

# HETEROGENEOUS REDUCTIONS OF (HOMOHYPOTROPHENE)DIALKYLPLATINUM(II) COMPLEXES PROVIDE A USEFUL SYSTEM FOR THE STUDY OF INTERMEDIATE SURFACE ALKYL ON PLATINUM [1]

T. RANDALL LEE and George M. WHITESIDES \*

*Department of Chemistry, Harvard University, Cambridge, MA 02138, U.S.A.*

Received 22 March 1991; accepted 13 May 1991

This paper reports a comparison of the ethyl moieties generated on the surface of platinum black during the heterogeneous, platinum-catalyzed hydrogenations of (1,5-cyclooctadiene)diethylplatinum(II) ((COD)PtEt<sub>2</sub>), of (homohypotrophene)diethylplatinum(II) ((HOP)PtEt<sub>2</sub>), and of ethylene using D<sub>2</sub> in ethyl alcohol-*d*. In reductions of the platinum complexes, the  $\pi$ -olefin and  $\sigma$ -alkyl organic ligands are converted to alkanes by reaction of the intermediate surface alkyls with surface hydrides, and the platinum(II) becomes part of the platinum(0) surface. These reductions are characterized by two kinetic regimes: one in which the rate of reaction is limited by the mass transport of hydrogen to the surface of the catalyst (the mass transport limited regime, MTL), and one in which the rate is limited by a reaction on the surface of the catalyst (the reaction rate limited regime, RRL). In the RRL regime, the isotopic compositions of the ethanes-*d<sub>n</sub>* produced from the reductions of the platinum complexes and of ethylene suggest that the surface ethyls (Et\*) generated from each precursor have similar relative rates of isotopic exchange (and thus of C-H bond activation) and of reductive elimination as ethane. In the MTL regime, the Et\* derived from each precursor have different reactivities: the Et\* generated from (HOP)PtEt<sub>2</sub> have reactivities that are more similar to the Et\* generated from ethylene than do the Et\* generated from (COD)PtEt<sub>2</sub>.

**Keywords:** Heterogeneous, hydrogenation, surface alkyls, platinum

## 1. Introduction

We use the heterogeneous, platinum-catalyzed hydrogenation of (diolefin)dialkylplatinum(II) complexes ((DO)PtR<sub>2</sub>, eq. (1)) to generate and study

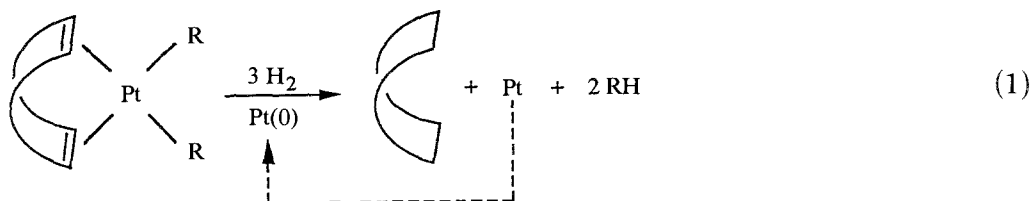


Table 1

Standard conditions for reductions under RRL and MTL conditions

Parameter	RRL	MTL	Remarks
Substrate (mg)	15–20	15–20	(DO)PtEt <sub>2</sub> and HOP <sup>a</sup>
Solvent (mL)	3	3	ethyl alcohol- <i>d</i>
Vessel (mL)	20	20	glass pressure tube
$P_{D_2}$ (atm)	2.4	0.17	
$T$ (°C)	–20	40	
Catalyst (mg)	30	40	platinum black
$S_{Pt}$ (μg-atom) <sup>b</sup>	15	20	established by H <sub>2</sub> /O <sub>2</sub> titration
Stirring (RPM)	1800	1800	rate of rotation of magnetic stir bar (10 × 6 mm)

<sup>a</sup> For reductions of ethylene, we used 1 mL (at 1 atm) of ethylene gas.<sup>b</sup>  $S_{Pt}$  is the quantity of platinum surface atoms ( $0.50 \pm 0.06$  μg-atom/mg Pt black).

surface alkyls on platinum under conditions representative of those used in heterogeneous catalytic hydrogenations of olefins [2–9]. Initial adsorption of the platinum atom in the complex onto the surface of the catalyst generates surface alkyls from the alkyl and diolefin moieties originally present in the soluble complex. Reaction of the surface alkyls with surface hydrides produces alkanes; the platinum(II) becomes part of the platinum(0) surface.

