

Reprinted from *Organometallics*, 1988, 7, 2379.

Copyright © 1988 by the American Chemical Society and reprinted by permission of the copyright owner.

Intermolecular Activation of C–D Bonds in Benzene- d_6 by *trans*-Neopentyl(trifluoromethanesulfonato)bis(trimethylphosphine)platinum(II)¹

Robert L. Brainard,² W. Rodger Nutt,² T. Randall Lee, and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received May 12, 1988

trans-(Me₃P)₂Pt(CH₂C(CH₃)₃)(SO₃CF₃) (L₂PtNpTf, 1) reacts with benzene- d_6 at 133 °C and gives *trans*-(Me₃P)₂Pt(C₆D₅)(SO₃CF₃) (2) and neopentane- d_1 as the major products. When this reaction is carried out in concentrated solutions ([1]₀ ≥ 0.04 M), small quantities of neopentane- d_0 (8–17%) and 1,1-dimethylcyclopropane (1–3%) are also detected; larger quantities of neopentane- d_0 are produced (32–45%) when the initial concentration of 1 is low ([1]₀ = 0.01–0.03 M). The rate of reaction is decreased by the addition of Bu₄N⁺Tf⁻ and increased by the addition of Bu₄N⁺BF₄⁻. A competitive kinetic isotope effect was estimated by allowing 1 to react with C₆D₅H and comparing the relative yields of neopentane- d_0 and neopentane- d_1 : k_H/k_D is large, but its quantitative value is uncertain because of experimental ambiguities. The mechanism for this reaction seems to involve generation of L₂PtNp⁺ as an essential intermediate. This intermediate appears to react with benzene by direct oxidative addition of a C–H bond, but electrophilic attack on the benzene ring cannot be rigorously excluded.

Introduction

Although intermolecular activation of C–H bonds by homogeneous organometallic compounds is an area of intensive research,^{3–12} examples based on soluble organo-

platinum species have only recently been reported.¹³ Clean platinum surfaces cleave C–H bonds under mild

(1) Supported by the National Science Foundation, Grant CHE-85-08702.

(2) Present address of R.L.B.: Polaroid Corp., Waltham, MA. W.R.N. was on sabbatical leave from Davidson College.

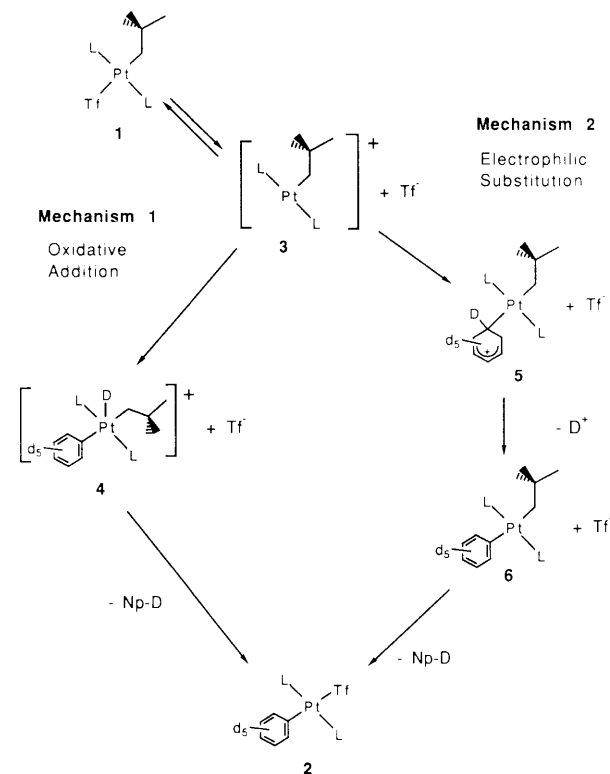
(3) Parshall, G. W. *Catal. (London)* 1977, 1, 335. Webster, D. E. *Adv. Organomet. Chem.* 1977, 15, 147. Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980. Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Boston, 1984.

(4) Garnett, J. L.; Hodges, R. J. *J. Am. Chem. Soc.* 1967, 89, 4546–47. Garnett, J. L.; West, J. C. *Aust. J. Chem.* 1974, 27, 129–42 and references therein.

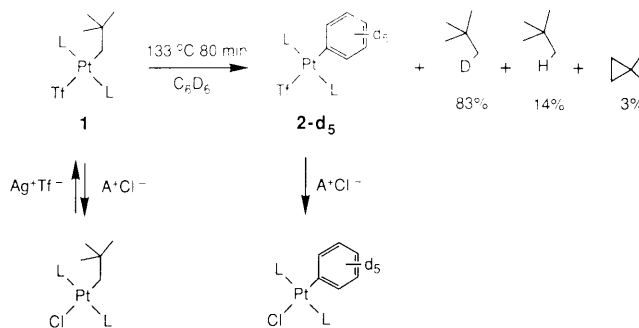
(5) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Russ. J. Phys. Chem. (Engl. Transl.)* 1969, 43, 1222–3.

(6) Shul'pin, G. B.; Shilov, A. E.; Kitagorodskii, A. N. *J. Organomet. Chem.* 1980, 201, 319–325. Shilov, A. E. *Organomet. Chem.* 1981, 212, 267–274. Shul'pin, G. B.; Nizova, G. V.; Shilov, A. E. *J. Chem. Soc., Chem. Commun.*, 1983, 671–672. *J. Organomet. Chem.* 1981, 220, 271–276. Kushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* 1983, 7, 729–733.

(7) For example: Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* 1979, 101, 1742–51. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* 1982, 104, 4240–42. Gomez, M.; Robinson, D. J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* 1983, 825–6. Fisher, B. J.; Eisenberg, R.; *Organometallics* 1983, 2, 764–67. Morris, R. H.; Shiralian, M. *J. Organomet. Chem.* 1984, 260, C47–C51. Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* 1983, 105, 305–306.

Scheme I. Two Possible Mechanisms for the Reaction of $L_2PtNpTf$ with Benzene- d_6 ($L = Me_3P$; $Tf = CF_3SO_3$)

conditions^{14,15} and organoplatinum complexes undergo facile *intramolecular* C–H activation.^{16,17} This paper describes the reaction of *trans*-(Me_3P)₂Pt($CH_2C(CH_3)_3$)- SO_3CF_3 (1) with benzene- d_6 . The immediate objective of this work was to examine the influence of the electrophilicity of the platinum center on reactivity toward C–D(H) bonds. We consider two mechanisms for this reaction (Scheme I). Both involve heterolytic dissociation of triflate: one involves oxidative addition of the C–H bond of benzene to the platinum center of the coordinatively unsaturated intermediate **3**; the other involves electrophilic reaction of **3** with the benzene. The distinction between these two mechanisms centers on the issue of the intermediacy of an η^1 -intermediate, **5**: does the platinum atom form a localized bond with carbon by electrophilic attack on the benzene with disruption of the aromatic π -system of benzene?¹⁸

Scheme II. Synthesis of $L_2PtNpTf$ (1) and Products of the Reaction of 1 with Benzene- d_6 ($L = Me_3P$; $Tf = CF_3SO_3$; $A^+ = n-C_{14}H_{29}NMe_2(CH_2Ph)^+$)

^a Yields of C-5 product (neopentane, dimethylcyclopropane) are relative yields. We estimate that these yields are, at most, 5% larger than the absolute yields.

Throughout this paper, the platinum complexes are named by reference to *trans*-neopentyl(trifluoromethanesulfonato)bis(trimethylphosphine)platinum(II) (1), $L_2PtNpTf$. Thus, for example, *trans*-(phenyl- d_5)-(trifluoromethanesulfonato)bis(trimethylphosphine)platinum(II) is called $L_2Pt(C_6D_5)Tf$ or **2- d_5** , and neopentane- d_1 is called **Np-D**.

