Reductive Elimination of a Carbon-Carbon Bond from Bis(trialkylphosphine)-3,3-dimethylplatinacyclobutanes Produces Bis(trialkylphosphine)platinum(0) and 1,1-Dimethylcyclopropane¹

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Abstract: The thermal decompositions of several platinacyclobutanes—bis(triethylphosphine)- (1), bis(triisopropylphosphine)-(2), and bis(tricyclohexylphosphine)-3,3-dimethylplatinacyclobutane (3)—have been examined in cyclohexane solution. Decomposition of 1 proceeds heterogeneously: it produces platinum metal, neopentane, 1,1-dimethylcyclopropane, and ethylene and seems to be autocatalytic. Decompositions conducted using reaction mixtures containing mercury(0) proceed homogeneously and produce predominately 1,1-dimethylcyclopropane; any platinum metal produced is apparently amalgamated by the Hg(0) and rendered catalytically inactive. Thermal decompositions of 2 and 3 proceed homogeneously, even in the absence of Hg(0), and yield 1,1-dimethylcyclopropane, bis(trialkylphosphine)platinum(0), and a small quantity of neopentane. The rates of decomposition are decreased by addition of trialkylphosphine, and a study of this dependence of rate on concentration of added phosphine for 2 indicates that one phosphine dissociates to produce a three-coordinate platinum(II) intermediate prior to reductive elimination of 1,1-dimethylcyclopropane. The Arrhenius activation parameters for decomposition of 2 and 3 are respectively $E_a = 46 \pm 3 \text{ kcal mol}^{-1}$, log $A = 23 \pm 2 \text{ and } E_a = 42 \pm 2 \text{ kcal mol}^{-1}$, log $A = 21 \pm 1$. Substitution of deuterium for hydrogen in the triisopropylphosphine groups of 2 produces no change in the rate of reaction. We cannot distinguish between mechanisms in which reductive elimination of 1,1-dimethylcyclopropane occurs directly from the three-coordinate intermediate and those in which oxidative addition of a C-H bond to platinum by cyclometalation of the phosphine produces a Pt(IV) intermediate in a step preceding rate-limiting reductive elimination of 1,1-dimethylcyclopropane.

Heterogeneous reactions of hydrocarbons with transition metals (cracking, reforming, hydrogenation) involve cleaving and reforming C-H and C-C bonds, and are believed to proceed through metallacyclic and surface-alkyl intermediates.³ Although studies of the mechanisms of these heterogeneous reactions have been difficult, the studies of related reactions in homogeneous transition-metal systems have provided examples of C-H and C-C bond cleavage and formation by metathesis,⁴ β -hydride elimination and insertion of olefins into metal-hydrogen bonds,5,6 oxidative addition and reductive elimination of C-H^{7,8} and C-C bonds.⁹⁻¹³ and cyclometalation.14-16 This paper is concerned with the

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Scheme I. Reaction of Triisopropylphosphine with (1,5-Cvclooctadiene)dineopentylplatinum(II) (L = *i*-Pr₃P; Yields Based on (1,5-Cyclooctadiene)dineopentylplatinum(II))



Scheme II. Reaction of Tricyclohexylphosphine with (1,5-Cyclooctadiene)dineopentylplatinum(II) (L = c-Hx, P; Yields Based on (1,5-Cyclooctadiene)dineopentylplatinum(II))



mechanism of carbon-carbon bond formation by reductive elimination from platinum. A previous study of the thermal decom-

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position of platinum(II) metallacycles¹⁷ indicated that reductive elimination of a C-C bond took place only after the oxidative addition of a halogenated solvent molecule (methylene chloride) to platinum(II) had occurred and generated a platinum(IV) intermediate. In nonhalogenated solvents, only β -hydride elimination of alkene was observed. Here we describe a study of the mechanism of thermal decomposition of bis(trialkylphosphine)-3,3dimethylplatinacyclobutanes to bis(trialkylphosphine)platinum(0) and 1,1-dimethylcyclopropane in hydrocarbon solvents. The reaction proceeds by an initial dissociation of one of the trialkylphosphine ligands and generation of a three-coordinate platinum(II) intermediate. The large Arrhenius preexponential frequency factors that are observed suggest that the reductive elimination of 1,1-dimethylcyclopropane is rate limiting. The possibility that oxidative addition of a C-H bond of the coordinated phosphine to Pt(II) to form a Pt(IV) intermediate preceeds reductive elimination of dimethylcyclopropane can neither be proved nor disproved.

Results

Preparation of Bis(triisopropylphosphine)-3,3-dimethylplatinacyclobutane (2) and Bis(tricyclohexylphosphine)-3,3-dimethylplatinacyclobutane (3). Platinacyclobutanes 2 and 3 were isolated in 19% and 17% yields, respectively, as air-stable, white crystalline solids from the reaction of 2 equiv of the corresponding trialkylphosphine with dineopentyl(1,5-cyclooctadiene)platinum-(II) in cyclohexane at 50 °C and were characterized by a combination of ¹H and ³¹Pl¹H} NMR spectroscopy, elemental analysis, and chemical reactions. Addition of DCl to a solution of 2 in cyclohexane generated 1 equiv of neopentane which was determined by GC/MS analysis to be \geq 95% (CH₃)₂C(CH₂D)₂; repeating the procedure with 3 produced 1 equiv of neopentane which was \geq 94% (CH₃)₂C(CH₂D)₂.