The rate-determining step in these reductions can be chosen to be the mass transport of dihydrogen to the surface of the catalyst (the mass transport limited (MTL) regime), or to be a reaction on the surface (the reaction rate limited (RRL) regime). We have rigorously defined these regimes for reductions of (1,5-cyclooctadiene)dimethylplatinum(II) ((COD)PtMe<sub>2</sub>) in *n*-heptane and in ethyl alcohol; either regime can be selected by appropriately adjusting the temperature and the pressure of dihydrogen (table 1) [2,6]. In both regimes, the kinetics show zero-order dependence on the concentration of the organometallic substrate. Zero-order kinetics are typically observed in heterogeneous hydrogenations of olefins, and are interpreted to indicate that all active sites on the surface of the catalyst are saturated with alkyl groups [10–15].

We rely on deuterium labelling to study the reactivities of surface alkyls on platinum. Interpretation of the isotopic distributions of deuterated alkanes produced from the reductions of (DO)PtR<sub>2</sub> complexes in aprotic solvents is complicated by three processes of H/D exchange: (1) between the surface alkyls derived from the diolefin and the R groups, (2) between H(D) \* and H<sub>2</sub> (or D<sub>2</sub>), and (3) between the surface alkyls and the solvent by activation of the C-H bonds of the solvent [3,6]. Deconvoluting the reactions involving the different species present on the surface can be difficult. We have found that interpretation of the isotopic data can be simplified by performing the reductions in protic solvents, ROH(D), where R = H(D) or alkyl [6,16,17]. The exchange of H/D between ROH(D) and H(D) \* [18–21] is sufficiently rapid that the surface hydrides

(deuterides) equilibrate isotopically essentially completely with the protons (deuterons) in the solvent (eq. (2)). Thus, for reactions carried out using  $H_2$  and ROD, the reducing species present on the surface



is predominantly (or exclusively)  $D^*$ . This rapid conversion of  $H^*$  to  $D^*$  by equilibration with ROD simplifies the study of the reactions of surface alkyls by making inconsequential the three processes of H/D exchange listed above for reductions in aprotic solvents. In addition, the  $H^*$  moieties generated via C-H bond activation of surface alkyls exchange into the solvent. *Thus, for reductions in ROD, most (if not all)  $C^*$  bonds present on the surface of the catalyst are converted to C-D bonds rather than C-H bonds, even when the reducing agent is  $H_2$ .*

This conversion of C-H to C-D by exchange with the surface (and hence with the solvent via the surface) affords a useful method of detecting and characterizing the reactivities of surface alkyls. Specifically, the isotopic composition of the alkanes produced by the reductions of olefins or of  $(DO)PtR_2$  complexes provides a measure of the relative rates of the two pathways summarized in eq (3): irreversible



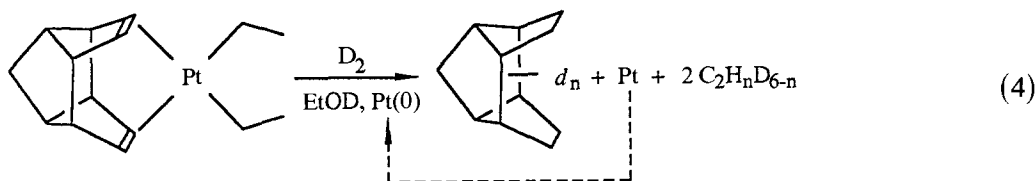
reductive elimination of  $R^*$  groups as alkanes ( $v_1$ ), and (formally reversible) exchange of H/D with the surface to generate partially deuterated surface alkyls  $R^D^*$  ( $v_2$ ). The rate of this exchange ( $v_2$ ) reflects the rate of C-H bond activation of the surface alkyls. By comparing the relative rates of these processes, we can characterize and compare surface alkyls derived from different sources.

