The Reduction of C* Bonds Proceeds with Retention of Configuration: Stereochemical Investigation of the Heterogeneous Reduction by Dideuterium of (Homohypostrophene)neopentyl(2-norbornyl)platinum(II) Complexes on Platinum Black[1]

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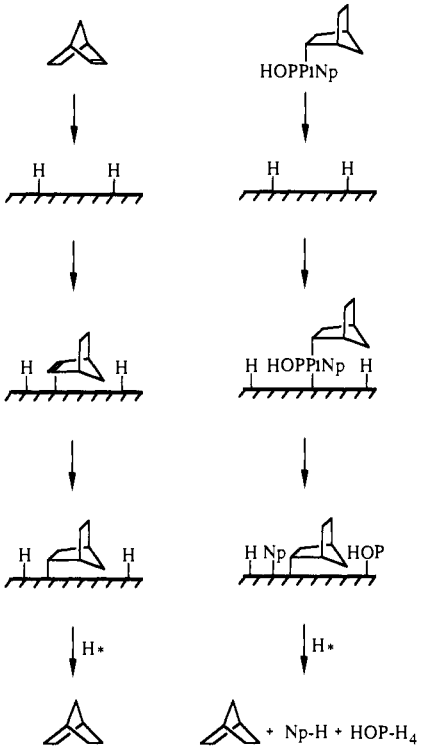
Abstract: This paper reports an investigation of the heterogeneous, platinum(0)-catalyzed reductions by dideuterium of (homohypostrophene)neopentyl(*exo*-2-norbornyl)platinum(II) (**1**) and (homohypostrophene)neopentyl(*endo*-2-norbornyl)-platinum(II) (**2**). The stereochemistries of bonding of the 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 alkanes 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-norbornyl* moieties undergo β-H activation at rates competitive with reductive elimination as norbornanes-d_n; in contrast, approximately 35% of the *endo*-2-norbornyl* moieties undergo α-H activation and epimerization to *exo*-2-norbornyl* at rates competitive with reductive elimination as norbornanes-d_n. 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 tetracyclo-[6.3.0.0^{4,11}.0^{5,9}]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 (diolefin)dialkylplatinum(II) complexes proceeds via initial adsorption of the platinum atom to the surface of the catalyst. Neopentane-d_1 is the major isotopomer of neopentane produced from the reductions of **1** and **2** by D_2.

Introduction

The stereochemical outcome of heterogeneous hydrogenations of olefins on noble metal catalysts has been examined extensively.[2] Despite these efforts and the continuing progress in understanding the structures of hydrocarbons on metal surfaces,[3-24] the stereochemistry of reduction of the C* bond has been defined only by inference. Determining the stereochemistry of reduction of C*

Scheme I. Proposed Analogy between Surface Alkyls Derived from Norbornene (Left) and Those Derived from (Homohypostophene)neopentyl(*exo*-2-norbornyl)platinum(II) (Right) (HOP = Homohypostrophene; Np = Neopentyl)



(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) For reviews, see: Bartók, M. *Stereochemistry of Heterogeneous Metal Catalysis*; Wiley: New York, 1985. Rylander, P. N. *Hydrogenation Methods*; Academic Press: San Diego, 1985. Ozaki, A. *Isotopic Studies of Heterogeneous Catalysis*: Academic: New York, 1977. Burwell, R. L., Jr. *Catal. Rev.* **1972**, *7*, 25-49. Rylander, P. N. *Catalytic Hydrogenation over Platinum Metals*; Academic: New York, 1967.

(3) Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 2288-2293.

(4) Wieckowski, A.; Rosasco, S. D.; Salaita, G. N.; Hubbard, A.; Bent, B. E.; Zaera, F.; Godbey, D.; Somorjai, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 5910-5920.

(5) Zaera, F. *J. Am. Chem. Soc.* **1989**, *111*, 4240-4244.

(6) Beebe, T. P., Jr.; Yates, J. T., Jr. *J. Phys. Chem.* **1987**, *91*, 254-257.

(7) Beebe, T. P., Jr.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1987**, *108*, 663-671.

(8) Soma, Y. *J. Catal.* **1982**, *75*, 267-274.

(9) Wang, P.-K.; Slichter, C. P.; Sinfelt, J. H. *Phys. Rev. Lett.* **1984**, *53*, 82-85.

(10) Wang, P.-K.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1985**, *89*, 3606-3609.

(11) Gay, I. D. *J. Catal.* **1987**, *108*, 15-23.

(12) Chin, Y.-H.; Ellis, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 7653-7654.

(13) George, P. M.; Avery, N. R.; Weinberg, W. H.; Tebbe, F. N. *J. Am. Chem. Soc*, **1983**, *105*, 1393-1394.

(14) Hills, M. M.; Parmeter, J. E.; Mullins, C. B.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 3554-3562.

(15) Parmeter, J. E.; Hills, M. M.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 3563-3569.

(16) Avery, N. R.; Sheppard, N. *Proc. R. Soc. London, A* **1986**, *405*, 1-25.

(17) Avery, N. R.; Sheppard, N. *Proc. R. Soc. London, A* **1986**, *405*, 27-39.

(18) de la Cruz, C.; Sheppard, N. *J. Chem. Soc., Chem. Commun.* **1987**, 1854-1855.

(19) Demuth, J. E. *Surf. Sci.* **1980**, *93*, L82-L88.

(20) Ogle, K. M.; Creighton, J. R.; Akhter, S.; White, J. M. *Surf. Sci.* **1986**, *169*, 246-266.

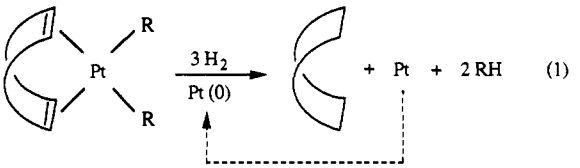
(21) Hitchcock, A. P.; Newbury, D. C.; Ishi, I.; Stöhr, J.; Horsley, J. A.; Redwing, R. D.; Johnson, A. L.; Sette, F. *J. Chem. Phys.* **1986**, *85*, 4849-4862.

(22) Netzer, F. P.; Goldman, A.; Rosina, G.; Bertel, E. *Surf. Sci.* **1988**, *204*, 387-404.

