

# Heterogeneous platinum-catalyzed hydrogenation of dialkyl-(diolefin)platinum(II) complexes: A new route to platinum surface alkyls

(catalysis/reaction mechanisms)

THOMAS J. MCCARTHY, YEN-SHIANG SHIH, AND GEORGE M. WHITESIDES

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

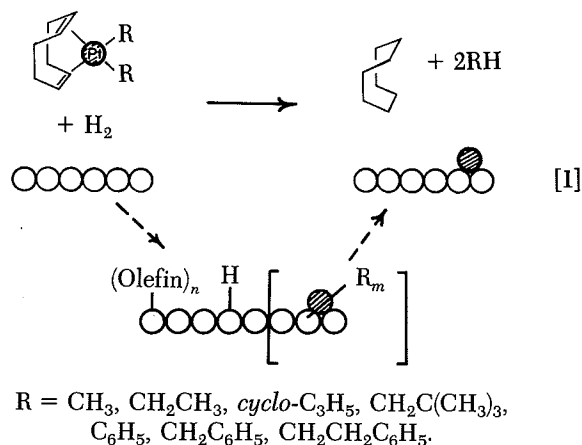
Contributed by George M. Whitesides, March 16, 1981

**ABSTRACT** Platinum metal catalyzes the reduction of dialkyl(diolefin)platinum(II) complexes by dihydrogen to alkanes and platinum(0). The reaction involves adsorption of the platinum(II) complex on the platinum(0) catalyst surface with conversion of the alkyl moieties to platinum surface alkyls; these appear as alkane products. The platinum atom originally present in the soluble organoplatinum species becomes part of the platinum(0) surface.

Platinum surface alkyls are believed to be intermediates in platinum-catalyzed heterogeneous reactions of hydrocarbons (1-8). Among the difficulties encountered in studying the mechanisms of these reactions is that of establishing simultaneously the structure and reactivity of the intermediates. The application of surface spectroscopy to problems in catalysis is beginning to yield valuable structural information concerning surface alkyls under certain conditions, and studies of product distributions, especially using isotopically labeled reactants, have established mechanistically informative patterns of reactivity for (usually) different alkyls under different conditions (9-12). Nonetheless, in no instance are both the structure and the characteristic reactivity of a platinum surface alkyl known, particularly under the conditions prevailing during use of a heterogeneous platinum catalyst in synthesis.

## DISCUSSION

Here we describe experiments in which the platinum-catalyzed heterogeneous hydrogenation of soluble dialkyl(diolefin) platinum(II) complexes (olefin<sub>2</sub>PtR<sub>2</sub>) was examined (Eq. 1).



We propose, on the basis of these experiments, that this reaction involves adsorption of the dialkylplatinum(II) moiety at

the platinum surface; it thus provides the basis for a new method of generating platinum surface alkyls. In this method, the *initial* structure of the organic portion of the surface alkyl is well defined, and these surface species are generated on a working platinum catalyst. The method is thus complementary to techniques used previously in examining heterogeneous reactions catalyzed by platinum and provides a new point of entry into catalytic cycles occurring on platinum.

The reaction of dialkyl(diolefin)platinum(II) complexes in hydrocarbon solution at ambient temperature with dihydrogen (1-3 atm; 1 atm = 1.013 × 10<sup>5</sup> Pa) in the presence of porous glass beads coated with platinum(0) rapidly and quantitatively yields the alkanes derived by hydrogenolysis of the PtR<sub>2</sub> group and hydrogenation of the diolefin. No alkyl dimers are formed. The platinum originally present in the soluble organoplatinum compound is deposited on the surface of the platinum catalyst and *becomes* the catalytic surface for subsequent reduction. The addition of small quantities of thiophene or triphenylphosphine (0.5 mol %, based on olefin<sub>2</sub>PtR<sub>2</sub>) blocks the reduction in a solution containing previously active catalyst; these poisoned catalysts are also inactive for the hydrogenation of cyclohexene.