In a previous study utilizing reductions in ethyl alcohol-*d* (EtOD), we compared the surface ethyl moieties ( $Et^*$ ) derived from (1,5-cyclooctadiene)-diethylplatinum(II) ((COD)PtEt<sub>2</sub>) with those derived from ethylene [6]. We found that under RRL conditions, the  $Et^*$  moieties derived from both sources had similar relative rates of isotopic exchange (and thus of C-H bond activation) and reductive elimination. Under MTL conditions, however, the  $Et^*$  moieties derived from (COD)PtEt<sub>2</sub> had a slower rate of isotopic exchange relative to the rate of reductive elimination than those derived from ethylene. We hypothesized that the difference under MTL conditions arose from a faster rate of reductive elimination of the  $Et^*$  moieties derived from (COD)PtEt<sub>2</sub> than those derived from ethylene. We proposed that the faster rate of reductive elimination was due to a higher concentration of H(D) $^*$  species near the  $Et^*$  moieties derived from (COD)PtEt<sub>2</sub> than near those derived from ethylene, and that the excess H(D) $^*$

species were generated by loss from coadsorbed COD \* moieties. (Note: although initial loss of hydrogen from COD \* moieties would strictly be as H \* rather than as D \*, we have written H(D) \* to indicate that H \* is converted rapidly to D \* by exchange with EtOD; in fact, the isotopic exchange between H(D) \* and EtOD is sufficiently rapid that interchange of isotopes of hydrogen between diolefin \* and R \* is completely intercepted by exchange with EtOD [6].) Comparison of the incorporation of deuterium into the COD \* moieties generated from (COD)PtEt<sub>2</sub> and free COD provided support for this interpretation: the content of deuterium in the cyclooctanes produced from (COD)PtEt<sub>2</sub> ( $d_{av} = 14.8$ ) was greater than that produced under similar conditions from COD ( $d_{av} = 13.2$ ) [6].

In order to further test these hypotheses, we chose to modify our system by substituting for COD in the (DO)PtR<sub>2</sub> complex a diolefin that is less likely to donate H \* to the surface of platinum via  $\alpha\alpha$ -activation,  $\alpha\beta$ -activation, and/or  $\pi$ -allyl formation [22]. We believed that the incorporation of a relatively inert diolefin would permit the R \* groups generated by reductions of (DO)PtR<sub>2</sub> complexes and olefins (R<sup>(-H)</sup>) to have similar reactivities under RRL conditions and MTL conditions.

This paper reports the reductions by D<sub>2</sub> of (homohypostrophene)diethylplatinum(II) ((HOP)PtEt<sub>2</sub>) on platinum black suspended in ethyl alcohol-*d* (eq. (4)).



We chose homohypostrophene (HOP) as the diolefin for three reasons. First, the rigid structure of HOP \* moieties should inhibit  $\pi$ -allyl formation. Second, the multiple bridgehead carbons in HOP \* moieties should limit  $\alpha\alpha$ - and  $\alpha\beta$ -activation to the carbon centers corresponding to the olefinic positions of HOP [23]. Third, we preferred homohypostrophene over the more readily available (and similarly reactive) norbornadiene (NBD) because (NBD)PtEt<sub>2</sub> undergoes spontaneous decomposition at 0 °C [24], probably by  $\beta$ -H elimination of the ethyl ligands. We chose platinum black as the catalyst in order to eliminate any issues concerning catalyst-support interactions or isotopic impurities originating in the support. We chose EtOD as the solvent because (DO)PtR<sub>2</sub> complexes are readily soluble in EtOD, and because we have a detailed understanding of the kinetics of reduction of these complexes in this solvent. Finally, in order to simplify comparisons between surface alkyls derived by the reductions of different precursors, we chose D<sub>2</sub> rather than H<sub>2</sub> to eliminate possible ambiguities in the origin of deuterium in the products from these reductions.

## 2. Experimental

### GENERAL

Ethyl alcohol-*d* (Aldrich, 99.5 + atom% D) was deoxygenated by purging with argon. The volumes of EtOD used in reductions were measured and transferred with gas-tight syringes. Platinum black (Aldrich, lot number 03019KT) was used as received. The surface area of this catalyst ( $0.50 \pm 0.06 \mu\text{g-atom/mg Pt black}$ ) was measured using standard  $\text{H}_2/\text{O}_2$  titrations [2]. Ethylmagnesium bromide (Aldrich, 3.0 *M* in diethyl ether), ethylene and  $\text{D}_2$  (Matheson, highest purity available) were used without modification. A 10% dideuterium-in-argon mixture was prepared for use in reductions in the MTL regime by evacuating a 10-L gas cylinder, filling it with 1 atm of  $\text{D}_2$ , and pressurizing it to 150 psig with argon.

