Activation of the C–H Bonds of Benzene by Reaction with [Bis(dicyclohexylphosphino)ethane]platinum(0), Generated by the Thermolysis of cis-[Bis(dicyclohexylphosphino)ethane]hydridoneopentylplatinum(II)[1]

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Abstract: Reductive elimination of neopentane from cis-[bis(dicyclohexylphosphino)ethane]hydridoneopentylplatinum(II) (**1**) generates the reactive intermediate [bis(dicyclohexylphosphino)ethane]platinum(0) (**2**), which forms cis-[bis(dicyclohexylphosphino)ethane]hydridophenylplatinum(II) (**3**) upon reaction with benzene. The rate-determining step is reductive elimination of neopentane: E_a = 28.0 (0.4) kcal/mol, log A = 14.3 (0.2), $\Delta G^{\ddagger}$(69 °C) = 25.7 (0.7) kcal/mol, $\Delta H^{\ddagger}$(69 °C) = 27.3 (0.3) kcal/mol, and $\Delta S^{\ddagger}$(69 °C) = 5 (1) eu. Kinetic and spectroscopic studies rule out coordination of benzene to the platinum center before or during the transition state. Variable-temperature NMR studies establish that the bis(phosphine) ligand remains chelated to the platinum atom during reductive elimination. The presumed intermediate, **2**, can be trapped by diphenylacetylene and bis(dicyclohexylphosphino)ethane as [bis(dicyclohexylphosphino)ethane](diphenylacetylene)platinum(0) (**4**) and bis[bis(dicyclohexylphosphino)ethane]platinum(0) (**5**), respectively. The X-ray crystal structure of **1** is reported. The compound crystallizes in space group C_{2h}^5-$P2_1/n$ of the monoclinic system with 4 molecules in a cell of dimensions a = 11.517 (8), b = 15.730 (11), c = 17.364 (13) Å, and β = 90.32 (3)°. The structure has been refined to an agreement index $R(F_o^2)$ of 0.069 for 311 variables and 10 182 observations. The Pt center has its expected pseudo-square-planar coordination with a Pt–H distance of 1.56 (5) Å.

Platinum is widely used as a catalyst for a variety of industrial processes that cleave carbon–hydrogen bonds.[4] In contrast, few soluble platinum complexes react with saturated hydrocarbons. Aqueous solutions of platinum chlorides and acetates catalyze deuterium exchange into saturated hydrocarbons, but the reactions are complex and mechanistic detail is incomplete.[5,6] Most recent insights into the mechanism of hydrocarbon activation by transition metals have come from studies of soluble complexes of iridium and rhodium.[7-9]

In this paper we report the synthesis of cis-[bis(dicyclohexylphosphino)ethane]hydridoneopentylplatinum(II) (**1**), the first phosphine-stabilized platinum complex that reacts cleanly with

Scheme I.[a] Synthesis of cis-[Bis(dicyclohexylphosphino)ethane]hydridoneopentylplatinum(II) (**1**)

[a] ⌒P P = Bis(dicyclohexylphosphino)ethane
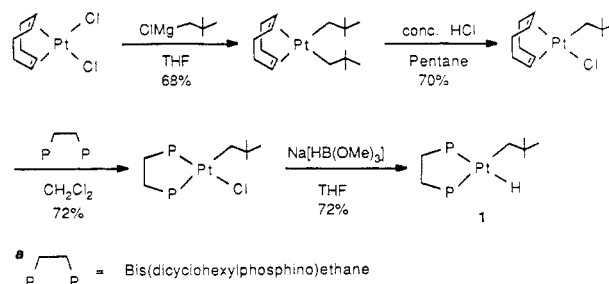
hydrocarbons.[10] When **1** is heated in benzene solution, neopentane is reductively eliminated. Oxidative addition of a C–H bond of benzene produces cis-[bis(dicyclohexylphosphino)ethane]hydridophenylplatinum(II) (**3**) (eq 1). The intermediate responsible for oxidative addition is believed to be [bis(dicyclohexylphosphino)ethane]platinum(0) (**2**).

⌒P P = Bis(dicyclohexylphosphino)ethane
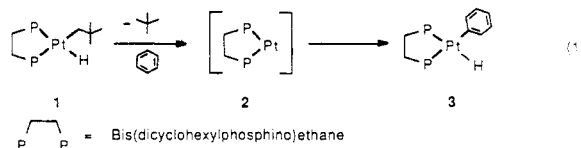
Results

Synthesis of 1. Scheme I outlines the synthesis of **1**. Treatment of (1,5-cyclooctadiene)dichloroplatinum(II) with excess neopentylmagnesium chloride, followed by cleavage of one neopentyl

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(4) Ciapetta, F. G.; Wallace, D. N. *Catal. Rev.* **1971**, *5*, 67–158.

(5) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Hingham, MA, 1984. Shilof, A. E. *Pure Appl. Chem.* **1978**, *50*, 725–733. Kushch, L. A.; Lavrushko, V. V.; Misharin, Yu. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729–733.

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(7) For leading references, see: Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620–631. Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624–626. Cameron, C. J.; Felkin, H.; Fillebeen-Khan, T.; Forrow, N. J.; Guittet, E. *J. Chem. Soc., Chem. Commun.* **1986**, 801–802. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941–7944.

(8) The activation of hydrocarbons by other transition metals, including tungsten, osmium, and rhenium, has also been reported. See: Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27–35. Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1346–1347. Jones, W. D.; Maguire, J. A. *Organometallics* **1986**, *5*, 590–591. Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358–4359.

(9) Several lanthanide and actinide complexes also activate hydrocarbons. In contrast to transition-metal complexes, which oxidatively add C–H bonds, these lanthanide and actinide complexes activate hydrocarbons via a four-center transition state. See: Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1–11. Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425–437.

(10) A preliminary account of this work has been reported: Hackett, M.; Ibers, J. A.; Jernakoff, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 8094–8095.
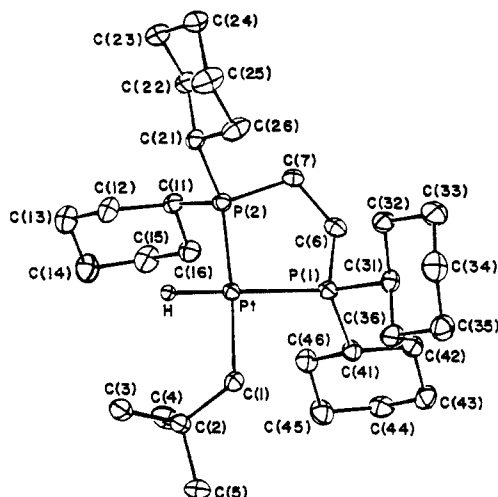
Figure 1. Structure of $PtH(CH_2CMe_3)(Cy_2PCH_2CH_2PCy_2)$ (**1**). Except for the hydride ligand, H atoms have been omitted for the sake of clarity. The thermal ellipsoids are shown at their 50% probability levels.

ligand with concentrated hydrochloric acid, produces (1,5-cyclooctadiene)chloroneopentylplatinum(II). Displacement of 1,5-cyclooctadiene by bis(dicyclohexylphosphino)ethane, and subsequent reduction of [bis(dicyclohexylphosphino)ethane]-chloroneopentylplatinum(II) by sodium trimethoxyborohydride,[11] yields **1**. The complex is stable with respect to water and dioxygen and has been characterized by ^{1}H and ^{31}P NMR, IR, and UV–vis spectroscopies, elemental analysis, and X-ray crystallography.

Both ^{1}H and ^{31}P NMR spectra of **1** show unusual features that proved to be characteristic of this class of compounds. The hydride ligand appears in the ^{1}H NMR spectrum at relatively low field (δ −0.15) as a doublet of doublets with platinum satellites that arise from coupling to the two inequivalent phosphorus atoms and the platinum atom. In the ^{31}P NMR spectrum, each of the inequivalent phosphorus atoms appears as a singlet flanked by platinum satellites. The marked downfield shift of the peaks (relative to the modest shift usually observed upon coordination of phosphines to transition metals[12]) and the negligible phosphorus–phosphorus coupling constant ($J_{P-P} < 3$ Hz) are characteristic of the five-membered ring formed by chelation of the platinum atom by the bis(phosphine) ligand.[13]

X-ray Crystal Structure of 1. Isolable cis transition-metal alkyl hydride complexes are rare in general, and those that have been characterized crystallographically are even fewer in number.[14] These facts, and our desire to understand why the bis(phosphine) ligand is resistant to cyclometalation, encouraged us to determine the crystal structure of **1**.

The crystal structure of **1** is shown in Figure 1; bond distances and angles are presented in Table I. The complex is pseudo square planar, as expected for a platinum(II) complex. There is a slight twist of the C(1)PtH plane relative to the P(1)PtP(2) plane such that atom C(1) is 0.169 (5) Å and atom H is −0.16 (5) Å from the best least-squares plane through the five atoms. Bond distances and angles are unexceptional. In particular, the length of the
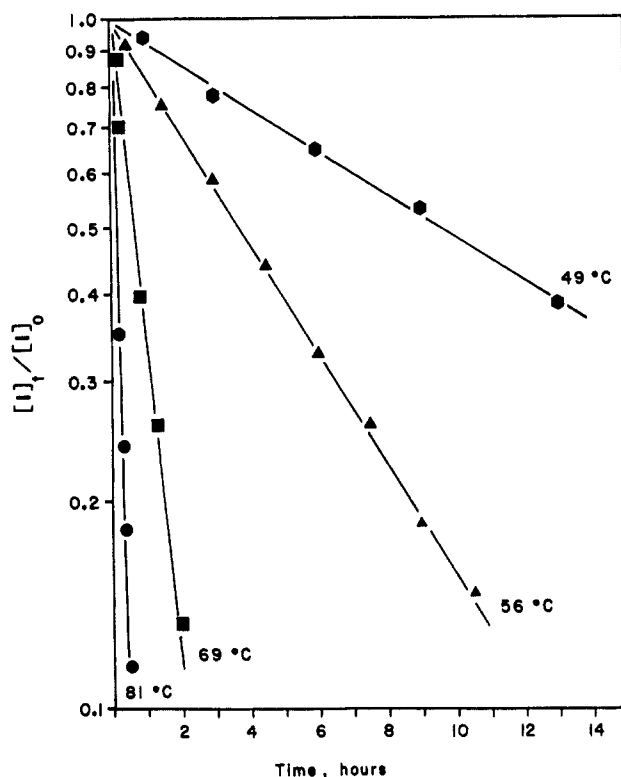

Figure 2. Thermal decomposition of **1** in benzene. $[1]_0 = 0.08$ M.

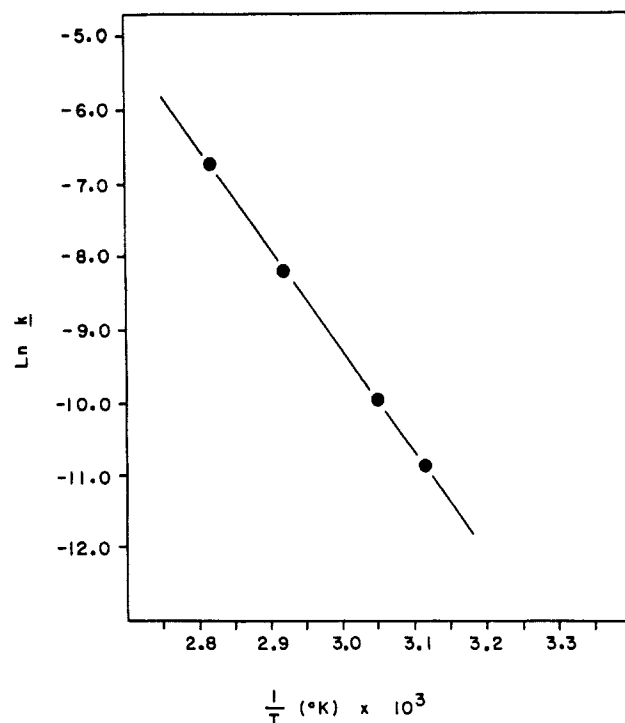**Figure 3.** Arrhenius plot for the decomposition of **1** in benzene.

platinum–hydride bond, 1.56 (5) Å, is typical of terminal metal hydrides.[15]

An important feature of the crystal structure is that the cyclohexyl groups on the phosphorus ligands are folded back from the platinum center. In addition, there are no significant non-

(11) Other hydride reagents were surveyed briefly. Aluminum hydrides such as $LiAlH_4$ and $Na[H_2Al(OCH_2CH_2OMe)_2]$ (Red Al) caused extensive decomposition to free bis(dicyclohexylphosphino)ethane; diisobutylaluminum hydride gave a mixture of products, none of which was readily identifiable. Treatment with polyhydrides such as lithium borohydride gave cationic platinum dimers, $(Cy_2PCH_2CH_2PCy_2)_2Pt_2H_3Cl$. Both $Li[HBEt_3]$ (Super-Hydride) and $Na[HB(OMe)_3]$ reduced $(Cy_2PCH_2CH_2PCy_2)Pt(CH_2CMe_3)Cl$ cleanly to **1**. Reduction with $Na[HB(OMe)_3]$ gave a more easily purified product and the air stability of $Na[HB(OMe)_3]$ made it a much more reliable reagent than Super-Hydride.

(12) Meriwether, L. S.; Leto, J. R. *J. Am. Chem. Soc.* **1961**, *83*, 3192–3196. Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 1104–1106.

(13) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171–185.

(14) To the best of our knowledge, the only other cis transition-metal alkyl hydride complex that has been characterized crystallographically is $(C_5Me_5)(PMe_3)Ir(Cy)H$: Buchanan et al., Reference 7.

(15) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; pp 532–540. Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University: Oxford, 1984; pp 353–355. Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 61.