Results

Preparation of $L_2PtNpTf$ (1). Reaction of *trans*- $L_2PtNpCl$ with silver triflate ($AgSO_3CF_3$) in benzene yields $L_2PtNpTf$ (1). Reaction of 1 with ($n-C_{14}H_{29}NMe_2$)($PhCH_2$) N^+Cl^- in THF regenerates *trans*- $L_2PtNpCl$ (Scheme II). We propose that the bond between the platinum atom and triflate group in 1 is covalent. We rationalize this structural proposal using the following arguments: (1) $L_2PtNpTf$ is very soluble in benzene (0.21 M) and is reasonable soluble in cyclohexane- d_{12} (>0.05 M) and *n*-hexane (>0.02 M). (2) While three-coordinate, 14-electron platinum(II) complexes have been proposed as intermediates in several mechanisms^{16,17,19–21} (including the mechanisms discussed here), they have never been isolated or observed spectroscopically: $[L_2PtNp]^+Tf^-$ is thus not a reasonable structure for 1. (3) The ³¹P NMR spectra of 1 in C_6D_6 and C_6D_{12} are similar (δ –9.33 ($J_{PPt} = 3030$ Hz) and δ –9.1 ($J_{PPt} = 3070$ Hz), respectively). We would expect that this change in solvent would have a greater effect on these spectra if 1 were a triflate salt. (4) The ³¹P NMR chemical shift of 1 is ca. 4 ppm *downfield* of $L_2PtNpCl$. We would expect that the chemical shift of 1 would be closer to those of $[L_2PtNp]^+Cl^-$ (5–10 ppm *upfield* of $L_2PtNpCl$) if 1 were a triflate salt.

Products. When a solution of $L_2PtNpTf$ (1) (0.05 M) in benzene- d_6 (99.5 atom %, 0.34 M benzene- d_5 as impurity) in a sealed 5-mm NMR tube is allowed to react for 2 half-lives (133 °C for 80 min), $L_2Pt(C_6D_5)Tf$ (**2- d_5**), neopentane- d_1 (83%), neopentane- d_0 (14%), and 1,1-dimethylcyclopropane (3%) are products²² (Scheme II). The only phosphorus-containing product observed by ³¹P NMR

(8) Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1983**, 478–9.

(9) For example: Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939. Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121–22. Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723–25. Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107–113. Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 88–89. Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1950–58.

(10) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–63.

(11) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–93.

(12) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214–16.

(13) Hackett, M.; Ibers, J. A.; Jernakoff, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436–1448. Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449–1462.

(14) Kool, L.; Whitesides, G. M. *J. Am. Chem. Soc.*, submitted for publication.

(15) For example: Tsai, M.-C.; Friend, C. M.; Muettterties, E. *J. Am. Chem. Soc.* **1982**, *104*, 2539–2543.

(16) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725.

(17) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948–49. DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *104*, 124–33.

(18) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581–4582. Silvestre, J.; Calhorda, M. J.; Hoffmann, R.; Stoutland, P. O.; Bergman, R. G. *Organometallics* **1986**, *5*, 1841–1851.

(19) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396–3403.

(20) Reamey, R. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 81–85.

(21) Brainard, R. L.; Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1481–1490.

(22) These are relative yields determined by GC. We estimate that they differ from the absolute yield by no more than $\pm 5\%$.

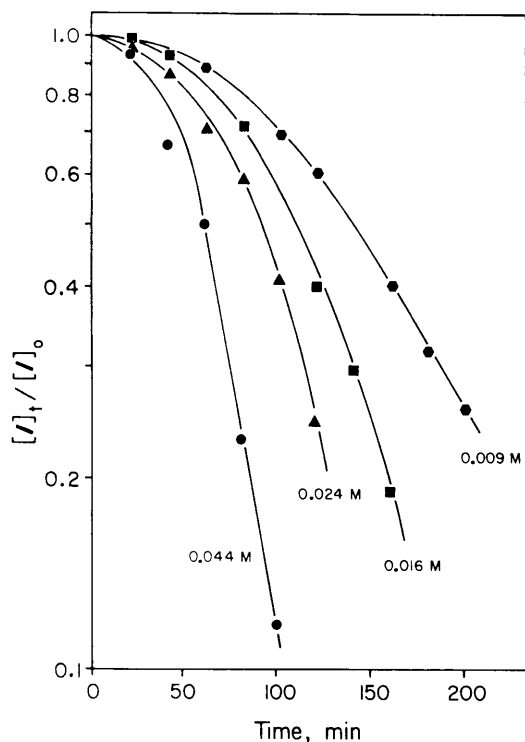
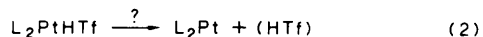
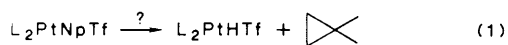


Figure 1. First-order kinetic plots of the reaction of $L_2PtNpTf$ with benzene- d_6 at different initial concentrations of **1** ($T = 133^\circ C$). $[L_2PtNpTf]_0$ is indicated on the figure for each curve.

spectroscopy is $L_2Pt(C_6D_5)Tf$ (**2-d**₅). As part of our proof of structure, samples of **2** and **2-d**₅ were converted to *trans*- $L_2Pt(C_6H_5)Cl$ and *trans*- $L_2Pt(C_6D_5)Cl$ by reaction with benzyldimethyltetradecylammonium chloride in THF. The relative amounts of neopentane-*d*₁ and neopentane-*d*₀ produced in these reactions vary from ~1:1 to ~10:1, depending on the initial concentration of $L_2PtNpTf$ (vide infra). The reaction mixtures are initially clear and colorless; at the conclusion of the reaction they become pale yellow and a small quantity of clear colorless gel forms on the walls of the NMR tubes. We did not determine the composition of this gel.

We believe that the 1,1-dimethylcyclopropane (1–5%) is a product of *intramolecular* activation of a methyl C–H bond in **3** followed by reductive elimination. This decomposition pathway is similar to that observed for *trans*-((*c*- C_5H_9)₃P)₂PtNpCl in which *trans*-((*c*- C_5H_9)₃P)₂PtHCl, 1,1-dimethylcyclopropane (96%), and neopentane (4%) are produced.²¹ By strict analogy with this reaction, L_2PtHTf should have been produced together with 1,1-dimethylcyclopropane (eq 1 and 2). Although L_2PtHTf was not observed by ³¹P NMR spectroscopy, it might have been present as the colorless gel.



Kinetics. Figure 1 shows kinetic plots derived from four experiments in which benzene-*d*₆ solutions were decomposed thermally at 133 °C. The initial concentration of **1** ($[1]_0$) in these four experiments varied from 0.009 to 0.044 M. The reactions were not first-order in starting material (1): the rates increased as the reaction proceeded and were greater when $[1]_0$ was greater. These trends in reaction rates suggest a reaction whose rate is accelerated by one or more reaction products.