Unlike the reaction of 2 equiv of triethylphosphine with (1,5cyclooctadiene)dineopentylplatinum(II), which cleanly produces dineopentybis(triethylphosphine)platinum(II),14 the corresponding reaction of (1,5-COD)Pt[CH₂C(CH₃)₃], with triisopropylphosphine (Scheme I) or tricyclohexylphosphine (Scheme II) gave a complex reaction mixture containing no dineopentylbis(trialkylphosphine)platinum(II) compounds (as determined by ³¹P{¹H} NMR spectroscopy). Instead, a bis(trialkylphosphine)-3,3-dimethylplatinacyclobutane and bis(trialkylphosphine)platinum(0) complex were produced as the major platinum-containing compounds, along with neopentane and 2,2,5,5-tetramethylhexane. Oxidative addition of an allylic C-H bond of 1,5-cyclooctadiene to platinum(II) is undoubtedly the source of some of the hydrogen atoms which participate in the subsequent reductive elimination of a C-H bond to form neopentane; a 15-20% yield of 1,3,5cyclooctatriene was obtained from the reaction of triisopropylphosphine with (1,5-cyclooctadiene)dineopentylplatinum(II).

The marked difference in the products of the reaction of (1,5-cyclooctadiene)dineopentylplatinum(II) and triisopropylphosphine, tricyclohexylphosphine, and triethylphosphine may be due to the larger steric bulk of the first two of these phosphines.¹⁸ A square-planar platinum(II) species composed of two neopentyl groups and two sterically demanding trialkylphosphine ligands is probably very unstable. The displacement of 1,5-cyclooctadiene by a bulky phosphine could produce a highly reactive, coordinatively unsaturated 14-electron platinum(II) species which could oxidatively add a C-H bond of a neopentyl group, cyclooctadiene, or phosphine alkyl group to yield the observed products.

Thermal Decomposition of Bis(trialkylphosphine)-3,3-dimethylplatinacyclobutanes. Products. The thermal decomposition of a cyclohexane solution of bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (1) in a sealed tube at 157 °C produces



Figure 1. First-order plots of the thermal decompositions of $2 (\blacksquare, \square)$, $2 \cdot (L^D)_2 (\Delta)$, and $3 (\bullet, O)$ in cyclohexane at 116 °C. Solid symbols represent data obtained by ³¹Pl⁴H} NMR spectroscopy; open symbols are based on GLC data.

a heterogeneous reaction mixture containing neopentane, 1,1dimethylcyclopropane, ethylene, and platinum metal.¹⁴ The formation of a platinum mirror and collodial platinum was probably due to the disproportionation of bis(triethylphosphine)platinum(0), formed by the reductive elimination of 1,1-dimethylcyclopropane from 1, to produce tris(triethylphosphine)platinum(0) and platinum metal. In fact, when the thermal decomposition of 1 was repeated at 178 °C in the presence of Hg(0), the reaction mixture remained homogeneous. 1,1-Dimethylcyclopropane and neopentane were produced in a ratio of 94:6 throughout the thermolysis. No other hydrocarbon products were observed by GLC when the reaction was repeated in isooctane or 2,2,4,4-tetramethylpentane. ³¹P{¹H} NMR spectroscopy revealed only the production of free triethylphosphine as 1 was consumed, and no $(Et_3P)_3Pt^0$ was observed, indicating that platinum metal was amalgamated with mercury and rendered inert. The small percentage of neopentane produced in the presence of Hg(0) indicates that its formation in larger quantities in the absence of Hg(0) may be due to reactions catalyzed by the platinum metal which is formed.

Heating a sealed tube containing a 0.08 M solution of 2 or 3in cyclohexane resulted in a homogeneous reaction which produced either bis(triisopropylphosphine)platinum(0) (4) or bis(tricycle hexylphosphine)platinum(0) (5), respectively, 1,1-dimethylcyclopropane, and a small quantity of neopentane (eq 1).¹⁹ The

$$\begin{array}{c} {}_{2}{}_{2}{}_{2}{}_{2}{}_{1} \left(\begin{array}{c} 126 \ ^{\circ}C}{C_{0}} + {}_{2}{}_{2}{}_{2}{}_{2}{}_{1}{}_{0}{}_{1}{}_{0}{}_{1} \right) + \left(\begin{array}{c} 126 \ ^{\circ}C}{C_{0}} + {}_{2}{}_{2}{}_{1}{}_{2}{}_{1}{}_{2}{}_{1}{}_{2}{}_{1}{}_{2}{}_{1}{}_{2}{}_{1}{}_{2}{}_{1}{}_{2}{}_{1}{}_{2}{}_{1}{}_{2}{}_$$

homogeneous nature of the reaction and the high yields of 1,1dimethylcyclopropane can be attributed to the stability of the bis(trialkylphosphine)platinum(0) complexes which are formed.²⁰ The source of the two hydrogen atoms which are required in the production of neopentane have not been positively identified, but they did not originate from the solvent, since the thermal decomposition of 2 in C_6D_{12} produced only neopentane- d_0 . When a cyclohexane solution of $2 \cdot (L^D)_2$ ($L^D = [(CD_3)_2CD]_3P$) was heated for 0.5 h at 178 °C, the neopentane produced was 80% d_0 , 15% d_1 , and 4% d_2 , indicating some transfer of hydrogen atoms originally present in the phosphine ligand to the platinacyclobutane ring to form neopentane.