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Table I. Bond Distances (Å) and Bond Angles (deg) in **1**

Pt–H	1.56 (5)	H–Pt–C(1)	82 (2)
Pt–C(1)	2.125 (5)	H–Pt–P(1)	173 (2)
Pt–P(1)	2.278 (2)	H–Pt–P(2)	96 (2)
Pt–P(2)	2.253 (2)	C(1)–Pt–P(1)	95.3 (1)
P(1)–C(31)	1.846 (5)	C(1)–Pt–P(2)	174.6 (1)
P(1)–C(41)	1.844 (5)	P(1)–Pt–P(2)	87.16 (6)
P(1)–C(6)	1.858 (5)	C(31)–P(1)–Pt	115.5 (2)
P(2)–C(11)	1.849 (5)	C(31)–P(1)–C(41)	104.6 (2)
P(2)–C(21)	1.843 (5)	C(31)–P(1)–C(6)	104.2 (2)
P(2)–C(7)	1.843 (5)	Pt–P(1)–C(41)	118.5 (2)
C(1)–C(2)	1.542 (7)	Pt–P(1)–C(6)	108.6 (2)
C(2)–C(3)	1.519 (7)	C(41)–P(1)–C(6)	104.0 (2)
C(2)–C(4)	1.544 (7)	C(11)–P(2)–Pt	111.9 (2)
C(2)–C(5)	1.525 (7)	C(11)–P(2)–C(21)	104.9 (2)
C(6)–C(7)	1.540 (7)	C(11)–P(2)–C(7)	105.1 (2)
C(11)–C(12)	1.529 (7)	Pt–P(2)–C(21)	119.3 (2)
C(12)–C(13)	1.540 (8)	Pt–P(2)–C(7)	110.2 (2)
C(13)–C(14)	1.520 (8)	C(21)–P(2)–C(7)	104.4 (2)
C(14)–C(15)	1.493 (8)	Pt–C(1)–C(2)	118.9 (3)
C(15)–C(16)	1.524 (8)	C(1)–C(2)–C(3)	112.3 (4)
C(16)–C(11)	1.525 (7)	C(1)–C(2)–C(4)	111.3 (4)
C(21)–C(22)	1.533 (7)	C(1)–C(2)–C(5)	109.7 (4)
C(22)–C(23)	1.529 (8)	C(3)–C(2)–C(4)	108.2 (4)
C(23)–C(24)	1.521 (8)	C(3)–C(2)–C(5)	107.8 (4)
C(24)–C(25)	1.527 (7)	C(4)–C(2)–C(5)	107.4 (4)
C(25)–C(26)	1.528 (8)	P(2)–C(7)–C(6)	112.8 (3)
C(26)–C(21)	1.523 (7)	C(7)–C(6)–P(1)	112.7 (3)
C(31)–C(32)	1.531 (7)		
C(32)–C(33)	1.525 (7)		
C(33)–C(34)	1.521 (8)		
C(34)–C(35)	1.525 (8)		
C(35)–C(36)	1.518 (7)		
C(36)–C(31)	1.538 (7)		
C(41)–C(42)	1.530 (7)		
C(42)–C(43)	1.532 (8)		
C(43)–C(44)	1.505 (8)		
C(44)–C(45)	1.531 (8)		
C(45)–C(46)	1.531 (8)		
C(46)–C(41)	1.528 (7)		
C–C(cyclohexyl)	1.525 (10^a)		

^{a} Estimated standard deviation of a single observation on the assumption that the 24 observations that were averaged are from the same population. The fact that this value is only slightly larger than those calculated from the inverse matrix suggests that standard deviations are correctly estimated.

bonding interactions between the platinum atom and any cyclohexyl or neopentyl C–H bonds. If the relative orientations in the crystal structure are maintained in solution, this lack of nonbonding interactions may explain why the bisphosphine and neopentyl ligands are inert to intramolecular activation by platinum. Intramolecular metalation of both phosphine and neopentyl ligands is well documented for platinum[16-18] and other metals,[19] but we have seen no evidence for either reaction in **1** (vide infra). Furthermore, reductive elimination of neopentane should leave an exposed, unencumbered platinum atom.

Reaction Products and Kinetics. The thermolysis of **1** in benzene yielded neopentane (0.95 equiv) and *cis*-[bis(dicyclohexylphosphino)ethane]hydridophenylplatinum(II) (**3**; quantitative yield) as the sole products. The rate of decomposition, as determined by quantitative ^{31}P NMR spectroscopy, was independent of the concentration of the starting material from 0.04 to 0.12 M, and plots of ln [**1**]/[**1**]$_0$ vs time were linear for greater than 3 half-lives. Representative data from thermolyses at 49, 56, 69,
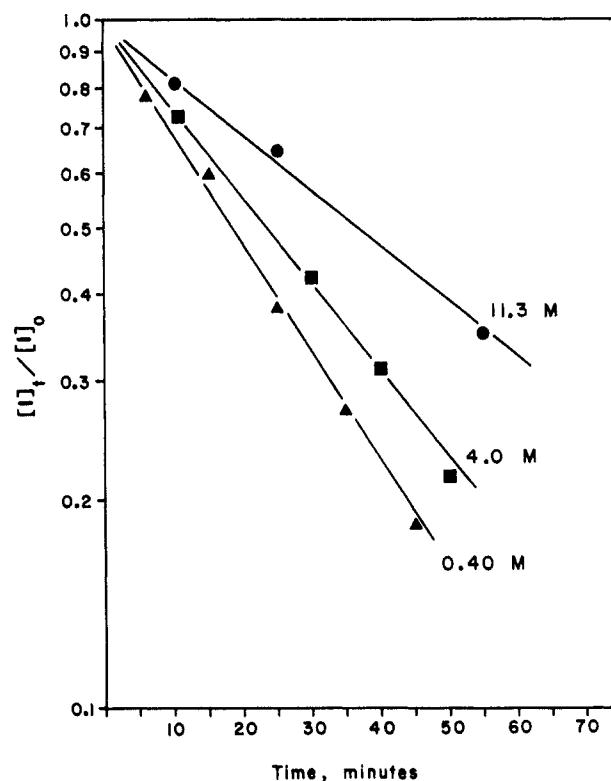

Figure 4. Thermal decomposition of **1** in benzene/cyclohexane solution at 69 °C. The concentration of benzene in cyclohexane is indicated next to each curve. [**1**]$_0$ = 0.04 M.

and 81 °C are shown in Figure 2. The Eyring parameters derived from these data are E_a = 28.0 (0.4) kcal/mol, log A = 14.3 (0.2), $\Delta G^{\ddagger}$(69 °C) = 25.7 (0.7) kcal/mol, $\Delta H^{\ddagger}$(69 °C) = 27.3 (0.3) kcal/mol, and $\Delta S^{\ddagger}$(69 °C) = 5 (1) eu (Figure 3).

No trace of 1,1-dimethylcyclopropane, bineopentyl, or neopentylbenzene was detected as a product. The minute quantities of cyclohexane and cyclohexene that were observed in the reaction solution were present in the same trace amounts in unreacted benzene; no decomposition of the bisphosphine was detected.[20]

Thermolysis of 1 in Benzene-*d***$_6$.** The rate of decomposition of **1** in C$_6$D$_6$ was indistinguishable from that observed in C$_6$H$_6$. The product of decomposition in C$_6$D$_6$ was *cis*-[bis(dicyclohexylphosphino)ethane]deuterido(phenyl-*d*$_5$)platinum(II). Analysis of the neopentane by GC/MS indicated that no deuterium from the solvent had been incorporated into neopentane.

Thermolysis of 1 in Mixed Benzene/Cyclohexane Solutions. In order to determine whether benzene was coordinated to the platinum center in the transition state, samples of **1** were thermolyzed in cyclohexane containing benzene in concentrations ranging from 0.40 to 6.0 M. (Neat benzene is 11.3 M.) If benzene were coordinated to platinum prior to or in the transition state, increased concentrations of benzene would accelerate decomposition. The opposite effect was observed: the rate of decomposition *decreases* as the concentration of benzene is increased (Figure 4). The decrease in rate is not dramatic; the decomposition in 0.40 M benzene/cyclohexane is 2.3 times as fast as decomposition in neat benzene. We believe that the decrease in rate does not indicate inhibition by benzene but merely reflects the effect of increased solvent polarity on the rate of reaction (vide infra).

Evidence against 1:1 Coordination of Benzene to 1. The fact that the rate of decomposition of **1** is lower at higher concentrations of benzene does not rule out the formation of a 1/1 complex between **1** and benzene. To determine whether such a complex did form, the UV–vis spectrum of **1** in neat cyclohexane was compared to that of a solution containing equimolar amounts of

(16) Cheney, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 754–763. Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235–271. Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327–352. Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73–86. Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139–144. Constable, E. C. *Polyhedron* **1984**, *3*, 1037–1057.

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

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

(19) See, for example: Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56.

(20) Compared to monodentate phosphines, chelating bis(phosphines) are relatively metalation-resistant. See: Clerici, M. G.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1973**, 516–517.
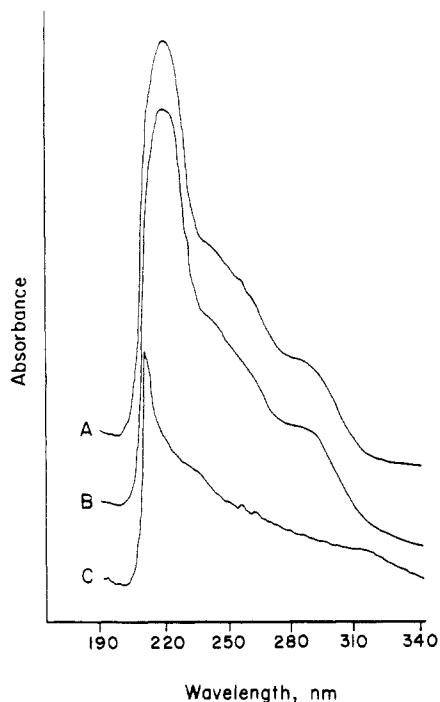
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Figure 5. (A) UV–vis spectrum of **1** in cyclohexane containing 1 equiv of benzene; [**1**] = [PhH] = 10^{-4} M. There are no peaks in the 340–750-nm range. (B) UV–vis spectrum of **1** in cyclohexane; [**1**] = 10^{-4} M. (C) UV–vis spectrum of benzene in cyclohexane; [PhH] = 10^{-4} M.

1 and benzene in cyclohexane. The two spectra were indistinguishable (Figure 5). These spectra argue against the formation of a coordination complex between **1** and benzene.

Effect of Solvent Polarity on the Reaction Rate. To determine the influence of the solvent polarity on the reaction rate, solutions of **1** in cyclohexane and THF were thermolyzed at 69 °C. In the absence of additives, the decomposition of **1** in cyclohexane does not obey first-order kinetics and the only product is an unidentified white precipitate. In the presence of diphenylacetylene or bis-(dicyclohexylphosphino)ethane, however, the decomposition is cleanly first order; the products are *cis*-[bis(dicyclohexylphosphino)ethane](diphenylacetylene)platinum(0) (**4**) and bis-[bis(dicyclohexylphosphino)ethane]platinum(0) (**5**), respectively (eq 2; P̑P = bis(dicyclohexylphosphino)ethane). The rates of decomposition of **1** in cyclohexane containing diphenylacetylene and in cyclohexane containing bis(dicyclophosphino)ethane are identical.

(2)
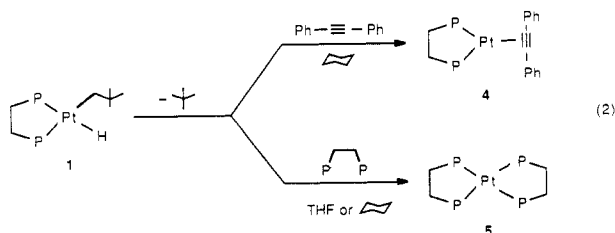
In contrast to the decomposition in neat cyclohexane, the decomposition of **1** in neat THF is cleanly first order. The major product results from oxidative addition of THF; it is tentatively identified as *cis*-[bis(dicyclohexylphosphino)ethane]hydrido(3-oxacyclopentyl)platinum(II). (See the Experimental Section.) In the presence of bis(dicyclohexylphosphino)ethane, the product is **5** and the rate of decomposition is the same as in neat THF. Representative data are shown in Figure 6. Comparison of the rates of decomposition in cyclohexane, benzene, and THF indicates that the rate of reaction decreases with increasing solvent polarity.

Kinetic Isotope Effect. Three sealed tubes, two containing benzene solutions of *cis*-[bis(dicyclohexylphosphino)ethane]deuteridoneopentylplatinum(II) (**1**-*d*) and one containing a benzene solution of **1**, were thermolyzed side by side at 69 °C. Comparison
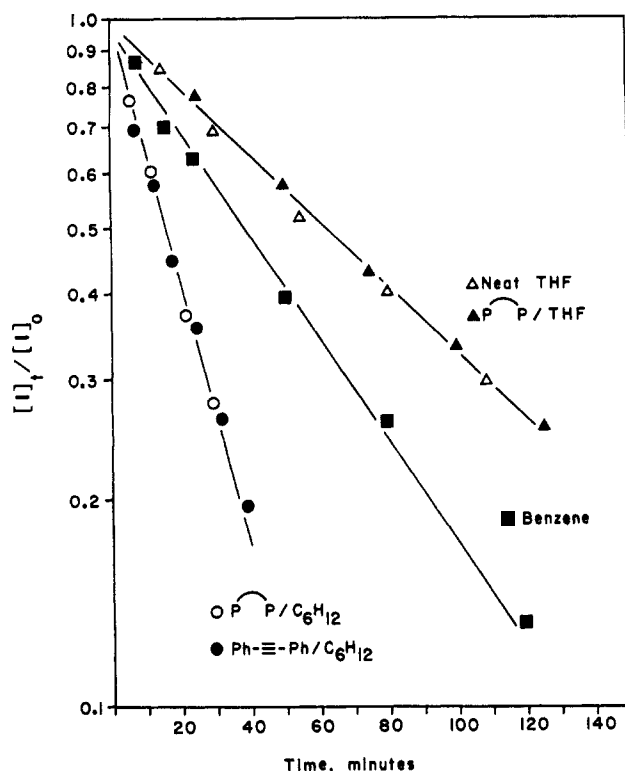

Figure 6. Thermolysis of **1** in various solvents at 69 °C. In C_6H_{12}, [**1**]$_0$ = 0.04 M; in benzene and THF, [**1**]$_0$ = 0.08 M. The solvent and additive (if any) are indicated next to each curve.
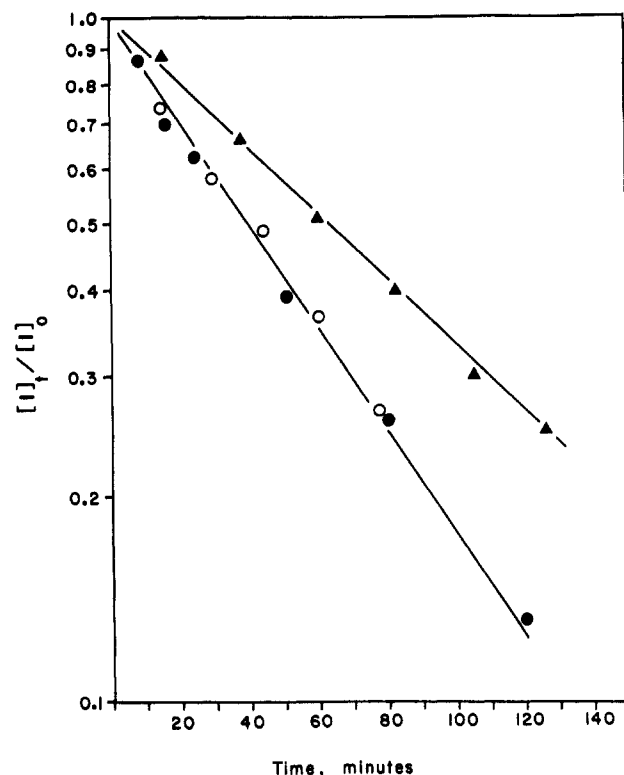

Figure 7. Thermal decomposition of **1** (●) and **1**-*d*$_1$ (▲) in C_6H_6 at 69 °C. Also shown is the decomposition of **1** in C_6D_6 (○). [**1**]$_0$ = 0.08 M.

of the rates of decomposition yielded k_H/k_D = 1.5 (Figure 7).