0002-7863/91/1513-8745$02.50/0

bonds using the reduction of olefins requires a critical assumption since the *initial* stereochemistry of the C* bond is not known.[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 bonds.[26-32] In addition, "anchoring" at sites remote from the double bonds increases the selectivity toward cis addition of H_2.[2,33-41] Several studies showed that cis addition of H_2 occurs to the less hindered face of the olefin.[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,[50-56] In this research, we showed that the heterogeneous, platinum-catalyzed hydrogenation of (diolefin)dialkylplatinum(II) complexes ((DO)PtR_2) on platinum black produces diolefin-H_4, 2 equiv of R-H, and platinum(0).[50] The platinum(0) becomes part of the surface of the catalyst, and is catalytically active in subsequent hydrogenations (eq 1).[50,55] This reaction involves (i) adsorption



(1)

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 diolefin moieties originally present in the organometallic complex, and (iii) final reaction of the surface alkyls with surface hydrides to produce alkanes by reductive elimination. This reaction can be used to generate R* of known *initial* structure.[51,52] 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 unspecified reaction occurring on the surface.[50] Under these conditions, the reduction by dideuterium of (1,5-cyclooctadiene)di-*n*-propylplatinum(II) produces 1-propane-d_1 as the major product, and that of (1,5-cyclooctadiene)diisopropylplatinum(II) produces 2-propane-d_1 as the major product. These observations suggest that the regiochemistries of the propylplatinum moieties are preserved on transfer to the surface and on reduction.[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 (homohypostrophene)neopentyl(*exo*-2-norbornyl)platinum(II) (**1**) and (homohypostrophene)neopentyl(*endo*-2-norbornyl)platinum(II) (**2**), and confirmed their structures using X-ray crystallography. We selected homohypostrophene (HOP) as the diolefin 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.[56] 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.[57] Second, the location of the deuterium atoms in the product norbornanes (exo vs endo) could be easily

(23) Land, D. P.; Pettiette-Hall, C. L.; McIver, R. T., Jr.; Hemminger, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 5970-5972.
(24) Pettiette-Hall, C. L.; Land, D. P.; McIver, R. T., Jr.; Hemminger, J. C. *J. Phys. Chem. Soc.* **1990**, *94*, 1948-1953.
(25) The stereochemistry of reduction of C* bonds generated via hydrogenolysis (the reductive cleavage of σ bonds) or hydrogenation of acetylenes is also poorly defined; the C* bonds generated by these methods are probably different (perhaps with the exception of the hydrogenolysis of C-C or C-H bonds) from those generated from olefins. For leading references on the stereochemistry of hydrogenolysis of C-H bonds, see: Kieboom, A. P. G.; van Benschop, H. J.; van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 231-233. Kieboom, A. P. G.; Breyer, A. J.; van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 186-189. Burwell, R. L., Jr.; Shim, B. K. C.; Rowlinson, H. C. *J. Am. Chem. Soc.* **1957**, *79*, 5142-5148. Rowlinson, H. C.; Burwell, R. L., Jr.; Tuxworth, R. H. *J. Phys. Chem.* **1955**, *59*, 225-231. Burwell, R. L., Jr.; Briggs, W. S. *J. Am. Chem. Soc.* **1952**, *79*, 5096-5102. For leading references on the stereochemistry of hydrogenation of acetylenes, see: Ulan, J. G.; Maier, W. F. *J. Mol. Catal.* **1989**, *54*, 243-261. Brunet, J.-J.; Caubere, P. *J. Org. Chem.* **1984**, *49*, 4058-4060. Marvel, E. N.; Li, T. *Synthesis* **1973**, 457-468. Meyer, E. F.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 2877-2880 and 2881-2887. Bond, G. C.; Wells, P. B. *Adv. Catal.* **1964**, *15*, 91-226. Reference 2.
(26) von Wessely, F.; Welleba, H. *Chem. Ber.* **1941**, *74*, 777-785.
(27) Siegal, S.; Smith, G. V. *J. Am. Chem. Soc.* **1960**, *82*, 6082-6087.
(28) Burwell, R. L., Jr.; Littlewood, A. B.; Cardew, M.; Pass, G.; Stoddart, C. T. H. *J. Am. Chem. Soc.* **1960**, *82*, 6272-6280.
(29) Siegal, S.; Smith, G. V.; Dmuchovsky, B.; Dubbel, D.; Halpern, W. *J. Am. Chem. Soc.* **1962**, *84*, 3136-3139.
(30) van Rantwijk, F.; van Vliet, A.; van Bekkum, H. *J. Mol. Catal.* **1980**, *9*, 283-292.
(31) Yanagawa, A.; Suzuki, Y.; Anazawa, I. *J. Mol. Catal.* **1985**, *29*, 41-54.
(32) Ojima, I.; Yatabe, M. *Chem. Lett.* **1982**, 1335-1338.
(33) Thompson, H. W.; Naipawer, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 6379-6386.
(34) Thompson, H. W.; McPherson, E.; Lences, B. L. *J. Org. Chem.* **1976**, *41*, 2903-2906.
(35) Gula, M. J.; Spencer, T. A. *J. Org. Chem.* **1980**, *45*, 805-809.
(36) Johns, W. F. *J. Org. Chem.* **1966**, *31*, 3780-3784.
(37) Horwell, D. C.; Timms, G. H. *Synth. Commun.* **1979**, *9*, 223-231.
(38) Warawa, E. J.; Campbell, J. R. *J. Org. Chem.* **1974**, *39*, 3511-3516.
(39) Mori, K.; Abe, K.; Washida, M.; Nishimura, S.; Shiota, M. *J. Org. Chem.* **1971**, *36*, 231-233.
(40) Powell, R. G.; Madrigal, R. V.; Smith, C. R., Jr.; Mikolajczak, K. L. *J. Org. Chem.* **1974**, *39*, 676-680.
(41) McMurry, J. E. *Tetrahedron Lett.* **1970**, 3731-3734.
(42) Stork, G.; Hill, R. K. *J. Am. Chem. Soc.* **1957**, *79*, 495-500.
(43) Eigenmann, G. W.; Arnold, R. T. *J. Am. Chem. Soc.* **1959**, *81*, 3440-3442.
(44) Cristol, S. J.; Lalonde, R. T. *J. Am. Chem. Soc.* **1959**, *81*, 1655-1659.
(45) Arcus, C. L.; Cort, L. A.; Howard, T. J.; Loc, L. B. *J. Chem. Soc.* **1960**, 1195-1200.
(46) Stork, G.; Schulenberg, J. W. *J. Am. Chem. Soc.* **1962**, *79*, 284-292.
(47) Arnold, D. R.; Trecker, D. J.; Whipple, E. B. *J. Am. Chem. Soc.* **1965**, *87*, 2596-2602.
(48) Cocker, W.; Shannon, P. V. R.; Staniland, P. A. *J. Chem. Soc. C* **1966**, 41-47.
(49) Franzus, B.; Baird, W. C., Jr.; Chamberlain, N. F.; Hines, T.; Snyder, E. I. *J. Am. Chem. Soc.* **1968**, *90*, 3721-3724. Franzus, B.; Baird, W. C., Jr.; Surridge, J. H. *J. Org. Chem.* **1968**, *33*, 1288-1290. Baird, W. C., Jr.; Surridge, J. H. *J. Org. Chem.* **1972**, *37*, 1182-1185.
(50) Miller, T. M.; Izumi, A. N.; Shih, Y.-S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3146-3156.
(51) Miller, T. M.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3156-3163.
(52) Miller, T. M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3164-3170.
(53) Lee, T. Randall; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 2576-2585.
(54) A portion of these results was communicated previously: Lee, T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 368-369.
(55) McCarthy, T. J.; Shih, Y.-S.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 4649-4651. Lee, T. R.; Laibinis, P. E.; Folkers, J. P.; Whitesides, G. M. *Pure Appl. Chem.* **1991**, *63*, 821-828.
(56) Surface alkyls produced from HOP are less reactive in hydrogen donation to the surface than those produced from 1,5-cyclooctadiene (COD): Lee, T. R.; Whitesides, G. M. *Catal. Lett.* **1991**, *9*, 461-472.
(57) Selective synthesis of (DO)Pt(*exo*-2-norbornyl)R seemed possible because the exo Grignard reagent was shown to be more reactive in mixtures of ca. 40% *exo*-2- and 60% *endo*-2-norbornylmagnesium bromide.[58-60] Synthesis of (DO)Pt(*endo*-2-norbornyl)R seemed possible because *endo*-2-norbornyl magnesium bromide can be produced selectively,[58-60] and has a half-life of ca. 30 h at 0 °C.[60]
(58) Jensen, F. R.; Nakamaye, K. L. *J. Am. Chem. Soc.* **1966**, *88*, 3437-3438.
(59) Davies, A. G.; Roberts, B. P. *J. Chem. Soc. B* **1969**, 317-321.
(60) Root, K. S.; Hill, C. L.; Whitesides, G. M. Unpublished results.

