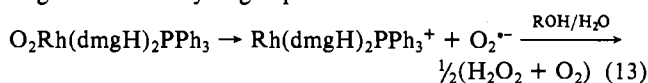


dissociate to a Rh(III) complex and superoxide ions, which in turn form hydrogen peroxide by disproportionation, as shown by eq 13.²⁵ In that case, 1 mol of the original rhodium dimer reacts to give 1 mol of hydrogen peroxide.



(25) We discount a possible reaction between the superoxo complex and additional Rh(dmgh)₂PPh₃, because (as pointed out by a reviewer) such a reaction, in competition with eq 4, would require an impossibly high bimolecular rate constant.

Acknowledgment is made to the National Science Foundation for support under Grant CHE-84-18084. Some of this work was accomplished with the facilities of Ames Laboratory, operated by Iowa State University for the U.S. Department of Energy under Contract W-7405-Eng-82.

Registry No. Rh(dmgh)₂PPh₃, 21057-94-3; CCl₄, 56-23-5; CHCl₃, 67-66-3; CBr₄, 558-13-4; CHBr₃, 75-25-2; CH₂Br₂, 74-95-3; CH₂CHC-H₂Br, 106-95-6; CH₂BrCH₂Br, 106-93-4; CH₃I, 74-88-4; CH₃CH₂I, 75-03-6; CH₃CH₂CH₂I, 107-08-4; CH₃CHICH₃, 75-30-9; *p*-MePhCH₂Br, 104-81-4; PhCH₂Br, 100-39-0; *p*-BrPhCH₂Br, 589-15-1; *m*-BrPhCH₂Br, 823-78-9; *p*-CF₃PhCH₂Br, 402-49-3; *m*-CF₃PhCH₂Br, 100-11-8.

Contribution from the Corporate Science and Technology Center and Corporate Research Services Department, Air Products and Chemicals, Inc., Allentown, Pennsylvania 18195

Synthesis and Characterization of *trans*-(PMe₃)₂PtHCl and an Investigation of Its Role in Olefin Hydration Catalysis

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Received March 11, 1988

Analytically pure *trans*-(PMe₃)₂PtHCl was synthesized and examined for its ability to catalyze the anti-Markovnikov hydration of terminal olefins. Although this catalyst has been reported to give high selectivities to primary alcohols, our attempts to hydrate 1-hexene in a basic aqueous medium in the presence of a phase-transfer agent or surfactant and pure *trans*-(PMe₃)₂PtHCl failed to yield any alcohol products. In addition, spectroscopic studies failed to confirm nucleophilic attack of hydroxide ion on coordinated olefins in this system. Instead, the predominant reaction under a variety of conditions was olefin isomerization.

Introduction

The catalytic hydration of terminal olefins to primary alcohols would be an important route to industrially useful alcohols. In a recent report, Jensen and Trogler¹ claimed the direct anti-Markovnikov hydration of terminal olefins using a soluble platinum catalyst. This would represent a revolutionary improvement over current methods of manufacturing primary alcohols² and has received a great deal of attention.³ The published results claim that *trans*-(PMe₃)₂PtHCl in a 1:1 mixture of 0.4 M aqueous NaOH and 1-hexene forms a species that, at 60 °C and in the presence of benzyltrimethylammonium chloride, catalyzes selective hydration to 1-hexanol.

Efforts in our laboratories to reproduce this catalysis have been unsuccessful. In this paper, we provide details of our attempts to effect the claimed catalysis and also present some interesting spectroscopic results observed during our studies.

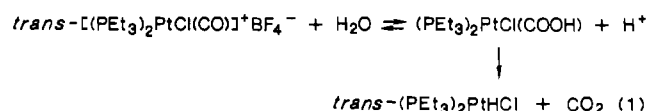
Our work was initially hampered by the fact that literature methods for the preparation of *trans*-(PMe₃)₂PtHCl do not yield analytically pure material or fail to provide any information on analytical purity. For example, *trans*-(PMe₃)₂PtHCl was first prepared by Chatt and Shaw in 1962 via the reduction of *cis*-(PMe₃)₂PtCl₂ with aqueous hydrazine.⁴ Their material was impure, and it was unstable during further purification attempts. We have confirmed these observations.

In 1984, Flood and Statler synthesized high yields of *trans*-(PMe₃)₂PtHCl by thermally decomposing platinum alkyl complexes.⁵ Although we have no reason to doubt the purity of their material, the synthesis requires a multistep procedure and no analytical data were published. Finally, Trogler's group has

synthesized the complex by sodium naphthalide reduction of *cis*-(PMe₃)₂PtCl₂ under an atmosphere of H₂ and has determined its structure by X-ray crystallography.⁶ Again, however, no analytical data on the bulk material were reported. Our efforts to synthesize active catalyst by this method gave catalytically inactive material that was difficult to purify. Because of the possibility that our inability to reproduce the reported catalysis was due to our use of impure material, one of our primary goals was to prepare analytically pure *trans*-(PMe₃)₂PtHCl.

Results and Discussion

Preparation of Analytically Pure *trans*-(PMe₃)₂PtHCl. Our first synthetic route (eq 1) was modeled after a procedure used



by Catellani and Halpern for preparing *trans*-(PEt₃)₂PtHCl.⁷ Because the cationic complex for the analogous trimethylphosphine complex was unknown, this complex was first prepared according to eq 2. The complex was characterized by IR, ¹H NMR (Table I), and ³¹P NMR spectroscopy (Table II) and by elemental analysis.

The carbonyl complex was dissolved in acetone, and an excess of water was added. Extraction of the solution with ether yielded a solid that was spectroscopically verified as *trans*-(PMe₃)₂PtHCl, but only in trace amounts. Problems were also encountered because of the low stability of the hydride in water-acetone solution. For these reasons, we investigated alternative synthetic approaches.