Thermolysis in the Presence of Bis(dicyclohexylphosphino)ethane. Solutions of **1** in benzene containing 0.5, 1.0, and 2.0 equiv of bis(dicyclohexylphosphino)ethane were thermolyzed at 69 °C. The rates of decomposition were independent of the concentration of bis(dicyclohexylphosphino)ethane and indistinguishable from the rate observed in the absence of added bis(phosphine) (Figure
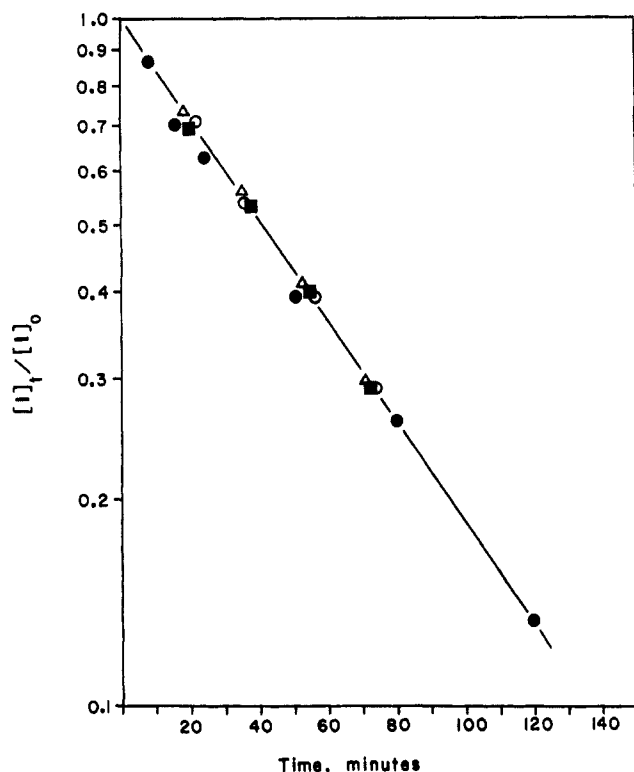
Figure 8. Thermal decomposition of 1 at 69 °C in benzene (●) and in 0.04 M (■), 0.08 M (O), and 0.16 M (△) solutions of bis(dicyclohexylphosphino)ethane in benzene. $[1]_0 = 0.08$ M.
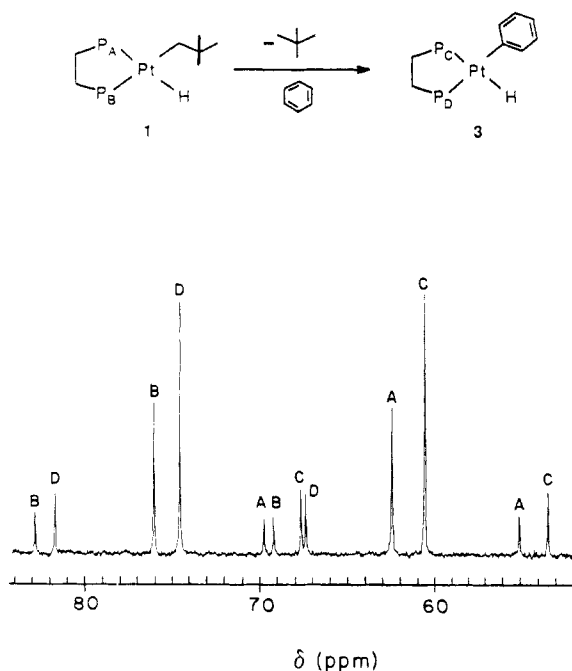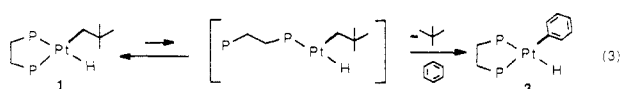

1   3

δ (ppm)

Figure 9. $^{31}P\{^1H\}$ NMR spectrum of a benzene solution of 1 and 3 at 64 °C. Satellites arise from coupling to ^{195}Pt (33.8% natural abundance).

8). Both 3 and 5 were obtained as products.

The lack of inhibition by added bis(phosphine) does not rule out dissociation of one end of the bis(phosphine) prior to reductive elimination of neopentane (eq 3; $\overline{P\ P}$ = bis(dicyclohexyl-
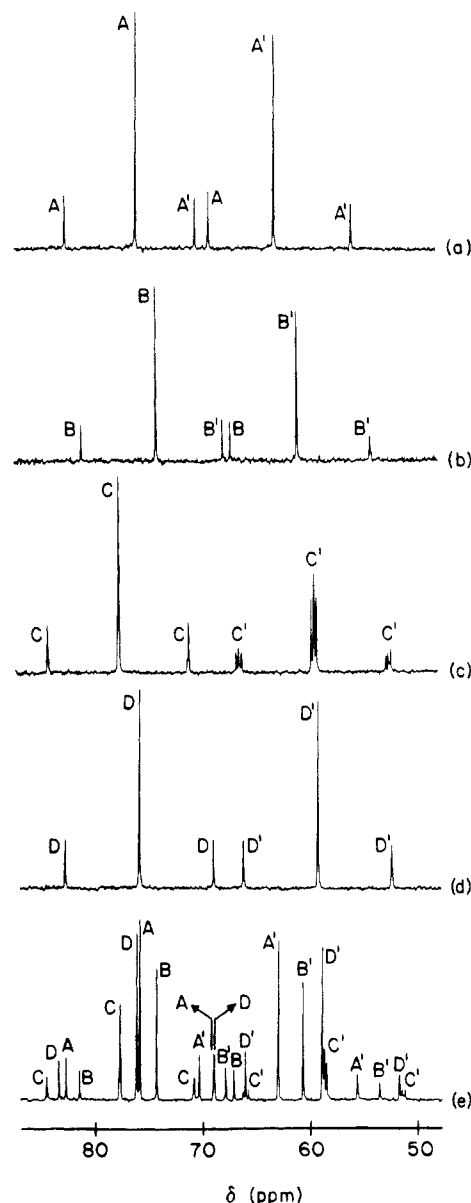

phosphino)ethane).[21] The added bis(phosphine) would be unable

δ (ppm)

Figure 10. $^{31}P\{^1H\}$ NMR spectra of 1 (A), 3 (B), 6-d_3 (C), 7 (D), and the reaction mixture produced by thermal decomposition of equimolar amounts of 1 and 6-d_3 in benzene (E).

to compete for the empty coordination site left by dissociation of one end of the ligand because the effective concentration of the noncoordinated end would be much greater than the concentration of added bis(phosphine).[22] Thus, even if such equilibration did occur, added bis(phosphine) would not inhibit the reaction. Note, however, that the observation of both 3 and 5 as products is compatible with the proposal of 2 as a common intermediate.

Evidence against Phosphine Dissociation. The ^{31}P NMR spectrum of a benzene solution of 1 and 3 was recorded at 64 °C and at room temperature. The line widths at half-height of the

(21) Inhibition by added phosphine has been used as evidence for rate-determining loss of phosphine. See, for example: Reamey, R. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 81–85. McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396–3403. DiCosimo, R.; Moore, S. S. Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124–133.

(22) The effective concentration of the free end of a monocoordinated bis(phosphine) has not been determined experimentally. In organic compounds, the effective concentration of a nucleophile in an intramolecular reaction that produces a five-membered ring is generally high but varies widely. For example, the effective concentration of an alcohol group in intramolecular lactonizations varies from 79 to 10^{16} M (the latter concentration being transparently impossible): Page, M. 1. *Chem. Soc. Rev.* **1973**, *2*, 295–323. See also: Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976; Vol. 1. Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95–102.
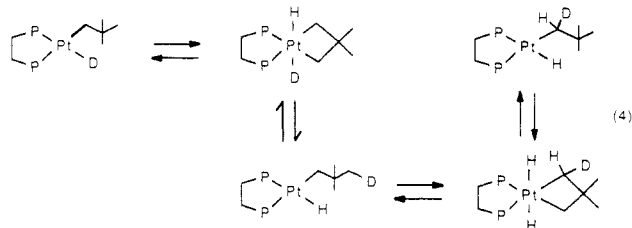
Activation of the C-H Bonds of Benzene

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peaks corresponding to 1 and 3 were the same at both temperatures, and only very small changes in the chemical shifts were observed. No loss of platinum-phosphorus coupling was observed, nor were any new peaks visible (Figure 9). These results suggest that the equilibrium shown in eq 3, if it occurs at all, strongly favors the chelating bis(phosphine).

Test for the Intramolecular Nature of Reductive Elimination. In order to test for the exchange of bis(phosphine), alkyl, and hydride ligands during the course of decomposition, 1 was thermolyzed in the presence of an equimolar amount of *cis*-[bis(dicyclopentylphosphino)ethane]deuterido(neopentyl-*1,1-d₂*)platinum(II) (**6-d_3**) in C_6H_6. (The isotopic purity of **6-d_3** was about 80%; some *cis*-[bis(dicyclopentylphosphino)ethane]hydrido(neopentyl-*1,1-d₂*)platinum(II) (**6-d_2**) was visible in the ³¹P NMR, ¹H NMR, and IR spectra.) The only species observed by ³¹P NMR spectroscopy during the course of the reaction were 1 and **6** and their respective products, 3 and *cis*-[bis(dicyclopentylphosphino)ethane]hydridophenylplatinum(II) (7) (Figure 10). None of the possible exchange products, e.g. *cis*-[bis(dicyclopentylphosphino)ethane]hydridoneopentylplatinum(II) or **1-d_1**, were observed.

Upon completion of the reaction, analysis of the neopentane indicated that it was a mixture of neopentane-d_0, -d_2, and -d_3. The ratio of neopentane-d_2 to neopentane-d_3 corresponds to the ratio of **6-d_2** to **6-d_3** calculated from integration of the ³¹P NMR spectrum and to the neopentane-d_2/neopentane-d_3 ratio calculated from GC/MS analysis of the neopentane produced when **6-d_3** is thermolyzed in C_6H_6. These results indicate that within experimental error the reductive elimination is strictly intramolecular.[23]

Test for Intramolecular Rearrangment in 1-d_1. Metalation of the neopentyl ligand, followed by reductive elimination of a C-H (or a C-D) bond, would eventually lead to complete scrambling of the deuterium from the platinum into the methylene and methyl positions of the neopentyl group (eq 4; $\overline{P\,P}$ = bis(dicyclohexyl-

phosphino)ethane).[24] To determine whether such scrambling was occurring, the thermolysis of **1-d_1** in C_6H_6 was monitored by ²H NMR spectroscopy. Initially, the only peaks observed were those of the deuterium ligand bonded directly to the platinum atom (Figure 11). As the thermolysis progressed, a new peak, corresponding to neopentane-d_1, appeared, but no peaks were observed at the chemical shifts expected for the methyl and the methylene groups. Thus, within the limits of detection (5%), no preequilibrium involving metalation and reductive elimination occurs in the thermolysis of **1-d_1**.

Test for Intermolecular Rearrangement of 3 in Benzene-d_6. In order to determine whether 3 was undergoing exchange with the solvent, the thermolysis of 3 in C_6D_6 was monitored by ³¹P NMR spectroscopy. Initially, only peaks corresponding to 3 were observed; however, peaks corresponding to *cis*-[bis(dicyclohexylphosphino)ethane]deuterido(phenyl-d_5)platinum(II) (**3-d_6**) began to appear (Figure 12). These results are consistent with reductive elimination of benzene followed by oxidative addition of the C-D bond of a solvent molecule.

Test for Intramolecular Rearrangement of *cis*-[Bis(dicyclohexylphosphino)ethane]hydrido(phenyl-d_5)platinum(II) (3-d_5). The
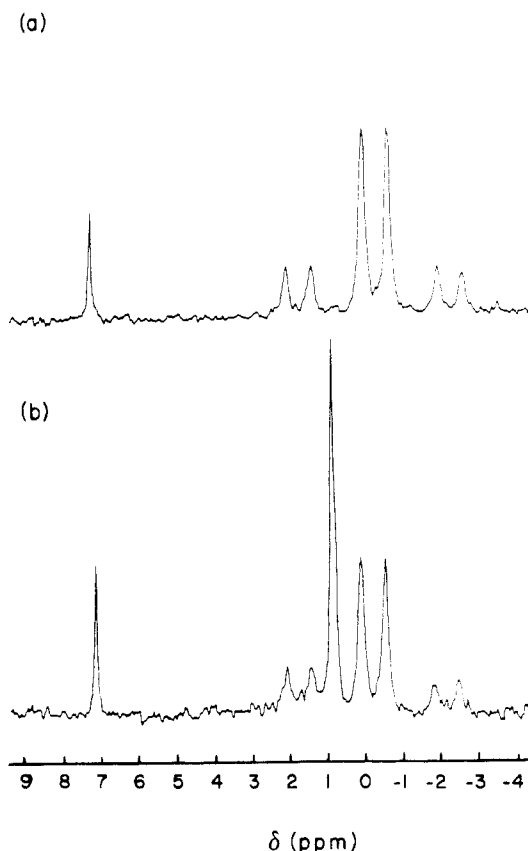
(23) Several cases of bimolecular reductive elimination have been documented. See: Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376-1386. Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139-145. Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34-41.

(24) Similar deuterium scrambling occurs in Os(D)(PMe₃)₄CH₂C-(CH₃)(CD₃)₂ and in *trans*-PtCl(PR₃)₂(CD₂CMe₃): Desrosiers et al., References 8 and 17.

Figure 11. ²H NMR spectra of **1-d_1** in C_6H_6 at t = 0 (a) and t = 65 min at 69 °C (b). The doublet at δ -0.20 corresponds to the deuterium ligand bonded directly to the platinum center; the singlet at δ 0.87 corresponds to neopentane-d_1. No peaks are observed at δ 2.53 (PtCHDCMe₃) or δ 1.70 (PtCH₂C(CH₃)₂(CH₂D)).
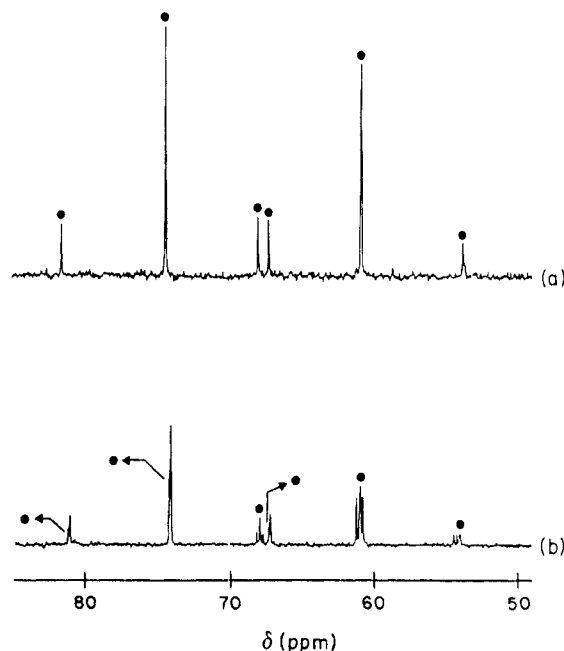
Figure 12. ³¹P{¹H} NMR spectrum of 3 (●) in C_6D_6 at t = 0 (a) and at t = 79 h at 69 °C (b). The new peaks in (b) correspond to **3-d_6**.

thermolysis of **3-d_5** in C_6H_6 was monitored by ²H NMR spectroscopy (Figure 13). Initially, only peaks in the aromatic region were observed. However, new peaks arose around δ 0.0, corresponding to deuterium bonded directly to the platinum center. Simultaneously, the "residual solvent peak" (actually benzene-d_5 as well as benzene containing the natural abundance of deuterium) increased in size. Eventually, the peaks in the aromatic and the

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Figure 13. ^{2}H NMR spectra of 3-d_5 in C_6H_6 at $t = 0$ (a), 2 h + 27 min (b), 4 h + 35 min (c), 9 h + 30 min (d), 22 h + 33 min (e), and 28 h + 36 min (f) at 69 °C. Directly above spectra c–e are insets that show the hydride region in greater detail.