The Relative Yields of Neopentane-*d*₁ and Neopentane-*d*₀. Solutions of $L_2PtNpTf$ in benzene-*d*₆ (99.5

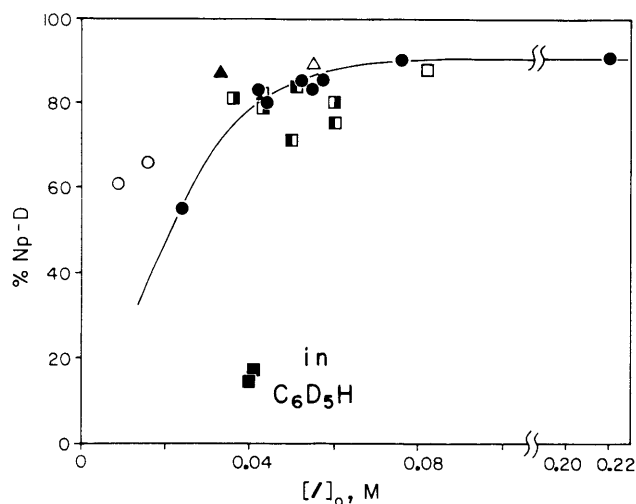


Figure 2. Percent neopentane-*d*₁ (relative to total neopentane) produced during the thermal decomposition of $L_2PtNpTf$ in benzene- d_6 (or benzene- d_5) at $133^\circ C$ plotted as a function of $[1]_0$. Thermal decompositions were conducted in sealed 5-mm NMR tubes in benzene- d_6 , except where noted: ●, standard conditions; ○, 10-mm glass NMR reaction tube; □, Vycor reaction tube; △, 5 mm NMR tube which was treated with DCl/ D_2O and dried under vacuum before use; ▲, 10 mg of D_2O added; ■, C_6D_5H used as solvent; ■, $Bu_4N^+Tf^-$ added; ■, $Bu_4N^+BF_4^-$ added.

atom %, 0.34 M benzene-*d*₅ as impurity) heated at 133 °C for 2 half-lives in sealed NMR tubes produced a mixture of neopentane-*d*₁ and neopentane-*d*₀. The amount of neopentane-*d*₁ produced (relative to total neopentane) increased as the initial concentration of $L_2PtNpTf$ ($[1]_0$) increased, reaching a limiting value of around 90% when the initial concentration of $L_2PtNpTf$ was high ($[1]_0 \geq 0.07$ M; Figure 2). The rationalization of low levels of ¹H incorporation into products in this type of reaction represents a problem that is always difficult and annoying when working with small quantities of dilute solutions of water-sensitive organometallic compounds. The protons may originate in water in the glassware, in the solvent, or, perhaps, adsorbed on the solid organoplatinum compound; from reaction with isotopic impurities in the solvent; or from intramolecular reaction with Np or phosphine ligands. We believe that both reactions with water adsorbed on the walls of the NMR tubes and with isotopic impurities in solvent are important: the former is important at low $[1]_0$; the latter for high $[1]_0$. Contributions from other sources of protons cannot, however, be excluded.

Reactions conducted in 10-mm NMR tubes (3.0 mL of solution) produced less neopentane-*d*₀ than would be expected on the basis of a comparison of the trends in deuterium incorporation observed for reactions conducted in 5-mm NMR tubes (Figure 2). This result is consistent with the hypothesis that the area of the glass tube in contact with the sample is important in determining the isotopic composition of neopentane, since 10-mm NMR tubes have a lower surface-to-volume ratio (ca. 5 cm²/mL) than do 5-mm NMR tubes (ca. 10 cm²/mL).

These and related experiments outlined in the Experimental Section suggest that at low $[1]_0$ (0.01–0.06 M), $L_2PtNpTf$ reacts with water at the interface of the glass NMR tubes to form neopentane-*d*₀.²³ Increases in the initial concentration of $L_2PtNpTf$, addition of D_2O , and H/D exchange of the protons on the surface of the glass

(23) Assuming that 10^{15} molecules/cm² constitute a monolayer of water molecules, we calculated that neopentane-*d*₀ is formed by the reaction of **1** with two monolayers of water on the surface of the NMR tube in contact with solution.

all helped to decrease the mole fraction of neopentane- d_0 to about 10%. We believe that this residual neopentane- d_0 was *not* a product of reaction of 1 with protons on glass surfaces but was instead a product of the reaction of 1 with residual protons in benzene- d_6 or of the intramolecular reaction of L_2PtNp^+ with the Me_3P protons (*vide infra*).

Reaction of $L_2PtNpTf$ in C_6D_5H . The relative amounts of neopentane- d_1 produced in two independent thermolyses of 0.04 M benzene- d_5 solutions of $L_2PtNpTf$ were 15% and 17% (Figure 2). The relative amount of neopentane- d_1 produced in thermolyses of benzene- d_6 solutions of 1 at the same concentration is around 80%. Neglecting the 20% neopentane- d_0 normally produced during the reaction of 1 with benzene- d_6 (99.5 atom %), the ratio of NpD vs NpH produced in C_6D_5H is 1:4, despite the fact that C_6D_5H is 5:1 in $[D]$ and $[H]$. Thus, 1 shows a very large kinetic isotope effect of $k_H/k_D \approx 20 \pm 6$.²⁴⁻³¹

This apparent value of k_H/k_D is sufficiently large that its numerical accuracy is clearly suspect. We are confident that the *qualitative* conclusion from this experiment—that cleavage of a C-H bond of the benzene substrate is strongly favored over cleavage of a C-D bond—is correct. The *quantitative* estimate of this isotope effect is complicated both by the requirement of obvious assumptions about mass balance in protons and by the fact that when attack on the benzene slows on deuteration, the importance of other proton sources—glass, trimethylphosphine, neopentyl groups, traces of water—increases. We have not compared the isotopic compositions of neopentanes produced in decompositions in C_6D_6 of $L_2PtNpTf$ and $[(CD_3)_3P]_2PtNpTf$, in order to check independently the source of the protons in these experiments. We can, however, check our numbers for consistency. In particular, the large value of k_H/k_D can account for the amount of neopentane- d_1 produced in reactions at high $[1]_0$ (90%). The benzene- d_6 used in these experiments was 99.5 atom % deuterium. This level of isotopic purity indicates that the relative concentration of hydrogen to deuterium was 1:200. On the basis of this value of $[H]/[D]$ and the magnitude of the competitive kinetic isotope effect ($k_H/k_D = 20$), we estimate that the maximum amount of neopentane- d_1 to be expected from the reaction of 1 with benzene- d_6 (99.5 atom %) is 91%. The observed value is 90%.

We conclude from the experiments that reaction of $L_2PtNpTf$ with C-H and C-D bonds in benzene shows a large normal isotopic effect. We are not confident of the magnitude of this effect.

Addition of Tetra-*n*-butylammonium Triflate. Several homogeneous solutions of $L_2PtNpTf$ (1) in benzene-

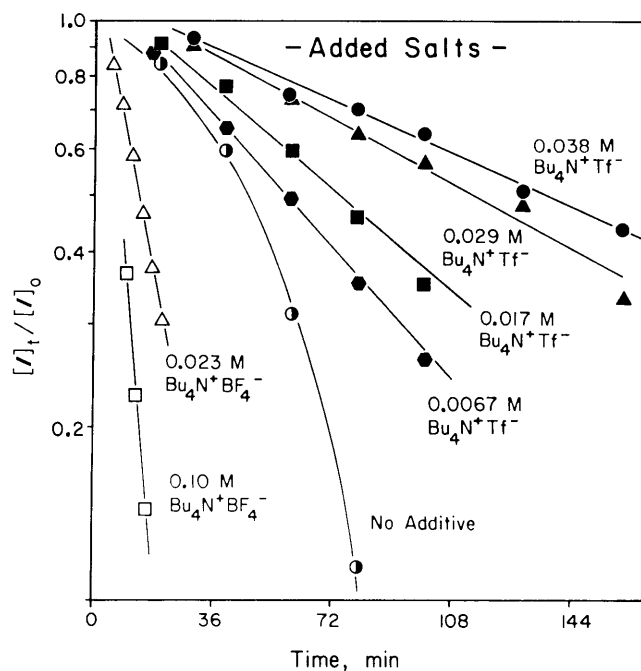


Figure 3. First-order kinetic plots of the reaction of $L_2PtNpTf$ with benzene- d_6 at 133 °C in the presence of added $Bu_4N^+Tf^-$ (filled figures), of added $Bu_4N^+BF_4^-$ (open figures), and with no additives (○): $[L_2PtNpTf]_0 = 0.04$ – 0.06 M; $[Bu_4N^+Tf^-]_0$ and $[Bu_4N^+BF_4^-]_0$ are indicated on the figure for each curve.