We found that the best way to synthesize *trans*-(PMe₃)₂PtHCl was by a modification of the methanolic NaBH₄ reduction used

- (1) Jensen, C. M.; Trogler, W. C. *Science (Washington, D.C.)* **1986**, *233*, 1069-1071.
- (2) *Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1978; Vol. 1, pp 716-754.
- (3) (a) *Chem. Eng. News* **1986**, *64* (April 28), 68-69. (b) *Chem. Week* **1986** *139* (Sept 24), 22. (c) *Technology Forecasts and Technology Surveys*; PWG: Beverly Hills, CA, 1986; p 9.
- (4) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075-5084.
- (5) Flood, T. L.; Statler, J. A. *Organometallics* **1984**, *3*, 1795-1803. Statler, J. A. Ph.D. Dissertation, University of Southern California, 1982.

- (6) Packett, D. K.; Jensen, C. M.; Cowan, R. L.; Strouse, C. E.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 3578-3583.
- (7) Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566-568.

Table I. Summary of ^1H NMR Data^{a,b}

platinum complex	solvent	δ [J, Hz]	previous citations (ref)
<i>trans</i> -(PMe_3) ₂ PtHCl	C_6D_6	Pt-H -16.15 (t) [$J(\text{Pt-H}) = 1310$, $J(\text{P-H}) = 17$]; Pt-PCH ₃ 1.21 (t) [$J(\text{Pt-H}) = 37$, $J(\text{P-H}) = 3.5$]	4, 5, 6
<i>cis</i> -(PMe_3) ₂ PtCl ₂	CD_2Cl_2	Pt-PCH ₃ 1.74 (d) [$J(\text{P-H}) = 10.4$, $J(\text{Pt-H}) = 35$]	6, 15
<i>trans</i> -[(PMe_3) ₂ Pt(CO)Cl] ⁺ PF ₆ ⁻	CD_2Cl_2	Pt-PCH ₃ 1.85 (t) [$J(\text{P-H}) = 4$, $J(\text{Pt-H}) = 26$]	
[(PMe_3) ₃ PtH] ⁺ PF ₆ ⁻	$\text{Me}_2\text{SO-d}_6$	Pt-H -5.7 (t, d) [$J(\text{P-H})(\text{cis}) = 17$, $J(\text{P-H})(\text{trans}) = 162$]; Pt-PCH ₃ 1.7 (br)	5, 9
<i>trans</i> -[(PMe_3) ₂ PtH(1-hx)] ⁺ PF ₆ ^{-c}	acetone- <i>d</i> ₆	Pt-H -8.73 (t) [$J(\text{Pt-H}) = 1024$, $J(\text{P-H}) = 14$]; PtH ₂ C=CHR 3.23 (m); PtH ₂ C=CHR 4.35 (m)	1
<i>trans</i> -[(PMe_3) ₂ PtH(1-hx)] ⁺ PF ₆ ^{-d}	acetone- <i>d</i> ₆	Pt-H -7.41 (t) [$J(\text{Pt-H}) = 1075$, $J(\text{P-H}) = 16.7$]; Pt-PCH ₃ 1.82 (t)	
<i>trans</i> -[(PEt_3) ₂ PtH(1-hx)] ⁺ PF ₆ ^{-d}	acetone- <i>d</i> ₆	Pt-H -7.92 (t) [$J(\text{Pt-H}) = 1021$, $J(\text{P-H}) = 13.2$]	
<i>cis,cis,trans</i> -PtCl ₂ H ₂ (PMe_3) ₂	C_6D_6	Pt-H -17.54 (t) [$J(\text{Pt-H}) = 1190$, $J(\text{P-H}) = 9.2$]	
<i>trans</i> -[(PMe_3) ₂ PtH(ac)] ⁺ PF ₆ ⁻	acetone- <i>d</i> ₆	Pt-H -23.7 (t) [$J(\text{Pt-H}) = 1475$]; Pt-PCH ₃ 1.55 (t) [$J(\text{P-H}) = 4$, $J(\text{Pt-H}) = 33$]	1 ^e

^a Values are from this work and were determined in our laboratories except where otherwise noted; multiplicities given exclude ^{195}Pt satellites.

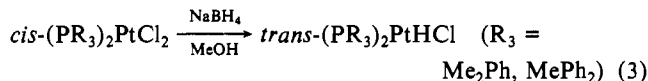
^b References indicate previous citations of specific complexes and are in general agreement with this work, except where noted in text. ^c Literature values. ^d Low concentrations prevented us from observing the olefinic references of the coordinated hexene. ^e No NMR data were given for this complex in the reference.

Table II. ^{31}P NMR Data for Platinum Complexes

complex	solvent	δ [J, Hz]
<i>trans</i> -[(PMe_3) ₂ Pt(CO)Cl] ⁺ PF ₆ ⁻	CD_2Cl_2	-7.4 [$J(\text{Pt-P}) = 1846$]
<i>trans</i> -[(PMe_3) ₂ PtH(1-hx)] ⁺ PF ₆ ^{-a}	acetone- <i>d</i> ₆	-8.2 [$J(\text{Pt-P}) = 2183$]
<i>trans</i> -[(PMe_3) ₂ PtH(1-hx)] ⁺ PF ₆ ⁻	acetone- <i>d</i> ₆	-23.4 [$J(\text{Pt-P}) = 2349$]
<i>trans</i> -(PMe_3) ₂ PtH(ac)] ⁺ PF ₆ ⁻	acetone- <i>d</i> ₆	-10.5 [$J(\text{Pt-P}) = 2540$]
<i>trans</i> -[(PEt_3) ₂ PtH(ac)] ⁺ PF ₆ ⁻	acetone- <i>d</i> ₆	24.8 [$J(\text{Pt-P}) = 2657$]
<i>trans</i> -[(PEt_3) ₂ PtH(1-hx)] ⁺ PF ₆ ⁻	acetone- <i>d</i> ₆	12.66 [$J(\text{Pt-P}) = 2420$]