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Figure 2. Dependence of the rate of thermal decomposition of 2 on the concentration of added triisopropylphosphine. Rate constants were measured at 126.5 °C in cyclohexane solution by ${}^{31}P{}^{1}H{}$ NMR spectroscopy.

Kinetics. The thermal decomposition of 1 in cyclohexane (in the presence of Hg(0)) was followed by monitoring the appearance of 1,1-dimethylcyclopropane by GLC. This reaction followed first-order kinetics ($k^{obsd} = 1.2 \times 10^{-5} \, \mathrm{s}^{-1}$, 178 °C) through the first half-life of the reaction. Free triethylphosphine was also generated as the reaction progressed due to amalgamation of Pt(0) by Hg(0). Because added trialkylphosphine was found to inhibit the rate of decomposition of 2 or 3 (vide infra) and because the effect of Hg(0) on the mechanism of thermal decomposition of 1 is unknown, further investigation of this reaction was deferred in favor of an examination of the simpler thermolysis of 2 and 3, which proceeded homogeneously at much lower temperatures than those necessary for the decomposition of 1.

Rates of decomposition of 2 and 3 were determined by following the disappearance of platinacyclobutane by ³¹Pl¹H} NMR spectroscopy and by monitoring the appearance of 1,1-dimethylcyclopropane by GLC (Figure 1). Rates determined by using these techniques were indistinguishable. Reaction rates were independent of the initial concentration of platinacyclobutane (from 2.4×10^{-2} M to 8.0×10^{-2} M), and the disappearance of 2 or 3 and appearance of 1,1-dimethylcyclopropane were both first order in platinacyclobutane to greater than 90% decomposition.

Addition of triisopropylphosphine or tricyclohexylphosphine to cyclohexane solutions of the corresponding platinacyclobutane inhibited the reaction, but the yields of 1,1-dimethylcyclopropane and neopentane were unchanged. An examination of the dependence of the rates of decomposition of 2 (0.08 M) in the presence of added triisopropylphosphine (0.005–0.040 M) yielded rate constants which obeyed the empirical rate eq 2 (Figure 2).

$$-d[\mathbf{2}]/dt = k^{\text{obsd}}[\mathbf{2}][((CH_3)_2CH)_3P]^{-0.97 \pm 0.12}$$
(2)

The inhibition in the decomposition produced by added trialkylphosphine is not due to an associative process (eq 3) since

$$-_2$$
Pt X + L \neq L₃Pt X (3)

the ³¹P{¹H} NMR spectra of the reaction mixtures containing various concentrations of added phosphine showed no compounds other than platinacyclobutane and free phosphine.

Phosphine dissociation was demonstrated to occur in a preequilibrium rather than rate-determining step by heating a cyclohexane solution of 2 (0.07 M) and 2-(L^D)₂ (0.07 M, L^D = [(CD₃)₂CD]₃P) at 50 °C and following the rate of exchange of phosphines by ³¹P{¹H} NMR spectroscopy. Complete equilibration of deuterated and nondeuterated phosphines among 2, 2- L^HL^D , and 2-(L^D)₂ was observed after 8 h, with no detectable decomposition of 2 to bis(triisopropylphosphine)platinum(0) (Figure 3).

Analysis of the temperature dependence of thermolyses of 2 and 3 over the range 90–120 °C yielded Arrhenius activation parameters of $E_a = 46 \pm 3$ kcal mol⁻¹, log $A = 23 \pm 2$ and E_a



Figure 3. ³¹P[¹H] NMR spectra (101.3 MHz) of a cyclohexane solution of $2 \cdot (L^{H})_{2}$ (0.07 M) and $2 \cdot (L^{D})_{2}$ (0.07 M), A, and after heating at 50 °C for 8 h to produce an equilibrium mixture of $2 \cdot (L^{H})_{2}$, $2 \cdot (L^{D})_{2}$, and $2 \cdot L_{H}L_{D}$, B. No decomposition to form 1,1-dimethylcyclopropane and $L_{2}Pt^{0}$ was observed. (¹⁹⁵Pt satellites are not shown; the underlined phosphine (L^{H(D)}) corresponds to the peak(s) indicated.)



Figure 4. Arrhenius plots for the thermal decompositions of $2 (\bullet)$ and $3 (\blacksquare)$ determined by ³¹P{¹H} NMR spectroscopy.

= 42 ± 2 kcal mol⁻¹, log $A = 21 \pm 1$, respectively (Figure 4). These activation parameters are similar in magnitude to those reported for the thermal decomposition of bis(2,2-dimethylaklyl)bis(triethylphosphine)platinum(II) complexes, which produce bis(triethylphosphine)platinacycloalkanes and hydrocarbon.¹⁴ The rate-limiting step for the cyclometalation reactions is believed to be reductive elimination of alkane from a Pt(IV) intermediate, based on the large Arrhenius preexponential frequency factor and the observation of a kinetic deuterium isotope effect $(k_{\rm H}/k_{\rm D} \approx$ 3) when deuterium is substituted for hydrogen in the alkyl groups. To examine the possibility that the thermal decomposition of 2 might proceed in a similar manner via a rate-limiting oxidative addition or reductive elimination of a triisopropylphosphine C-H bond, the rate of decomposition of **2** and $2 \cdot (L^D)_2$ at 116 °C were compared (Figure 1); a $k_{\rm H}/k_{\rm D} = 0.98 \pm 0.04$ was obtained, indicating the absence of a rate-limiting oxidative addition or reductive elimination of a C-H bond of the coordinated phosphine.