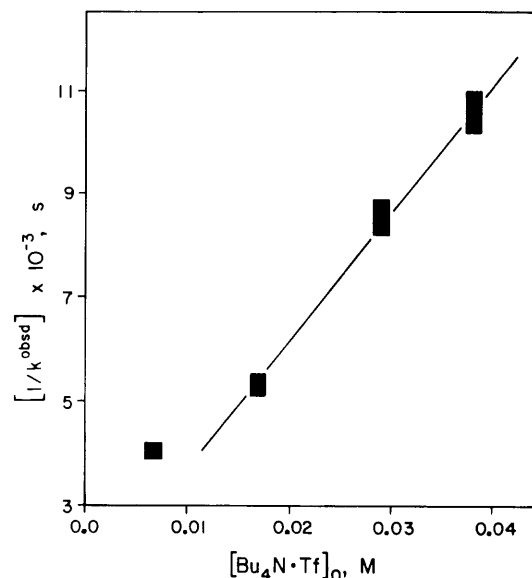


Figure 4. Reciprocal of the first-order rate constant ($1/k^{obsd}$) for the reaction of 1 with benzene- d_6 plotted as a function of $[Bu_4N^+Tf^-]_0$ ($T = 133$ °C, $[1]_0 = 0.04$ – 0.06 M).

ene- d_6 containing tetra-*n*-butylammonium triflate ($0.007 \leq Bu_4N^+Tf^- \leq 0.038$ M) were allowed to decompose at 133 °C. During the first 20 min of thermolysis, a brown oil separated from these solutions, with the greatest amount of oil appearing in those solutions initially having the highest concentrations of $Bu_4N^+Tf^-$. We estimate that the volume of this oil was 10–30% of the volume of the $Bu_4N^+Tf^-$ added and suspect it to have been predominantly $Bu_4N^+Tf^-$. The products of these reactions were similar to those observed in the absence of added $Bu_4N^+Tf^-$, although the yields of neopentane- d_0 and 1,1-dimethylcyclopropane increased slightly (Figure 2).

These reaction rates appeared to be first-order in $L_2PtNpTf$ after a short induction period and were found to *decrease* when the initial concentration of $Bu_4N^+Tf^-$

(24) Error limits for this kinetic isotope effect were determined from the 95% confidence limits for the percent of neopentane- d_1 produced in each reaction ($\pm 5\%$).

(25) The value of $k_H/k_D = 20$ is larger than the semiclassical upper limit for a primary KIE of $k_H/k_D = 4.2$ based on complete bond breaking of a benzene C-H(D) bond at 133 °C.²⁶ A number of large kinetic isotope effects are known that exceed this semiclassical upper limit: $k_H/k_D = 16$, 21, 27, 45, >1000.²⁶⁻³¹

(26) O'Ferrall, R. A. M. In *Proton-Transfer Reaction*; Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975; Chapter 8. Lewis, E. S. In *Proton-Transfer Reaction*; Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975; Chapter 10 and references therein.

(27) Stewart, R.; van der Linden, R. *Discuss. Faraday Soc.* **1960**, 29, 211.

(28) Lewis, E. S.; Funderburk, L. H. *J. Am. Chem. Soc.* **1967**, 89, 2322–27. Lewis, E. S.; Robinson, J. K. *J. Am. Chem. Soc.* **1968**, 90, 4337–44.

(29) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1975**, 97, 907–8. Roecker, L.; Meyer, T. J. *J. Am. Chem. Soc.* **1986**, 4066–4073.

(30) Caldin, E. F.; Mateo, S. *J. Chem. Soc., Chem. Commun.* **1973**, 854–55.

(31) Wang, J.-T.; Williams, F. *J. Am. Chem. Soc.* **1972**, 2930–34.

increased (Figure 3). The reciprocals of these first-order rate constants³² were plotted as a function of $[\text{Bu}_4\text{N}^+\text{Tf}^-]$ (where $[\text{Bu}_4\text{N}^+\text{Tf}^-]_0$ is the initial concentration of $\text{Bu}_4\text{N}^+\text{Tf}^-$) and were found to give a straight line at the higher values of $[\text{Bu}_4\text{N}^+\text{Tf}^-]_0$ (0.017–0.038 M, Figure 4).^{33,34} If the triflate concentration in these reactions were proportional to $[\text{Bu}_4\text{N}^+\text{Tf}^-]_0$, this correlation would strongly support a mechanism for the thermal decomposition of L_2PtNpTf in which triflate dissociates before and remains dissociated during the rate-limiting transition state. As it is, the formation of the brown oil makes it difficult to know the triflate concentration exactly or even whether the triflate concentration is proportional to the initial concentration of $\text{Bu}_4\text{N}^+\text{Tf}^-$, since these solutions may be saturated in $\text{Bu}_4\text{N}^+\text{Tf}^-$. The linear dependence of rate on the initial concentration of $\text{Bu}_4\text{N}^+\text{Tf}^-$ argues, however, that the concentration of triflate ion does increase with $[\text{Bu}_4\text{N}^+\text{Tf}^-]_0$ and that the rate at which 1 reacts with benzene- d_6 is decreased by the presence of triflate anion. This behavior is consistent with a rate-limiting transition state in which triflate is dissociated.³⁵

Addition of Tetra-*n*-butylammonium Tetrafluoroborate. Solutions of L_2PtNpTf and $\text{Bu}_4\text{N}^+\text{BF}_4^-$ in benzene- d_6 (0.023 and 0.10 M) decomposed much faster than solutions *not* containing $\text{Bu}_4\text{N}^+\text{BF}_4^-$ and gave better first-order kinetics (after a brief induction period, Figure 3). The solution with the higher initial concentration of $\text{Bu}_4\text{N}^+\text{BF}_4^-$ (0.10 M) reacted faster than the solution with the lower initial concentration (0.023 M). Only the solution that was initially 0.10 M in $\text{Bu}_4\text{N}^+\text{BF}_4^-$ produced a brown oil; the solution containing 0.023 M $\text{Bu}_4\text{N}^+\text{BF}_4^-$ remained homogeneous. The products of these reactions were similar to those observed in the absence of added $\text{Bu}_4\text{N}^+\text{BF}_4^-$ (Figure 2).

These kinetic results are consistent with the mechanisms outlined in Scheme I, as both involve an ionic rate-limiting transition state; the increase in ionic strength of the solvent is probably responsible for the increase in the reaction rate.³⁵ Addition of $\text{Bu}_4\text{N}^+\text{BF}_4^-$ also probably helps to maintain a fairly constant level of ionic strength (as with the addition of $\text{Bu}_4\text{N}^+\text{Tf}^-$) and allows the reaction of L_2PtNpTf with benzene- d_6 to occur by first-order kinetics.