^a Reference 1.

by Clark and Kurosawa for the preparation of the PMe_2Ph and PMePh_2 analogues (eq 3).⁸ This method involves the dropwise



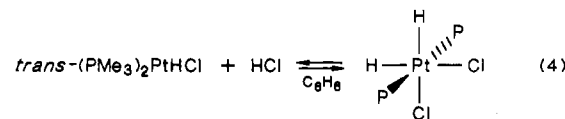
addition of methanolic sodium borohydride to a suspension of *cis*-(PR_3)₂PtCl₂ (R = Me_2Ph , MePh_2) in methanol. After acidification with methanolic hydrochloric acid, the solvent is removed, and the solid is extracted into benzene and precipitated with pentane.

When this procedure was used for a suspension of *cis*-(PMe_3)₂PtCl₂, several problems were experienced. First, the solid obtained after extraction and precipitation consisted of a mixture of 95% *trans*-(PMe_3)₂PtHCl and 5% of an unidentified hydride impurity (^1H NMR (PtH) δ -17.54 ($J(\text{Pt-H}) = 1190$ Hz) in C_6D_6). Second, consistent results were difficult to achieve. At times, the benzene extracts turned red, and no products could be obtained from these solutions.

To circumvent these problems, we modified the procedure as follows. An excess of borohydride was used, and the reaction time was increased to 2 h. After acidification and removal of solvent, the extraction was done with hot hexane, followed by filtration through Celite and animal charcoal. This method gave a reproducible synthesis of analytically pure *trans*-(PMe_3)₂PtHCl. The spectroscopic parameters are identical with those reported earlier for this complex (see Tables I and II). Further details of the preparation are discussed in the Experimental Section.

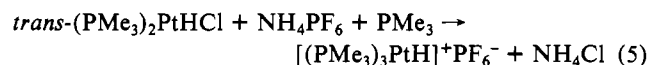
Reactions Using *trans*-(PMe_3)₂PtHCl. Because repeated attempts failed to reproduce the catalysis reported by Jensen and Trogler, we undertook a study of the reaction chemistry of *trans*-(PMe_3)₂PtHCl in order to better understand its behavior. The complex obtained via the borohydride method was stable as a solid when stored in an inert (N_2) atmosphere. However, it was very unstable in aqueous solution and showed a propensity to form a tris(phosphine) species (vide infra). In its reactions with other

substrates, this complex was similar to the well-known *trans*-(PEt_3)₂PtHCl. For example, the 6-coordinate complex *cis,cis,trans*-PtCl₂H₂(PMe_3)₂ was formed by bubbling anhydrous HCl through a solution of *trans*-(PMe_3)₂PtHCl in benzene (eq 4).



Attempts to isolate this complex led to its partial decomposition back to *trans*-(PMe_3)₂PtHCl.

Reaction of the hydrido chloride with phosphine in the presence of an appropriate anion gave the tris(phosphine) hydride as shown in eq 5.⁹ This reaction was initially run with a large excess of



phosphine in acetone. After the solvent was filtered and removed in vacuo, the residue was extracted with dichloromethane. A white solid was precipitated by the addition of diethyl ether. The ^1H NMR spectrum of this complex in CD_2Cl_2 showed a doublet at δ 1.7 and a sharp hydride singlet at δ -12.8 ($J(\text{Pt-H}) = 618$ Hz). This spectrum is consistent with that reported by Flood and Statler for [(PMe_3)₃PtH]⁺Cl⁻; however, the ratio of the phosphine methyl protons to the hydridic protons by integration did not match the proposed structure and indicated the presence of extra phosphine. Elemental analysis was consistent with this interpretation, as the carbon and hydrogen percentages were abnormally high. Flood and Statler also reported difficulties in obtaining an acceptable analysis for this material.

We therefore repeated the experiment using a stoichiometric amount of trimethylphosphine and were able to isolate a cream-colored solid that gave acceptable analysis. The ^1H NMR spectrum (Table I) showed the characteristic doublet of triplets pattern for the hydridic signals, consistent with the structure [(PMe_3)₃PtH]⁺. Addition of phosphine to an NMR tube containing pure [(PMe_3)₃PtH]⁺ in CD_2Cl_2 gave the ^1H NMR spectrum observed by Flood and Statler, with loss of Pt-P coupling.

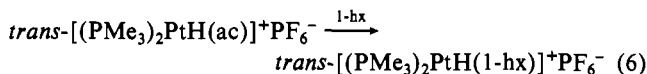
Spectroscopic Study of Olefin Complexes. The analytically pure *trans*-(PMe_3)₂PtHCl we prepared via the borohydride route failed to act as an olefin hydration catalyst under the conditions published by Jensen and Trogler (see Experimental Section). For this reason, we decided to examine their proposed mechanism in detail. In this mechanism, the hydrido-olefin complex *trans*-[(PMe_3)₂PtH(CH₂=CHR)]⁺ was postulated as an important intermediate.¹ The

(9) We later learned that Trogler's group has synthesized the complex as the analytically pure BPh_4^- salt by an independent route: Packett, D. L.; Swepston, P. N.; Syed, A.; Trogler, W. C. *Organometallics* 1988, 7, 159-166.