resolved by using ^1H (or ^2H) NMR spectroscopy.[47,51,61] 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)PtNpCl was selective (≥90% **1** produced), but analogous reaction with (HOP)PtMeCl was not. Second, the substitution of neopentyl groups for methyl groups improved the crystallinity of (DO)PtR_2 complexes.

Reduction of these complexes with dideuterium over platinum black in alkane solvents generated deuterated norbornanes via intermediate 2-norbornyl* moieties of known stereochemistry. We determined the location of the deuterium atoms in these norbornanes using ^1H and ^2H NMR spectroscopy, and analyzed the alkanes produced in these reductions by GC/MS. Finally, ^1H NMR spectroscopy was used to locate the deuterium atoms in the homohypostrophanes produced in the reductions by D_2 of free homohypostrophene, and of samples containing **1** and **2**.

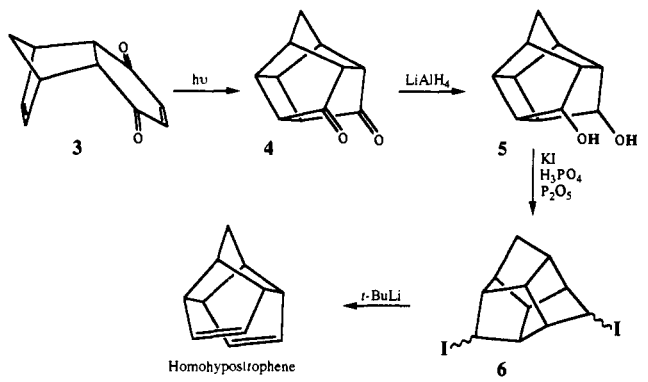
Experimental Section

General Procedure. We purchased *n*-pentane (99+%, 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 (Mallinckrodt) was distilled from Na/benzophenone. We purchased platinum black (lot numbers 10410HT and 03019KT), neopentyl chloride (99%), *exo*-2-bromonorbornane (98%), norbornene (99%), benzophenone (99%), pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (98%), *tert*-butyllithium (1.7 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(μ-chloro)dichlorobis(ethylene)diplatinum(II) (Zeise's dimer, Strem) and dideuterium (99.5 atom % D, Matheson) were used as received. Cyclopentadiene was distilled from dicyclopentadiene (Aldrich, 97%), and benzoquinone (Baker) was recrystallized from petroleum ether.

We collected the ^2H NMR spectra on a Bruker WM 300 spectrometer operating at 46.03 MHz with broad-band ^1H decoupling, and referenced to C_6D_6 (δ 7.15 ppm). Melting points were obtained in capillaries sealed under vacuum. We used a Hewlett-Packard 5992A 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 from kinetics run on a Gilford 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 ^1H NMR coupling constants of homohypostrophane (HOPH) were calculated with Macromodel V2.0 using the MM2(85) parameter set.[62] Oneida Research Co. performed the elemental analyses.

Procedure for Reductions. Each reduction was performed as follows. A 20-mL pressure-bottle reactor (purchased from Lab Glass, and silanized as described previously[50]) was charged with 30 mg of platinum black and a football-shaped (10 × 6 mm) magnetic 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/ethylene glycol (1:1, v/v) regulated by a Neslab Cryocool at −20 ± 1 °C. Solvent (1 mL) was added, and dideuterium was admitted to the reactor through 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; the pressure reported is probably accurate to ±5%). 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)[63] was cooled to −20 °C and added to the catalyst via 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.

Scheme II. Synthesis of Homohypostrophene



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)PtR_2 in alkane[50] and protic solvents[53] under the conditions used here showed that, for a wide variety of diolefins 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, (norbornadiene)dimethylplatinum(II), react autocatalytically with H_2,[50] 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*-heptane without any catalyst present. Immediately after addition of the dissolved platinum complexes, we removed an aliquot (t = 0)[64] 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 μL 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^{4,11}.0^{5,9}]undeca-2,6-diene (Homohypostrophene). We synthesized homohypostrophene (ca. 50-g scale) using the method of Smith and Barborak (Scheme II).[65] The details of this synthetic strategy are provided as supplementary material. Since we observed that homohypostrophene 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 homohypostrophene when desired.

Synthesis of Tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecane (Homohypostrophane, HOPH). Homohypostrophane (HOPH) is the product from the reduction of homohypostrophene with H_2 over platinum black. Following the procedure for reductions outlined above, we hydrogenated 0.104 g (0.72 mmol) of homohypostrophene 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 (0.52 mmol; 72%) of HOPH as a waxy white solid. Mp: sublimed. MS: m/e (rel intens) 148 (38) M$^+$, 119 (49), 91 (55), 81 (51), 80 (64), 79 (76), 77 (40), 67 (100), 66 (95), 41 (76), 39 (94), 27 (68). ^1H NMR ($CDCl_3$, 500 MHz, Figure 6):[66] δ 2.06 (m, 2 H, H_a), 1.98 (br s, 4 H, H_b), 1.56 (br d, 4 H, J = 8 Hz, H_c), 1.46 (s, 2 H, H_d), 1.45 (br d, 4 H, $J \approx 8$ Hz, H_e). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 48.1, 43.0, 30.4, 25.5. Anal. Calcd for $C_{11}H_{16}$: 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

(61) Kitching, W.; Atkins, A. R.; Wickham, G.; Alberts, V. *J. Org. Chem.* **1981**, *46*, 563–570.
(62) Still, W. C.; Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T. *MacroModel V2.0*; Department of Chemistry, Columbia University, New York, NY.
(63) Reductions of homohypostrophene and norbornene were performed similarly.
(64) In ref 50, we described in detail 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 ^1H NMR analysis (COSY), and coupling constants calculated by using MacroModel V2.0:[62] for HOPH, MacroModel V2.0 predicts that the coupling between H_b and H_e is 8 Hz, and that between H_b and H_c is 1 Hz; a 2D COSY spectrum confirms that, on the basis of our assignment, the coupling between H_b and H_e is greater than that between H_b and H_c.

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[67] of these solutions typically showed the solutions to be 0.6–0.7 M in 2-norbornylmagnesium bromide (ca. 60–70% yield). According to prior reports, these solutions contained a mixture of ca. 40% *exo*- and 60% *endo*-2-norbornylmagnesium bromide.[58,60]

***endo*-2-Norbornylmagnesium Bromide.** This Grignard reagent was synthesized using a variation on established procedures.[58,60] We transferred under argon 50.0 mL (30.0 mmol) of a 0.6 M solution of 2-norbornylmagnesium 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 a −10 °C salt/ice–water bath, and stirring was initiated. We added via cannula a 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-norbornylmagnesium bromide,[58,60] was stored at −78 °C, and used shortly thereafter.