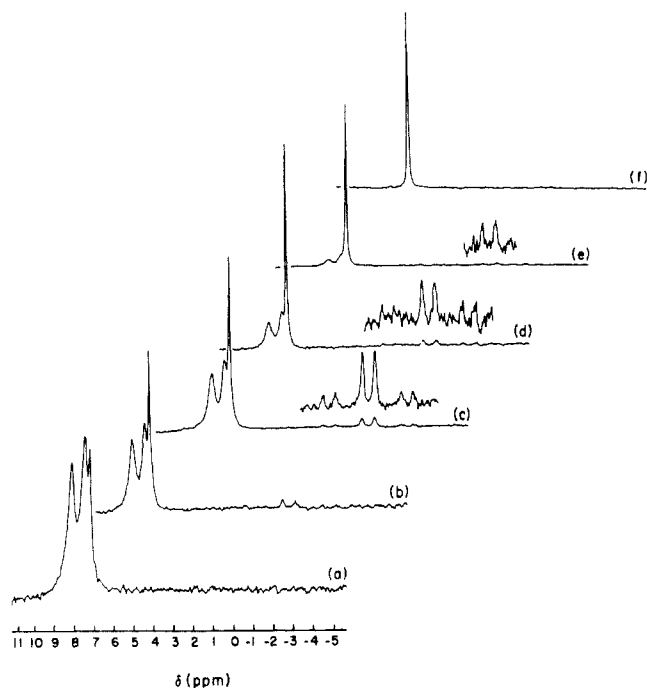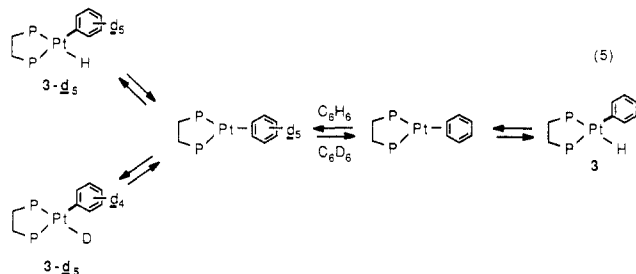hydride regions disappeared, leaving only the solvent peak. These results suggest that reductive elimination of benzene generates an η^2-benzene complex that can undergo either oxidative addition (resulting in intramolecular deuterium scrambling) or exchange with the solvent (eq 5; P͡P = bis(dicyclohexylphosphino)ethane).


(5)

Discussion

Literature precedent suggested that reductive elimination of an alkane from a *cis*-[bis(phosphine)]alkylhydridoplatinum(II) species would be facile and that the bent [bis(phosphine)]platinum(0) species generated by reductive elimination would be highly reactive. For example, *cis*-hydridomethyl[bis(triphenylphosphine)]platinum(II) reductively eliminates methane at −25 °C to generate bis(triphenylphosphine)platinum(0).[25] The [bis(phosphine)]platinum(0) complex is unstable and disproportionates to [tris(triphenylphosphine)]platinum(0) and platinum metal in the absence of additives such as diphenylacetylene or triphenylphosphine.

In contrast, the highly reactive bent [bis(phosphine)]platinum(0) species generated by sodium–mercury amalgam reduction of *cis*-[bis(di-*tert*-butylphosphino)ethane]dichloroplatinum(II) reacts with the solvent, THF, to form *cis*-[bis(di-*tert*-butylphosphino)ethane]dihydridoplatinum(II) (eq 6; R = *tert*-butyl).[26]

(6)
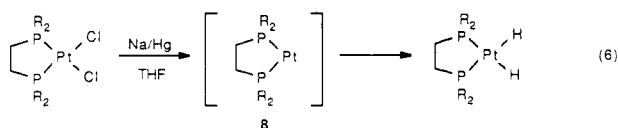
(25) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916.

Scheme II.^{a} Mechanism of Decomposition of **1** in Benzene

^{a} = Bis(dicyclohexylphosphino)ethane
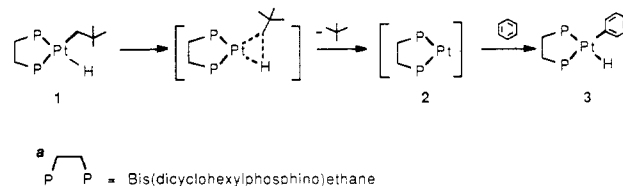
The mechanism by which [bis(di-*tert*-butylphosphino)ethane]-platinum(0) reacts with THF was not investigated, but by analogy with the results presented here, an intermediate of structure **8** is possible.

As expected, **1** readily eliminates neopentane to form **2**, which then oxidatively adds benzene to yield **3** (eq 1). We assume that the driving force for this reaction is the formation of a strong platinum–aryl bond at the expense of a relatively weak platinum–alkyl bond. The exact bond dissociation energies are not known, but transition-metal–aryl bonds are generally considered to be at *least* 10 kcal/mol stronger than transition-metal–alkyl bonds.[27] We propose that conversion of **1** to **3** follows the mechanism summarized in Scheme II.

The observed first-order kinetics suggests that reductive elimination of neopentane is the rate-determining step; labeling experiments rule out the possibility of reversible intramolecular metalation (eq 4) prior to reductive elimination. The small but real kinetic isotope effect ($k_H/k_D = 1.5$) suggests that the rate-determining step involves the formation or cleavage of a C–H bond and that the transition state is nonlinear.[28] The preexponential factor A is consistent with a transition state in which one particle is converted to two.[29] The results of variable-temperature NMR studies indicate that the bis(phosphine) ligand remains chelated to the platinum center throughout the course of the reaction.

Both UV–vis spectroscopy and the results of kinetic studies in mixed benzene/cyclohexane solutions indicate that benzene is *not* coordinated to the platinum center either in the ground state or in the rate-determining step. The decrease in rate with increasing solvent polarity suggests a nonpolar transition state, i.e. one with minimal charge separation. Radical mechanisms involving homolysis of the platinum–carbon bond are excluded by several results: the absence of radical-derived products, such as bineopentyl and neopentylbenzene; the absence of deuterium incorporation from the solvent into neopentane; and the absence of crossover products in experiments designed to investigate the intramolecular nature of the reaction. In addition, labeling studies used in the crossover experiments indicate that reductive elimination is strictly intramolecular.

The assumed intermediate, **2**, can be trapped by diphenylacetylene, bis(dicyclohexylphosphino)ethane, or benzene. Note, however, that [bis(dicyclohexylphosphino)ethane](η^2-benzene)-platinum(0) is equally plausible as a reactive intermediate in benzene. Scrambling of deuterium from the phenyl ring of 3-d_5 into the hydride position suggests the existence of such an η^2-benzene complex.[30] The fact that the rate of decomposition is

(26) Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063–2073.

(27) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41–48. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663. Buchanan et al., Reference 7.

(28) Saunders, W. H., Jr. In *Techniques of Chemistry*, 3rd ed.; Lewis, E. S., Ed.; Wiley: New York, 1974; Vol. 6, Chapter 5. We note that the interpretation of isotope effects in other reactions, e.g. those involving coordination of the substrate prior to oxidative addition of the C–H bond, is considerably less straightforward. (See ref 7 for examples of such reactions.)

(29) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968; Chapter 3. Page, M. I.; Jencks, W. P. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1678–1683. Page, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 449–459. Bennett, L. E. *Prog. Inorg. Chem.* **1973**, *18*, 1–176.

indistinguishable in C_6H_6 and C_6D_6 rules out the oxidative addition of benzene as the rate-determining step in the decomposition of **1**.

The reactivity of **2** can be rationalized by considering it as a homogeneous model of an "edge" platinum atom in a heterogeneous platinum catalyst.[31]   High-vacuum studies on single platinum crystals have shown that these sites are reactive with respect to the cleavage of C–H bonds.   Linear [bis(phosphine)]platinum(0) complexes, which are completely unreactive with respect to hydrocarbon addition, are analogous to the less reactive terrace platinum atoms in the heterogeneous catalyst.[32] The intermediate **2** is also isolobal with singlet methylene.[33]

Experimental Section

General Procedures. Diethyl ether and THF were distilled from sodium benzophenone under argon. Hexane and cyclohexane were stirred over 1/4 v/v nitric acid/sulfuric acid, washed with distilled water, dilute aqueous sodium hydroxide, distilled water, and brine, dried over magnesium sulfate, passed through silica and distilled from Na/K alloy under argon. Benzene was stirred over sulfuric acid and then treated similarly. Bis(dicyclohexylphosphino)ethane was recrystallized twice from degassed 95% ethanol for kinetic experiments; for preparative use, it was used as received from Strem Chemicals. Bis(dichlorophosphino)ethane was used as received from Strem Chemicals; NaD (98% isotopic purity) was purchased from the Pressure Chemical Co. Diphenylacetylene was recrystallized twice from 95% ethanol. (1,5-Cyclooctadiene)dichloroplatinum(II),[34] (1,5-cyclooctadiene)dineopentylplatinum(II),[18] and chloro(1,5-cyclooctadiene)neopentylplatinum(II)[17] were prepared according to the literature procedures. (1,5-Cyclooctadiene)di(phenyl-d_5)platinum(II)[35] and chloro(1,5-cyclooctadiene)(phenyl-d_5)platinum-(II)[36] were prepared by analogy to published procedures. Literature procedures were used to prepare $(CH_3)_3CCD_2OH$,[18] $(CH_3)_3CCD_2OTs$,[18,37] and $(CH_3)_3CCD_2Cl$.[38] The Grignard reagent was prepared from Mg turnings and $(CH_3)_3CCD_2Cl$ in THF; the mixture was refluxed for several days to ensure complete reaction. (1,5-Cyclooctadiene)[di(neopentyl-$1,1$-d_2)platinum(II)[18] and chloro(1,5-cyclooctadiene)(neopentyl-$1,1$-d_2)platinum(II)[17] were prepared by analogy to the literature procedures. Triply sublimed magnesium turnings (Alfa) were used in Grignard reactions. Alkyllithium and Grignard reagents were titrated with 2-butanol/toluene under argon with N,N-naphth-1-

(30) The thermolysis of **1** in benzene-$1,3,5$-d_3 and in a 1/1 mixture of C_6H_6 and C_6D_6 might clarify whether [bis(dicyclohexylphosphine)ethane](η^2-benzene)platinum(0) is a precursor to **3** and whether coordination of benzene or oxidative addition of the C–H bond of benzene is rate-determining in the reaction of **2** with benzene. These experiments are precluded by the fact that the products of oxidative addition are not stable under the reaction conditions. For example, 3-d_5 undergoes exchange with C_6H_6 at 69 °C (Figure 13b). The observed deuterium scrambling also suggests that the determination of –d[3]/dt would not be trivial. Presumably, a series of equilibria are involved; separation of the various rate constants would be difficult, even if an appropriate ArH were found.

3
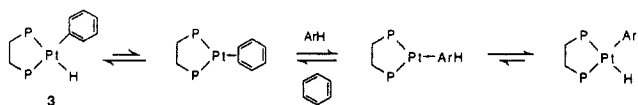
(31) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University: Ithaca, NY, 1981; Chapter 9. Somorjai, G. A. *Acc. Chem. Res.* **1976**, *9*, 392–398.

(32) The enhanced reactivity of bent [bis(phosphine)]platinum(0) species such as **2** relative to linear complexes can be explained by molecular orbital theory. In linear L_2Pt^0 complexes, the HOMO is sheltered between the phosphine ligands, whereas in the bent [bis(phosphine)]platinum(0) species the HOMO extends into space, apparently more appropriately oriented for oxidative addition of C–H bonds. See: Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 6928–6937. Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191–205. Zeigler, T. *Inorg. Chem.* **1985**, *24*, 1547–1552. Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482–7492.

(33) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711–724. Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

(34) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1970**, *13*, 52–55. McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.

(35) Kistner, C. R.; Hutchinson, J. H.; Doyle, J. R.; Storlie, J. C. *Inorg. Chem.* **1963**, *2*, 1255–1261.

(36) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411–428.

(37) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; p 1180.

(38) The compound was prepared as described except HMPA was used as the solvent instead of diethylacetamide. Sowinski, A. J.; Whitesides, G. M. *J. Org. Chem.* **1979**, *44*, 2369–2376.

ylphenylamine[39] as an indicator. The latter was recrystallized twice from 3/1 v/v distilled water/95% ethanol; any purple oil that fell out of the hot solution was removed with a pipet. Melting and boiling points are uncorrected. ¹H NMR spectra were recorded at 250, 300, and 500 MHz; ²H NMR spectra were recorded at 46.1 MHz; ³¹P NMR spectra were recorded at 121.5 MHz; ¹³C NMR spectra were recorded at 62.9 MHz; ¹¹B NMR spectra were recorded at 96.3 MHz. ¹H, ²H, and ¹³C NMR shifts are relative to tetramethylsilane; the residual solvent peak (C_6HD_5, δ 7.15; $CHCl_3$, δ 7.25; C_6HD_{11}, δ 1.38; $CHDCl_2$, δ 5.35) was used as an internal reference. ³¹P NMR shifts are relative to 85% H_3PO_4 at δ 0.0, with shifts downfield of the reference considered positive. ¹¹B NMR shifts are relative to BF_3–THF at δ 0.00. GC analyses were performed on a Perkin-Elmer 3920B gas chromatograph; GC/MS analyses were performed on a Hewlett-Packard 5992A GC/MS at 7 eV. Elemental analyses were performed by Spang and Galbraith.