(8) Clark, H. C.; Kurosawa, H. *J. Organomet. Chem.* 1972, 36, 399-409.

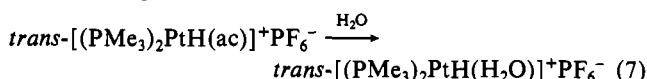
insertion of the olefin into the Pt-H bond is a potential competing reaction.¹⁰

Jensen and Trogler have suggested that the insertion of the olefin into the Pt-H bond is slow. In support of this, they have reacted trans-(PMe₃)₂PtHCl with 1 equiv of silver hexafluorophosphate in acetone-d₆ to generate trans-[(PMe₃)₂PtH(acetone)]⁺PF₆⁻ and then added 5 equiv of 1-hexene to form trans-[(PMe₃)₂PtH(1-hx)]⁺PF₆⁻ (eq 6).¹ The hydrido olefin



ac = acetone; 1-hx = 1-hexene

complex was claimed to be stable in solution at 25 °C for up to 45 min, indicating that the olefin insertion reaction is slow. An additional proposed intermediate was generated and observed spectroscopically by adding water to the acetone complex to give an aquo complex (eq 7).¹



We sought to reproduce Jensen and Trogler's NMR experiments, in order to identify trans-[(PMe₃)₂PtH(H₂O)]⁺PF₆⁻ and trans-[(PMe₃)₂PtH(1-hx)]⁺PF₆⁻ and to use them as catalysts for olefin hydration instead of trans-(PMe₃)₂PtHCl. Unfortunately, we could not reproduce those experiments. The reaction of trans-(PMe₃)₂PtHCl with 1 equiv of silver hexafluorophosphate in acetone at room temperature gave brown solutions containing no detectable hydride. Because of the instability problems associated with this system, we turned to the seemingly more stable trans-(PEt₃)₂PtHCl and spectroscopically monitored reactions of this complex with AgPF₆ and 1-hexene.

Clark and co-workers have studied the reactions of trans-[(PEt₃)₂PtH(ac)]⁺PF₆⁻ with ethylene in detail.¹⁰ They found that trans-[(PEt₃)₂PtH(C₂H₄)]⁺PF₆⁻ is stable at room temperature, but heating to 40 °C in acetone causes insertion of the olefin into the platinum-hydride bond. On this basis, we hoped that the analogous reaction with 1-hexene at room temperature would yield trans-[(PEt₃)₂PtH(1-hx)]⁺PF₆⁻.

Thus, a solution of trans-[(PEt₃)₂PtHCl] in acetone-d₆ was reacted with 1 equiv of silver hexafluorophosphate, and the silver chloride was removed by centrifugation. An excess of 1-hexene was added, and a ¹H NMR spectrum was recorded at room temperature. No hydridic signals due to the π-olefin complex trans-[(PEt₃)₂PtH(1-hx)]⁺PF₆⁻ were detected. Only trans-[(PEt₃)₂PtH(ac)]⁺PF₆⁻ (δ -24.8 (J(Pt-H) = 1484 Hz)) was observed. In addition, the signals due to the vinylic protons of 1-hexene were not present; instead, a multiplet was observed at δ 5.4, indicating that total isomerization of 1-hexene to internal olefin(s) had occurred. (The vinylic protons of 1-hexene in acetone-d₆ occur at δ 5.0 and 5.8.)

In order to more fully understand the isomerization process, the ¹H and ³¹P NMR spectra were obtained as a function of temperature. trans-(PEt₃)₂PtHCl was dissolved in acetone and reacted with 1 equiv of silver hexafluorophosphate, also in acetone. After the silver chloride was centrifuged and removed, the solution was cooled to -38 °C and ¹H NMR and ³¹P NMR spectra were recorded. The ¹H NMR spectrum showed a hydride signal at δ -24.3, indicative of the complex [(PEt₃)₂PtH(ac)]⁺PF₆⁻. The ³¹P NMR spectrum (Figure 1a) gave a signal at δ 24.8 (J(Pt-P) = 2657 Hz). Addition of excess 1-hexene gave the spectrum shown in Figure 1b (δ 12.66 (J(Pt-P) = 2420 Hz)). We assign this signal to trans-[(PEt₃)₂PtH(1-hx)]⁺PF₆⁻, which is supported by the appearance of a new hydridic signal at δ -7.8 in the ¹H NMR spectrum.

The temperature was then raised to 3 °C. The ³¹P NMR spectrum shown in Figure 1c shows an increase in the relative intensity of the signal due to the acetone complex. At 20 °C, the ³¹P NMR spectrum shows almost total depletion of the hexene