We measured the UV absorbances of aliquots of  $(\text{DO})\text{PtEt}_2$  in EtOD on a Gilford 240 single-beam spectrophotometer. Procedures for the removal of aliquots have been described previously [2]. Mass spectra were obtained with a Hewlett Packard 5992A GC/MS (70 eV electron impact ionization) using the software for Selected Ion Monitoring from Hewlett Packard. We measured stirring rates (the number of revolutions per minute (RPM) of the football-shaped ( $10 \times 6 \text{ mm}$ ) magnetic stir bars) with a calibrated strobe light.

We conducted the reductions in 20-mL pressure-bottle reactors (Lab Glass) silanized with octadecyltrichlorosilane as described previously [2]. For reductions under RRL conditions, the neoprene septa used to cap the bottles were used as purchased; for reductions under MTL conditions, they were extracted with methylene chloride, and rinsed with ethyl alcohol before use. Reactors were immersed to within  $\sim 1 \text{ cm}$  of their metal crown caps in a large bath of water/ethylene glycol (1 : 1, v : v). The temperature of the bath was controlled to  $\pm 1^\circ \text{C}$  with a Neslab Cryocool ( $T < 0^\circ \text{C}$ ), or a Fisher circulating bath ( $T > 0^\circ \text{C}$ ). The low pressures of  $\text{D}_2$  required for MTL conditions were generated using 10%  $\text{D}_2$ -in-argon mixtures. Dideuterium and 10%  $\text{D}_2$ -in-argon mixtures were admitted to the reactors via syringe needles inserted through the septa of the reactors, and the pressures inside the reactors were measured by similar insertion of a syringe needle attached to a pressure gauge. The pressures reported are probably accurate to  $\pm 5\%$ .

Under MTL conditions, the headspace of the reactors contained insufficient  $\text{D}_2$  for complete reduction of the substrate; consequently, we conducted these reductions with slow leaks ( $\sim 5 \text{ mL/min}$ ) of gas from the reactors. The leaks provided constant pressures of  $\text{D}_2$  over the solutions, and were regulated by fine-metering valves connected to syringe needles inserted through the septa of the reactors.

We performed the reductions as follows. A reaction vessel equipped with a magnetic stir bar was charged with catalyst, capped, purged for  $\sim 10 \text{ min}$  with argon, and placed in the constant-temperature bath. We added 1 mL of EtOD to the reactor by syringe, and initiated stirring. After being purged for 30 s with  $\text{D}_2$

(under RRL conditions) or 10% D<sub>2</sub>/Ar (under MTL conditions), the reactor was held at constant pressure for 10 min. Stirring of the catalyst was stopped; the catalyst was allowed to settle, and the solvent was carefully removed via cannula. For reductions of (DO)PtEt<sub>2</sub> and HOP, we dissolved ca. 15 mg of the substrate in 3 mL of EtOD, and added the solution to the reactor via cannula; for reductions of ethylene, we simply added an additional 3 mL of solvent by syringe, and then 1 mL (at 1 atm) of ethylene gas by gas-tight syringe. Stirring was initiated; simultaneously, a stopwatch was started. The reductions performed under MTL conditions were stopped after 0.5 h, and those performed under RRL conditions were stopped after 1.5 h. For all substrates, analysis by UV, GC, and/or <sup>1</sup>H NMR indicated that conversion to products was complete in the allotted times.

#### SYNTHESIS

Homohydroporphene (HOP) [7], (1,5-cyclooctadiene)diethylplatinum(II) ((COD)PtEt<sub>2</sub>) [25], and (homohydroporphene)platinum(II)dichloride ((HOP)PtCl<sub>2</sub>) [7] are literature compounds. In the following paragraphs, we detail the synthesis of (homohydroporphene)diethylplatinum(II) ((HOP)PtEt<sub>2</sub>).