***cis*-[Bis(dicyclohexylphosphino)ethane]chloroneopentylplatinum(II).** A 100-mL round-bottomed flask with a side arm was equipped with a stirring bar and a pressure-adjusted addition funnel topped by an argon inlet. The flask was charged with (1,5-cyclooctadiene)chloroneopentylplatinum(II) (3.01 g, 7.39 mmol) and purged with argon. The platinum complex was dissolved in 40 mL of degassed CH_2Cl_2, and the addition funnel was charged with a solution of bis(dicyclohexylphosphino)ethane (3.44 g, 8.13 mmol) in 30 mL of CH_2Cl_2. The bis-(phosphine) solution was added at room temperature. After ca. 2 h, the solvent was removed by rotary evaporation. The oily yellow residue was crystallized from hot acetone; cooling to –10 °C produced colorless crystals. A small second crop was isolated from the mother liquor. After a second recrystallization, the product was isolated by suction filtration and air-dried before being ground between a mortar and pestle and dried in vacuo at 69 °C (0.02 Torr). The yield of white powder was 72% (3.86 g, 5.33 mmol). Mp (capillary sealed under argon): 225–226 °C. ¹H NMR ($CDCl_3$): δ 2.35–2.0 (m, 8 H), 1.9–1.1 (m, 51 H). ³¹P NMR ($CDCl_3$): δ 65.0 (s with Pt satellites, $J_{Pt–P}$ = 1611 Hz), 54.2 (s with Pt satellites, $J_{Pt–P}$ = 4334 Hz). IR (KBr): 2930 (s), 2860 (s), 1480 (m), 1450 (s), 1423 (m), 1410 (m), 1385 (m), 1359 (m), 1335 (w), 1310 (w), 1300 (w), 1272 (m), 1240 (w), 1212 (m), 1185 (m), 1179 (m), 1160 (w), 1115 (m), 1095 (w), 1082 (w), 1055 (w), 1048 (w), 1030 (w), 1008 (m), 920 (m), 892 (m), 869 (m), 852 (s), 825 (m), 798 (m), 750 (s), 675 (m), 655 (m), 542 (m), 490 (w), 475 (w), 442 (w), 410 (w), 402 (w), 380 (w), 360 (w), 350 (w), 290 (m) cm⁻¹. Anal. Calcd for $C_{31}H_{59}ClP_2Pt$: C, 51.41; H, 8.21; Cl, 4.90; P, 8.55. Found: C, 51.42; H, 8.35; Cl, 4.82; P, 8.55.

***cis*-[Bis(dicyclohexylphosphino)ethane]hydridoneopentylplatinum(II) (1).** A 125-mL round-bottomed flask was charged with *cis*-[bis(dicyclohexylphosphino)ethane]chloroneopentylplatinum(II) (2.60 g, 3.59 mmol) and purged with argon. The complex was then dissolved in 100 mL of THF and treated with a solution of $Na[HB(OMe)_3]$ (1.40 g, 10.9 mmol) in 25 mL of THF. After ca. 2 h, the initially clear solution had become cloudy. The reaction was quenched at 0 °C with distilled water. Diethyl ether was added to separate the aqueous and organic layers. The aqueous layer was extracted several times with ether; the combined organic extracts were washed with water and dried over magnesium sulfate. Removal of solvent via rotary evaporation left a colorless oil. The oil was dissolved at room temperature in the minimum volume of ether; an equal volume of methanol was added, and the solution was refrigerated at –10 °C overnight. The colorless crystals isolated by suction filtration were recrystallized a second time; a second crop of crystals was isolated from the mother liquor. The colorless prisms were dried over KOH in vacuo (0.025 Torr). The yield was 72% (1.78 g, 2.58 mmol). Mp (capillary sealed under argon): 120–130 °C dec. ¹H NMR (C_6D_6): δ 2.52 ("t" with Pt satellites, $J_{P–H}$ = 7, $J_{Pt–H}$ = 78 Hz, 2 H), 2.25–1.95 (m, 6 H), 1.95–1.0 (m, 51 H), –0.15 (dd with Pt satellites, $J_{P–H}$ = 18, $J_{P'–H}$ = 194, $J_{Pt–H}$ = 1175 Hz, 1 H). ³¹P NMR (C_6D_6): δ 75.9 (s with Pt satellites, $J_{Pt–P}$ = 1664 Hz), 62.9 (s with Pt satellites, $J_{Pt–P}$ = 1798 Hz). IR (neat): 2920 (vs), 2860 (vs), 2010 (s), 1450 (s), 1420 (w), 1380 (w), 1355 (m), 1303 (w), 1299 (w), 1275 (w), 1239 (w), 1200 (w), 1185 (w), 1175 (w), 1140 (w), 1110 (w), 1085 (w), 1045 (w), 1030 (w), 1008 (m), 918 (w), 892 (m), 855 (m), 820 (m), 800 (m), 748 (m), 660 (m), 645 (m) cm⁻¹. Anal. Calcd for $C_{31}H_{60}P_2Pt$: C, 53.97; H, 8.77; P, 8.98. Found: C, 54.11, 53.94; H, 8.69, 8.74; P, 8.92, 8.96.

Sodium Trimethoxyborodeuteride. The compound was prepared from NaD (98% isotopic purity) and trimethylborate according to the literature procedure.[40] ¹H NMR (THF-d_8): δ 3.1 (s). ¹¹B NMR (THF-d_8): δ 48.4. ¹³C NMR (THF-d_8): δ 3.25 (s).

***cis*-[Bis(dicyclohexylphosphino)ethane]deuteridoneopentylplatinum(II) (1-d_1).** The complex was prepared from *cis*-[bis(dicyclohexyl-

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phosphino)ethane]chloroneopentylplatinum(II) and sodium trimethoxyborodeuteride in 75% yield according to the procedure described for 1. Mp (capillary sealed under argon): ca. 120–130 °C dec. ^{1}H NMR (C_6D_6): δ 2.55 ("t" with Pt satellites, J_{P-H} = 7, J_{Pt-H} = 78 Hz, 2 H), 2.25–1.95 (m, 6 H), 1.95–1.0 (m, 51 H). ^{31}P NMR (C_6D_6): δ 75.7 (s with Pt satellites, J_{Pt-P} = 1665 Hz), 62.9 ("t" with Pt satellites, J_{P-D} = 30, J_{Pt-P} = 1777 Hz). ^{2}H NMR (C_6D_6): δ –0.20 (br d with Pt satellites, J_{P-D} = 30, J_{Pt-D} = 180 Hz. IR (neat): 2930 (vs), 2860 (vs), 2020 (w), 1450 (s), 1375 (w), 1350 (m), 1305 (w), 1295 (w), 1275 (w), 1235 (w), 1200 (w), 1175 (w), 1110 (w), 1005 (m), 890 (m), 855 (m), 820 (w), 790 (w), 745 (m), 660 (m), 640 (m), 580 (w), 530 (w) cm^{-1}. The complex was ca. 85% isotopically pure; unlabeled 1 is visible in the ^{1}H NMR, ^{31}P NMR, and IR spectra. Quenching and washing with D_2O instead of H_2O did not improve the isotopic purity of the product.

Bis(dicyclopentylphosphino)ethane. A 250-mL round-bottomed flask equipped with a stirring bar, a pressure-adjusted dropping funnel, and a Liebig condenser topped by an argon inlet was flame-dried under argon. Once the flask had cooled, it was charged with an ethereal solution of cyclopentylmagnesium bromide (1.2 M, 40 mL, 48 mmol). The addition funnel was charged with a solution of bis(dichlorophosphino)ethane (2 g, 9 mmol) in 40 mL of diethyl ether. The phosphine was added at –78 °C; a thick white solid formed immediately. The mixture was allowed to warm to room temperature overnight and then heated under reflux for ca. 3 h. The mixture (yellow solution, white solid) was cooled to 0 °C, and the reaction was quenched with 50 mL of degassed aqueous ammonium chloride (1/1 v/v saturated ammonium chloride/distilled water). The ethereal layer was removed via cannula; the aqueous layer was extracted twice with ether. The combined extracts were dried over degassed magnesium sulfate. The yellow supernatant was filtered through a coarse frit into an argon-purged flask equipped with a distillation head. The solvent was distilled off under argon, leaving a yellow oil that solidified upon cooling. The solid was recrystallized twice from degassed 95% ethanol and dried in vacuo (0.02 Torr). The yield of soft white crystals, mp (capillary sealed under argon) 77–80 °C, was 56% (1.77 g, 4.83 mmol). ^{1}H NMR (C_6D_6): δ 1.91–1.1 (m). ^{31}P NMR (C_6D_6): δ 1.0 (s).

***cis*-[Bis(dicyclopentylphosphino)ethane]chloro(neopentyl-*1,1-d$_2$*)platinum(II).** A 100-mL round-bottomed flask with a side arm was equipped with a stirring bar and a pressure-adjusted dropping funnel topped by an argon inlet. The flask was charged with chloro(1,5-cyclooctadiene)(neopentyl-*1,1-d$_2$*)platinum(II) (0.75 g, 1.9 mmol) and purged with argon. The complex was then dissolved in 25 mL of degassed CH_2Cl_2; the addition funnel was charged with a solution of bis(dicyclopentylphosphino)ethane in 20 mL of degassed CH_2Cl_2. The bis(phosphine) was added at room temperature. After 1 h, the solvent was removed by rotary evaporation, leaving a yellow oil. The oil was dissolved in the minimum amount of warm acetone and cooled to –80 °C. The white solid that formed was separated, dissolved in warm acetone, and cooled to –10 °C. The colorless crystals isolated by Buchner filtration were powdered with a mortar and pestle and dried in vacuo at 69 °C (0.05 Torr). The yield of white powder, mp (capillary sealed under argon) 135 °C, was 51% (0.63 g, 0.94 mmol). ^{1}H NMR (C_6D_6): δ 2.63 (m, 2 H), 2.37 (m, 2 H), 2.3–2.0 (m, 6 H), 1.85–1.4 (m, 33 H), 1.4–1.15 (m, 3 H), 1.15–0.95 (m, 3 H). ^{31}P NMR (C_6D_6): δ 60.5 (s with Pt satellites, J_{Pt-P} = 1594 Hz), 48.7 (s with Pt satellites, J_{Pt-P} = 4218 Hz). IR (KBr): 2950 (s), 2882 (s), 2120 (m), 2105 (w), 2080 (w), 1472 (w), 1450 (m), 1410 (w), 1380 (w), 1352 (m), 1300 (w), 1212 (m), 1122 (m), 1065 (w), 1029 (w), 910 (m), 865 (w), 850 (w), 800 (m), 675 (m), 650 (w), 530 (m), 485 (w), 470 (w), 280 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{49}D_2ClP_2Pt$: C, 48.39; Cl, 5.29; P, 9.24. Found C, 48.66, 48.70; Cl, 5.33, 5.30; P, 9.22.

***cis*-[Bis(dicyclopentylphosphino)ethane]deuterido(neopentyl-*1,1-d$_2$*)platinum(II) (6).** A 100-mL recovery flask was charged with *cis*-[bis(dicyclohexylphosphino)ethane]chloro(neopentyl-*1,1-d$_2$*)platinum(II) (0.30 g, 0.45 mmol) and purged with argon. The complex was then dissolved in 20 mL of THF and treated with a solution of Na[DB(OMe)$_3$] (0.25 g, 1.9 mmol) in 20 mL of THF. After 3 h at room temperature, the reaction was quenched at 0 °C with distilled water. Diethyl ether was added to the solution, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic extracts were washed with water and dried over magnesium sulfate. The solvent was removed by rotary evaporation, leaving an oily solid. The solid was dissolved in the minimum volume of ether; an equal amount of methanol was added, and the solution was cooled to –80 °C. The white solid that formed was dissolved a second time in 1/1 v/v ether/methanol and cooled to –10 °C. The yield of colorless prisms, mp (capillary sealed under argon) 100–108 °C dec, was 55% (0.16 g, 0.25 mmol). ^{1}H NMR (C_6D_6): δ 2.2 (m, 2 H), 2.0–1.05 (m, 47 H). ^{31}P NMR (C_6D_6): δ 77.7 (s with Pt satellites, J_{Pt-P} = 1662 Hz), 58.7 ("t" with Pt satellites, J_{P-D} = 30, J_{Pt-P} = 1771 Hz). ^{2}H NMR (C_6H_6) δ 2.47

(br s), –0.32 (br d with Pt satellites, J_{P-D} = 30, J_{Pt-D} = 179 Hz). IR (neat): 2960 (vs), 2880 (vs), 2120 (m), 2105 (m), 2055 (m), 2005 (m), 1455 (s), 1380 (w), 1350 (m), 1305 (m), 1235 (m), 1115 (m), 1050 (m), 907 (m), 872 (m), 801 (m), 673 (s), 525 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{49}D_3P_2Pt$: C, 50.93; P, 9.73. Found: C, 51.00, 51.09; P, 9.56, 9.52. The isotopic purity was about 80%; some *cis*-[bis(dicyclohexylphosphino)ethane]hydrido(neopentyl-*1,1-d$_2$*)platinum(II) (*6-d$_2$*) was observed by ^{1}H NMR, ^{31}P NMR, and IR spectroscopy.

***cis*-[Bis(dicyclopentylphosphino)ethane]hydridophenylplatinum(II).** A sealed NMR tube containing 6 (19.8 mg, 0.031 mmol) in 0.50 mL of benzene was thermolyzed to completion at 69 °C. The contents of the tube were transferred to a 10-mL recovery flask, and the solvent was removed by rotary evaporation. The white solid was dried over KOH in vacuo (0.02 Torr); the yield was 18.9 mg (95%). Mp (capillary sealed under argon): ca. 170 °C dec. ^{1}H NMR (CD_2Cl_2): δ 7.43 ("t" with Pt satellites, J_{P-H} = 7, J_{Pt-H} = 58 Hz, 2 H), 6.97 (t, J = 7 Hz, 2 H), 6.71 (t, J = 7 Hz, 1 H), 2.5–1.2 (m, 40 H), –1.10 (dd with Pt satellites, J_{P-H} = 17, $J_{P'-H}$ = 183, J_{Pt-H} = 1158 Hz, 1 H). ^{31}P NMR (C_6H_6): δ 76.2 (s with Pt satellites, J_{Pt-P} = 1758 Hz), 58.8 (s with Pt satellites, J_{Pt-P} = 1745 Hz). IR (neat): 3045 (m), 1985 (m), 1570 (m) cm^{-1}. The complex reacts with CD_2Cl_2 at room temperature.

***cis*-[Bis(dicyclohexylphosphino)ethane]hydridophenylplatinum(II) (3)** was isolated from a completely thermolyzed sample of 1 in benzene. The complex was dissolved in the minimum amount of THF at room temperature; an equal amount of MeOH was added, and the solution was cooled to –10 °C. The colorless plates so obtained were recrystallized a second time. The yield was 24%. (The yield, as determined by ^{31}P NMR spectroscopy, is quantitative; the isolated yield of the twice-recrystallized complex is low, owing to the small scale of the reaction.) Mp (capillary sealed under argon): 187–188 °C dec. ^{1}H NMR (CD_2Cl_2): δ 7.42 ("t" with Pt satellites, J = 7, J_{Pt-H} = 58 Hz, 2 H), 6.97 (m, 2 H), 6.70 (m, 1 H), 2.1–0.8 (m, 48 H), –1.05 (dd with Pt satellites, J_{P-H} = 17, $J_{P'-H}$ = 181, J_{Pt-H} = 1159 Hz, 1 H). ^{31}P NMR (C_6H_6): δ 74.3 (s with Pt satellites, J_{Pt-P} = 1751 Hz), 60.6 (s with Pt satellites, J_{Pt-P} = 1739 Hz). IR (neat): 3050 (w), 2923 (vs), 2855 (vs), 1985 (s), 1570 (m), 1460 (w), 1450 (s), 1415 (w), 1347 (w), 1330 (w), 1307 (w), 1298 (w), 1270 (w), 1200 (w), 1185 (w), 1172 (w), 1110 (w), 1024 (w), 1005 (w), 955 (w), 908 (w), 890 (w), 852 (m), 820 (w), 792 (w), 765 (w), 745 (m), 718 (m), 703 (m), 662 (w), 650 (w) cm^{-1}. Anal. Calcd for $C_{32}H_{54}P_2Pt$: C, 55.24; H, 7.82; P, 8.90. Found: C, 54.94, 55.16; H, 7.82, 7.84; P, 9.02, 9.06.