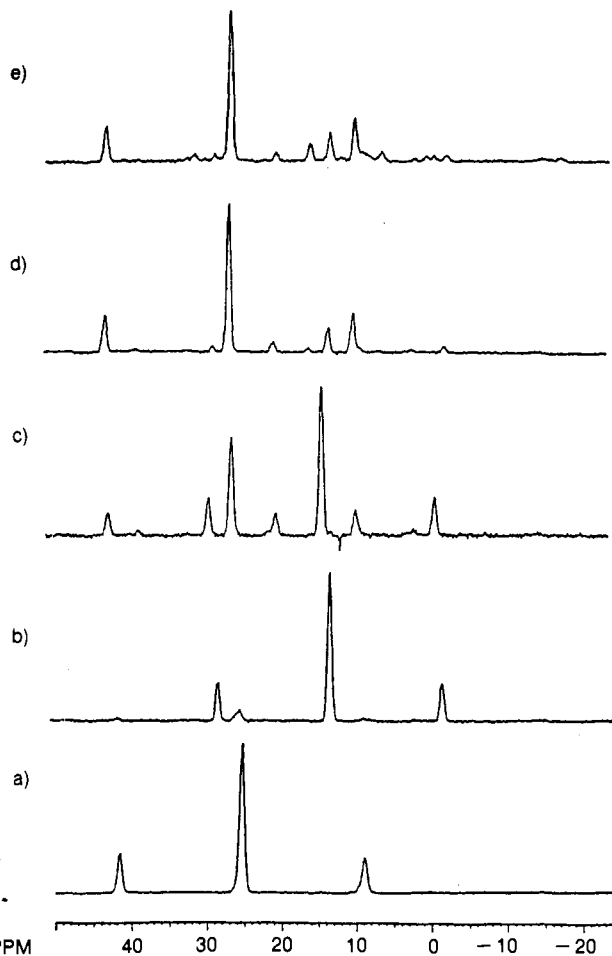


Figure 1. ³¹P NMR spectra of triethylphosphine complexes of platinum: (a) [trans-(PEt₃)₂PtH(ac)]⁺ at -38 °C; (b) 1-hexene added to form [trans-(PEt₃)₂PtH(1-hx)]⁺, also at -38 °C; (c-e) the latter complex at (c) 3 °C, (d) 20 °C, and (e) 20 °C for 18 h.

complex and the ¹H NMR spectrum indicates that there has been total isomerization of 1-hexene. These results demonstrate that trans-[(PEt₃)₂PtH(1-hx)]⁺PF₆⁻ is stable in acetone only at low temperatures (<0 °C). At room temperature, the complex may undergo fast insertion of the olefin into the Pt-H bond, eliminate the internal isomers of 1-hexene, and re-form the hydrido acetone complex. Alternative isomerization mechanisms are, of course, possible.¹¹

We then returned to the PMe₃ analogue, this time at low temperatures. Thus, trans-(PMe₃)₂PtHCl in acetone-d₆ was reacted with 1 equiv of silver hexafluorophosphate at -78 °C. After the silver chloride was removed, the ¹H and ³¹P NMR spectra were recorded at -54 °C. The ¹H NMR spectrum showed a hydride signal at δ -23.7 (J(Pt-H) = 1476 Hz), which we assign to the complex trans-[(PMe₃)₂PtH(ac)]⁺PF₆⁻. Figure 2a shows that the ³¹P NMR spectrum of this sample is a single resonance at δ -10.5 (J(Pt-P) = 2540 Hz). An excess of 1-hexene was added, and the ¹H and ³¹P NMR spectra were determined once again at -54 °C. Figure 2b shows a new ³¹P NMR signal at δ -23.4 (J(Pt-P) = 2349 Hz). The corresponding ¹H NMR spectrum showed a hydride at δ -7.4 (J(Pt-H) = 1075 Hz). We ascribe these signals as being due to the formation of the complex trans-[(PMe₃)₂PtH(1-hx)]⁺PF₆⁻.

The sample was next warmed to -32 °C. The ³¹P NMR spectrum (Figure 2c) discloses the reappearance of the acetone complex. The ¹H NMR spectrum again shows evidence of some isomerization of 1-hexene. At -12 °C, no hydridic signals were observed, and the olefin had completely isomerized. The ³¹P NMR

(10) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* 1972, 11, 1275-1280.

(11) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986; pp 372-374.

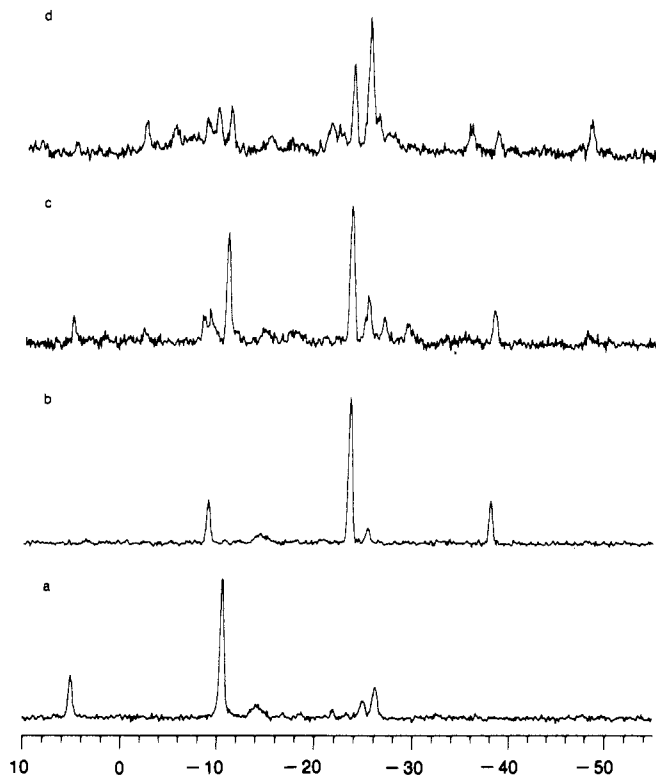


Figure 2. ^{31}P NMR spectra of trimethylphosphine complexes of platinum: (a) $[\text{trans}-(\text{PMe}_3)_2\text{PtH}(\text{ac})]^+$ at -54°C ; (b) 1-hexene added to form $[\text{trans}-(\text{PMe}_3)_2\text{PtH}(1\text{-hx})]^+$, also at -54°C ; (c, d) the latter complex at (c) -32°C and (d) -12°C .

spectrum (Figure 2d) reveals the presence of several decomposition products.