Discussion

The thermal decomposition of bis(trialkylphosphine)-3,3-dimethylplatinacyclobutane to bis(trialkylphosphine)platinum(0) and 1,1-dimethylcyclopropane can be explained by one of two possible mechanisms. Either mechanism is supported by the observation that dissociation of trialkylphosphine and formation of a coordinatively unsaturated 14-electron Pt(II) species is required for the reaction to occur. The large Arrhenius preexponential factor (log $A \approx 21-23$) is also consistent with a mechanism

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Scheme III. Proposed Mechanism for Thermal Decomposition of Bis(trialkylphosphine)-3,3-dimethylplatinacyclobutane in Which a C-C Bond Is Reductively Eliminated from a Pt(II) Intermediate



Scheme IV. Proposed Mechanism for Thermal Decomposition of Bis(trialkylphosphine)-3,3-dimethylplatinacyclobutane in Which a C-C Bond Is Reductively Eliminated from a Pt(IV) Intermediate



in which three particles (phosphine, 1,1-dimethylcyclopropane, and the remaining Pt moiety) are generated in the transition state from one particle in the ground state.

One mechanism of reaction would involve dissociation of trialkylphosphine, rate-limiting reductive elimination of a C-C bond to produce 1,1-dimethylcyclopropane and LPt⁰, and recombination of LPt⁰ with dissociated phosphine (Scheme III). Dissociation of a phosphine ligand prior to reductive elimination of a C-C bond from a three-coordinate intermediate has been reported for thermal decompositions of LAu(CH₃)₂R, L₂Pd(CH₃)₂, and ArNiMeL₂.²¹ In the absence of a polar, coordinating solvent, the L_2Pd^0 formed after reductive elimination of ethane disproportionates to metallic palladium and L₄Pd⁰, and for Au(III), the LAu(I)R species produced upon reductive elimination of R₂ undergoes further intermolecular decomposition to produce Au metal and free phosphine; in contrast, the thermal decomposition of ArNiMeL₂ in cyclohexane or benzene proceeds homogeneously to produce L_2Ni^0 as a stable product. Thus, the production of LPt^0 (an intermediate which is probably highly unstable) in a nonpolar solvent such a cyclohexane would have to be followed by rapid recombination with dissociated phosphine to prevent the formation of platinum metal.

An alternate mechanism could involve initial dissociation of trialkylphosphine, oxidative addition of a C-H bond of the remaining coordinated phosphine to produce a Pt(IV) intermediate, rate-limiting reductive elimination of 1,1-dimethylcyclopropane, and recombination of dissociated phosphine with reductive elimination of the phosphine C-H bond from the remaining Pt(II) intermediate to produce L_2Pt^0 (Scheme IV). The absence of a kinetic deuterium isotope effect upon substitution of ((CD₃)₂CD)₃P for $((CH_3)_2CH)_3P$ in the thermolysis of **2** $(2-(L^D)_2)$ indicates only that the oxidative addition of a phosphine C-H bond, if it does occur, does not take place in the rate-limiting step. A number of reactions have been reported in which the oxidative addition of a trialkylphosphine C-H bond to Pt(II) has resulted either in the formation of a cyclometalated phosphine Pt(II) compound via a Pt(IV) intermediate²² or in the exchange of ²H for ¹H in the alkyl groups of coordinated phosphines (in reactions performed in D_2O/CH_3COOD).²³ The observation of incorporation of ²H into the ca. 1% neopentane produced from the thermal decom-



Figure 5. Gibbs free energy-reaction coordinate diagram illustrating the relative free energies of activation for reaction of 1 with neopentane or decomposition to L_2Pt^0 ($T\Delta S$ calculated for 0.1 M reactants and products)

position of $2-(L^D)_2$ might be due to a phosphine cyclometalation reaction in which the reductive elimination of a C-²H bond instead of a C-C bond occurs a small percentage of the time. Since reductive elimination of a C-C bond from Pt(IV) is well documented^{9,24} and reports of this same reaction for Pt(II) are few,²⁵ the possibility of cyclometalation of a trialkylphosphine to produce a Pt(IV) intermediate from which reductive elimination of 1,1dimethylcyclopropane could occur cannot be ignored, though no concrete evidence has been produced by this investigation to indicate such a reaction does take place.

Our study of the reactions of homogeneous Pt(II) compounds has been directed toward achieving the oxidative addition of an unactivated C-H bond of a hydrocarbon solvent to a homgeneous platinum species, so that comparisons of the mechanisms of the homogeneous and heterogeneous C-H bond activation reactions can be made. We have now completed the study of one particular system, that of the thermal decompositions of dineopentylbis-(trialkylphosphine)platinum(II) and its product, bis(trialkylphosphine)-3,3-dimethylplatinacyclobutane (eq 4). One may ask

$$L_{2}Pt \underbrace{\bigwedge}_{i \in H_{12}} \begin{array}{c} L_{2}Pt X \\ \xrightarrow{i \in H_{12}} \\ \xrightarrow$$

why the reaction proceeds only to the right, with no observable back reaction via oxidative addition of a C-H bond of neopentane or the solvent. The results of this investigation can be used to construct an argument which outlines the problems of trying to oxidatively add "unactivated" C-H bonds of hydrocarbon solvents to homogeneous platinum(II) species.