Synthesis of Platinum Complexes. (Homohypostrophene)platinum(II) Dichloride (HOP)PtCl$_2$. Under argon, we added 3.51 g of a 3:1 mixture of homohypostrophene/trishomocubane (ca. 18 mmol of homohypostrophene) 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)PtCl$_2$ as white needles (53% yield based on platinum). Mp: 252–300 °C dec. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.38 ("t" with Pt satellites, J_{Pt-H} = 78 Hz, 4 H), 3.27 ("t" with Pt satellites, J_{Pt-H} = 26 Hz, 4 H), 3.21 (m, 2 H), 1.85 (s, 2 H). Anal. Calcd for $C_{11}H_{12}PtCl_2$: C, 32.21; H, 2.95. Found: C, 32.22; H, 2.65.

(Homohypostrophene)platinum(II) Diiodide, (HOP)PtI$_2$. The diiodide was obtained in quantitative yield from (HOP)PtCl$_2$ by suspending the dichloride in acetone, 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)PtI$_2$ as yellow needles. Mp: 247–285 °C dec. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.47 ("t" with Pt satellites, J_{Pt-H} = 78 Hz, 4 H), 3.30 (sep, J = 1.8 Hz, 2 H), 3.15 ("t" with Pt satellites, J_{Pt-H} = 27 Hz, 4 H), 1.93 (s, 2 H). Anal. Calcd for $C_{11}H_{12}PtI_2$: C, 22.28; H, 2.04. Found: C, 22.25; H, 2.02.

(Homohypostrophene)dineopentylplatinum(II), (HOP)PtNp$_2$. This compound could be synthesized from either 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)PtI$_2$ in diethyl ether (50 mL) was cooled to −78 °C under an atmosphere of argon. We added a 0.6 M solution of neopentylmagnesium 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 H_2O 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 off the column (yellow, absorbs 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)PtNp$_2$. Mp: 106–107 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 5.62 ("t" with Pt satellites, J_{Pt-H} = 51 Hz, 4 H), 2.66 (sep, J = 1.8 Hz, 2 H), 2.43 (br s, 4 H), 2.12 ("t" with Pt satellites, J_{Pt-H} = 92 Hz, 4 H), 1.37 (s, J_{Pt-C} = 124 Hz, 18 H), 1.09 (s, 2 H). Anal. Calcd for $C_{21}H_{34}Pt$: C, 52.37; H, 7.12. Found: C, 52.63; H, 6.95.

(Homohypostrophene)neopentylplatinum(II) Chloride, (HOP)Pt(Np)Cl. In a 50-mL round-bottom flask equipped with a magnetic stir bar, we dissolved 1.05 g (2.18 mmol) of (HOP)PtNp$_2$ in a minimum amount of *n*-pentane, and added 1 mL of concentrated HCl. After stirring for 2 h at room temperature, a white precipitate had formed, and analysis by TLC (1:1 *n*-pentane/diethyl ether) indicated that the reaction was complete. The solution was neutralized by adding saturated sodium bicarbonate solution. We extracted the aqueous phase with diethyl ether, and dried the organic phase over magnesium sulfate. After filtration, rotary evaporation yielded an off-white solid that was chromatographed on silica gel (1:1 *n*-pentane/diethyl ether), and recrystallized from diethyl ether to afford glassy pale yellow plates of (HOP)Pt(Np)Cl (0.888 g, 1.99 mmol; 91% yield). Mp: 148–149 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.40 (t of "t" with Pt satellites, J = 3, J_{Pt-H} = 44 Hz, 2 H), δ 5.20 (t of "t" with Pt satellites, J = 3, J_{Pt-H} = 91 Hz, 2 H), 3.23 (m, 1 H), 3.10 (m, 1 H), 3.04 (br m, 2 H), 2.91 (br m, 2 H), 1.66 ("t" with Pt satellites, J_{Pt-H} = 76 Hz, 2 H), 1.59 (br s, 2 H), 1.07 (s, J_{Pt-C} = 124 Hz, 9 H). Anal. Calcd for $C_{16}H_{23}PtCl$: C, 43.10; H, 5.20. Found: C, 43.21; H, 4.99.

(Homohypostrophene)neopentylplatinum(II) Iodide, (HOP)Pt(Np)I. This compound was obtained from the corresponding chloride in quantitative yield by dissolving the chloride in a minimum amount of acetone, saturating the solution with KI (the solution turns from clear to yellow immediately upon addition of KI), and stirring for 2 days. Aqueous workup and extraction with diethyl ether followed by recrystallization from hot diethyl ether yielded (HOP)Pt(Np)I as yellow prisms. Mp: 143–144 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.41 (t of "t" with Pt satellites, J = 3, J_{Pt-H} = 48 Hz, 2 H), δ 5.35 (t of "t" with Pt satellites, J = 3, J_{Pt-H} = 89 Hz, 2 H), 3.26 (m, 1 H), 3.10 (m, 1 H), 2.97 (br m, 2 H), 2.91 (br m, 2 H), 2.07 ("t" with Pt satellites, J_{Pt-H} = 81 Hz, 2 H), 1.63 (br s, 2 H), 1.09 (s, J_{Pt-C} = 124 Hz, 9 H). Anal. Calcd for $C_{16}H_{23}PtI$: C, 35.76; H, 4.31. Found: C, 35.87; H, 4.21.

(Homohypostrophene)neopentyl(*exo*-2-norbornyl)platinum(II), 1. Under argon, we added via cannula 30.0 mL (18.0 mmol) of a 0.6 M solution of 2-norbornylmagnesium bromide (ca. 45% exo and 55% endo) in diethyl ether to a flame-dried 100-mL Schlenk flask equipped with a magnetic stir bar. We placed the flask in a −10 °C salt/ice–water bath, and added dropwise via cannula a yellow solution containing 0.252 g (0.565 mmol) of (HOP)Pt(Np)Cl in diethyl ether. After 1 h, the solution had darkened; analysis by TLC (1:1 diethyl ether/*n*-pentane) showed that the reaction was complete. We added H_2O to destroy the excess Grignard reagent, extracted the aqueous phase with diethyl ether, combined the organic phases, and dried them over magnesium sulfate. After decolorizing carbon (Norit) was added, the solution was filtered into a round-bottomed flask, and concentrated to a yellow oil. This oil was chromatographed on silica gel with *n*-pentane as the eluant. The first few fractions (yellow, absorbs in the UV) were collected, and evaporated to dryness. The resulting yellow solid, recrystallized from diethyl ether/methanol, gave 83 mg (0.164 mmol, 29% yield) of a mixture of **1** (96%) and **2** (4%).[68] Mp: 98–120 °C dec. ^{1}H NMR (C_6D_6, 500 MHz): δ 5.55–5.80 (complex m, 4 H), 2.6–2.7 (complex m, 2 H), 2.35–2.55 (complex m, 6 H), 2.02 (m, 1 H), 1.88–1.98 (complex m, 1 H), 1.88 and 1.85 (J_{AB} = 11 Hz, 2 H), 1.79 (m, 1 H), 1.63 (m, 1 H), 1.51 (m, 2 H), 1.40 (m, 1 H), 1.35 (s, 9 H), 1.28 (m, 1 H), 1.09 (s, 2 H). ^{13}C NMR (C_6D_6, 125.8 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, 43.3, 42.4, 41.5, 41.3, 39.7, 38.8, 37.5, 36.13, 36.06, 35.97, 29.9. Anal. Calcd for $C_{23}H_{34}Pt$: C, 54.64; H, 6.78. Found: C, 54.62; H, 6.56.