We therefore conclude that the chemistries of $\text{trans}-[(\text{PMe}_3)_2\text{PtH}(1\text{-hx})]^+$ and $\text{trans}-[(\text{PEt}_3)_2\text{PtH}(1\text{-hx})]^+$ are similar. Both are unstable and result in the isomerization of 1-hexene. The systems differ somewhat in that the PMe_3 complexes appear to be less stable. Comparison of the NMR parameters reported by Jensen and Trogler with those observed by us for $\text{trans}-[(\text{PMe}_3)_2\text{PtH}(1\text{-hx})]^+\text{PF}_6^-$ (Tables I and II) is interesting. The values differ significantly (^{31}P δ -8.2^1 vs δ -23.4).

We also attempted to generate the π -olefin complexes in other solvents. $\text{trans}-(\text{PEt}_3)_2\text{PtHCl}$ was dissolved in deuteriated methanol and reacted with 1 equiv of silver hexafluorophosphate. After the silver chloride was filtered, an excess of 1-hexene was added. The ^1H NMR spectrum indicated the presence of two complexes, $\text{trans}-[(\text{PEt}_3)_2\text{PtH}(1\text{-hx})]^+\text{PF}_6^-$ and $\text{trans}-[(\text{PEt}_3)_2\text{PtH}(\text{CD}_3\text{OD})]^+\text{PF}_6^-$, with their hydridic signals at -8.13 and -26.07 ppm, respectively. Thus, the π -olefin complex appears to be more stable at room temperature in methanol than in acetone. The spectrum did show a small multiplet at δ 5.4 between the signals due to the vinylic protons of 1-hexene, resulting from the isomerization of 1-hexene. After 2 h, the 1-hexene isomerized completely. In a separate experiment, when the base $\text{NMe}_4^+\text{OH}^- \cdot 5\text{H}_2\text{O}$ (1 equiv) was added to the π -olefin complex at room temperature, a new hydridic signal was observed at δ -11.3 ppm, and more isomerization of 1-hexene resulted. No primary alcohol was detected.

Because of our success in stabilizing the olefin complex $\text{trans}-[(\text{PEt}_3)_2\text{PtH}(1\text{-hx})]^+\text{PF}_6^-$ at room temperature in methanol, similar attempts were made with $\text{trans}-[(\text{PMe}_3)_2\text{PtH}(1\text{-hx})]^+\text{PF}_6^-$. However, this led to decomposition. A low-temperature NMR experiment was then performed. $\text{trans}-[(\text{PMe}_3)_2\text{PtH}(1\text{-hx})]^+$ was generated in deuteriated methanol at -59°C and identified by its hydride resonance at δ -7.45 ($J(\text{Pt}-\text{H}) = 1072$ Hz). Addition of 1 equiv of $\text{NMe}_4^+\text{OH}^- \cdot 5\text{H}_2\text{O}$ at -59°C produced a new hydridic signal at δ -22.08 ($J(\text{Pt}-\text{H}) = 1136$ Hz). The chemical shift of this hydride is consistent with the formation of $\text{trans}-(\text{PMe}_3)_2\text{PtH}(\text{OH})$ and is similar to the chemical shift observed

for $\text{trans}-\text{P}(i\text{-Pr})_3)_2\text{PtH}(\text{OH})$ by Otsuka and co-workers.¹² Warming this solution to room temperature did not cause any primary alcohols to form, as determined by both NMR and GC/MS spectra. The main reaction appears to be substitution of the olefin, rather than OH^- attack on the olefin. The latter process would lead to the formation of hydrido alkyl complexes,¹³ no signals assignable to such complexes were detected.

Conclusions

Despite repeated attempts, we were unable to reproduce the catalytic hydration of olefins to yield primary alcohols using the $\text{trans}-(\text{PMe}_3)_2\text{PtHCl}$ catalyst preparation and reaction methodology reported by Jensen and Trogler. An analytically and spectroscopically pure form of this complex prepared by an alternate route also failed to catalyze the conversion of terminal alkenes to primary alcohols according to conditions reported in the literature. The π -olefin complexes $\text{trans}-[(\text{PR}_3)_2\text{PtH}(1\text{-hx})]^+\text{PF}_6^-$ ($\text{R} = \text{Me}, \text{Et}$) were found to be stable at low temperatures. At room temperature, these complexes were unstable and isomerization of 1-hexene to internal olefins was observed.

Reaction of these π -olefin complexes with the base $\text{NMe}_4^+\text{OH}^- \cdot 5\text{H}_2\text{O}$ did not produce any 1-hexanol or any hydridoalkylplatinum complexes that would be consistent with the proposed olefin hydration mechanism. In addition, the spectroscopic parameters reported previously for $\text{trans}-[(\text{PMe}_3)_2\text{PtH}(1\text{-hx})]^+\text{PF}_6^-$ are considerably different from those observed by us. On the basis of these observations, we believe that the process of olefin hydration is considerably more complex than Jensen and Trogler report and requires extensive clarification.

Experimental Section

Materials. The following compounds were used without purification: trimethylphosphine (Strem), potassium tetrachloroplatinate (Aldrich), silver iodide-trimethylphosphine complex (Aldrich), silver hexafluorophosphate (Aldrich), sodium borohydride (Alfa), ammonium hexafluorophosphate (Aldrich), sodium hydroxide pellets (Fisher), methanol- d_4 (Aldrich), methylene chloride (Fisher), acetone- d_6 (Aldrich-Gold Label), diethyl ether (Fisher), petroleum ether (Fisher), and animal charcoal (Darco G-60, Aldrich No. 24,227-6). Hexane (Fisher) and 1-hexene (Aldrich) were distilled under N_2 from CaH_2 . Methanol (Fisher) was distilled from $\text{Mg}(\text{OMe})_2$ under N_2 . Water was obtained from Aldrich (HPLC grade) and thoroughly degassed before use. The following compounds were prepared by literature methods: $\text{trans}-(\text{PEt}_3)_2\text{PtHCl}$,⁴ $\text{cis}-(\text{Et}_2\text{S})_2\text{PtCl}_2$,¹⁴ and $\text{cis}-(\text{PMe}_3)_2\text{PtCl}_2$.⁶