For the reaction $(Et_3P)_2Pt[CH_2C(CH_3)_3]_2 \rightarrow 1$ + neopentane (178 °C), $k^{cald} = 3.8 \times 10^{-2} \text{ s}^{-1}$;¹⁴ this rate corresponds to a $\Delta G^* \simeq 30$ kcal mol⁻¹. Two particles are produced from one in the reaction, resulting in a $T\Delta S(\text{translation}) = 15-17$ kcal mol⁻¹ (178 °C, 0.1 M reactants and products).²⁶ The sums of bond energies in the reactant and products are the same to a first approximation (neglecting ring strain, vide infra), and one can make the sim-

⁽²¹⁾ For LAuR₃, L = Ph₃P and R = CH₃, C₂H₅, *n*-C₃H₇, *i*-C₃H₇, and t-C₄H₉.¹⁰ For L₂Pd(CH₃)₂, L = PPh₃ and PPh₂CH₃ and L₂ = Ph₂PCH₂CH₂PPh₂.¹¹ For ArNiMeL₂, L = Et₃P and Ar = o-tolyl.¹³

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⁽²⁴⁾ The reaction of cyclohexane solutions of 1 or 2 with bromine or iodine at 25 °C results in the immediate reductive elimination of 1,1-dimethylcyclopropane and formation of $trans-L_2PtX_2$ (X = Br, I); this reaction most likely proceeds through a Pt(IV) intermediate, from which reductive elimination of a C-C bond is rapid.

⁽²⁵⁾ The thermal decomposition of solid samples of cis-L₂PtR₂ (R = C₆H₅, *p*-CH₃C₆H₄, L = P(C₆H₅)₃, P(*p*-CH₃C₆H₄)₃; L₂ = dppe, dppm) in the absence of solvent resulted in the concerted, intramolecular reductive elimination of R₂; rates of decomposition were found to increase upon addition of added phosphine: Braterman, P. S.; Cross, R. J.; Young, G. B. J. Chem. Soc., Dalton Trans. 1976, 1306–1314. Glockling, F.; McBride, T.; Pollock, R. J. I. J. Chem. Soc., Chem. Commun. 1973, 650.

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plifying assumption that $\Delta H \simeq 0$ and that ΔG for the reaction is primarily controlled by entropic effects. For the subsequent reaction of $\mathbf{1} \rightarrow L_2 Pt^0 + 1,1$ -dimethylcyclopropane (178 °C, with Hg(0)), $k^{obsd} = 1.2 \times 10^{-5} \text{ s}^{-1}$. The actual reaction rate could be up to 10^2 faster than observed, since free triethylphosphine is produced during the reaction due to amalgamation of Pt(0) with Hg(0) and may inhibit the rate of decomposition as was observed for thermolyses of **2** and **3**. This range of rate constants corresponds to a $\Delta G^* = 33-37$ kcal mol^{-1,27} From this information one can construct a reaction coordinate diagram which illustrates the relative free energies of activation for the forward and back reactions of **1** (Figure 5); $\Delta G^*(\text{back}) - \Delta G^*(\text{forward}) \simeq 8-14$ kcal mol⁻¹.

The oxidative addition of a C-H bond of a solvent molecule to 1 should be more favorable than reaction with neopentane because of its greater relative concentration (eq 5); $\Delta S = R \ln$

[solvent]/[neopentane] $\simeq R \ln 100 \simeq 9.1$ eu. The hypothetical reaction of 1 with solvent should therefore have $T\Delta S = 4.1$ kcal mol⁻¹ (178 °C) more favorable than reaction of 1 with neopentane but still have a $\Delta G^* = 4-10$ kcal mol⁻¹ greater than that for reductive elimination of 1,1-dimethylcyclopropane from 1.

This entire argument is only qualitative in that it ignores changes in bond strengths and strain energies in proceeding from reactants to products and that it is based on very qualitative estimates of $T\Delta S$. Entropic factors alone are not necessarily the dominant contributors to ΔG for these reactions: steric crowding in $(Et_3P)_2Pt[CH_2C(CH_3)_3]_2$ is relieved upon loss of neopentane,²⁸ and ring strain in the platinacyclobutane which is produced is small but significant (<5 kcal mol⁻¹ greater than an analogous platinacyclopentane).^{14,29} Although the relative importance of entropic and enthalpic contributions in determining the free energy of these reactions have not been established, the above argument suggests that the highly favorable change in entropy in producing two particles from one, both for the production of 1 and for its subsequent decomposition, is significant in determining the direction of the reaction.

Experimental Section

General Data. All reactions involving organometallic compounds were performed under argon or prepurified dinitrogen by using standard anaerobic techniques.³⁰ The procedures followed for performing sealed tube reactions have been described previously.¹⁴ Boiling points are uncorrected. Melting points were determined on a Thomas-Hoover Apparatus and are uncorrected. ³¹P[¹H] NMR spectra were recorded at 36.2 and 101.3 MHz on Jeol FX-90Q and Bruker WP-250 spectrometers, respectively. Spectra are reported at 36.2 MHz unless otherwise noted, and chemical shifts are reported relative to external 85% phosphoric acid

(28) Steric crowding about transition metal alkyls has been reported to result in a decrease of metal-carbon bond energies by 19–20 kcal mol⁻¹ for $[M(CH_2C(CH_3)_3)_4]$ (M = Ti, Zr, or Hf) with respect to sterically less demanding alkyl substituents (Lappert, M. F.; Patil, D. S.; Padley, J. B. J. Chem. Soc., Chem. Commun. 1975, 830–831). Differences in cobalt n-propyl and cobalt neopentyl bond energies of ~7 kcal mol⁻¹ have been observed in certain organocobalt complexes (Tsou, T.-T.; Loots, M.; Halpern, J. J. Am. Chem. Soc. 1982, 104, 623–624).