Kinetic information concerning the reaction was obtained by carrying out reductions using a preformed active platinum catalyst under conditions such that the catalyst surface area remained effectively constant throughout the course of the reaction: reduction of dimethyl(1,5-cyclooctadiene)platinum(II) (CODPtMe<sub>2</sub>) in *n*-decane at 25°C obeyed the empirical rate equation given below:

$$-d[\text{CODPtMe}_2]/dt = k(S_{\text{Pt}})^{0.9 \pm 0.2}(P_{\text{H}_2})^{1.1 \pm 0.2}[\text{CODPtMe}_2]^{0.0 \pm 0.1}, \quad [2]$$

where  $S_{\text{Pt}}$  is the quantity of platinum exposed on the catalyst surface, as measured by titration with H<sub>2</sub> and O<sub>2</sub> and expressed in g-atoms, and  $k = 9 \times 10^{-3} \text{ atm}^{-1} \text{ sec}^{-1}$ . Rate equations of the same form are observed for the hydrogenation of olefins over platinum (13). Reduction of the dialkyl(diolefin)platinum(II) complexes studied here was 2-20% as fast as reduction of cyclohexene. The activation energy ( $E_a$ ) for hydrogenation of CODPtMe<sub>2</sub> is  $\approx 12 \text{ kcal mol}^{-1}$  (1 cal = 4.184 J). This activation energy was derived from rates obtained over a limited temperature range (-15°C to 45°C) and is not very accurate. Its magnitude, and the observation that the rate constant for reaction is independent of agitation, are however sufficient to establish that the rate of reaction is not diffusion or mass-transfer limited.

These observations show that the reduction of CODPtMe<sub>2</sub> by H<sub>2</sub> over platinum is a heterogeneous reaction that resembles the hydrogenation of olefins in its kinetics. In particular, they

The publication costs of this article were defrayed in part by page charge payment. This article must therefore be hereby marked "advertisement" in accordance with 18 U. S. C. §1734 solely to indicate this fact.

Abbreviations: COD, 1,5-cyclooctadiene; CODPtMe<sub>2</sub>, dimethyl(1,5-cyclooctadiene)platinum(II).

establish that the reaction does not proceed by *homogeneous* reaction between  $H_2$  and  $CODPtR_2$  with generation of soluble platinum(0) followed by deposition of this species on a solid surface. They do not, by themselves, establish that the (di)alkylplatinum moieties reach the platinum surface. Evidence supporting adsorption of these alkyl groups on the surface, and suggesting their conversion to surface alkyls, is summarized in Table 1. The observed interchange of hydrogen (deuterium) between diolefin and methyl groups and the formation of multiply labeled methanes are most easily rationalized by a mechanism in which platinum methyl groups exchange hydrogen (deuterium) with a pool of mobile platinum surface hydrogen (deuterium) atoms. The production of deuterated ethane and cyclooctane by hydrogenation of a mixture of  $CODPt(CH_2CH_3)_2$  and (norbornadiene)  $Pt(C^2H_3)_2$  and the observation that both  $C^2H_3O^2H$  and  $^2H_2O$ -saturated ether effectively intercept hydrogen from the surface before it can be incorporated into RH suggest that this hydrogen transfer is not exclusively "intramolecular" in the sense of involving a specific pathway between the diolefin and alkyl moieties originally bonded to a common platinum atom: instead, the hydrogen lost from the diolefin and  $Pt-R$  is accessible to all the other reactants in the system. The catalytic interchange of hydrogen (deuterium) between alkyl groups and a protic solvent during catalytic hydrogenation is, of course, well known (8, 15-17). It is most easily explained by exchange of surface platinum hydrides (as protons) with protons in the solvent. This type of exchange is also rapid for  $d^8$ -transition metal hydrides in homogeneous solution (18, 19).

No  $H^2H$  (<0.01%) is observed in the reduction of  $CODPt(C^2H_3)_2$  with  $H_2$ . As the observation of multiply exchanged methane establishes hydrogen donation from the methyl group to the platinum surface, the absence of  $H^2H$  indicates that dihydrogen chemisorption on the surface is irreversible under the conditions of the reaction.

These experiments, taken together, argue persuasively that the catalytic heterogeneous hydrogenation of (diolefin) $PtR_2$  on platinum involves the production of platinum-surface alkyls derived from the alkyl moieties R. They do not define the extent to which these platinum-surface alkyls resemble those formed in other platinum-catalyzed heterogeneous reactions. Although we have only begun to explore this problem, we have conducted one experiment that demonstrates a similarity in the reactivities of the surface ethyl groups prepared by reduction of  $CODPtEt_2$  and  $CH_2=CH_2$ : that is, the exchange of hydrogen for deuterium. Fig. 1 shows the patterns for isotopic distribution of the deuterated ethanes produced by reaction of  $CODPtEt_2$  and of  $CH_2=CH_2$  with  $^2H_2$  in  $C^2H_3O^2H$ : these patterns differ significantly only in that the ethanes from ethylene contain, as expected from their method of preparation, one additional deuterium. These experiments suggest that the relative rates of exchange (presumably by  $\beta$ -hydride elimination) and alkane formation are similar for these two surface ethyl species. They also establish that the reduction of  $CODPtEt_2$  does not proceed by initial formation of ethylene.