***cis*-[Bis(dicyclohexylphosphino)ethane]deuterido(phenyl-*d$_5$*)platinum(II) (3-*d$_6$*).** Two NMR tubes containing 0.5 mL of a 0.08 M solution of 1 in C_6D_6 were thermolyzed at 69 °C for 6 h. The tubes were cracked open, and their contents were transferred to a 10-mL pear-shaped flask. The solvent was removed by rotary evaporation, and the residue was dried over KOH in vacuo (0.010 Torr). The yield of white solid, mp (capillary sealed under argon) 183–184 °C dec, was qantitative (61 mg). ^{1}H NMR (CD_2Cl_2): δ 2.1–1.6 (m, 28 H), 1.5–0.90 (m, 2 H). ^{31}P NMR (CD_2Cl_2): δ 73.7 (s with Pt satellites, J_{Pt-P} = 1769 Hz), 60.6 ("t" with Pt satellites, J_{P-D} = 28, J_{Pt-P} = 1794 Hz). IR (KBr): 2915 (s), 2850 (s), 2290 (w), 2280 (w), 2230 (w), 1538 (m), 1450 (s), 1425 (s), 1350 (w), 1332 (w), 1310 (w), 1298 (w), 1275 (w), 1250 (w), 1202 (w), 1182 (w), 1172 (w), 1125 (w), 1112 (w), 1090 (w), 1050 (w), 1020 (w), 1005 (m), 915 (w), 890 (w), 865 (w), 855 (m), 820 (w), 793 (w), 750 (m), 740 (m), 660 (m), 642 (w), 560 (w), 542 (s), 530 (w), 518 (w), 486 (w), 465 (w), 440 (w), 420 (w), 400 (w), 350 (w) cm^{-1}. Traces of incompletely deuteriated complex were visible by ^{1}H NMR, ^{31}P NMR, and IR spectroscopy.

***cis*-[Bis(dicyclohexylphosphino)ethane]chloro(phenyl-*d$_5$*)platinum(II)-THF.** A 100-mL recovery flask equipped with a stirring bar and a pressure-adjusted dropping funnel topped by an argon inlet was charged with chloro(1,5-cyclooctadiene)(phenyl-*d$_5$*)platinum(II) (0.541 g, 1.41 mmol) and purged with argon. The complex was dissolved in 20 mL of CH_2Cl_2; the addition funnel was charged with a solution of bis(dicyclohexylphosphino)ethane (0.662 g, 1.57 mmol) in 20 mL of CH_2Cl_2. The bis(phosphine) solution was added at room temperature, and the resulting solution was stirred under argon for 3 h. The solvent was removed by rotary evaporation. The white powder was dissolved in warm THF; slow cooling to –10 °C produced colorless crystals. A small second crop was recovered from the mother liquor. After a second recrystallization, the crystals were ground with a mortar and pestle and dried in vacuo at 89 °C (0.015 Torr). The yield of white powder, mp (capillary sealed under argon) 220–260 °C dec, was 55% (0.631 g, 0.782 mmol). The complex retains one molecule of THF of complexation, as ascertained by ^{1}H NMR and elemental analysis. ^{1}H NMR (CD_2Cl_2): δ 3.74 (m, 4 H), 2.27 (br m, 4 H), 2.1–1.1 (m, 46 H), 0.85 (br m, 2 H). ^{31}P NMR (CD_2Cl_2): δ 62.5 (s with Pt satellites, J_{Pt-P} = 1725 Hz), 52.5 (s with Pt satellites, J_{Pt-P} = 4023 Hz). IR (neat): 2930 (vs), 2850 (s), 2260 (w), 1535 (w), 1450 (s), 1415 (w), 1350 (w), 1335 (w), 1305 (w), 1295 (w), 1272 (w), 1210 (w), 1200 (w), 1180 (w), 1172 (w), 1125 (w), 1100 (w),

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1080 (w), 1050 (w), 1005 (m), 955 (w), 915 (w), 890 (w), 850 (m), 820 (w), 795 (w), 745 (m), 710 (w), 665 (m) cm^{-1}. Anal. Calcd for $C_{32}H_{48}D_5ClP_2Pt \cdot C_4H_8O$: C, 53.55; Cl, 4.39; P, 7.67. Found: C, 53.81, 53.86; Cl, 4.42, 4.51; P, 7.76.

cis-[Bis(dicyclohexylphosphino)ethane]hydrido(phenyl-d_5)platinum(II) (3-d_5). A 100-mL recovery flask equipped with a stirring bar was charged with cis-[bis(dicyclohexylphosphino)ethane]chloro(phenyl-d_5)-platinum(II)-THF (0.542 g, 0.671 mmol) and purged with argon. The complex was suspended in 40 mL of THF and treated at room temperature with a solution of Na[HB(OMe)$_3$] (0.35 g, 2.7 mmol) in 20 mL of THF. The suspension rapidly became homogeneous and then clouded again. After 3 h, the reaction was quenched at 0 °C with distilled water. Methylene chloride was added to the mixture to induce separation of the aqueous layer. The aqueous layer was extracted with CH$_2$Cl$_2$ several times; the combined organic extracts were washed with water and dried over MgSO$_4$. Removal of the solvent by rotary evaporation left an amorphous white solid. The crude product was dissolved in the minimum amount of THF at room temperature; an equal volume of MeOH was added, and the solution was cooled to -10 °C. After two more recrystallizations, the colorless crystals were isolated by suction filtration and dried in vacuo (0.025 Torr) over KOH. A second crop was isolated from the mother liquor and similarly recrystallized. The yield of colorless crystals, mp (capillary sealed under argon) 194–195 °C dec, was 39% (0.181 g, 0.259 mmol). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.1–1.5 (m, 28 H), 1.5–1.1 (m, 18 H), 1.0–0.85 (m, 2 H), -1.05 (dd with Pt satellites, J_{P-H} = 17, J_{P-H} = 181, J_{Pt-H} = 1160 Hz, 1 H). ^{31}P NMR (CD$_2$Cl$_2$): δ 73.8 (s with Pt satellites, J_{Pt-P} = 1769 Hz), 60.6 (s with Pt satellites, J_{Pt-P} = 1816 Hz). ^{2}H NMR (C$_6$H$_6$): δ 8.0 (br s), 7.4 (br s). IR (neat): 2910 (vs), 2840 (vs), 2250 (w), 1980 (s), 1530 (m), 1445 (s), 1410 (w), 1345 (w), 1330 (w), 1304 (w), 1292 (w), 1267 (w), 1198 (w), 1180 (w), 1170 (w), 1110 (w), 1080 (w), 1045 (w), 1000 (m), 950 (vw), 914 (w), 887 (w), 850 (m), 815 (w), 790 (w), 760 (w), 740 (w), 715 (vw), 659 (m), 640 (w), 620 (w) cm^{-1}.

[Bis(dicyclohexylphosphino)ethane](diphenylacetylene)platinum(0) (4). A 10-mm-o.d. Pyrex thermolysis tube was charged with diphenylacetylene (0.058 g, 0.33 mmol) and 1 (0.102 g, 0.148 mmol) and evacuated to 0.010 Torr. The tube was back-filled with argon, and cyclohexane (2.5 mL) was added via syringe. The tube was sealed under vacuum (0.010 Torr) after three freeze–pump–thaw degassing cycles. The sample was heated at 69 °C for 3.0 h. The tube was cracked open; the yellow solution was transferred to a recovery flask and concentrated to dryness by rotary evaporation. The yellow oil was extracted with hexanes to remove diphenylacetylene, and the hexane-insoluble residue was recrystallized from warm acetone. Cooling to -10 °C produced yellow needles. After two more recrystallizations, the product was dried over KOH in vacuo (0.025 Torr). The yield of yellow needles, mp (capillary sealed under argon) 225–226 °C, was 22% (26 mg, 0.033 mmol). (The yield is low, owing to the small scale of the reaction; the yield as determined by quantitative ^{31}P NMR spectroscopy is ca. 80%.) ^{1}H NMR (CD$_2$Cl$_2$): δ 7.64 ("d", 4 H), 7.34 ("t", 4 H), 7.16 ("t", 2 H), 2.03 (m, 8 H), 1.9–1.6 (m, 20 H), 1.4–1.0 (m, 20 H). ^{31}P NMR (CD$_2$Cl$_2$): δ 67.6 (s with Pt satellites, J_{Pt-P} = 3010 Hz). IR (KBr): 3070 (w), 3050 (w), 3020 (w), 3010 (w), 2910 (vs), 2840 (vs), 1935 (vw), 1875 (vw), 1777 (w), 1727 (s), 1590 (s), 1480 (m), 1440 (s), 1420 (w), 1410 (w), 1342 (w), 1327 (w), 1293 (w), 1267 (w), 1195 (w), 1180 (w), 1170 (w), 1108 (w), 1066 (w), 1050 (vw), 1040 (vw), 1025 (w), 1000 (m), 912 (w), 905 (w), 887 (w), 862 (w), 850 (m), 820 (w), 790 (w), 755 (s), 740 (s), 689 (s), 655 (m), 625 (w), 598 (w), 561 (w), 530 (m), 512 (m), 483 (w), 465 (w), 435 (w), 400 (w), 375 (w), 350 (w) cm^{-1}. MS (EI) *m/e* (relative intensity): 796 (26), 795 (49), 794 (33; ^{194}M$^+$), 618 (16), 617 (14), 616 (60; ^{194}M$^+$ - PhCCPh), 615 (84), 614 (90), 613 (12), 534 (21), 533 (57), 532 (54), 531 (29), 530 (22), 529 (11), 451 (23), 450 (26), 449 (22), 448 (20), 447 (14), 368 (20), 367 (17), 289 (15), 288 (14), 287 (17), 286 (11), 180 (24), 179 (34), 178 (66; M$^+$, PhCCPh), 176 (12), 165 (13), 83 (49; C$_6$H$_{11}$$^+$), 81 (20), 77 (11), 67 (20), 55 (100), 54 (11), 53 (14), 51 (14), 50 (13). Exact mass for C$_{40}$H$_{58}$P$_2$Pt ($^{194.9662}$Pt): calcd, 795.3676; obsd, 795.3668. Anal. Calcd for C$_{40}$H$_{58}$P$_2$Pt: C, 60.36; H, 7.35; P, 7.78. Found: C, 60.32; H, 7.09; P, 8.17.

Bis[bis(dicyclohexylphosphino)ethane]platinum(0) (5). The complex was isolated as colorless crystals by cooling a completely thermolyzed solution of 1 in THF that contained a slight excess of bis(dicyclohexylphosphino)ethane. Mp (capillary sealed under argon): 245–247 °C dec. ^{1}H NMR (C$_6$D$_6$): δ 2.37 (br s, 8 H), 2.0–1.5 (m, 48 H), 1.5–1.1 (m, 40 H). ^{31}P NMR (C$_6$D$_6$): δ 32.1 (s with Pt satellites, J_{Pt-P} = 3588 Hz). MS (EI) *m/e* (relative intensity): 1039 (35; ^{195}M$^+$), 957 (100), 956 (65; ^{195}M$^+$ - Cy), 873 (75; ^{195}M$^+$ - 2 Cy). (The characteristic Pt "envelope" is observed for each of the assigned peaks.) Anal. Calcd for C$_{52}$H$_{96}$P$_4$Pt: C, 60.04; H, 9.30; P, 11.91. Found: C, 59.42; H, 8.94; P, 11.52.

Product of Thermolysis in THF. A sealed NMR tube containing 28 mg of 1 in 0.5 mL of THF was thermolyzed at 69 °C for 10 h. The

Table II. Crystallographic Data for 1

formula	$C_{31}H_{60}P_2Pt$
formula wt	689.86
space grp	C_{2h}^5-$P2_1/n$
a, Å	11.517 (8)
b, Å	15.730 (11)
c, Å	17.364 (13)
β, deg	90.32 (3)
V, Å^3	3146
Z	4
temp, °C	-150^a
ρ_{obsd}(25 °C), g/cm^3	1.39
ρ_{calcd}(-150 °C), g/cm^3	1.456
cryst faces	{001} (0.301),^{b} {101} (0.294), {10$\bar{1}$} (0.500), {010} (0.600), (111) (0.256)
cryst vol, m^3	0.0610
radiatn (λ, Å)	Mo Kα (λ(Kα$_1$) = 0.709 30)
linear abs coeff, cm^{-1}	46.22
transmssn factor	0.203–0.366^c
detector aperture	2.75 mm wide, 3 mm high, 17.3 cm from crystal
take-off angle, deg	4.0
scan speed, deg/min	4 in ω; reflcns having F_o^2 < 3σ(F_o^2) rescanned to achieve 3σ level up to max of 60 s
2θ limits	2° ≤ 2θ ≤ 62°
scan mode	ω–2θ
bkgd counts	$^1/_4$ of scan range on each side of reflcn
scan range	-1.2° below Kα$_1$ to 1.20° above Kα$_2$ in 2θ
std reflcn	6 in diverse regions of reciprocal space remeasd every 3.0 h of X-ray exposure
data colld	+*h*,+*k*,±*l*
no. of unique data	10 182
no. of unique data with F_o^2 > 3σ(F_o^2)	7056
p factor	0.03
no. of variables	311
$R(F_o)$ for F_o^2 > 3σ(F_o^2)	0.044
$R_w(F_o)$	0.043
$R(F_o^2)$	0.069^d
$R_w(F_o^2)$	0.091
error observn of unit weight	1.26

^{a} The low-temperature system is from a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Solerem, Z. T. de Vic, 31320 Castanet-Tolosan, France. ^{b} The numbers in parentheses are the distances in millimeters between the Friedel pairs of the preceding form; for the face (111), the distance is from the center as defined by the other faces. ^{c} The analytical method, as employed in the Northwestern absorption program AGNOST, was used for the absorption correction: de Meulenaer, J.; Tompa, H. *Acta. Crystallogr.* **1965**, *19*, 1014–1018. ^{d} Final refinement on F^2, using all the data.

yellow solution contained a small amount of white solid. The yield of neopentane, as determined by GC with an internal standard of *n*-pentane, was quantitative. The contents of the tube were transferred to a 10-mL recovery flask; the solvent was removed via rotary evaporation, and the resulting yellow oil was dried in vacuo (0.010 Torr). The yield was 29 mg. ^{31}P NMR (C$_6$D$_6$): δ 76.1 (s with Pt satellites, J_{Pt-P} = 1722 Hz), 64.0 (s with Pt satellites, J_{Pt-P} = 1785 Hz). The ^{1}H NMR spectrum was complicated. Four multiplets of equal intensity were observed in the range δ 4.8–3.9; one of the peaks was flanked by platinum satellites (δ 4.66, J_{Pt-H} = 38 Hz). In addition to numerous peaks in the aliphatic region (δ 2.9–0.9), a hydride peak was observed at higher field (δ -0.44, J_{P-H} = 18, $J_{P'-H}$ = 193, J_{Pt-H} = 1184 Hz). On the basis of these data, the product is tentatively identified as cis-[bis(dicyclohexylphosphino)-ethane]hydrido(3-oxacyclopentyl)platinum(II).[41] The reaction was not investigated further.

