2.1 H are lost from the exo positions. This observation indicates that deuterium adds predominantly to the endo positions of the HOP moiety originally coordinated to platinum in 1 and 2.

Qualitatively, these data suggest that the reduction of coordinated homohypostrophene proceeds with stereochemistry that is predominantly opposite to that of the reduction of free homohypostrophene. The observation that deuterium is incorporated predominantly into the faces of the olefins in homohypostrophene that were coordinated to the platinum atoms in 1 and 2 is consistent with our earlier proposal that adsorption of (DO)PtR3 complexes onto the surface occurs through initial attachment of the platinum atoms of these complexes.50,56 The rationale for this proposal was based on the following: (i) the platinum atom is the most polarizable part of the organometallic complex, (ii) the platinum atom in the complex becomes part of the surface of the catalyst,50 and (iii) the reduction of coordinated nobornadiene (NBD) in (NBD)PtMe2 proceeds with stereochemistry that is predominately opposite to that of the reduction of free NBD.51 Taken together, the stereochemical results from this and the earlier study argue that the adsorption of the diolefin moieties of (DO)PtR2 on the surface of the catalyst proceeds with retention of configuration, and are consistent with our assumption that the adsorption of the nobornyl moieties from 1 and 2 proceeds with retention of configuration (vide supra).

**Mass Spectral Data for the Homohypostrophanes.** Figure 7 provides the mass spectral data for the homohypostrophanes produced in the reductions by D2 of homohypostrophene and mixtures of I and 2. In all cases, the major deuterium isomer produced is HOPH-d4. The reduction of homohypostrophene produces HOPH-d4 relatively cleanly (>60%). Reductions of 1 and 2, however, produce significant quantities of other isomers, HOPH-dn (n = 5–8). The broader distribution of isomers of HOPH produced from the reductions of 1 and 2 relative to that produced from the reduction of homohypostrophene probably results from steric destabilization of the endo,endo-bound surface diolefin, or the endo surface alkyl. This additional strain energy probably allows the rate of other processes (e.g., isomerization of endo-HOP* to exo-HOP*) to become competitive with the rate of reductive elimination from the surface.

**Conclusions**

The major conclusions from this work are the following.

1. The stereochemistry of the reduction of C* bonds by H* (D*) proceeds with retention of configuration. This conclusion is based on the observation that the reduction of I with D2 incorporates deuterium into the exo position of nobornane, and that the reduction of 2 with D2 incorporates deuterium predominantly into the endo position of nobornane. Our proposed mechanisms for the reductions of exo-2-nobornyl* and endo-2-nobornyl* moieties (Schemes III and IV) argue that final reductive elimination of C* bonds from the surface proceeds with absolute retention of configuration. These arguments rely, however, on the correctness of the assumption that the adsorptions of I and 2 to form 2-nobornyl* moieties proceeds without loss of the stereochemistry of bonding between the 2-nobornyl moieties and platinum(II). Support for this assumption is detailed in the Results and Discussion.

2. The reduction of exo-2-nobornyl* moieties is relatively clean; the reduction probably proceeds via simple reductive elimination from the surface (major pathway, ca. 70%), and β-H elimination and incorporation of deuterium prior to reductive elimination from the surface (minor pathway, ca. 20%). The results that support this conclusion are (i) the incorporation of excess deuterium into the exo position of nobornane in the reduction by D2 of a sample containing 90% 1 and 10% 2 and (ii) the distribution of isotopomers of nobornane produced from this reduction.

3. The reduction of endo-2-nobornyl* moieties is less straightforward; the reduction probably proceeds via simple reductive elimination from the surface (major pathway, ca. 65%), and α-H activation and epimerization to exo-2-nobornyl* moieties followed by the reduction of these species as described in conclusion 2 (minor pathway, ca. 35%). This conclusion is supported by (i) the incorporation of excess deuterium into the exo position of nobornane in the reduction by D2 of a sample containing 97% 2 and 3% 1 and (ii) the distribution of isotopomers of nobornane produced in this reaction.

The differences in reactivity between exo* moieties and endo* moieties probably result from greater steric destabilization of endo* moieties.
than of exo*. Repulsions between the surface of platinum and the endo hydrogens of the endo* moieties are responsible for this additional destabilization.

4. The reduction of (DO)PtR₂ complexes occurs via initial adsorption of the platinum atom in the organometallic complex. We proposed this mechanism of adsorption in earlier papers on the basis of the following: (1) the platinum atom is the most polarizable part of the complex; (2) it is incorporated into the surface of the catalyst; (3) stereochemical probes showed that the reduction of norbornadiene by D₂ incorporated deuterium predominantly into the exo positions of norbornane, but the similar reduction of (norbornadiene)dimethylplatinum(II) incorporated deuterium predominantly into the endo positions of norbornane. In this paper, we provide further stereochemical support for this conclusion with the observation that the reduction of homohypostrophe by D₂ incorporates deuterium exclusively into the exo positions of homohypostrophe, but similar reductions of 1 and 2 incorporate deuterium predominantly into the endo positions of homohypostrophe.

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Registry No. 1, 131130-30-8; 2, 131130-31-9; 3, 51175-59-8; 4, 2958-72-7; 5, 54397-80-7; 6, 112710-38-0; HOP, 30114-57-9; HOPH, 59015-02-0; (HOP)PtCl₂, 131130-32-0; (HOP)PtBr₂, 135773-43-2; (HOP)PtN₂, 131130-33-1; (HOP)Pt(NpCl), 131130-34-2; (HOP)Pt(NpI), 131130-35-3; neopentylmagnesium chloride, 13132-23-5; exo-2-norbornylmagnesium bromide, 13058-86-1; endo-2-norbornylmagnesium bromide, 13058-87-2; exo-2-bromonorbornane, 2534-77-2; Zeise’s dimer, 12073-36-8; cyclopentadiene, 542-92-7; benzoquinone, 106-51-4.

Supplementary Material Available: Details of the syntheses of homohypostrophe and its precursors (3–6) and the synthesis of neopentylmagnesium chloride and procedures for the determination of structure, summary of the crystallographic data, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, complete tables of bond distances and angles, anisotropic displacement parameters for non-hydrogen atoms, coordinates for hydrogen atoms, packing diagrams, and UV absorption spectra for 1 and 2 (24 pages); listing of observed and calculated structure factors for 1 and 2 (22 pages). Ordering information is given on any current masthead page.