In summary, we propose that the heterogeneous hydrogenation of (diolefin) $PtR_2$  complexes over platinum involves generation of platinum surface alkyls, most plausibly by a pathway involving initial adsorption of  $PtR_2$  moieties at the platinum surface (Eq. 1). The structure of these alkyls *after* adsorption is not defined: we do not know whether the two alkyl groups remain attached to the same platinum atom or are mobile on the surface. In at least one reaction, however (exchange of the hydrogens of platinum surface ethyl with surface deuterium), their reactivity is similar to that of analogous surface alkyls produced by hydrogenation of olefins. Thus, whatever the details of bonding between the alkyl and the platinum surface in these two reactions, they are probably similar. This observation suggests either that the surface alkyl groups *are* mobile or that the rel-

Table 1. Isotopic distribution in hydrocarbon products from heterogeneous hydrogenation of dialkyl(diolefin)platinum(II) compounds

Exp.	Diolefin	Alkyl group	Reducing agent	Solvent	Isotopic distribution, %										Interpretation/comment
					C-1 or C-2					C-7 or C-8					
					$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	
1	$[^2H_{12}]DCD$	$C^2H_3$	$^2H_2$	$C^2H_3O^2H$	0	0	0	5	95						Controls: Ostensibly perdeuterated systems yield 5-8% $C^2H_3H$
2	$[^2H_{12}]DCD$		$^2H_2$	$C_6^2H_{12}$	0	0	0	8	92					No hydrogen exchange from cyclohexane to methyl	
3	$[^2H_{12}]DCD$	$C^2H_3$	$^2H_2$	$C_6H_{12}$	0	0	0	8	92					$^2H$ 0.3 transferred from olefin to methyl	
4	$[^2H_{12}]DCD$	$CH_3$	$H_2$	$C_6H_{12}$	85	12	3	0	0						
5	$[^2H_{12}]DCD$	$C^2H_3$	$^2H_2$	$C_6H_{12}$	0	0	5	37	58					Relative rate of H transfer from olefin to alkyl is $COD > DCD > NBD$	
6	COD	$C^2H_3$	$^2H_2$	$C_6H_{12}$	0	2	15	35	49						
7	NBD	$C^2H_3$	$^2H_2$	$C_6H_{12}$	0	0	0	15	85						
8	NBD	$C^2H_3$	$H_2$	$C_6H_{12}$	0	0	18	80	2	77	19	3	1	0	An average of $\approx 0.34$ $^2H$ is lost per $(C^2H_3)_2$ unit; an average of $\approx 0.37$ $^2H$ reappears in reduced diolefin
9	COD	$C^2H_3$	$H_2$	$C_6H_{12}$	0	0	19	80	1	64	28	6	2	0	
10	COD	$CH_3$	$H_2$	$C_6^2H_{12}$	100	0	0	0	0						
11	COD	$CH_3$	$H_2$	$C^2H_3O^2H$	15	39	23	14	9					Exchange occurs between methyl and protic solvents; multiple exchange occurs at methyl	
12	COD	$CH_3$	$H_2$	$Et_2O/^2H_2O$	23	43	14	12	7						
13	NBD	$C^2H_3$	$^2H_2$	$C^2H_3O^2H$	0	0	0	8	92					With experiments 6 and 7; exchange with protic solvent intercepts hydrogen from olefin	
14	COD	$C^2H_3$	$^2H_2$	$C^2H_3O^2H$	0	0	0	11	89						
15	COD	$C_2H_5$	$H_2$	$C_6H_{12}/8$ equiv. NBDPt- $(C^2H_3)_2$	94	6	0	0	0	73	18	7	2	0	Isotopic distributions for ethane and cyclooctane; deuterium from $C^2H_3$ of one platinum atom reaches alkyl and olefin of another

Reductions were carried out at 25°C and 3 atm  $H_2(^2H_2)$ . The starting concentration of (diolefin) $PtR_2$  was  $\approx 0.01$  M. Isotopic distributions were estimated from literature fragmentation patterns for  $CH_2^2H_2$  (14). Reference spectra for  $C^2H_4$ ,  $C^2H_3H$ ,  $CH_3^2H$ ,  $CH_4$ ,  $C_2H_5^2H$ ,  $C_2H_6$ ,  $C_7H_{12}$ , and  $C_8H_{16}$  were obtained in our laboratory. DCD, dicyclopentadiene; NBD, norbornadiene.