(41) Reduction of $\overline{RuCl_2[(Me_2PCH_2CH_2CH_2)_3P]}$ with lithium in THF yields $Ru(\overline{CHOCH_2CH_2CH_2})[(Me_2PCH_2CH_2CH_2)_3P]$: Antberg, M.; Dahlenberg, L. *J. Organomet. Chem.* **1986**, *312*, C67–C70. (Cyclopentadiene)-bis(triphenylphosphine)dihydridorhenium(III) catalyzes deuterium exchange between benzene-d_6 and both the α- and β-hydrogen nuclei of THF. See: Jones, W. D.; Maguire, J. A. *Organometallics* **1986**, *5*, 590–591.

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Table III. Positional Parameters and B(eq) for PtH(CH₂CMe₃)₃(Cy₂PCH₂CH₂PCy₂) (1)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
Pt	0.203989 (15)	0.224503 (12)	-0.179474 (10)	1.383 (4)	H(1)C(14)	0.224	0.320	0.081	4.0
P(1)	0.13439 (10)	0.090246 (82)	-0.196666 (71)	1.55 (3)	H(2)C(14)	0.153	0.339	0.154	4.0
P(2)	0.02271 (10)	0.261815 (81)	-0.145043 (73)	1.60 (3)	H(1)C(15)	0.126	0.200	0.117	3.9
C(2)	0.47519 (38)	0.22682 (35)	-0.14684 (27)	1.76 (10)	H(2)C(15)	0.009	0.248	0.113	3.9
C(31)	0.11738 (42)	0.05599 (31)	-0.29779 (28)	1.80 (11)	H(2)C(16)	0.148	0.209	-0.014	3.2
C(21)	-0.04918 (41)	0.35127 (30)	-0.19460 (29)	1.72 (11)	H(2)C(16)	0.028	0.168	0.003	3.2
C(41)	0.21088 (42)	0.00135 (32)	-0.14924 (29)	1.87 (11)	H(1)C(22)	-0.222	0.331	-0.174	3.1
C(7)	-0.07734 (39)	0.17158 (32)	-0.15880 (27)	1.67 (11)	H(2)C(22)	-0.164	0.388	-0.111	3.1
C(42)	0.15790 (47)	-0.08683 (35)	-0.16141 (29)	2.21 (12)	H(1)C(23)	-0.291	0.468	-0.190	3.4
C(16)	0.07301 (45)	0.21893 (35)	0.00634 (30)	2.23 (12)	H(2)C(23)	-0.165	0.502	-0.194	3.4
C(46)	0.22841 (48)	0.01915 (34)	-0.06348 (30)	2.30 (13)	H(1)C(24)	-0.271	0.403	-0.307	3.4
C(6)	-0.01499 (42)	0.08496 (33)	-0.15703 (30)	1.96 (12)	H(2)C(24)	-0.234	0.497	-0.317	3.4
C(4)	0.44495 (46)	0.20970 (41)	-0.06170 (32)	2.83 (15)	H(1)C(25)	-0.104	0.403	-0.377	4.0
C(22)	-0.16963 (43)	0.37662 (34)	-0.16531 (30)	2.07 (12)	H(2)C(25)	-0.042	0.461	-0.317	4.0
C(32)	0.03421 (44)	0.11565 (34)	-0.34059 (29)	2.11 (12)	H(1)C(26)	-0.104	0.291	-0.292	3.5
C(3)	0.49437 (45)	0.32173 (37)	-0.15657 (35)	2.64 (14)	H(2)C(26)	0.023	0.324	-0.299	3.5
C(1)	0.37998 (41)	0.19245 (33)	-0.20132 (29)	1.92 (11)	H(1)C(32)	-0.041	0.111	-0.318	3.1
C(11)	0.01389 (40)	0.28797 (30)	-0.04144 (28)	1.71 (11)	H(2)C(32)	0.062	0.172	-0.336	3.1
C(36)	0.23636 (45)	0.05402 (37)	-0.33753 (30)	2.23 (13)	H(1)C(33)	-0.007	0.037	-0.431	3.6
C(44)	0.25057 (48)	-0.13735 (37)	-0.03771 (32)	2.59 (14)	H(2)C(33)	-0.025	0.132	-0.451	3.6
C(35)	0.22539 (48)	0.03344 (36)	-0.42266 (31)	2.39 (13)	H(1)C(34)	0.135	0.077	-0.516	3.6
C(25)	-0.09645 (52)	0.41619 (40)	-0.32390 (34)	3.0 (2)	H(2)C(34)	0.174	0.150	-0.462	3.6
C(24)	-0.21463 (46)	0.44464 (38)	-0.29395 (33)	2.47 (13)	H(1)C(35)	0.197	-0.023	-0.429	3.4
C(43)	0.23085 (50)	-0.15575 (36)	-0.12184 (34)	2.63 (14)	H(2)C(35)	0.300	0.038	-0.446	3.4
C(12)	0.07130 (50)	0.37433 (35)	-0.02764 (31)	2.47 (13)	H(1)C(36)	0.273	0.108	-0.332	3.3
C(15)	0.08459 (57)	0.24302 (37)	0.09106 (32)	2.9 (2)	H(2)C(36)	0.283	0.011	-0.314	3.3
C(5)	0.58990 (42)	0.18209 (38)	-0.16326 (33)	2.56 (14)	H(1)C(42)	0.082	-0.087	-0.140	3.2
C(45)	0.30400 (50)	-0.04924 (38)	-0.02556 (32)	2.78 (14)	H(2)C(42)	0.154	-0.098	-0.215	3.2
C(26)	-0.05306 (47)	0.33718 (37)	-0.28136 (30)	2.50 (13)	H(1)C(43)	0.191	-0.209	-0.127	3.7
C(34)	0.14316 (51)	0.09427 (37)	-0.46421 (30)	2.65 (14)	H(2)C(43)	0.304	-0.159	-0.147	3.7
C(33)	0.02487 (48)	0.09255 (38)	-0.42568 (31)	2.62 (14)	H(1)C(44)	0.178	-0.140	-0.012	3.6
C(23)	-0.21364 (45)	0.45603 (36)	-0.20697 (33)	2.45 (13)	H(2)C(44)	0.302	-0.179	-0.017	3.6
C(14)	0.14811 (54)	0.32514 (41)	0.10053 (32)	3.1 (2)	H(1)C(45)	0.310	-0.038	0.028	3.7
C(13)	0.08430 (54)	0.39603 (37)	0.05848 (33)	2.82 (15)	H(2)C(45)	0.379	-0.048	-0.048	3.7
H	0.2547 (43)	0.3162 (34)	-0.1780 (28)	0.2 (1.1)	H(1)C(46)	0.266	0.073	-0.057	3.3
H(1)C(11)	-0.066	0.292	-0.027	2.7	H(2)C(46)	0.155	0.020	-0.039	3.3
H(1)C(21)	-0.001	0.399	-0.187	2.7	H(1)C(1)	0.385	0.132	-0.200	2.9
H(1)C(31)	0.086	0.000	-0.299	2.8	H(2)C(1)	0.398	0.212	-0.251	2.9
N(1)C(41)	0.286	-0.001	-0.171	2.8	H(1)C(3)	0.554	0.340	-0.123	3.6
H(1)C(6)	-0.059	0.045	-0.187	3.0	H(2)C(3)	0.516	0.333	-0.208	3.6
H(2)C(6)	-0.011	0.066	-0.105	3.0	H(3)C(3)	0.425	0.351	-0.145	3.6
H(1)C(7)	-0.133	0.173	-0.119	2.7	H(1)C(4)	0.376	0.239	-0.049	3.8
H(2)C(7)	-0.115	0.178	-0.207	2.7	H(2)C(4)	0.433	0.150	-0.054	3.8
H(1)C(12)	0.146	0.374	-0.050	3.5	H(3)C(4)	0.507	0.229	-0.030	3.8
H(2)C(12)	0.025	0.417	-0.051	3.5	H(1)C(5)	0.578	0.122	-0.163	3.6
H(1)C(13)	0.127	0.447	0.064	3.8	H(2)C(5)	0.617	0.199	-0.213	3.6
H(2)C(13)	0.010	0.403	0.080	3.8	H(3)C(5)	0.645	0.197	-0.125	3.6

X-ray Crystal Structure of 1. Colorless rectangular crystals of 1 were grown from 1/1 diethyl ether/methanol at -10 °C. A suitable crystal was mounted in the cold stream (-150 °C) of an Enraf-Nonius CAD4 diffractometer. Crystallographic data are summarized in Table II. These data were collected by standard procedures.[42] Similarly, the structure was solved and refined by standard procedures.[42] The position of the hydride ligand was determined from a difference electron density synthesis that was based on the anisotropic refinement of all non-hydrogen atoms. That this was the position from an atom and not from noise was established through a succession of difference electron density syntheses with successively smaller scattering shells.[43] The positions of the hydrogen atoms of the three methyl groups were also located from difference electron density syntheses. These positions were idealized (C–H = 0.95 Å; B(H) = B_{eq}(C) + 1.0 Å²). The hydrogen atoms of the methylene and cyclohexyl groups were placed at their calculated positions. While the positional parameters and isotropic thermal parameter of the hydride ligand were varied in ensuing calculations, those of the other hydrogen atoms were held fixed. In the final cycle of refinement on F_o^2, all 10 182 F_o^2 values were used to determine the values of 311 variables. An analysis of $\sum w(F_o^2 - F_c^2)^2$ as a function of F_o^2, setting angles, and Miller indices shows no unusual trends. Fractional coordinates and isotropic or equivalent isotropic thermal parameters are presented in Table III; anisotropic thermal parameters are given in Table IV;[44] calculated and observed structure amplitudes are given in Table V.[44]

Sealed-Tube Reactions. General Methods. A 14/20 inner joint was sealed onto a 5-mm-o.d. medium-walled NMR tube. The tube was washed with distilled water and acetone and dried in the oven at 140 °C. The tube was attached to a vacuum line and flame-dried in vacuo. It was charged with 14–42 mg of 1 and reevacuated for at least 1 h. Freshly distilled benzene (0.50 mL) was added via syringe under cover of argon. The contents of the tube were degassed by three freeze–pump–thaw cycles; on the fourth cycle, the tube was sealed under vacuum (0.010 Torr), with care taken to avoid a metallic mirror at the seal.

The sample tubes were heated in the vapors of refluxing solvents (acetone, 56 °C; hexanes, 69 °C; cyclohexane, 81 °C) or in a temperature-controlled water bath (49 °C). The disappearance of 1 was monitored for 2–3 half-lives by quantitative ³¹P NMR spectroscopy. The 5-mm NMR tubes used for the thermolyses were positioned coaxially in a 10-mm-o.d. NMR tube containing the lock solvent (C₆D₆) and a sealed capillary of aqueous H₃PO₄. A 90° pulse and a relaxation delay of at least 5T_1 were used to ensure accurate quantitation. The area of the two central peaks of 1 relative to that of H₃PO₄ was determined by electronic integration.

Analysis of the Reaction Products. The samples were thermolyzed to completion (8–10 half-lives), and the yields of products were determined by quantitative ³¹P NMR spectroscopy. The samples were cooled to -78 °C, cracked open, and capped with a septum. A stock solution of *n*-pentane in hexanes (0.50 mL) was added as a GC standard. The samples were warmed to 0 °C and shaken well. The solution was analyzed by

(42) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

(43) La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511–519.

(44) Supplementary material.

GC for neopentane and 1,1-dimethylcyclopentane at room temperature with the use of a 12-ft 4% UCW-98 on 80/100 Chromosorb P column. The electronically determined peak areas were corrected for the differences in response factors (*n*-pentane, 1.00; neopentane, 1.02). The same column and conditions were used for GC/MS analysis of neopentane.

The solution was analyzed for bineopentyl and neopentylbenzene at 120 °C with the use of a 12-ft 4% UCW-98 on 80/100 Chromosorb P column and for cyclohexane and cyclohexene with a 20-ft 25% AgNO$_3$/TEG on 80/100 Chromosorb P column at room temperature.

Thermolysis of 1 in Benzene. Sealed NMR tubes containing 0.04, 0.08, 0.10, and 0.12 M solutions of **1** in C$_6$D$_6$ were thermolyzed at 69.0 °C. The rate constants for these decompositions were 2.90, 2.71, 2.79, and 2.80 × 10^{-4} s^{-1}, respectively. (Each rate constant is the average of two runs.) After 8 half-lives, the sole product observed was **3** (quantitative yield, as determined by ^{31}P NMR spectroscopy). Neopentane was quantified (0.95 equiv) by GC and identified by GC/MS. No trace of 1,1-dimethylcyclopropane, bineopentyl, or neopentylbenzene was detected. Minute amounts of cyclohexane and cyclohexene were detected in the benzene; these contaminants were present in unreacted benzene and thus are not the products of bis(phosphine) decomposition.

Arrhenius Parameters. Rate constants for the decomposition of **1** (0.08 M) in benzene at 49.2, 56.1, 69.0, and 81.0 °C were 0.199, 0.516, 2.80, and 11.9 × 10^{-4} s^{-1}, respectively. (The rate constant for the decomposition at 69.0 °C is the average of eight runs; the other rate constants are each the average of two runs.) The activation parameters are given in the text.[45]

Thermolysis of 1 in Benzene-d_6. Each of two NMR tubes was charged with ca. 28 mg of **1**. The tubes were attached to a vacuum line and evacuated. Benzene-d_6 (0.50 mL) was vacuum-transferred from LiAlH$_4$ into each tube. The samples were degassed as usual and sealed in vacuo (0.010 Torr). The rate of decomposition at 69.0 °C was 2.72 × 10^{-4} s^{-1} (average of two runs). The tubes were heated for 8 half-lives (ca. 6 h); when the tubes were cooled to room temperature, the product, 3-d_6, separated as crystals. Neopentane was quantified (0.96 equiv) by GC and identified by GC/MS: *m/e* (relative intensity) 57 (100), 58 (4.6).

Thermolysis of 1 in Benzene/Cyclohexane. Five sealed tubes, each containing ca. 14 mg of **1** in 0.50 mL of benzene/cyclohexane solution, were prepared from 0.40, 0.80, 2.0, 4.0, and 6.0 M stock solutions of benzene in cyclohexane. The samples were thermolyzed at 68.9 °C, and the rate of decomposition was determined by quantitative ^{31}P NMR spectroscopy. The rate constants for the 0.40, 0.80, 2.0, 4.0, and 6.0 M benzene/cyclohexane solutions were 6.44, 6.13, 5.98, 4.99, and 4.39 × 10^{-4} s^{-1}, respectively. The only product observed by ^{31}P NMR spectroscopy was **3**.

Test for 1/1 Benzene Coordination. A 10^{-4} M solution of **1** in cyclohexane was prepared by dissolving 7 mg of **1** in 10 mL of deolefinated cyclohexane in a volumetric flask. A 1.0-mL aliquot of this solution was then diluted to 10 mL in a second volumetric flask. The UV–vis spectrum of the solution was recorded against a blank of deolefinated cyclohexane: λ_{max} (log ϵ) 282 nm (3.5), 256 (sh, 3.6), 240 (sh, 3.8), 217 (4.0).