(downfield shifts positive). ¹H NMR spectra were recorded at 90 and 250 MHz, respectively, on these same spectrometers and are reported at 90 MHz unless otherwise specified. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra were recorded on a Hewlett-Packard 5990A GC/MS at an ionizing voltage of 70 eV. Diethyl ether and tetrahydrofuran were distilled from disodium benzophenone dianion under argon. Cyclohexane and cyclopentane were stirred over concentrated sulfuric acid for 48 h, washed with saturated sodium bicarbonate solution and then water, dried with phosphorus pentoxide, and distilled under argon. Triethyl phosphate was distilled and stored under argon. DCl (38% in D₂O, 99% D, Stohler), triisopropylphosphine (Strem), and tricyclohexylphosphine (Strem) were used as received. Dineopentyl(1,5-cyclooctadiene)platinum¹⁴ and bis(triethylphosphine)-3,3-dimethylplatinacyclobutane $(1)^{14}$ were prepared as previously described. A published procedure was used to prepare 2-bromopropane- d_7 from 2-propanol- d_8 (Stohler, 99.5% D).³¹ Organoplatinum compounds were stored in tightly sealed vials in the dark at -15 °C and were freshly recrystallized before performing thermolyses.

Tris(isopropyl-d₇)phosphine. To a 500-mL round-bottomed flask equipped with stirring bar, addition funnel, and reflux condenser was added 7.0 g (0.29 mol) of magnesium metal and 200 mL of ether. The addition funnel was charged with a solution of 31 g (0.24 mol) of 2-bromopropane- d_7 in 30 mL of ether. This solution was added dropwise with stirring at a rate sufficient to maintain gentle reflux. The mixture was stirred for 3 h after the addition was complete and then filtered through a plug of glass wool to yield 230 mL of 0.97 M (isopropyl- d_7)-magnesium bromide (0.22 mol, 94% yield).

The deuterated phosphine was prepared according to a variation of a published procedure.³² To a flame-dried, argon-filled 500-mL roundbottomed flask equipped with stirring bar and addition funnel was added 6.1 mL (9.6 g, 0.070 mol) of freshly distilled phosphorous trichloride and 100 mL of ether. The addition funnel was charged with the Grignard solution described above, which was then added dropwise with stirring under argon at -10 °C. After the addition was complete, the mixture was refluxed for 2 h and cooled to room temperature. Degassed, distilled water (10 mL) was added *slowly* by syringe with stirring, followed by 50 mL of degassed 2 N HCl and 66 mL of degassed 2 N NH_4OH which dissolved the salts from the reaction and left two phases containing no solids. The organic layer was transferred by cannula to an argon-filled flask containing ca. 20 g of anhydrous sodium sulfate, the remaining aqueous layer was stirred with an additional 150 mL of ether, and the organic layers were combined and fractionally distilled under argon at atmospheric pressure. The fraction boiling at 170-175 °C (lit.³⁰ bp 175 °C) was collected and filtered under argon through a 0.5-cm \times 2.0-cm column of alumina (Woelm, Activity I) to yield 5.3 g (42% yield) of tris(isopropyl- d_7)phosphine: ³¹P{¹H} NMR (C₆D₆) δ 17.3.

Reaction of Dineopentyl(1,5-cyclooctadiene)platinum(II) with Triisopropylphosphine and Tricyclohexylphosphine. Into a flame-dried, argon-filled 0.5-mL thermal decomposition tube was weighed 15 mg (0.034 mmol) of dineopentyl(1,5-cyclooctadiene)platinum(II); the tube was capped with a rubber septum and flushed with argon. To the tube was then added by syringe 0.10 mL (0.068 mmol) of a 0.68 M solution of triisopropylphosphine in cyclohexane or 0.25 mL (0.068 mmol) of a 0.27 M solution of tricyclohexylphosphine in cyclohexane, followed by 0.15 mL of a 0.102 M solution of cyclopentane (GLC internal standard) in cyclohexane. The contents of the tube were degassed by three freezepump-thaw cycles, and the tube was sealed under vacuum (0.01 torr). The tube was heated at 50 °C for 15 h, then frozen in liquid nitrogen, and opened under argon, and the reaction mixture examined by GLC for neopentane and 2,2,5,5-tetramethylhexane by using a 10-ft, 1/8-in. 20% SE-30 on Chromosorb P column and for 1,5-cyclooctadiene and 1,3,5cyclooctatriene using a 10-ft, $^{1}/_{8}$ -in. 15% $\beta_{\beta}\beta'$ -oxydipropionitrile on Chromosorb P column. The yields of neopentane, 2,2,5,5-tetramethylhexane, 1,5-COD, and 1,3,5-cyclooctatriene were 80%, 36%, 80%, and 14%, respectively, for reaction with triisopropylphosphine and 85%, 15%, 30% and 3%, respectively, for reaction with tricyclohexylphosphine. Addition of 0.10 mL of concentrated HCl to these reaction mixtures produced an additional 53 and 83% yield of neopentane from the reactions with triisopropylphosphine and tricyclohexylphosphine, respectively, accounting for all the neopentyl groups originally on platinum.