In a flame-dried 250-mL Schlenk flask equipped with a magnetic stir bar, a suspension of 0.813 g (1.98 mmol) of (HOP)PtCl<sub>2</sub> in dry diethyl ether (ca. 100 mL) was cooled to -78 °C under an atmosphere of argon. To this suspension, we added 2.0 mL (6.0 mmol) of 3.0 M solution of ethylmagnesium bromide in diethyl ether dropwise via cannula. The solution was stirred, allowed to warm slowly to 0 °C, and held at this temperature for 1 h. Analysis of the resulting brown solution by thin layer chromatography (1:1, pentane/diethyl ether; neutral Al<sub>2</sub>O<sub>3</sub> plates) showed the reaction to be complete. We carefully added 20 mL of water to quench any excess Grignard reagent, and poured the mixture into a 250 mL separatory funnel using water and diethyl ether. The layers were separated, and the aqueous phase was extracted twice with 50 mL of diethyl ether. To the combined organic phases, we added MgSO<sub>4</sub> and decolorizing carbon (Norit). Filtration yielded a yellow solution that was concentrated to dryness by rotary evaporation. The resulting yellow solid was chromatographed on silica gel using pentane as the eluant. The fractions containing the product were collected, combined, and evaporated to dryness. Recrystallization from diethyl ether/methyl alcohol yielded 0.440 g (56%) of (HOP)PtEt<sub>2</sub> as yellow plates. Mp (capillary sealed under vacuum): 56–66 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 5.39 ("t" with Pt satellites, *J*<sub>Pt-H</sub> = 52 Hz, 4H), 2.61 (sep, *J* = 1.7 Hz, 2H), 2.38 (br s, 4 H), 1.80 ("t" of q, *J*<sub>Pt-H</sub> = 86 Hz, *J* = 8 Hz, 4H), 1.54 ("t" of t, *J*<sub>Pt-H</sub> = 74 Hz, *J* = 8 Hz, 6H), 1.07 (s, 2H). Anal. calcd. for C<sub>15</sub>H<sub>22</sub>Pt: C, 45.33; H, 5.58. Found: C, 45.50; H, 5.51.

#### ISOTOPIC ANALYSIS

The isotopic compositions of the ethanes-*d*<sub>n</sub> were determined using mass spectral analysis as detailed in a previous report [6]. The location and content of

deuterium in the homohypostrophanes- $d_n$  was determined using  $^1\text{H}$  NMR and mass spectral analyses as reported previously [7]. The average content of deuterium,  $d_{\text{av}}$  (eq. (5)), describes the isotopic composition of the

$$d_{\text{av}} = 1/100 \sum_{n=1}^m n(\% \text{ alkane-}d_n) \quad (5)$$

alkanes- $d_n$  produced from the reductions. Values of  $d_{\text{av}}$  are probably accurate to  $\pm 5\%$  absolute.

### 3. Results and discussion

#### REDUCTIONS IN THE REACTION RATE LIMITED (RRL) REGIME

We compared the isotopic compositions of the ethanes- $d_n$  produced in the platinum-catalyzed reductions of (COD)PtEt<sub>2</sub>, (HOP)PtEt<sub>2</sub>, and ethylene in

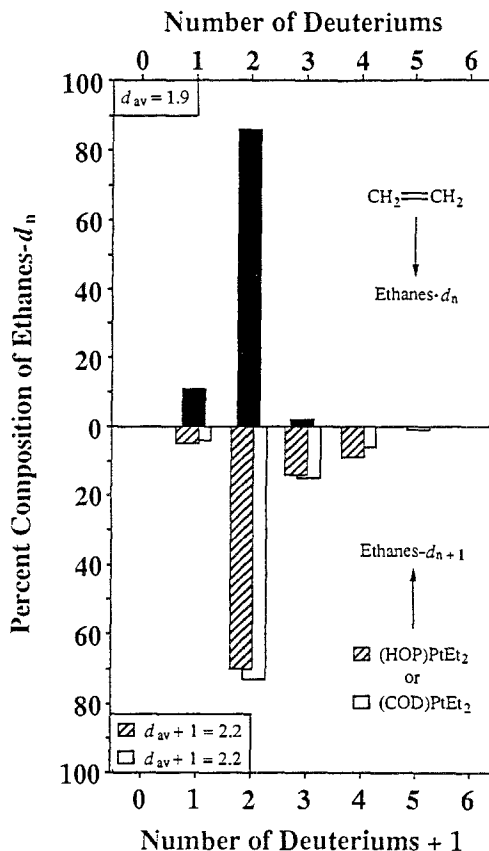


Fig. 1. Percent composition of the isotopomers of ethane as a function of the number of deuterium atoms in the ethanes from the reductions of ethylene (top), and of (COD)PtEt<sub>2</sub> and (HOP)PtEt<sub>2</sub> (bottom) in EtOD under RRL conditions. Values of  $d_{\text{av}}$  from duplicate runs differed by no more than  $\pm 0.2$ .

order to compare the platinum-surface alkyls generated as intermediates in these reactions. In reductions involving  $D^*$ , the  $Et^*$  moieties derived from ethylene should, in principle, incorporate approximately one more deuterium atom than those derived from the  $(DO)PtEt_2$  complexes if the surface ethyls derived from these two types of precursors have similar reactivities (eqs. (6,7)).