A 10^{-4} M solution of benzene in cyclohexane was prepared by diluting 85 mg of benzene with deolefinated cyclohexane in a 100-mL volumetric flask. A 1.0-mL aliquot of this solution was then diluted to 100 mL with additional cyclohexane. Then 7 mg of **1** was dissolved in the benzene/cyclohexane solution. The final concentration of both benzene and **1** was 10^{-4} M. The UV–vis spectrum of this solution, recorded against a blank of cyclohexane, was indistinguishable from the UV–vis spectrum of **1** in neat cyclohexane.

Thermolysis of 1 in Cyclohexane Containing Diphenylacetylene. A sealed tube containing ca. 14 mg of **1** and 6 mg of diphenylacetylene in 0.50 mL of cyclohexane was prepared. The rate of decomposition at 68.8 °C was 7.23 × 10^{-4} s^{-1}. The major product was **4**. A few very small, spurious peaks were also present in the ^{31}P NMR spectrum; these are probably from the products of oxidative addition of the phenyl C–H bonds.

Thermolysis of 1 in Cyclohexane Containing Bis(dicyclohexylphosphino)ethane. Two sealed tubes, each containing ca. 14 mg of **1** in 0.50 mL of a 0.16 M solution of bis(dicyclohexylphosphino)ethane in cyclohexane, were prepared. The rate of decomposition at 68.9 °C was

7.30 × 10^{-4} s^{-1} (average of two runs).

Thermolysis of 1 in THF. Two sealed tubes, each containing ca. 28 mg of **1** in 0.50 mL of THF, were thermolyzed at 68.6 °C. Linear first-order kinetics was observed, but the initially colorless solutions turned pink and a small amount of white precipitate formed. The rate of decomposition was 1.91 × 10^{-4} s^{-1} (average of two runs). The major product is tentatively identified as *cis*-[bis(dicyclohexylphosphino)ethane]hydrido(3-oxacyclopentyl)platinum(II); several minor products were also observed. The reaction was not investigated in depth.

Thermolysis of 1 in THF Containing Bis(dicyclohexylphosphino)ethane. Two sealed tubes, each containing ca. 28 mg of **1** in 0.50 mL of 0.24 M bis(dicyclohexylphosphino)ethane in THF, were thermolyzed at 68.4 °C. The rate of decomposition was 1.86 × 10^{-4} s^{-1} (average of two runs). The major product was **5**; a small amount of the hydride also formed.

Thermolysis of 1-d_1. Two sealed tubes, each containing 28 mg of **1-d_1** in 0.50 mL of benzene, were thermolyzed at 69.2 °C side by side with a sealed tube containing 28 mg of **1** in 0.50 mL of benzene. The rate of decomposition was determined by quantitative ^{31}P NMR spectroscopy. Monitoring the disappearance of the peaks corresponding to **1-d_1** was complicated by the presence of peaks from **1**. (The starting material was only ca. 85% isotopically pure.) The downfield peak of **1-d_1** (δ 75.7) was sufficiently well resolved from that of **1** (δ 75.9) to permit accurate integration, but the upfield peak of **1** (δ 62.9) coincided with the center peak of the upfield "triplet" of **1-d_1** (δ 62.9, J_{P-D} = 30 Hz). The amount of **1-d_1** was taken as proportional to the area of the peak at δ 75.7 plus 1.5 times the combined area of the outer peaks of the "triplet". The rate of decomposition of **1-d_1** was 1.92 × 10^{-4} s^{-1} (average of two runs). Alternatively, the amount of **1-d_1** was taken as proportional to twice the area of the peak at δ 75.7. Corrected in this manner, the rate of decomposition was 1.90 × 10^{-4} s^{-1} (average of two runs). The rate of decomposition of **1** was 2.94 × 10^{-4} s^{-1}. The kinetic isotope effect calculated from these data was the same regardless of which "corrected" rate constant was used: k_H/k_D = 1.5.

Thermolysis of 1 in the Presence of Bis(dicyclohexylphosphino)ethane. A 0.16 M solution of bis(dicyclohexylphosphino)ethane was prepared by dissolving 0.34 g of bis(dicyclohexylphosphino)ethane in benzene in a 5-mL volumetric flask under argon. More dilute solutions (0.080 and 0.040 M) were prepared by diluting 2.50- and 1.25-mL aliquots of this stock solution to 5.0 mL. Three sealed tubes, each containing 28 mg of **1** in 0.50 mL of bis(phosphine)/benzene solution, were prepared from the 0.040, 0.080, and 0.16 M stock solutions. The rates of decomposition at 69.0 °C were 2.82, 2.88, and 2.86 × 10^{-4} s^{-1}, respectively. Both **3** and **5** were produced.

Test for Phosphine Dissociation. Variable-Temperature NMR Experiments. A medium-walled 5-mm-o.d. NMR tube was charged with 28 mg **1**, 0.10 mL of C$_6$D$_{12}$, and 0.40 mL of benzene. The sample was freeze–pump–thaw degassed three times and then back-filled with 1 atm of argon and sealed. The sample was placed in a preheated NMR probe, and the ^{31}P NMR spectrum was recorded at 337 K. (The accuracy of the thermometer in the NMR spectrometer is estimated to be ±5 K.) The sample was then removed and the probe temperature was lowered to 305 K. (The decoupler generates enough heat to maintain the probe at this temperature even when no additional heat is supplied.) Once the probe temperature had stabilized, a second ^{31}P NMR spectrum was recorded. The line widths at half-height (6–7 Hz, including a line broadening of 3 Hz) of the peaks corresponding to **1** were the same at both temperatures; no loss of platinum–phosphorus coupling was observed at 337 K, and no new peaks were visible down to δ –3. (The chemical shift of uncoordinated bis(dicyclohexylphosphino)ethane is δ 1.7; presumably, the free end of the monocoordinated ligand would have a similar chemical shift.) Only small changes (10–50 Hz) in the chemical shifts were observed. Similarly, the line widths at half-height of the peaks corresponding to **3** (6 Hz, including a line broadening of 3 Hz) were identical at both temperatures, and the chemical shifts varied only slightly (10–20 Hz).

Thermolysis of 6 in Benzene. A sealed NMR tube containing 19 mg of **6** in 0.50 mL of benzene was thermolyzed at 68.9 °C. The rate of decomposition was 3.77 × 10^{-4} s^{-1}; linear first-order kinetics was observed for greater than 2 half-lives. After 8 half-lives, the sole product was **7** (96% yield). The yield of neopentane was 90%, as quantified by GC with *n*-pentane as a standard. Neopentane was also analyzed by GC/MS: *m/e* (relative intensity) 57 (31.6), 58 (5.1), 59 (23.0), 60 (100; M$^+$ – CH$_3$), 61 (4.5).

Test for the Intramolecular Nature of Reductive Elimination. Two sealed NMR tubes, each containing equimolar amounts of **1** (21 mg) and **6** (19 mg) in benzene (0.50 mL), were thermolyzed at 68.9 °C. The rate of decomposition of **1** was 2.66 × 10^{-4} s^{-1} (average of two runs); the rate of decomposition of **6** was 3.67 × 10^{-4} s^{-1} (average of two runs). The only complexes observed by ^{31}P NMR spectroscopy during the course of

(45) The uncertainty in the thermodynamic parameters was determined as follows. Rate constants for fourteen separate kinetic experiments (eight experiments at 69 °C, two experiments each at 49, 56, and 81 °C) were determined by a linear regression analysis of the data. The values of log k were plotted against $10^3/T$ (K), and the slope of the line was determined by linear regression. The standard deviation in the slope was adjusted to the 95% confidence level, and the maximum and minimum values of the slope were used to determine the uncertainty in the thermodynamic parameters. The uncertainty in the temperature was considered to be ±1 °C.
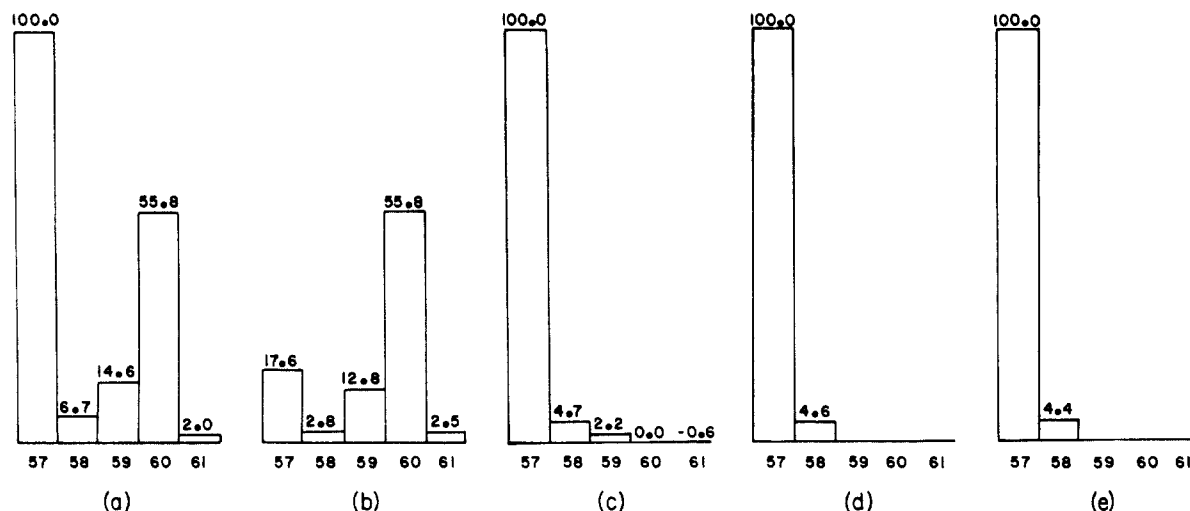
100.0   100.0   100.0   100.0   100.0

55.8   55.8

17.6

14.6   12.8

6.7   4.7   4.6   4.4
2.0   2.8   2.5   2.2   0.0 -0.6

57 58 59 60 61   57 58 59 60 61   57 58 59 60 61   57 58 59 60 61   57 58 59 60 61

(a)   (b)   (c)   (d)   (e)

Figure 14. GC/MS analysis of neopentane: (a) neopentane from the thermal decomposition of equimolar amounts of 1 and 6-d_3 in C_6H_6 at 69 °C; (b) neopentane from the thermolysis of 6-d_3 in C_6H_6 at 69 °C, normalized such that the intensity of the base peak, m/e 60, is 55.8%; (c) spectrum a − spectrum b, normalized so that the intensity of the base peak, m/e 57, is 100%; (d) mass spectrum of authentic neopentane; (e) MS of the neopentane produced by thermal decomposition of 1 in C_6D_6.

the thermolyses were 1, 6, 3, and 7. No crossover products, e.g. 1-d_1, were observed. After 6 h, the only products observed were 3 and 7, both of which were formed in quantitative yield. The neopentane formed in the reaction was analyzed by GC/MS: m/e (relative intensity) 57 (100), 58 (6.7), 59 (14.6), 60 (55.8), 61 (2.0). The mass spectrum of the neopentane produced by the thermolysis of 6 was normalized so that the intensity of the base peak (m/e 60) was the same as the intensity of this peak in the mass spectrum of the neopentane from the crossover experiment (55.8): m/e (relative intensity) 57 (17.6), 58 (2.8), 59 (12.8), 60 (55.8), 61 (2.5). The mass spectrum of the neopentane from the thermolysis of 6 was subtracted from the mass spectrum of the neopentane from the crossover experiment. The resulting mass spectrum was normalized so that the intensity of the base peak (m/e 57) was 100: m/e (relative intensity) 57 (100), 58 (4.7), 59 (2.2), 60 (0), 61 (−0.6). This mass spectrum is very similar to the mass spectrum of authentic neopentane (Matheson, 99.2% pure): m/e (relative intensity) 57 (100), 58 (4.6). The mass spectral data are presented graphically in Figure 14. Both ^{31}P NMR and GC/MS data indicate that crossover during reductive elimination was minimal; the reductive elimination of neopentane is strictly intramolecular and perforce monomolecular.

Test for Intramolecular Rearrangement in 1-d_1. A sealed NMR tube containing 42 mg of 1-d_1 in 0.50 mL of benzene was prepared. Initially, the ^{2}H NMR spectrum showed a broad doublet with platinum satellites (δ −0.20, J_{P-D} = 30, J_{Pt-D} = 180 Hz). After 65 min (ca. 1 half-life) at 69 °C, the only new peak observed in the ^{2}H NMR spectrum was that of neopentane-d (δ 0.87). No peaks were observed at δ 2.52 (corresponding to cis-[bis(dicyclohexylphosphino)ethane]hydrido(neopentyl-1-d_1)platinum(II)) or at δ 1.7 (corresponding to cis-[bis(dicyclohexylphosphino)ethane]hydrido(neopentyl-3-d_1)platinum(II)).

Test for Intermolecular Exchange. Thermolysis of 3 in Benzene-d_6. A 5-mm-o.d. NMR tube was charged with 8 mg of 3 and evacuated. Then C_6D_6 (0.5 mL) was vacuum-transferred from LiAlH$_4$ into the NMR tube. After three freeze–pump–thaw cycles, the tube was sealed in vacuo (0.010 Torr). The initial ^{31}P NMR spectrum showed only 3:

δ 74.3 (s with Pt satellites, J_{Pt-P} = 1749 Hz); 60.7 (s with Pt satellites, J_{Pt-P} = 1737 Hz). When the tube was heated to 69 °C, peaks corresponding to 3-d_6 began to appear: δ 74.2 (s with Pt satellites, J_{Pt-P} = 1749 Hz), 60.7 ("t" with Pt satellites, J_{P-D} = 29, J_{Pt-P} = 1718 Hz). In accord with these data, the signals from the phenyl and hydride hydrogen nuclei were greatly diminished in the ^{1}H NMR spectrum.

Test for Intra- and Intermolecular Rearrangement in 3-d_5. A sealed NMR tube containing 7 mg of 3-d_5 in 0.50 mL of benzene was prepared. The initial ^{2}H NMR spectrum showed two broad peaks at δ 8.04 and 7.41, as well as the residual solvent peak at δ 7.15. The sample was heated to 69 °C, and ^{2}H NMR spectra were recorded periodically. The peaks at δ 8.04 and 7.41 decreased in size, while the "residual solvent" peak (actually benzene-d_5, as well as benzene containing the natural abundance of deuterium) grew. In addition, a doublet with platinum satellites appeared in the high-field region (δ 0.15, J_{P-D} = 29, J_{Pt-D} = 180 Hz). With time the peaks at δ 8.04, 7.41, and 0.15 completely vanished, and after ca. 28 h, only the residual solvent peak was observed. The ^{31}P NMR spectrum was identical with that of 3, indicating that the complex had not decomposed in the process of exchange.

Supplementary Material Available: Table IV, anisotropic thermal parameters (2 pages); Table V, a listing of calculated and observed structure amplitudes (41 pages). Ordering information is given on any current masthead page.