Thermal Decomposition of L_2PtNpTf in Toluene. Thermolysis of a solution of L_2PtNpTf in toluene (0.07 M) at 133 °C, for 80 min, yielded $\text{L}_2\text{Pt}(m\text{-tolyl})\text{Tf}$, $\text{L}_2\text{Pt}(p\text{-tolyl})\text{Tf}$, neopentane (99%), and 1,1-dimethylcyclopropane (1%). The rate of this reaction was indistinguishable from that observed in benzene- d_6 ($[1]_0 = 0.07$ M) under the same conditions (Figure 5). The products of this thermal decomposition yielded $\text{L}_2\text{Pt}(m\text{-tolyl})\text{Cl}$ (65%) and $\text{L}_2\text{Pt}(p\text{-tolyl})\text{Cl}$ (35%) after reaction with benzyldimethyltetradecylammonium chloride in THF. The identities of these products were determined by comparison with ^1H NMR

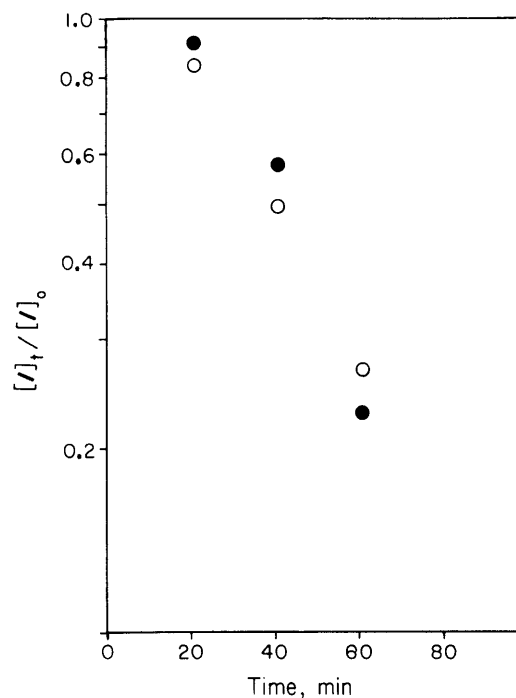
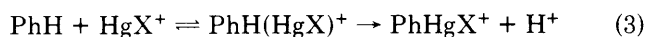


Figure 5. Reaction of L_2PtNpTf with toluene (●) and benzene- d_6 (○) at 133 °C ($[1]_0 = 0.07$ M).

and ^{31}P NMR spectra of authentic samples of $\text{L}_2\text{Pt}(m\text{-tolyl})\text{Cl}$ and $\text{L}_2\text{Pt}(p\text{-tolyl})\text{Cl}$ synthesized independently. Relative yields were determined by comparison of the integrated intensities of appropriate peaks in the ^{31}P NMR and the ^1H NMR spectra. No products (<5%) of ortho or benzylic substitution were observed by either ^1H or ^{31}P NMR spectroscopy.

The lack of selectivity between meta and para toluene C-H bonds (1:1 para/meta rate ratio), and the similar rates observed in the reactions of 1 with benzene and toluene indicate that the product-determining steps in these reactions do not involve a large localization of positive charge on the aromatic ring. Mercuration of aromatic compounds is believed to proceed by the mechanism outlined in eq 3.³⁶



The perchloric acid catalyzed mercuration of toluene shows a pronounced kinetic selectivity for para over meta (11:1 to 15:1 para/meta ratio of rates), and reaction with toluene is 6–8 times faster than reaction with benzene.³⁷ The bromination of aromatic compounds is even more selective. Toluene is brominated 600 times faster than is benzene, and the para position of toluene is brominated 440 times faster than the meta position.³⁸ Thus, the statistically determined relative selectivities calculated here for para and meta metalation of toluene and the insignificant difference in rate of reaction of benzene are both inconsistent with mechanisms involving electrophilic attack on the aromatic ring.

Addition of Trimethylphosphine. A 0.09 M solution of L_2PtNpTf and trimethylphosphine (3.5 equiv) in benzene- d_6 reacted within 5 min at room temperature to produce $[\text{L}_3\text{PtNp}]^+\text{Tf}^-$. Most of this compound separated from solution as a clear, colorless oil, although a detectable concentration remained in the upper benzene- d_6 layer.³⁹

(32) The first-order rate constants used in Figure 4 were derived from the linear portions of the kinetic plots shown in Figure 3.

(33) When these data were plotted as $\ln k_{\text{obsd}}$ vs $\ln [\text{Bu}_4\text{N}^+\text{Tf}^-]_0$, the order in $[\text{Bu}_4\text{N}^+\text{Tf}^-]_0$ was determined to be -0.86 ± 0.14 (95% confidence) for this reaction. We believe that this value departs from (the expected) -1.0 because increases in $[\text{Bu}_4\text{N}^+\text{Tf}^-]_0$ produce increases both in $[\text{Tf}^-]$ and in the ionic strength. The mass-law effect of increased free triflate ion concentration is partly offset by the increases in ionic strength. This phenomenon is similar to that observed in $\text{S}_{\text{N}}1$ solvolysis of alkyl halides.³⁴

(34) For an excellent review of ion effects in solvolysis reactions, see: Raber, D. J.; Harris, J. M.; Schleyer, P. V. R. In *Ions and Ion pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1974; Vol. II, Chapter 3.

(35) The rate of this reaction should be increased in media of greater ionic strength because any of the possible rate-limiting transition states have more charge separation than the starting material 1. This reactivity is similar to that observed in $\text{S}_{\text{N}}1$ solvolysis reactions of alkyl halides.³⁴

(36) Kitching, W. *Organomet. Chem. Rev.* **1968**, *3*, 35–60.

(37) Brown, H. C.; McGary, C. W. *J. Am. Chem. Soc.* **1955**, *77*, 2300–2306.

(38) Brown, H. C.; Stock, L. M. *J. Am. Chem. Soc.* **1957**, *79*, 1421–1425.

This compound, the solution, and the colorless oil remained unchanged (by ^{31}P NMR and by visual inspection) after heating at 133 °C for 13 h in a sealed NMR tube.

The displacement of triflate by trimethylphosphine makes it impossible to examine the rate of reaction between L_2PtNpTf and benzene- d_6 in the presence of added phosphine, and it is therefore impossible to rule out completely a mechanism in which phosphine dissociates. Nevertheless, we think that the evidence for triflate dissociation argues against such a mechanism, since we consider it highly unlikely that two ligands must dissociate before oxidative addition to a benzene C–H(D) bond can occur.

Thermal Decomposition of L_2PtNpTf in Cyclohexane- d_{12} . A 0.05 M solution of L_2PtNpTf in cyclohexane- d_{12} was thermally decomposed at 133 °C for 2 h. The neopentane produced in this reaction contained only 1% neopentane- d_1 . Thus, L_2PtNpTf did not react with the C–D bonds in cyclohexane- d_{12} and form stable products.

Discussion

We cannot rigorously exclude either mechanism of Scheme I but strongly favor that involving direct oxidative addition of a C–H bond to L_2PtNp^+ .

Mechanism 1. In this mechanism, triflate dissociation is followed by oxidative addition of a benzene C–H(D) bond to the platinum center. Reductive elimination of neopentane- d_1 followed by recombination with triflate gives $\text{L}_2\text{Pt}(\text{C}_6\text{D}_5)\text{Tf}$. Triflate dissociation is reversible, and either oxidative addition or reductive elimination is probably rate-limiting.

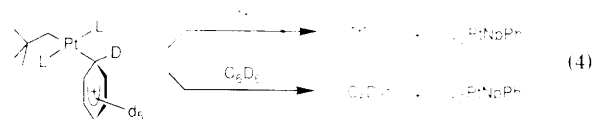
We suggest that the reaction in the absence of added salts is intrinsically first-order in $[\text{I}]_0$ but is accelerated by ionic side products. The linear first-order kinetics obtained in the presence of added $\text{Bu}_4\text{N}^+\text{BF}_4^-$ or added $\text{Bu}_4\text{N}^+\text{TF}^-$ are consistent with this proposal: these added salts should maintain a constant level of ionic strength. The rate depression in the presence of $\text{Bu}_4\text{N}^+\text{TF}^-$ and the rate acceleration in the presence of $\text{Bu}_4\text{N}^+\text{BF}_4^-$ are consistent with triflate dissociation. This behavior parallels the effect of adding a common ion or an uncommon ion to the $\text{S}_{\text{N}}1$ solvolysis of alkyl halides.³⁴

The lack of any reactivity difference between benzene- d_6 C–D bonds, toluene meta C–H bonds, and toluene para C–H bonds is consistent with this mechanism as neither aryl C–H(D) activation nor reductive elimination of neopentane should develop positive charge on the aryl rings.