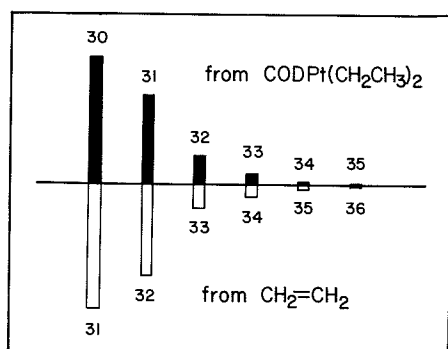


FIG. 1. Relative abundance of ions in the  $M^+$  region of ethane- $^2H_2$ , obtained by platinum-catalyzed reduction of  $CODPt(CH_2CH_3)_2$  and  $CH_2=CH_2$  with  $^2H_2$  in  $C^2H_3O^2H$ . Each value of  $m/e$  is labeled; the spectra are displaced by one mass unit to facilitate comparison.

ative rates of isotopic exchange and reduction are insensitive to details of surface bonding.

This technique has several potential attractions as a method of generating and studying the reactivity of platinum surface alkyls. First, it provides a route to platinum surface organic groups whose *organic* fragment structure (although not organic group-metal bonding) is exceptionally clearly defined and amenable to systematic variation. Thus, it can generate types of surface organic moieties that cannot be obtained by hydrogenation of olefins (e.g., methyl, neopentyl, phenyl, and others that lack a hydrogen  $\beta$  to the C-Pt bond, as well as specifically deuterated species such as  $CH_2C^2H_3$ ) and organic groups that have defined regiochemistry incompatible with alkane exchange reactions (e.g., propyl, isopropyl, benzyl,  $\beta$ -phenylethyl). Further, it generates these organic groups at a platinum surface on which olefin hydrogenation is taking place simultaneously. Thus, the conditions are comparable with those used in catalytic hydrogenation and milder than those used for alkane exchange. Second, its nature [a quantitative reaction forming alkanes and platinum(0)] makes it well suited for the collection of the types of thermochemical data required to characterize catalytic reactions.

This reaction should be useful in defining the characteristic reactivities of species proposed as intermediates in platinum-catalyzed hydrogenation—exchange and dehydrocyclization of alkanes and olefins. Obvious extensions of the technique to organometallic derivatives of other metals should contribute to the elaboration of mechanisms of other heterogeneous catalytic reactions.

## EXPERIMENTAL SECTION

Organoplatinum compounds were prepared by using procedures described elsewhere (20–23).

Catalysts were prepared by reducing  $CODPt(Me)_2$  (100 mg) onto controlled porosity glass (Sigma PG-700-120, 150 mg) with  $H_2$  in cyclohexane. These catalysts had  $\approx 3.5 \times 10^{-5}$  mol of surface platinum per g of catalyst (i.e., platinum plus glass) as measured by dihydrogen-dioxygen titration (24). The measured area of the platinum surface of these catalysts did not change during the course of four kinetic runs.

The form of the platinum deposited during a catalytic reduction of  $CODPtR_2$  depended on the surface available. Reactions initiated in clean vessels containing no solid platinum(0) exhibit pronounced induction periods, followed by rapid reaction accompanied by deposition of platinum metal. This induction period is eliminated by the addition of platinum metal to the reaction mixture before hydrogenation. When no porous

glass or platinum is present, a smooth mirror is formed on the walls of the reaction vessel; when porous glass is added, the platinum coats it as a black solid. Clean platinum foil (25) becomes coated with a dull metallic film. The platinum catalysts used in kinetics studies undergo no qualitative change visible on visual inspection or by scanning electron microscopy.