A similar synthesis on somewhat larger scale (0.256 g, 0.574 mmol (HOP)Pt(Np)Cl) produced 0.163 g (0.322 mmol, 58% yield) of a mixture of **1** (90%) and **2** (10%).[68] We used this mixture for the isotopic reductions.

(Homohypostrophene)neopentyl(*endo*-2-norbornyl)platinum(II), 2. A flame-dried, septum-capped, 200-mL round-bottomed flask equipped with a magnetic stir bar was charged with 0.253 g (0.471 mmol) of (HOP)Pt(Np)I 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-norbornylmagnesium 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 ($R_f \approx 0.5$), and possible product ($R_f \approx 0.9$). Elution with *n*-pentane showed that the spot at $R_f \approx 0.9$ had several components. We quenched the reaction by adding H_2O. 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 oil 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

(67) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–168.

(68) We determined the relative percentages of **1** and **2** by comparing the integrals of the resonances at 1.35 (**1**) and 1.33 (**2**). These resonances correspond to the methyl groups of the neopentyl moieties.

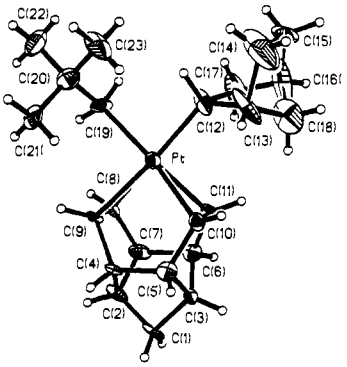


Figure 1. ORTEP drawing (30% probability level, showing atomic labeling scheme) for (homohypostrophene)neopentyl(*exo*-2-norbornyl)platinum-(II) (**1**). The molecule crystallizes in a noncentrosymmetric space group; the absolute configuration *R* was determined crystallographically. The data for this structure were collected at 0 °C.

product. Recrystallization from diethyl ether/methanol yielded 30 mg (0.059 mmol, 13% yield) of **2** as yellow needles. Mp: 111–180 °C dec. ^{1}H NMR (C_6D_6, 500 MHz): δ 5.79 (t of "t" with Pt satellites, J = 4.5, J_{Pt-H} = 52 Hz, 2 H), 5.62 (t of "t" with Pt satellites, J = 4.5, J_{Pt-H} = 48 Hz, 1 H), 5.55 (t of "t" with Pt satellites, J = 4.5, J_{Pt-H} = 52 Hz, 1 H), 3.03 (br s, 1 H), 2.80 ("t" with Pt satellites, J_{Pt-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 (J_{AB} = 11 Hz, 2 H), 1.92 (complex m, 3 H), 1.70 (m, 2 H), 1.35–1.55 (complex m, 4 H), 1.33 (s, 9 H), 1.09 (s, 2 H). Anal. Calcd for $C_{23}H_{34}Pt$: 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%).[68] We used the latter mixture for the isotopic reductions.

Isotopic Analysis of Alkanes-d_n. For analyses by GC/MS, we used the average content of deuterium, d_{av} (eq 2), to describe the isotopic

$$d_{av} = 1/100\sum_{n=1}^{m} n(\%\ \text{alkane-}d_n) \qquad (2)$$

compositions of the alkanes produced in the reductions.[51-53] In analyses by NMR, the values of d_{av} simply reflect the content of deuterium derived from integrations (vide infra). We believe that all values of d_{av} are accurate to ±5% absolute.

Isotopic analyses by GC/MS were conducted using procedures analogous to those described earlier.[51-53] 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 (8.7). Distributions 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 nth peak, and normalizing the resulting distribution. Distributions of ions for both molecules were corrected for natural abundance of ^{13}C by iteratively subtracting from the nth 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 ^{1}H NMR, standard integration techniques using Bruker software were used to determine the isotopic content of norbornane-d_n and HOPH-d_n. For analyses of norbornane-d_n, we integrated H_b and (H_c + H_d) relative to H_a (see Figure 3); for analyses of HOPH-d_n, we integrated (H_d + H_e) and H_c relative to H_a and H_b (see Figure 6). We used a 10-s relaxation delay (relaxation delay + acquisition time totalled 13 s) to acquire the spectra.

We used an acquisition time of 2 s to collect the ^{2}H 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

(69) For analyses of norbornanes, we corrected for $(M - 1)^+$ prior to correcting for natural abundance of ^{13}C. Reversal of this order changed the individual abundances by no more than 1%.

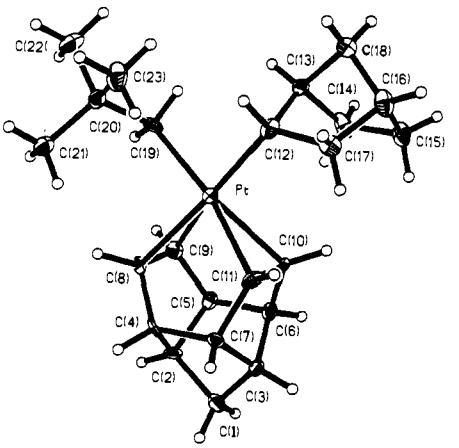


Figure 2. ORTEP drawing (30% probability level, showing atomic labeling scheme) for (homohypostrophene)neopentyl(*endo*-2-norbornyl)platinum-(II) (**2**). The molecule crystallizes in a centrosymmetric space group; the *S* enantiomer is shown. The data for this structure were collected at −58 °C.

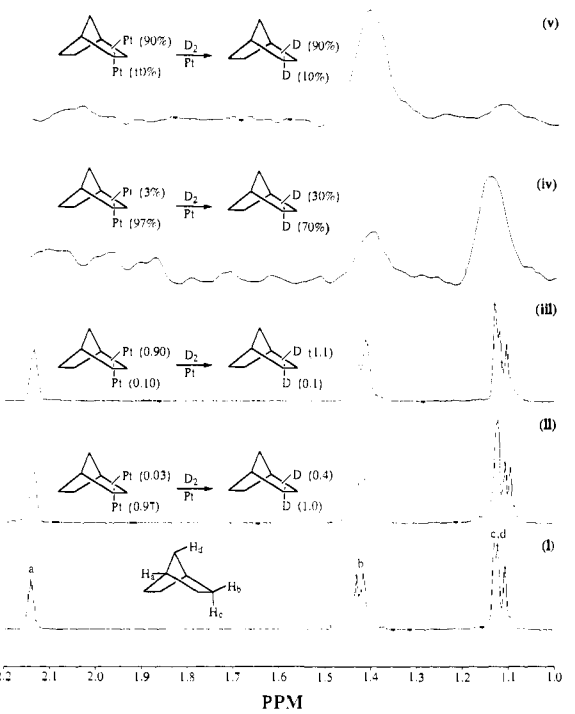


Figure 3. ^{1}H NMR spectra (C_6D_6, 500 MHz) of (i) norbornane-d_0 and the norbornanes from the reduction by D_2 of samples containing (ii) 97% **2** and 3% **1**, and (iii) 90% **1** and 10% **2**; ^{2}H NMR spectra (C_6D_6, 46.03 MHz) of the norbornanes from the reductions by D_2 of samples containing (iv) 97% **2** and 3% **1**, and (v) 90% **1** and 10% **2**.