Mechanism 2. According to this mechanism, reversible triflate dissociation is followed by association of benzene, yielding the η^1 -product of electrophilic attack of Pt(II) on the benzene ring. Deprotonation of this intermediate yields $\text{L}_2\text{PtNp}(\text{C}_6\text{D}_5)$ (6) and D^+ . Reaction of 6 with D^+ gives $\text{L}_2\text{Pt}(\text{C}_6\text{D}_5)\text{Tf}$ (2) and neopentane- d_1 .

As in mechanism 1, we would ascribe the autocatalytic kinetics in the absence of added salts to an ionic rate-limiting step that is accelerated by ionic side products. The linear first-order kinetics in the presence of added salts and the rate acceleration in the presence of added $\text{Bu}_4\text{N}^+\text{BF}_4^-$ are consistent with this proposal. The rate depression in the presence of added $\text{Bu}_4\text{N}^+\text{TF}^-$ could only be rationalized if, under these conditions ($[\text{Bu}_4\text{N}^+\text{TF}^-]_0 > 0.02 \text{ M}$), the deprotonation of the η^1 -complex were rate-limiting, and it were deprotonated by benzene rather than

triflate (eq 4). If this complex were deprotonated by



triflate instead of benzene or if some step other than deprotonation were rate-limiting, then the reaction would show no rate depression in the presence of added $\text{Bu}_4\text{N}^+\text{TF}^-$, since both 1 and the rate-limiting transition state would contain triflate.

The lack of any selectivity for benzene- d_6 vs toluene or of discrimination between the meta and para positions of toluene provide evidence against this mechanism, since it should be very similar to electrophilic substitution reactions showing pronounced differences in reactivity for these positions.

Conclusion

Both possible mechanisms for the reaction of 1 with benzene- d_6 have the species L_2PtNp^+ as the reactive intermediate; the mechanism involving electrophilic attack of this moiety on the aromatic ring seems less attractive than that in which a C–H bond adds oxidatively to this group. It is difficult to construct any variant of an electrophilic mechanism placing positive charge on the aromatic ring that is consistent with the low positional selectivity observed between the meta and para positions of toluene and the low substrate selectivity observed between benzene and toluene;⁴⁰ this low selectivity seems much more consistent with direct oxidative addition of a C–H bond to the platinum(II) center. The observation that the rate is suppressed on addition of triflate is compatible with the hypothesis that triflate dissociation is reversible.

A more detailed study of this mechanism might be possible but would be rendered difficult by the problems of working with highly polar or ionic species in the solvents with low dielectric constants. An important qualitative conclusion emerges, however, from the fact that no reaction appears to occur between 1 and cyclohexane- d_{12} . Until recently, the reluctance of soluble organoplatinum compounds to react with unactivated C–H bonds stood in surprising contrast with the high reactivity exhibited by platinum metal and by many other soluble organometallic species. The reactivity of 1 (or, more precisely, of $\text{L}_2\text{PtNp}^+\text{Tf}$) toward benzene suggests that increasing the electrophilicity of the platinum center does increase reactivity toward C–H bonds relative to intramolecular reaction but not sufficiently to favor intermolecular reaction with alkanes. By contrast, reaction of $(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)\text{Pt}^0$ with alkanes occurs readily.¹³ Thus, the essential ingredient in favoring intermolecular C–H activation seems *not* to be increasing the electrophilicity at the metal center but some presently unresolved combination of decreasing steric congestion around this center, hindering intramolecular access to C–H bonds, and decreasing the P–Pt–P bond angle.

Experimental Section

General Data. Silver trifluoromethanesulfonate (Alfa Products) was recrystallized from diethyl ether. Trimethylphosphine (Strem Chemicals) and $\text{Bu}_4\text{N}^+\text{BF}_4^-$ (Aldrich) were used as received. Benzene- d_6 (99.5 atom %), benzene- d_5 (MSD), toluene, and *p*-xylene were distilled from Na/K alloy and stored over

(39) $[\text{L}_3\text{PtNp}]^+\text{Tf}^-$ was observed in the upper benzene- d_6 layer and in the lower oil layer by adjusting the position of the NMR tube so that the appropriate layer was in the center of the spectrometer's probe during ^{31}P NMR experiments.

(40) This type of selectivity would require essentially encounter-controlled reaction of the platinum center with carbon centers.

LiAlH₄. Diethyl ether was freshly distilled from Na/benzophenone before use. Cyclohexane-*d*₁₂ and *n*-hexane were stirred over 10% concentrated nitric acid in concentrated sulfuric acid for several weeks, washed with aqueous NaHCO₃, passed through silica gel, distilled from Na/K alloy, and stored over LiAlH₄.

The ¹H and ³¹P NMR spectra were recorded on a Bruker WM 300 spectrometer. The ¹H chemical shifts are reported in parts per million with respect to Me₄Si (δ 0.0) and were measured relative to the ¹H resonance of the C₆D₅H impurity (δ 7.15). The ³¹P chemical shifts are relative to 85% phosphoric acid (downfield shifts positive); all ³¹P NMR spectra were proton decoupled. Melting points were obtained in sealed tubes under argon and are uncorrected.

All experiments were performed under an oxygen-free dry nitrogen or argon atmosphere using Schlenk and glovebox techniques.⁴¹ Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Analyses for phosphorus in (Me₃P)₂Pt(Ar)Cl (Ar = phenyl, *m*-tolyl, and *p*-tolyl) were consistently low and are not reported.

trans-Chloro(neopentylbistrimethylphosphine)platinum(II). A suspension of (COD)PtNpCl²¹ (1.355 g, 3.31 mmol) in diethyl ether (25 mL) was cooled to 0 °C. Trimethylphosphine (0.67 mL, 8.45 mmol, 2.56 equiv) was added in one portion. The reaction was stirred at 0 °C for 1.5 h and then allowed to warm to room temperature over 2.5 h. Ether was removed by rotary evaporation giving a white solid which was recrystallized from ca. 20 mL of petroleum ether. An ethereal solution of this solid was passed through silica gel (60 mL), recrystallized from diethyl ether, and yielded *trans*-L₂PtNpCl (1.17 g, 78%) as white crystals: mp 170–170.5 °C; ¹H NMR (C₆D₆) δ 1.68 (t of t, *J*_{HP} = 9, *J*_{HPt} = 83 Hz, 2 H),^{42,43} 1.24 (t of t, *J*_{HP} = 3.5, *J*_{HPt} = 28 Hz, 18 H), 1.20 (br s, 9 H); ³¹P NMR (C₆D₆) δ -13.3 (*J* = 2936 Hz). Anal. Calcd for C₁₁H₂₉ClP₂Pt: C, 29.11; H, 6.46; Cl, 7.81; P, 13.65. Found: C, 28.86; H, 6.43; Cl, 7.89; P, 13.62.

trans-(Me₃P)₂Pt(CH₂C(CH₃)₃)(SO₃CF₃) (1). A solution of L₂PtNpCl (6.0 mL, 0.20 M, 1.19 mmol) in benzene was added to a solution of AgSO₃CF₃ (35 mL, 0.034 M, 1.19 mmol) in benzene at room temperature and a white solid precipitated immediately. The reaction mixture was stirred at room temperature for 3 h and filtered. Benzene was removed from the filtrate by vacuum distillation, leaving an air-sensitive white solid. Recrystallization of the solid from hexane gave *trans*-L₂PtNpTf (420 mg, 62%) as white crystals: mp 125–126 °C; ¹H NMR (C₆D₆) δ 1.55 (t of t, *J*_{HPt} = 90, *J*_{HP} = 9.6 Hz, 2 H),^{42,43} 1.11 (t of t, *J*_{HPt} = 28, *J*_{HP} = 3.6 Hz, 18 H), 1.10 (t, *J*_{HPt} = 4.3 Hz, 9 H); ³¹P NMR (C₆D₆) δ -9.33, *J* = 3030 Hz. Anal. Calcd for C₁₂H₂₅F₃O₃P₂SPt: C, 25.40; H, 5.15; S, 5.65. Found: C, 25.20; H, 5.04; S, 5.28.