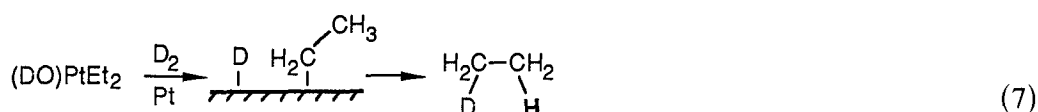
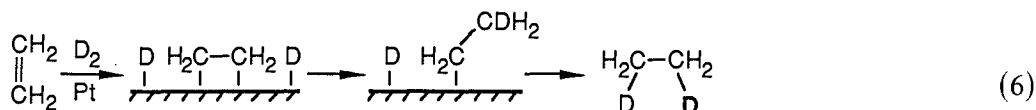
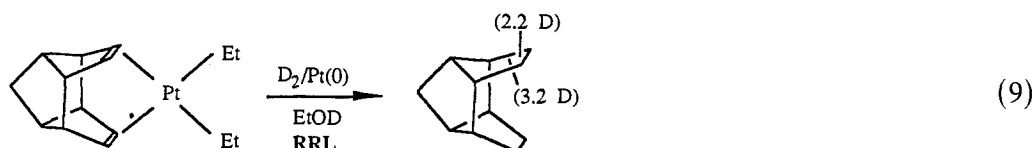
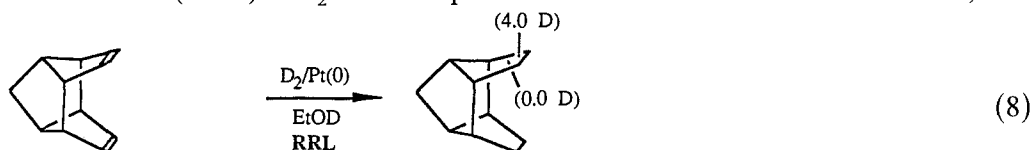


Fig. 1 summarizes the isotopic compositions of the ethanes- $d_n$  produced from these reductions under RRL conditions. These data demonstrate that under RRL conditions, the  $Et^*$  moieties derived from both platinum complexes are very similar, and they have relative rates of reductive elimination and isotopic exchange (and thus C-H bond activation) similar to those derived from ethylene: after correction for one additional deuterium atom, the values of  $d_{av}$  and the isotopic distributions of the ethanes- $d_n$  generated from the platinum complexes are similar to those generated from ethylene.

Eqs. (8) and (9) compare the incorporation of deuterium in the homohypophosphanes (HOPH) produced from the reductions under RRL conditions of HOP and of  $(HOP)PtEt_2$ . These equations show that in reductions of HOP,



deuterium is incorporated into the *exo* positions of  $HOPH-d_n$ , but in reductions of  $(HOP)PtEt_2$ , deuterium is incorporated predominantly into the *endo* positions of  $HOPH-d_n$ . The difference probably results from the different mechanisms of adsorption of the two substrates: adsorption of free HOP occurs on the less sterically congested *exo* faces (forming an *exo* adsorbed species), and adsorption of  $(HOP)PtEt_2$  occurs at platinum (forming an *endo* adsorbed species) [3,7]. Since the reduction of  $C^*$  bonds proceeds with retention of configuration [7],



deuterium is incorporated predominantly into those positions initially attached to the surface of platinum.

The substantial content of deuterium in the *exo* positions of HOPH- $d_n$  derived from the platinum complex results from isomerization of an *endo* adsorbed species to an *exo* adsorbed species. Although we have not investigated the mechanism of this isomerization, the absence of deuterium in the *endo* positions of HOPH- $d_n$  derived from free HOP suggests that isomerization from an *exo* adsorbed species to an *endo* adsorbed species does not occur under these conditions. These data are therefore consistent with the hypothesis that the *endo* adsorbed species are sterically destabilized relative to the *exo* adsorbed species [7]. We believe that this steric destabilization is ultimately responsible for the greater content of deuterium in HOPH- $d_n$  produced in the reduction of (HOP)PtEt<sub>2</sub> ( $d_{av} = 5.4$ ) than that produced in the reduction of free HOP ( $d_{av} = 4.0$ ).