norbornyl group to platinum (exo vs endo). The observation that the thermal ellipses 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 ^{1}H and ^{2}H NMR spectra of the norbornanes resulting from the reductions by D_2 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). Stereochemical[51] and kinetic[50] data provide support

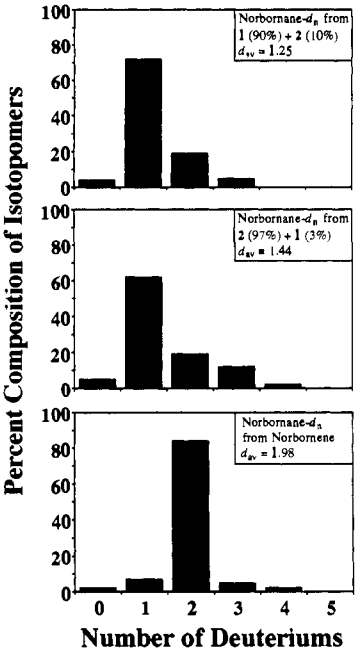


Figure 4. Isotopic distributions determined from the mass spectra of the norbornanes produced from the reductions by D_2 of norbornene (bottom), a mixture of 97% **2** and 3% **1** (middle), and a mixture of 90% **1** and 10% **2** (top). The percent composition shown for each isotopomer is probably accurate to ±5%.

for this contention: the stereochemistry of reduction of the diolefin moieties of (DO)PtR_2 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)PtR_2 complexes has not been unambiguously identified, but the activation energy for the reduction of (1,5-cyclooctadiene)dimethylplatinum(II) ((COD)$PtMe_2$) over platinum black in *n*-heptane is 15 ± 2 kcal/mol,[50] and that for inversion at a methyl carbon (e.g., S_N2 displacement on MeI and MeBr) is typically 15–20 kcal/mol.[70] The similar magnitude of these activation energies suggests that if inversion at carbon occurs in the reductions of (DO)PtR_2 complexes, the rates of these reductions should be influenced by structure in ways similar to those well established for S_N2 reactions. In fact, the reductions of (COD)PtR_2 complexes and S_N2 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)$PtMe_2$ (1.0), (COD)$PtEt_2$ (1.0), (COD)Pt(iso-Pr)$_2$ (0.69), (COD)Pt(iso-Bu)$_2$ (0.40), (COD)$PtNp_2$ (0.23), and (COD)$PtPh_2$ (0.60);[50] for the latter, the relative rates of displacement by Cl^- with inversion at carbon are MeI (1.0), EtI (0.090), iso-PrI (0.0029), iso-BuI (0.0034), NpI (0.0000013), and PhI (0.0).[70] The absence of a correlation between the rates of reduction of (DO)PtR_2 complexes and the rates of inversion at carbon in S_N2 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 D_2 of norbornene, and samples containing 90% **1** and 10% **2**, and 97% **2** and 3% **1**. Norbornane-d_1 is the major product from reductions of the platinum complexes, and norbornane-d_2 is the major product from the reduction of norbornene.

Table I gives the values of d_{av} 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 H_a and H_d (more correctly, incorporation of deuterium into these positions)

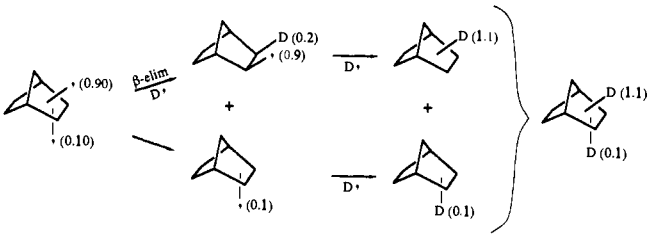
(70) Streiweiser, A., Jr. *Chem. Rev.* **1956**, *56*, 571–752.

Table I. Isotopic Compositions (d_{av}) of the Alkanes-d_n from the Reductions by D_2 of **1**, **2**, Homohypostrophene, and Norbornene[a]

alkane-d_n	substrate	d_{av} (MS)	d_{av} (^1H NMR)
homohypostrophane	**1** (90%) + **2** (10%)	5.22	5.26
	2 (97%) + **1** (3%)	5.24	5.30
	homohypostrophene	3.88	3.84
norbornane	**1** (90%) + **2** (10%)	1.25	1.17
	2 (97%) + **1** (3%)	1.44	1.35
	norbornene	1.98	*b*

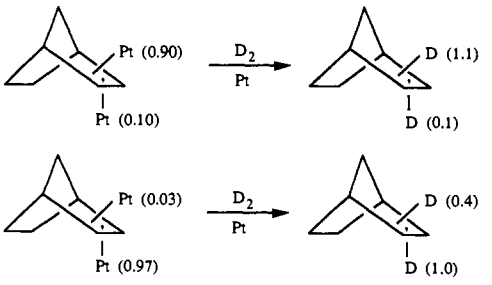
[a] The values of d_{av} are probably accurate to ±5% absolute. [b] The content of deuterium was not determined by ^1H NMR for this substrate.

Scheme III. Proposed Reactions of the Norbornyl* Moieties Generated in the Reduction by D_2 of a Mixture of 90% **1** and 10% **2** (Hydrogen Atoms Omitted for Clarity)



does not occur. The norbornanes produced from both platinum complexes contain more than 1.0 D (the number of equivalents of deuterium expected on the basis of the stoichiometry of the reaction). The incorporation of excess deuterium probably results from either (or both) α-H activation, or β-H activation (β-H elimination) prior to reductive elimination of 2-norbornyl* moieties from the surface (vide infra). Since it is unlikely under these conditions that every activation of a C–H bond results in subsequent incorporation of deuterium, we define an activation–incorporation event as an incorporation (e.g., α incorporation or β incorporation).

The isotopic compositions of the norbornanes produced from the reductions by D_2 of samples containing **1** and **2** are summarized in eqs 3 and 4. Equation 3 shows, for example, that the reduction by D_2 of a mixture of 90% **1** and 10% **2** produces norbornanes, containing 1.1 D in the exo position, and 0.1 D in the endo position. The observation that the incorporation of

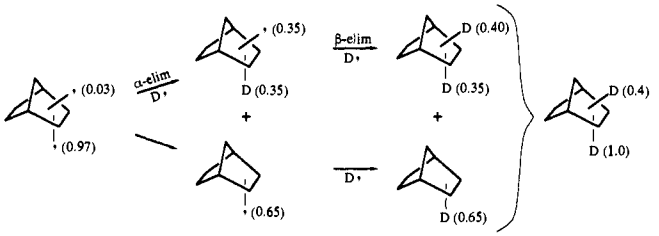


deuterium into the endo position does not exceed 0.1 D suggests that excess deuterium does not result from β incorporation into *endo*-2-norbornyl* (endo*) moieties, nor from α incorporation into *exo*-2-norbornyl* (exo*) moieties. On the other hand, β incorporation[71] of deuterium into ca. 20% of the exo* moieties adequately accounts for the excess deuterium, and is qualitatively consistent with the isotopic distributions shown in Figure 4 (ca. 70% norbornane-d_1 and 20% norbornane-d_2) for the reduction of this mixture. Scheme III summarizes these proposals.