Sample Preparation. In a typical experiment, a 5-mm NMR tube (526-PP Wilmad) was sealed to a 14/20 inner joint, filled with concentrated HNO₃, heated, rinsed with deionized water, and dried in an oven (110 °C). The tube was attached to a vacuum manifold, evacuated to 0.005 Torr, and flamed out for ca. 10 min. The evacuated tube was taken into a glovebox and loaded with a weighted sample of L₂PtNpTf. The loaded tube was evacuated to 0.005 Torr for several hours prior to the addition of degassed solvent by trap-to-trap distillation (benzene-*d*₆, benzene-*d*₀, benzene-*d*₅, toluene, and cyclohexane-*d*₁₂). The tube was sealed under vacuum.

Thermolysis Reactions. Sample NMR tubes were immersed in a solvent-vapor bath (chlorobenzene, 133 °C), removed at regular intervals, and immersed in water. The temperature of the solvent-vapor bath was determined with a calibrated thermometer and was found to be constant to ±0.7 °C. The mole fraction of L₂PtNpTf remaining at each time was calculated from ³¹P NMR spectra taken of the reaction mixture by this equation: $[1]_t/[1]_0 = [1]_t/([1]_t + [2-d_5]_t)$.⁴⁴

(41) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

(42) Platinum is composed of one-third ¹⁹⁵Pt (spin 1/2) and two-thirds other isotopes (spin 0). A characteristic coupling pattern is the 1:4:1 platinum "triplet".

(43) *J*_{HP} for methyl protons in phosphine ligands are virtual coupling constants. Pregosin, P. S.; Kunz, R. W. ³¹P and ¹³C NMR of Transition Metal Phosphine Complexes; Springer-Verlag: New York, 1979; pp 28–31, 66–68.

L₂Pt(C₆H₅)Tf (2) and L₂Pt(C₆H₅)Cl. A solution of L₂PtNpTf (1.0 mL, 0.16 M, 0.16 mmol) in benzene-*d*₀ was heated at 133 °C for 1 h in a sealed NMR tube. The ³¹P NMR spectrum of this solution showed that it contained 10% 1 and 90% L₂Pt(C₆H₅)Tf (2): ³¹P (C₆H₆) δ -8.49 (*J* = 2815 Hz). This solution was transferred to a suspension of benzyltrimethyltetradecylammonium chloride (72 mg, 0.20 mmol, 1.25 equiv) in 12 mL of tetrahydrofuran at -78 °C. The stirred reaction mixture was allowed to warm to room temperature over 1 h, reduced in volume by rotary evaporation, and purified by preparatory TLC yielding L₂PtNpCl (8 mg, 110% yield based on ³¹P NMR) and L₂Pt(C₆H₅)Cl (56 mg, 85% yield). Similar results were obtained when 1 was allowed to react with benzene-*d*₆, followed by reaction with benzyltrimethyltetradecylammonium chloride, except that 2-*d*₅ and L₂Pt(C₆D₅)Cl are obtained.

Alternate Syntheses of *trans*-(Me₃P)₂Pt(Ar)Cl (Ar = Phenyl, *m*-Tolyl, and *p*-Tolyl). These compounds were independently synthesized and analyzed to confirm product identification. A typical synthesis was performed as follows (yields were not optimized). A 100-mL round-bottomed flask with a side arm was equipped with a stirring bar. The flask was charged with (COD)PtCl₂ (0.503 g, 1.34 mmol), capped with a rubber septum, and purged with argon. Diethyl ether (25 mL) was then added to the flask, and the stirred suspension was cooled to -78 °C. A THF solution of phenylmagnesium bromide (3.1 mmol) was added dropwise, and the solution was allowed to warm slowly to 0 °C. Methanol (1 mL) was added to destroy any excess Grignard. Methylene chloride (10 mL) was added to increase dissolution, and the solution was filtered. The solvent was removed by rotary evaporation leaving a light brown solid (crude CODPtPh₂). The solid was dissolved in benzene and filtered through silica gel. Benzene was removed until the solution became saturated in (COD)PtPh₂. A huge excess of concentrated HCl was added, and a white precipitate formed immediately upon stirring. The solid was collected by suction filtration and rinsed with ether yielding crude (COD)Pt(Ph)Cl (0.325 g, 58%).

(COD)Pt(Ph)Cl (0.151 g, 0.36 mmol) was dissolved in benzene (20 mL) and cooled to 10 °C. Exactly 2 equiv (0.72 mmol) of trimethylphosphine were added to the stirred solution. After TLC analysis showed the reaction to be complete, the solvent was removed by rotary evaporation leaving a white solid. The solid was dissolved in a minimum amount of CH₂Cl₂ and chromatographed on silica gel using 2:1 petroleum ether/diethyl ether as the eluant. The fractions were collected, and solvent was removed by rotary evaporation. Two recrystallizations from diethyl ether yielded white needles of *trans*-(Me₃P)₂Pt(Ph)Cl (0.116 g, 69%, mp 215–216 °C): ¹H NMR (CDCl₃) δ 7.31 (t of d, *J*_{HPt} = 64, *J*_{HH} = 7 Hz, 2 H), 6.91 (m, 2 H), 6.84 (m, 1 H), 1.25 (t of t, *J*_{HPt} = 31, *J*_{HP} = 4 Hz, 18 H); ³¹P NMR (CDCl₃) δ -14.9, *J* = 2766 Hz. Anal. Calcd for C₁₂H₂₃ClP₂Pt: C, 31.35; H, 5.04; Cl, 7.71. Found: C, 31.38; H, 5.02; Cl, 7.33.

trans-(Me₃P)₂Pt(*m*-tolyl)Cl was recrystallized twice from 2:1 petroleum ether/diethyl ether: ¹H NMR (CDCl₃) δ 7.15 (t, *J*_{HPt} = 65 Hz, 1 H), 7.09 (t of d, *J*_{HPt} = 64, *J*_{HH} = 7 Hz, 1 H), 6.79 (m, 1 H), 6.64 (br d, *J*_{HH} = 7 Hz, 1 H), 2.19 (s, 3 H), 1.25 (t of t, *J*_{HPt} = 31, *J*_{HP} = 4 Hz, 18 H); ³¹P NMR (CDCl₃) δ -14.7 (*J* = 2754 Hz). Anal. Calcd for C₁₃H₂₅ClP₂Pt: C, 32.95; H, 5.32; Cl, 7.48. Found: C, 33.18; H, 5.32; Cl, 7.73.

trans-(Me₃P)₂Pt(*p*-tolyl)Cl was recrystallized twice from petroleum ether: ¹H NMR (CDCl₃) δ 7.17 (t of d, *J*_{HPt} = 64, *J*_{HH} = 8 Hz, 2 H), 6.74 (br d, *J*_{HH} = 8 Hz, 2 H), 2.17 (s, 3 H), 1.24 (t of t, *J*_{HPt} = 31, *J*_{HP} = 4 Hz, 18 H); ³¹P NMR (CDCl₃) δ -15.1 (*J* = 2759 Hz). Anal. Calcd for C₁₃H₂₅ClP₂Pt: C, 32.95; H, 5.32; Cl, 7.48. Found: C, 33.06; H, 5.35; Cl, 7.58.