Repeating the above procedure and heating the tube an additional 2 h at 126 °C after 15 h at 50 °C produced 1,1-dimethylcyclopropane and additional neopentane in 26% and 26% yields, respectively, for reaction

⁽²⁷⁾ At this same temperature (178 °C), the free energy of activation for decomposition of 2 or 3 is calculated to be $\Delta G^* \simeq 26-27$ kcal mol⁻¹. A comparison of the free energies of activation for addition of a C-H bond to 2 or 3 with their thermal decomposition to L_2Pt^0 and 1,1-dimethylcyclopropane is more difficult to construct than for 1, since the corresponding dineopentylbis(trialkylphosphine)platinum(II) compounds could not be prepared in order to determine ΔG for formation of the platinacyclobutanes.

⁽²⁹⁾ The ring strain in the platinacyclobutane moiety of platinum(IV) complexes (e.g., PtCl₂(C₃H₆)(bpy)) has been estimated at ~12 kcal mol⁻¹ by comparisons of heats of decomposition measured by using differential scanning calorimetry (Puddephatt, R. J. Coord. Chem. Rev. **1980**, 33, 149–194). Comparison of this estimate with that derived for similar platinum(II) complexes¹⁴ may not be appropriate, since steric crowding, bond strengths, and electronic structures of the two complexes may be different.

 ⁽³⁰⁾ Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

⁽³¹⁾ Coulson, E. J.; Gerrard, W.; Hudson, H. R. J. Chem. Soc. 1965, 2364-2369.

⁽³²⁾ Lorenz, H. J.; Zintl, A. R.; Volker, F. (Deutsche Advance Production G.m.b.H.) US 3499 039 (Cl. 260-606.5; C 07F), Mar 3, 1970, Appl. Nov 10 1966 (CA 72 P132967s); Neth. Appl. 6,614,945 (Cl. C 07F), Apr 24, 1967; Ger. Appl. Oct 21, 1966 (CA 67 P108757z).

with triisopropylphosphine and in 44% and 41% yields for reaction with tricyclohexylphosphine. The yield of 1,1-dimethylcyclopropane corresponds to the fraction of the reaction of trialkylphosphine with dincopentyl(1,5-cyclooctadiene)platinum(II) which produces platinacyclobutane, determined by heating a reaction mixture at 50 °C for 15 h, removing all volatile components under vacuum, redissolving the remaining oil in dry cyclohexane, and adding 0.10 mL of 38% DCl in D₂O. The yields of $(CH_3)_2C(CH_2D)_2$ produced in this manner for reactions using triisopropylphosphine and tricyclohexylphosphine were 27% and 39%, respectively (Schemes I and II), as determined by GC/MS analysis on a 20-ft, $\frac{1}{8}$ -in. 3% UCW-98 on Chromosorb P column.

Bis(triisopropylphosphine)-3,3-dimethylplatinacyclobutane (2 and 2- $(L^{D})_{2}$). Into each of three 12-in. × 0.5-in. medium-wall thermal decomposition tubes was weighed 0.89 g (2.0 mmol) of dineopentyl(1,5cvclooctadiene)platinum(II); the tubes were capped with a rubber septum and flushed with argon. To each tube was then added by syringe 10 mL of dry, degassed cyclohexane and 0.83 mL (0.64 g, 4.0 mmol) of triisopropylphosphine; the tubes were degassed by three freeze-pump-thaw cycles and sealed under vacuum (0.01 torr). The tubes were heated at 50 °C for 18 h, then frozen in liquid nitrogen, opened, and capped with rubber septa under argon. The reaction mixtures were transferred by cannula to a flame-dried, argon-filled 100-mL round-bottomed flask equipped with stirring bar, and the solvent was removed under vacuum with stirring. The remaining yellow-brown solid was dissolved in 50 mL of degassed acetone and the solution cooled to -78 °C. The yellow precipitate was collected by suction filtration and redissolved in 25 mL of degassed acetone. The volume of the solution was reduced by rapidly flowing argon over the solution at -78 °C. The fine, white crystalline precipitate was collected by suction filtration and remaining acetone removed under vacuum to yield 0.68 g (19%) of 2: mp 126-129 °C dec; ³¹P[¹H] NMR (C₆D₆) δ 33.0 (t, J_{Pt-P} = 1831 Hz); ¹H NMR (C₆D₆) δ 0.86 (4 H, t, J_{Pt-H} = 75.2 Hz, J_{P-H} = 10.3 Hz, PtCH₂), 1.05 (36 H, d of d, J_{P-H} = 11.7 Hz, J = 6.8 Hz, (CH₃)₂CHP), 1.49 (6 H, b s. C- $(CH_3)_2$, 2.17 (6 H, septet, J = 7.3 Hz, CHP); IR (KBr) 2990–2750 (vs br), 1450 (s), 1370 (s), 1350 (s), 1340 (m), 1235 (s), 1038 (s), 1019 (s). 915 (m), 872 (s), 757 (m), 632 (vs), 519 (c) cm⁻¹. Anal. $(C_{23}H_{52}P_2P_1)$ C, H.