In the reduction of samples containing 97% **2** and 3% **1**, the presence of 3% **1** is not significant, and will not be considered in the discussion here. The total amount of deuterium incorporated into the norbornanes (1.4 D) is described by eq 4: 1.0 D in the

(71) A recent report argues that CH_3CH_2* moieties undergo β-hydride elimination on platinum: Zaera, F. *J. Am. Chem. Soc.* **1990**, *94*, 5090–5095.

Scheme IV. Proposed Reactions of the Norbornyl* Moieties Generated in the Reduction by D_2 of a Mixture of 97% **2** and 3% **1** (Hydrogen Atoms Omitted for Clarity)



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 incorporation[72,73] 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-d_1, 20% norbornane-d_2, and 10% norbornane-d_3) for the reduction of 97% **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 rationalizations[75] 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.[50-53]

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 hydrogens and the surface of platinum; consequently, the barrier to conversion

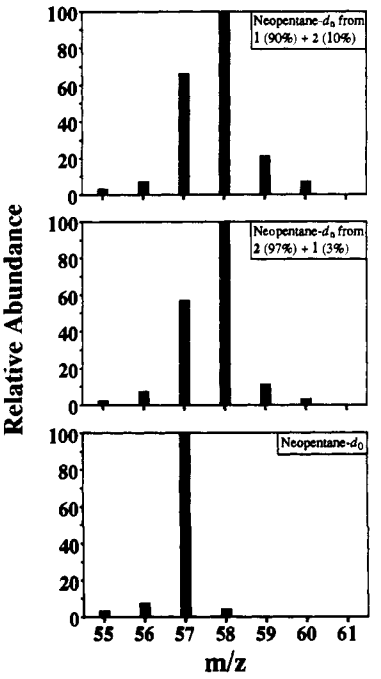


Figure 5. Mass spectra of neopentane-d_0 (bottom) and the neopentanes produced from the reductions by D_2 of a mixture of 97% **2** and 3% **1** (middle) and 90% **1** and 10% **2** (top).

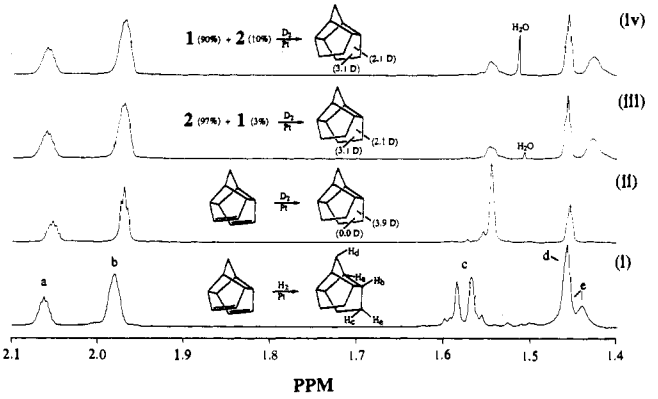


Figure 6. ^1H NMR spectra ($CDCl_3$, 500 MHz) of the tetracyclo-[6.3.0.$0^{4,11}$.$0^{5,9}$]undecanes (homohypostrophanes) from (i) the reduction by H_2 of homohypostrophene,[66] and the reduction by D_2 of (ii) homohypostrophene, (iii) samples containing 97% **2** and 3% **1**, and (iv) samples containing 90% **1** and 10% **2**. The changes in chemical shifts upon substitution of deuterium for hydrogen are probably due to isotope effects.[76]

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-norbornyl 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-norbornyl 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 disfavored 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*

(72) There is much support in the literature for the existence of $\alpha\alpha$-di-σ-absorbed species. See for example: Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *Chem. Phys. Lett.* **1978**, *56*, 267–271. Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *J. Chem. Phys.* **1979**, *70*, 2180–2188. Albert, M. R.; Sneddon, L. G.; Eberhardt, W.; Greuter, F.; Gustafsson, T.; Plummer, E. W. *Surf. Sci.* **1982**, *120*, 19–37. References 6 and 10.

(73) We have indicated that the epimerization of endo* to exo* occurs via $\alpha\alpha$-di-σ-absorbed species. The epimerization might occur, however, via σ-absorbed olefins. See for example: Zaera, F.; Hall, R. B. *J. Phys. Chem.* **1987**, *91*, 4318–4323. Naito, S.; Mitsutoshi, T. *J. Catal.* **1986**, *102*, 377–385. Mintsa-Eya, V.; Hilaire, L.; Choplin, A.; Tourode, R.; Gault, F. G. *J. Catal.* **1983**, *82*, 267–278. References 5 and 19.

(74) We did not detect norbornene during reductions of **2**; this observation does not, however, rule out the possibility that desorption of norbornene occurs during the reduction.

(75) We phrase the arguments in terms of kinetics; thermodynamics might, however, be responsible for the observations: we believe that exo* is lower in potential energy than endo*; this difference in potential energy could influence the incorporation of deuterium even if these species are in equilibrium.

is probably less sterically 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-d_0, and the neopentanes produced in the reductions by D_2 of mixtures of **1** and **2**. No M^+ ion is observed in the mass spectrum of neopentane; the base peak is the expected $(M - CH_3)^+$ ion. We are reluctant to infer detailed isotopic compositions of the neopentanes from these data since we do not know isotope effects for loss of, for example, CH_3 relative to CH_2D; we can, however, infer qualitatively that the neopentanes from the reduction of **1** and **2** are predominantly composed of neopentane-d_1, and that the same isotopic species is (are) produced from both **1** and **2**.