#### REDUCTIONS IN THE MASS TRANSPORT LIMITED (MTL) REGIME

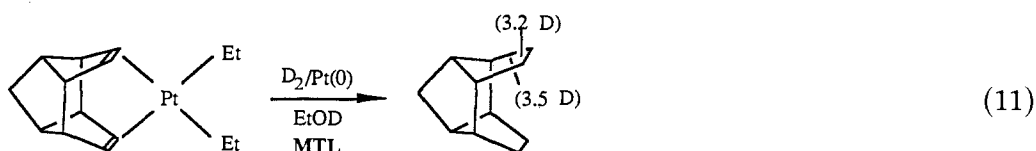
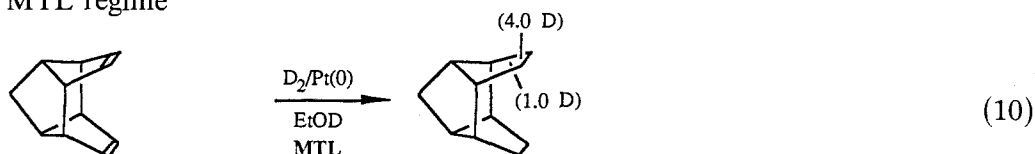
Fig. 2 shows the isotopic distributions and the values of  $d_{av}$  of the ethanes- $d_n$  produced from the reductions of (COD)PtEt<sub>2</sub>, (HOP)PtEt<sub>2</sub>, and ethylene under MTL conditions. The isotopic distributions from ethylene and (COD)PtEt<sub>2</sub> are very different. Ethylene, under these conditions, shows incorporation of approximately 2.2 deuterium atoms in excess of what would be expected from a stoichiometric reduction, and gives rise to C<sub>2</sub>D<sub>6</sub> as the major isotopomer. The excess deuterium atoms plausibly reflect rapid (relative to reductive elimination as ethane), reversible  $\alpha\beta$ -activation and/or  $\alpha\alpha$ -activation of Et \* moieties [26–28].

The incorporation of excess deuterium into Et \* species in substantially less starting from (COD)PtEt<sub>2</sub>: only 0.8D in excess of that required by stoichiometry is incorporated on average, and there are only low yields of highly deuterated isotopomers of ethane. The difference between the isotopic distributions of ethanes from (COD)PtEt<sub>2</sub> and ethylene could have several origins. One obvious possibility that our data argue against [6] is that the conversion of H \* to D \* by exchange with EtOD is slower (or less efficient) in the former than in the latter reaction. Other possibilities are: (1) that coadsorbed COD \* moieties influence the relative rates of reactions of Et \* moieties electronically or (2) by increasing the local concentrations of H(D) \* near the surface ethyl species, (3) that the freshly deposited platinum from (COD)PtEt<sub>2</sub> influences the reactivities of Et \* species or (4) some other reason.

The isotopic distribution of ethanes from (HOP)PtEt<sub>2</sub> lies in between those from ethylene and (COD)PtEt<sub>2</sub>. (HOP)PtEt<sub>2</sub> generates a broad distribution with 1.6 excess deuterium atoms (compared with 0.8 from (COD)PtEt<sub>2</sub> and 2.2 from ethylene) and with substantial ethane- $d_5$  and ethane- $d_6$ , but with ethane- $d_1$  still the major isotopomer. This distribution is compatible with the hypothesis that H(D) \* generation from coadsorbed COD \* moieties is responsible for the restricted range of ethanes- $d_n$  from (COD)PtEt<sub>2</sub>: generation of H(D) \* from

HOP\* moieties would plausibly be slower. These data do not exclude other hypotheses.

Eqs. (10) and (11) compare the incorporation of deuterium in HOPH- $d_n$  produced from the reductions under MTL conditions of HOP and of (HOP)PtEt<sub>2</sub>. For each reduction, the location of deuterium (*exo* vs. *endo*) is qualitatively similar to that observed under RRL conditions. Reduction of free HOP in the MTL regime



does, however, incorporate some deuterium into the *endo* positions of HOPH- $d_n$ . This observation suggests that isomerization of the *exo* adsorbed species to the *endo* adsorbed species occurs only under MTL conditions (where the relatively high temperature affords access to reaction channels not accessible under RRL conditions [6,17]). Nevertheless, the greater content of deuterium found in the *exo* positions (eq. (11); 3.2 D) than that found in the *endo* positions (eq. (10); 1.0 D), argues that isomerization of *endo* to *exo* is favored over the reverse process, and is consistent with our hypothesis that the *endo* adsorbed species are sterically destabilized relative to the *exo* adsorbed species. Again, we propose that this steric destabilization is responsible for the greater content of deuterium in HOPH- $d_n$  produced in the reduction of (HOP)PtEt<sub>2</sub> ( $d_{\text{av}} = 6.7$ ) than that produced in the reduction of free HOP ( $d_{\text{av}} = 5.0$ ).