Physical Measurements. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 684 spectrophotometer. Gas chromatographic (GC) measurements were performed with a Hewlett-Packard 5840A instrument with capillary capability and equipped with a 15 m \times 0.53 mm column containing a 1.5- μm film of SPB-5 as the stationary phase (Supelco Catalogue No. 2-5304). The ^1H NMR spectra were determined on an IBM SY-200 FT spectrometer with a proton, fluorine-19 5-mm dual probe. The ^{31}P NMR spectra were determined at 81.026 MHz with use of a 10-mm multinuclear probe. Low-temperature NMR experiments were determined with a 10-mm pretuned phosphorus probe, and the ^1H NMR spectra were determined on the decoupler channel of the probe. Proton chemical shifts were referenced to tetramethylsilane at 0.0 ppm. Phosphorus chemical shifts were referenced to the deuterium resonance of the solvent by using the internal frequency lock of the spectrometer calibrated such that a capillary tube containing 85% H_3PO_4 centered in a 10-mm NMR tube containing the deuteriated solvent appeared at 0 ppm at 20°C . All samples for the NMR spectroscopic analysis were prepared in 5-mm NMR tubes under an argon atmosphere and sealed with Suba-Seals (Aldrich). Elemental analyses were performed at Air Products and at the Schwarzkopf Microanalytical Laboratory.

$\text{trans}-(\text{PMe}_3)_2\text{PtHCl}$. The complex $\text{cis}-(\text{PMe}_3)_2\text{PtCl}_2$ (0.5 g, 1.2 mmol) was placed in a 100-mL Schlenk flask with a stir bar and degassed in vacuo for 15 min. To this was added 15 mL of dry methanol, and the

- (12) (a) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027-2039. (b) A reviewer has suggested that this NMR signal may be due to a methoxide complex. We agree that this is a possibility and cannot rule it out.
- (13) Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263-267.
- (14) Pidcock, A. L. *Inorg. Synth.* **1960**, *6*, 211-215.
- (15) Duddell, D. A.; Evans, J. G.; Goggin, P. L.; Goodfellow, R. J.; Rest, A.; Smith, J. G. *J. Chem. Soc. A* **1969**, 2134-2140.

mixture was then degassed by means of two freeze-pump-thaw cycles. Meanwhile, 3 mL of 12 M hydrochloric acid was added to 20 mL of methanol in a Schlenk flask; this was degassed by three freeze-pump-thaw cycles. The flask that contained the *cis*-(PMe₃)₂PtCl₂ and methanol was allowed to thaw after the second freeze-pump operation and then immediately fitted with a glass funnel under a positive flow of nitrogen. Sodium borohydride (1.5 g, 39 mmol) was added in small batches to this cold solution with stirring over a period of 5 min. The thick suspension was stirred for at least 2 h, and the color progressed from light yellow to gold to lime green. Methanolic hydrochloric acid was then added dropwise via a syringe until the solution was just acidic (pH ~3 or 4). At this stage the solution was brown.

The solvent was removed in vacuo, yielding a crusty brown solid. After the solid was dried overnight in the Schlenk flask, it was scraped into a beaker in air containing 100 mL of dry hexane. The solution was then boiled and filtered in air through a 150-mL medium-porosity frit covered with a mixture of animal charcoal and Celite. At this stage the product is not particularly air sensitive but can be filtered under N₂ if desired. The filtrate was allowed to stand for about 10 min and then placed in an ice bath for 0.5 h. Snow white crystals of *trans*-(PMe₃)₂PtHCl formed in the filtrate; these were filtered, dried in vacuo, and stored in an inert-atmosphere box. The yield was 0.135 g (0.35 mmol), 29%. Anal. Calcd for C₆H₁₉ClPt: C, 18.78; H, 4.99; P, 16.14; Cl, 9.25; Pt, 50.87. Found: C, 19.05; H, 4.87; P, 15.60; Cl, 9.94; Pt, 50.80.

[(PMe₃)₃PtH]⁺PF₆⁻. Into a Schlenk tube were placed 0.055 g (0.144 mmol) of *trans*-(PMe₃)₂PtHCl and 0.035 g (0.212 mmol) of NH₄PF₆. Then 5 mL of acetone was added to dissolve the solids, and this solution was degassed by means of two freeze-pump-thaw cycles. In another Schlenk flask, a stock solution was prepared by adding 0.3 mL of trimethylphosphine to 25 mL of degassed methylene chloride. This stock solution (1 mL) was added to the stirred acetone solution containing the platinum complex. After 2 h, the white precipitate of ammonium chloride was collected by filtration and the filtrate was evaporated to dryness in vacuo. The residue was extracted with a minimum of methylene chloride, and a cream-colored product was obtained by the addition of diethyl ether to the filtrate; yield 25 mg (27%). Anal. Calcd for C₂H₂₈F₆P₄Pt: C, 18.99; H, 4.92. Found: C, 18.57; H, 4.89.

trans-[(PMe₃)₂Pt(CO)Cl]⁺PF₆⁻. A Schlenk flask was charged with 0.5 g (1.1 mmol) of *cis*-(PMe₃)₂PtCl₂ and 0.398 g (2.2 mmol) of NH₄PF₆. The solids were dissolved in 30 mL of a 1:1 mixture of methylene chloride and acetone. Carbon monoxide was bubbled in slowly for several hours, after which the solution was stirred overnight under a CO atmosphere. The solution was then filtered to remove precipitated ammonium chloride, and the filtrate was evaporated to dryness by rotary evaporation. The residue was extracted with 15 mL of methylene chloride, and the mixture was filtered. A white solid was obtained by the addition of excess diethyl ether accompanied by scratching the flask with a spatula. The liquid was decanted, and the white solid was dried in vacuo and recrystallized from dichloromethane-diethyl ether; yield 0.346 g (56%); ν(CO) 2115 cm⁻¹ (Nujol). Anal. Calcd for C₇H₁₈ClF₆OP₃Pt: C, 15.13; H, 3.26. Found: C, 15.23; H, 3.25.