^{1}H NMR Spectra of the Homohypostrophanes. Figure 6 compares the ^{1}H NMR spectra of the homohypostrophanes (HOPH-d_n) produced in the reduction by H_2 of homohypostrophene, and the reductions by D_2 of homohypostrophene and samples containing **1** and **2**. The assignments of the ^{1}H resonances are described in the Experimental Section.[66,76] In the reduction of homohypostrophene by D_2, the loss of the resonance attributed to the exo protons of HOPH indicates that deuterium adds exclusively to the exo positions of HOPH. Analogous reductions of samples containing predominantly **1** or **2** are indistinguishable from one another, and less isotopically clean than the reduction of homohypostrophene. In the reductions of **1** 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 $(DO)PtR_2$ 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 norbornadiene (NBD) in $(NBD)PtMe_2$ proceeds with stereochemistry that is predominantly 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 $(DO)PtR_2$ on the surface of the catalyst proceeds with retention of configuration, and are consistent with our assumption that the adsorption of the norbornyl 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 D_2 of homohypostrophene and mixtures of **1** and **2**. In all cases, the major isotopomer produced is HOPH-d_4. The reduction of homohypostrophene produces HOPH-d_4 relatively cleanly (>60%). Reductions of **1** and **2**, however, produce significant quantities of other isotopomers, HOPH-d_n (n = 5–8). The broader distribution of isotopomers 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

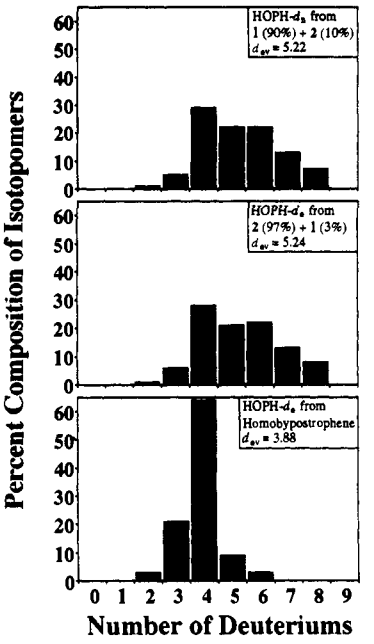


Figure 7. Isotopic distributions determined from the mass spectra of the tetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undecanes (homohypostrophanes) produced in the reductions by D_2 of homohypostrophene (bottom), a mixture of 97% **2** and 3% **1** (middle), and a mixture of 90% **1** and 10% **2** (top). The percent composition shown for each isotopomer is probably accurate to ±5%.

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 **1** with D_2 incorporates deuterium into the exo position of norbornane, and that the reduction of **2** with D_2 incorporates deuterium predominantly into the endo position of norbornane. Our proposed mechanisms for the reductions of *exo*-2-norbornyl* and *endo*-2-norbornyl* 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 **1** and **2** to form 2-norbornyl* moieties proceeds without loss of the stereochemistry of bonding between the 2-norbornyl moieties and platinum(II). Support for this assumption is detailed in the Results and Discussion.

2. *The reduction of exo-2-norbornyl* 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 norbornane in the reduction by D_2 of a sample containing 90% **1** and 10% **2** and (ii) the distribution of isotopomers of norbornane produced from this reduction.

3. *The reduction of endo-2-norbornyl* 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-norbornyl* 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 norbornane in the reduction by D_2 of a sample containing 97% **2** and 3% **1** and (ii) the distribution of isotopomers of norbornane produced in this reaction.

The differences in reactivity between exo* moieties and endo* moieties probably result from greater steric destabilization of endo*

(76) The changes in the chemical shifts of HOPH upon incorporation of deuterium are not due to concentration effects: a mixture (ca. 1:1) of HOPH-d_0 and HOPH-d_4 (from the reduction by D_2 of homohypostrophene) gave chemical shifts consistent with those shown in Figure 6.

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)PtR$_2$ complexes occurs via initial adsorption of the platinum atom in the organometallic complex.* We proposed this mechanism of adsorption in earlier papers[50-56] 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 D_2 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 homohypostrophene by D_2 incorporates deuterium exclusively into the exo positions of homohypostrophane, but similar reductions of **1** and **2** incorporate deuterium predominantly into the endo positions of homohypostrophane.

Acknowledgment. We thank Dr. Shaw Huang for assistance with the ^{2}H NMR experiments. We thank Watson Lees for assistance with the force field calculations and the 2D (COSY) ^{1}H NMR experiments.

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)PtCl$_2$, 131130-32-0; (HOP)PtI$_2$, 135773-43-2; (HOP)PtNp$_2$, 131130-33-1; (HOP)Pt(Np)Cl, 131130-34-2; (HOP)Pt(Np)I, 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 homohypostrophene 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.

Electrochemical Reduction of CO_2 Catalyzed by [Pd(triphosphine)(solvent)]$(BF_4)_2$ Complexes: Synthetic and Mechanistic Studies

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Abstract: The free radical addition of phosphorus-hydrogen bonds to carbon-carbon double bonds has been used to prepare a number of new tridentate ligands containing phosphorus. Reactions of these tridentate ligands with [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ yield the corresponding [Pd(tridentate)(CH$_3$CN)](BF$_4$)$_2$ complexes. These complexes catalyze the electrochemical reduction of CO_2 to CO in acidic dimethylformamide or acetonitrile solutions if the tridentate ligand is a linear triphosphine ligand. Complexes in which one or more of the phosphorus atoms of the tridentate ligand have been substituted with a nitrogen or sulfur heteroatom do not catalyze the electrochemical reduction of CO_2. Kinetic studies on [Pd(etpC)(CH$_3$CN)](BPh$_4$)$_2$ (where etpC is bis[(dicyclohexylphosphino)ethyl]phenylphosphine) show that, at acid concentrations above 1.0×10^{-2} M, the reaction is first order in catalyst, first order in CO_2, and independent of acid concentration. At acid concentrations less than 4.0×10^{-3} M, the catalytic rate is first order in catalyst, second order in acid, and independent of CO_2. The rate is also solvent dependent. A mechanism is proposed to account for these data. Comparison of the rate constants for catalysts with different alkyl and aryl substituents on the terminal phosphorus atoms indicates that the rate of reaction of the palladium(I) intermediates with CO_2 increases with the electron-donating ability of the R groups, and that steric interactions are of less importance. In contrast, the rate constants decrease with increasing steric bulk for substituents on the central phosphorus atoms of the triphosphine ligand. Other relationships between ligand structure and catalyst activity, selectivity, and stability are also discussed. An X-ray diffraction study of the catalytic decomposition product [Pd(etp)]$_2$(BF$_4$)$_2$ (where etp is bis[(diphenylphosphino)-ethyl]phenylphosphine) has been carried out. [Pd(etp)]$_2$(BF$_4$)$_2$ crystallizes in the monoclinic space group $P2_1/n$ with a = 13.842 (6) Å, b = 28.055 (8) Å, c = 19.596 (7) Å, β = 95.80 (3)°, v = 7571 (5) Å^3, and Z = 4. The structure was refined to R = 0.057 and R_w = 0.0809 for 10352 independent reflections ($F > 6\sigma(F)$). This Pd(I) dimer is bridged by two triphosphine ligands. A dihedral angle of 67° exists between the two nearly square planar PdP$_3$ fragments of [Pd(etp)]$_2$(BF$_4$)$_2$. This dimer can be reoxidized to regenerate the catalytically active complexes.

Introduction

The majority of homogeneous catalysts for the electrochemical reduction of CO_2 contain either nitrogen macrocycles[1-8] or bipyridine ligands.[9-13] A number of structurally characterized CO_2 complexes contain phosphine and arsine ligands,[14-16] and metal phosphine complexes catalyze a wide variety of homogeneous reactions.[17,18] However, there have been few reports of transition-metal phosphine complexes catalyzing the electrochemical

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(1) Collin, J.-P.; Sauvage, J.-P. *Coord. Chem. Rev.* **1989**, *93*, 245. This paper is an excellent review of the electrochemical reduction of carbon dioxide.
(2) Meshitsuka, S.; Ichikawa, M.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1974**, 158.
(3) Fischer, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7363.
(4) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 1153.

0002-7863/91/1513-8753$02.50/0