#### THE MTL REGIME VS THE RRL REGIME

In all of the reductions reported here, the content of deuterium in the product alkanes was greater under MTL conditions than under RRL conditions. We have shown that this behavior is general for surface alkyls on platinum, and reflects the faster rate of C-H bond activation of surface alkyls (relative to the rate of reductive elimination as alkanes) under MTL conditions than under RRL conditions [6,16,17].

#### 4. Conclusion

The heterogeneous platinum-catalyzed reductions of (COD)PtR<sub>2</sub> and (HOP)PtR<sub>2</sub> complexes generate surface alkyls (derived from the R groups) that

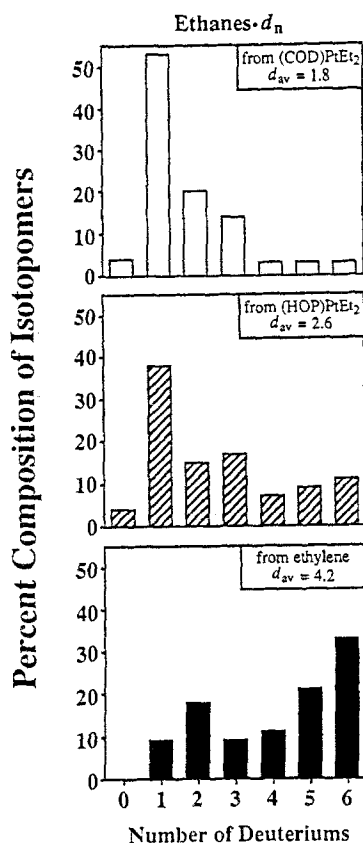


Fig. 2. Percent composition of the isotopomers of ethane as a function of the number of deuterium atoms in the ethanes from the reductions of (COD)PtEt<sub>2</sub> (top), (HOP)PtEt<sub>2</sub> (middle) and ethylene (bottom) in EtOD under MTL conditions. Values of  $d_{av}$  from duplicate runs differed by no more than  $\pm 0.3$ .

are similar, under RRL conditions, to those obtained by reductions of olefins. Specifically, the surface alkyls derived from both types of reactions under RRL conditions have similar relative rates of reductive elimination as alkanes and of isotopic exchange (and thus of C-H bond activation). This conclusion is based on a comparison of the isotopic compositions of the ethanes- $d_n$  produced in the reductions of (COD)PtEt<sub>2</sub>, (HOP)PtEt<sub>2</sub>, and ethylene in EtOD, a solvent that maintains the isotopic composition of the surface hydrides as D \*.

Under MTL conditions, the reductions of (COD)PtEt<sub>2</sub>, (HOP)PtEt<sub>2</sub>, and ethylene generate distinct patterns of isotopomers of ethane, with the extent of incorporation deuterium in excess of that required stoichiometrically increasing in that order. The distribution of ethanes- $d_n$  from (HOP)PtEt<sub>2</sub> is qualitatively intermediate between that from (COD)PtEt<sub>2</sub> and that from ethylene. We propose that (HOP)PtEt<sub>2</sub> differs from (COD)PtEt<sub>2</sub> in being slower to donate H(D) \* to the surface of platinum by loss from the diolefin \* group. In the reductions of

(COD)PtEt<sub>2</sub> complexes under hydrogen-starved MTL conditions, the COD \* moieties provided a source of H(D) \* that led to a faster rate of reductive elimination (relative to the rate of isotopic exchange) than surface ethyls derived from ethylene. The generation of relatively inert HOP \* moieties from (HOP)PtEt<sub>2</sub> decreases the relative rate of production of H(D) \*.

Reductions of (HOP)PtR<sub>2</sub> complexes appear to provide a system for the generation and study of surface alkyls on platinum that is closer to the reduction of olefins than does the reduction of (COD)PtR<sub>2</sub> complexes. Although the isotopic composition of the ethanes produced from (HOP)PtEt<sub>2</sub> and ethylene are still distinct, they are more similar than those from (COD)PtEt<sub>2</sub> and ethylene.

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