Relative Yields of Neopentane-*d*₁ and Neopentane-*d*₀. The structure of Vycor glass differs considerably from the structure of Pyrex glass. To test whether these differences can account for the formation of neopentane-*d*₀ during the thermolysis of 1 in glass NMR tubes, a solution of 1 (0.082 M) in benzene-*d*₆ was thermally

(44) The assumption that the mole fraction of 1 is equal to the integral of the ³¹P NMR signal for 1 divided by the sum of those integrals for 1 and 2-*d*₅ is, of course, not rigorously correct. A discrepancy between the values of *T*₁ for 1 and 2-*d*₅ will produce a systematic error in each rate determination. These systematic errors will not, however, cause a first-order reaction to give nonlinear kinetics.

decomposed in a sealed Vycor tube (Figure 2). The neopentane produced was 88% d_1 —essentially the same as in other reactions conducted in 5-mm NMR tubes in this concentration range. This change in the surface structure of the reaction vessel had very little effect on the relative amount of neopentane- d_1 produced in this experiment and indicates that protons on the surface of the glass are probably not involved in the formation of neopentane- d_0 at this concentration.

A sealed 5-mm NMR tube containing 1 mL of 38% DCl in D_2O was heated at 158 °C for 3 days, cracked open, rinsed with D_2O , and flame-dried under vacuum.⁴⁵ This tube was then used for the thermolysis of a 0.055 M benzene- d_6 solution of $L_2PtNpTf$. The neopentane produced in this reaction contained slightly more neopentane- d_1 (89%, Figure 2) than the neopentane produced in reactions having similar $[1]_0$ in untreated NMR tubes, but the amount of neopentane- d_1 produced did not exceed the usual 90%.

A 0.033 M benzene- d_6 solution of **1** was thermally decomposed for 60 min with 10 mg of D_2O (22 equiv). Unlike most other reactions presented here, no ^{31}P NMR signal for $L_2Pt(C_6D_6)Tf$ (or any other product) appeared over the course of this reaction.⁴⁶ The neopentane included much more monodeuterated material (87%, Figure 2) than would have been expected from a reaction at the same $[1]_0$ without added D_2O . Again, however, the amount of neopentane- d_1 produced did not exceed 90%.

Tetrabutylammonium Trifluoromethanesulfonate ($Bu_4N^+Tf^-$). Silver triflate (704 mg, 2.74 mmol) and tetrabutylammonium bromide (888 mg, 2.75 mmol) in a 200-mL round-bottomed flask equipped with a magnetic stir bar and a septum were placed under an argon atmosphere. Diethyl ether (100 mL) was added, and the reaction solution was stirred at room temperature for 1 h. This solution was reduced in volume by rotary evaporation. The resulting green solid was dissolved in CH_2Cl_2 , filtered through Celite, and recrystallized. Two recrystallizations from CH_2Cl_2/Et_2O yielded $Bu_4N^+Tf^-$ (771 mg, 72%) as white crystals: mp 91–94 °C; 1H NMR (C_6D_6) δ 2.97 (br t, $J = 7$ Hz, 8 H), 1.33 (m, 16 H), 0.95 (t, $J = 7$ Hz, 12 H); ^{13}C NMR (C_6D_6) δ 58.4, 24.0, 19.9, 13.8. Anal. Calcd for $C_{17}H_{36}F_3NO_3S$: C, 52.15; H, 9.27; N, 3.58; S, 8.17. Found: C, 51.98; H, 8.98; N, 3.42; S, 7.95.

Addition of Trimethylphosphine. Trimethylphosphine (10 μ L, 0.112 mmol, 3.5 equiv) was added to an NMR tube containing a solution of $L_2PtNpTf$ (0.35 mL, 0.09 M) in benzene- d_6 under a steady stream of argon. This solution was freeze–thaw–degassed three times, and the NMR tube was sealed under vacuum. A clear,

colorless oil (ca. 0.05 mL) separated from solution and sank to the bottom of the tube. Both layers contained $[L_3PtNp]^+Tf^-$ (^{31}P NMR), although the lower layer gave broadened signals which were shifted slightly from the signals observed in the upper layer. $[L_3PtNp]^+Tf^-$ in the upper layer: ^{31}P NMR (C_6D_6) δ –20.7 (d of t, $J_{PP} = 25$, $J_{PPt} = 2799$ Hz, 2 L), –24.4 (t of t, $J_{PP} = 25$, $J_{PPt} = 1561$ Hz, 1 L). $[L_3PtNp]^+Tf^-$ in lower layer: ^{31}P NMR (C_6D_6) δ –20.3, –24.8. No change was observed by ^{31}P NMR spectroscopy, nor did the appearance of the two layers change, after this sample was heated at 133 °C for 13 h. These ^{31}P NMR spectra are similar to that observed for $[(Et_3P)_3PtH]^+Cl^-$ at –61 °C. This compound is formed upon addition of Et_3P to solutions of *trans*-(Et_3P) $_2PtHCl$.⁴⁷

Gas Chromatographic and GC/MS Analysis of Reaction Mixtures. Reaction mixtures in sealed NMR tubes which had been thermally decomposed until ca. 25% of $L_2PtNpTf$ remained were cooled with liquid nitrogen to condense volatiles, cracked open, and sealed with a septum. The liquid phase of each sample was analyzed by GC and GC/MS. The relative yields of neopentane and 1,1-dimethylcyclopropane were determined by direct comparison of their GC integrals. (Within experimental error, the GC response factors for these compounds are identical.)

Mass spectra were obtained by using a Hewlett-Packard 5990A GC/MS, with a 70-eV ionization voltage. For each injection into the GC/MS instrument, each GC peak was sampled six to eight times over a broad range of retention times. Each of these samples yielded eight individual spectra. The resulting 48–64 individual spectra were statistically weighted according to their base peak abundance to produce one composite mass spectrum. The relative quantities of neopentane (d_0 vs d_1) were determined by comparing the relative abundance of the (M – methyl) peaks of authentic neopentane- d_0 (57/100%, 58/4.7%) and authentic neopentane- d_1 (57/35%, 58/100%).⁴⁸

Acknowledgment. We thank Alaric Naiman and Marifaith Hackett for many helpful discussions. The NMR spectrometers used at Harvard were purchased in part through NSF CHE 80-08891 and through NIH BRS Shared Instrument Grant Program 1 S10 RR01748-01A1.

Registry No. **1**, 116563-64-5; **2**, 116563-65-6; *trans*- $L_2PtNpCl$, 116563-66-7; *trans*- $L_2Pt(C_6H_5)Cl$, 90065-11-5; (COD)Pt(Ph)Cl, 51177-65-2; *trans*- $L_2Pt(m\text{-tolyl})Cl$, 116563-67-8; *trans*- $L_2Pt(p\text{-tolyl})Cl$, 116563-68-9; $Bu_4N^+Tf^-$, 35895-70-6; $[L_3PtNp]^+F^-$, 116563-70-3; (COD)PtNpCl, 102307-58-4; (COD)PtCl $_2$, 12080-32-9; benzene- d_6 , 1076-43-3.

(45) This procedure is very similar to that used to prepare all the other NMR tubes, except for the use of DCl/ D_2O and D_2O instead of the usual HNO_3 and H_2O (see Experimental Section).

(46) Since the extent of decomposition in most of these experiments was followed by comparing the electronic integrations of **1** and **2-d₅**, it was not possible to determine the rate of decomposition of **1** in the presence of added D_2O . The signal to noise ratio of the ^{31}P NMR spectrum of **1** decreased during the 60 min of thermal decomposition, but some signal was still visible at the end.

(47) Brainard, R. L.; Whitesides, G. M. *Organometallics* **1985**, *4*, 1550–1557.

(48) Neopentane- d_1 was produced by using two different methods. (i) Addition of DCl/ D_2O (99 atom %) to a solution of (Et_3P) $_2PtNp_2^{13}$ in dry methylene chloride produced Np-D. (ii) A sample of neopentylmagnesium bromide which had been dried under vacuum was quenched with D_2O and yielded Np-D. Neopentane- d_1 produced by these two methods gave similar mass spectra.