Kinetics: Rates were followed by monitoring the UV absorbance of the platinum complexes at 280 nm. Products were identified by gas chromatography/mass spectrometry using a Hewlett-Packard model 5990. Mass spectral analysis for  $H^2H$  was carried out on a DuPont 491 instrument.

Isotopic analyses were carried out by using standard techniques (20), making certain to average spectra taken across the width of the gas chromatographic peak. The fact that hydrogen (deuterium) from water ( $^2H_2O$ ) and protic solvents is readily incorporated into hydrocarbon products is an experimental problem: solvents must be thoroughly dried in isotopic exchange experiments.

We are grateful to Mr. James W. Nicoletti for constructing the apparatus used for dihydrogen-dioxygen titration (surface area determination) and to Mr. James Hill for performing the mass spectroscopic analyses of dihydrogen samples (National Institutes of Health Grant DRR 00317 to Prof. K. Biemann). The research was supported by the National Science Foundation through the Massachusetts Institute of Technology Materials Research Laboratory (DMR 78-24185), Grant 80-12722CHE, and a predoctoral fellowship (to T.J.M., 1978–1981). The Materials Research Laboratory provided the electron microscope facilities used in the work.

- Clarke, J. K. A. & Rooney, J. J. (1976) *Adv. Catal.* **25**, 125–183.
- Siegel, S., Outlaw, J., Jr. & Garti, N. (1978) *J. Catal.* **52**, 102–115.
- Webb, G. (1978) in *Catalysis*, Specialist Periodical Reports (Chem. Soc. London, London), Vol. 2, pp. 145–175.
- Csicsery, S. M. (1979) *Adv. Catal.* **28**, 293–321.
- Leclercq, G., Leclercq, L. & Maurel, R. (1973) *J. Catal.* **50**, 87–97.
- Sinfelt, J. H. (1973) *Adv. Catal.* **23**, 91–119.
- Inone, Y., Herrmann, J. M., Schmidt, H., Burwell, R. L., Butt, J. B. & Cohen, J. B. (1978) *J. Catal.* **53**, 401–413.
- Ozaki, A. (1977) *Isotopic Studies of Heterogeneous Catalysis* (Kadansha, Tokyo).
- Muetterties, E. L., Rhodin, T. N., Band, E., Brucker, C. F. & Pretzer, W. R. (1979) *Chem. Rev.* **79**, 93–137.
- Somorjai, G. A. (1977) *Adv. Catal.* **26**, 1–68.
- Prentice, J. D., Lesuinas, A. & Sheppard, N. (1976) *J. Chem. Soc. Chem. Commun.* 76–77.
- Demuth, J. E. (1977) *Chem. Phys. Lett.* **45**, 12–17.
- Thompson, S. J. & Webb, G. (1968) *Heterogeneous Catalysis* (Oliver & Boyd, London), p. 118.
- American Society for Testing Materials (1963) *Index of Mass Spectral Data*, Special Technical Publication No. 356 (A. S. T. M., Philadelphia).
- Garnett, J. L. (1971) *Catal. Rev.* **5**, 229–268.
- Burwell, R. L., Jr. (1973) *Catal. Rev.* **7**, 25–49.
- Frennet, A. (1975) *Catal. Rev.* **10**, 37–68.
- Yoshida, T., Matsuda, T., Okano, T., Kitani, T. & Otsuka, S. (1979) *J. Am. Chem. Soc.* **101**, 2027–2038.
- Walker, H. W., Kresge, C. T., Ford, P. C. & Pearson, R. G. (1979) *J. Am. Chem. Soc.* **101**, 7428–7429.
- Foley, P., DiCosimo, R. & Whitesides, G. M. (1980) *J. Am. Chem. Soc.* **102**, 6713–6725.
- Kistner, C. R., Hutchinson, J. H., Doyle, J. R. & Storlie, J. C. (1963) *Inorg. Chem.* **2**, 1255–1261.
- Clark, H. C. & Manner, L. E. (1973) *J. Organomet. Chem.* **59**, 411–428.
- Müller, J. & Göser, P. (1967) *Angew. Chem. Int. Ed. Engl.* **6**, 364–365.
- Carballo, L., Serrano, C., Wolf, E. E. & Carberry, J. J. (1978) *J. Catal.* **52**, 507–514.
- Richard, M. A., Deutch, J. & Whitesides, G. M. (1978) *J. Am. Chem. Soc.* **100**, 6613–6625.