Catalytic Procedure. In a glovebox, a stirring bar and 10 mg of each *trans*-(PMe₃)₂PtHCl and benzyltrimethylammonium chloride were placed in a glass reaction tube equipped with a high-vacuum Teflon valve (Kontes) and a side arm for inert-atmosphere manipulations. (On other occasions, sodium dodecyl sulfate¹⁶ was used instead of benzyltrimethylammonium chloride.) The vessel was then attached to a Schlenk line. A solution of 0.4 M NaOH in degassed water was prepared, and

the solution itself was degassed by means of three freeze-pump-thaw cycles. Under a stream of N₂, 0.5 mL each of 1-hexene and of the NaOH solution were added via syringe. The solution was immediately frozen, and the vessel was evacuated. The Teflon valve was then closed, and after the mixture had thawed, the reactor was placed in an oil bath heated to 60 °C. After being stirred at this temperature for 3 h, the mixture was cooled and analyzed by GC.

Reaction of *trans*-[(PEt₃)₂PtH(ac)]⁺PF₆⁻ and 1-Hexene at Low Temperature. A Schlenk tube was charged with 100 mg (0.214 mmol) of *trans*-(PEt₃)₂PtHCl, placed under argon, and capped with a Suba-Seal. Also, 55 mg (0.218 mmol) of AgPF₆ was placed with a stir bar under argon in a centrifuge tube, which was capped with a Suba-Seal. A 5-mm NMR tube containing a methanol capillary tube was also capped with a Suba-Seal under argon. In the meantime, acetone-*d*₆ and 1-hexene were degassed by means of three freeze-pump-thaw cycles. To each of the tubes, enough acetone-*d*₆ (0.2–0.3 mL) was added to dissolve the solids. The solution of (PEt₃)₂PtHCl in acetone-*d*₆ was added via a syringe to the centrifuge tube containing AgPF₆ in acetone-*d*₆. After the mixture had been stirred for 0.5 h, AgCl was removed by centrifugation and the solution was transferred via syringe to the NMR tube containing argon. The temperature of the NMR spectrometer probe was monitored via the chemical shift difference of the OH and CH₃ protons of the methanol capillary. After determining the ¹H NMR and ³¹P NMR spectra, we cooled the sample in a dry ice-acetone bath and added ~0.1 mL of degassed 1-hexene via syringe. The ¹H and ³¹P NMR spectra were recorded at low temperatures, and the tube was gradually warmed. All spectroscopic parameters are reported in Tables I and II.

Reaction of *trans*-[(PMe₃)₂PtH(acetone)]⁺PF₆⁻ and 1-Hexene at Low Temperatures. For this experiment, we had to maintain low temperatures to prevent decomposition of the acetone complex. In an argon glovebox, 50 mg (0.013 mmol) of *trans*-(PMe₃)₂PtHCl and 23 mg (0.013 mmol) of AgPF₆ were placed in separate centrifuge tubes equipped with stir bars and capped with Suba-Seals. Both solids were dissolved in 0.3 mL of acetone-*d*₆, and the AgPF₆ solution was added quickly to the platinum complex via syringe at -78 °C. The reaction was kept in the cold bath except for periodic stirring. After a few minutes, the solution was cooled (but not allowed to freeze) in liquid N₂ for an instant and then centrifuged for ca. 1 min to remove AgCl. The solution was transferred via a precooled glass syringe to a 5-mm NMR tube equipped with a methanol capillary tube and kept at -78 °C. The ¹H and ³¹P NMR spectra were recorded at low temperature (-54 °C). The sample was then placed in a dry ice-acetone bath, and 0.1 mL of degassed 1-hexene was added via syringe. The spectra were determined at various temperatures (see Tables I and II).

Reaction of *trans*-[(PEt₃)₂PtH(CD₃OD)]⁺PF₆⁻ and 1-Hexene at Room Temperature. Samples of 73 mg (0.016 mmol) of *trans*-(PEt₃)₂PtHCl and 40 mg of AgPF₆ were weighed in two separate centrifuge tubes in an argon-containing drybox. Each of the solids was dissolved in 0.2 mL of degassed methanol-*d*₄; the solutions were then combined. After several minutes of stirring, AgCl was centrifuged and the solution transferred to a 5-mm NMR tube for ¹H NMR determination. Then 0.1 mL of 1-hexene was added to the tube, and the spectrum was recorded.

Reaction of *trans*-[(PMe₃)₂Pt(CD₃OD)]⁺PF₆⁻ and 1-Hexene at Low Temperature. The procedure followed was the same as that for *trans*-[(PMe₃)₂PtH(ac)]⁺PF₆⁻, except for the substitution of methanol-*d*₄ for acetone-*d*₆.

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(16) It is believed that the role of benzyltrimethylammonium chloride is that of a surfactant; sodium dodecyl sulfate has been reported to be more effective: Troglor, W. C. *Abstracts of Papers*, 194th National Meeting of the American Chemical Society, New Orleans, LA; American Chemical Society: Washington, DC, 1987; CHED 23.