Compound 2-(L^D)₂ was prepared in the same manner as described for 2, using 0.94 mL (0.72 g, 4.0 mmol) of tris(isopropyl- d_7)phosphine for each 0.89 g (2.0 mmol) of dineopentyl(1,5-cyclooctadiene)platinum(11) (21% yield): mp 129.0–130.5 °C dec; ³¹P{¹H} NMR (C₆D₆) δ 31.8 (t, $J_{PI-P} = 1834$ Hz); ¹H NMR (C₆D₆) δ 0.85 (4 H, t, $J_{PI-H} = 76.2$ Hz, $J_{P-H} =$ 9.8 Hz, PtCH₂), 1.49 (6 H, b s, C(CH₃)₂); IR (KBr) 2920 (s), 2860 (s), 2820 (m), 2205 (m), 2190 (s), 2130 (m), 2100 (m), 2060 (m), 1450 (m), 1360 (m), 1310 (m), 1055 (m), 1018 (s), 805 (m), 785 (m), 595 cm⁻¹. Anal. (C₂₃H₁₀D₄₂P₂Pt) C, P.

Bis(tricyclohexylphosphine)-3,3-dimethylplatinacyclobutane (3). Into each of three 12-in. \times 0.5-in. medium-wall thermal decomposition tubes was weighed 0.60 g (1.4 mmol) of dineopentyl(1,5-cyclooctadiene)platinum(II); the tubes were capped with a rubber septum and flushed with argon. To each tube was added 8.0 mL (2.8 mmol) of a 0.34 M solution of tricyclohexylphosphine in cyclohexane. The tube walls were washed down with an additional 2.0 mL of cyclohexane, and the resulting solutions were degassed by two freeze-pump-thaw cycles and sealed under vacuum (0.01 torr). The tubes were heated at 50 °C for 15 h and then opened under argon and the reaction mixtures transferred by cannula to an argon-filled 50-mL round-bottomed flask equipped with stirring bar. The volatile components of the reaction mixture were removed under vacuum while being heated at 40-50 °C, and the remaining red-brown oil was redissolved in 150 mL of degassed acetone and cooled to -10 °C for 12 h. The pale yellow solid which precipitated was collected by suction filtration and dissolved in ca. 100 mL of THF. The resulting solution was filtered through a 0.5-µm millipore filter and the filtrate reduced in volume to 10 mL by rotary evaporation at 25 °C. Acetone (50 mL) was added, and the resulting solution was cooled to -78 °C. The white, crystalline solid which precipitated was collected by suction filtration and remaining solvent removed under vacuum to yield 0.56 g (17%) of 3: mp 155–156 °C (dec); ³¹P NMR (C₆D₆) δ 22.3 (t, J_{Pt-P} = 1797 Hz); ¹H NMR (C₆D₆) δ 0.98 (4 H, m, J_{Pt-H} = 75.1 Hz, PtCH₂), 1.27 (18 H, m, CH₂), 1.58 (6 H, s, C(CH₃)₂), 1.59-1.99 (30 H, b m), 2.14 (18 H, m); IR (KBr) 2990-2870 (vs br), 2845 (vs), 1443 (s), 1345 (m), 1295 (m), 1268 (m), 1172 (m), 1122 (m), 1002 (m), 845 (s), 729 (m) cm⁻¹. Anal. ($C_{41}H_{76}P_2Pt$) C, H, P.

Thermal Decomposition of Bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (1) in the Presence of Hg(0). Into each of nine flame-dried, argon-filled 0.5-mL medium-wall thermal decomposition tubes was placed 0.40 g of triply distilled mercury. The tubes were capped with rubber septa and flushed with argon, and then 0.10 mL of a solution of 0.150 g (0.299 mmol) of freshly recrystallized 1 dissolved in 1.50 mL of a 0.102 M solution of cyclopentane in cyclohexane was added to each tube by syringe. The constriction in each tube was rinsed with 0.03 mL of cyclohexane. The contents of the tubes were degassed and the tubes sealed under vacuum (0.01 torr). The tubes were heated for predetermined intervals at 178 °C, then frozen in liquid nitrogen, and opened and the reaction mixtures analyzed by GLC for production of 1,1-dimethylcyclopropane. The observed rate constant for the reaction was measured from data collected through 1 half-life of the reaction; $k^{obsd} = 1.2 \times 10^{-5} \text{ s}^{-1}$. At the completion of the reaction, the yields of 1,1-dimethylcyclopropane and neopentane were 92% and 9%, respectively.

Thermal Decomposition of 2 and 3. Into a 5-mm NMR tube was weighed 30 mg (0.052 mmol) of **2**; the tube was capped with a rubber septum and flushed with argon. To the tube was added by syringe 0.50 mL of a 0.108 M solution of cyclopentane in cyclohexane; the contents of the tube were degassed, and the tube was sealed under vacuum. The tube was then heated for 2 h at 126 °C and the pale yellow, homogeneous reaction mixture examined by ${}^{31}P_{1}^{1}H_{1}$ NMR. No starting material remained, and the only product observed was bis(triisopropylphosphine)-platinum(0)³³ δ 73.2 (t, 1:4:1, $J_{Pt-P} = 4229$ Hz) (lit.³⁴ (octane) δ 72.8 ($J_{Pt-P} = 4202$ Hz)). The tube was opened under argon and the reaction mixture examined by GLC on a 10-ft, ${}^{1}/_{8}$ -in. 20% SE-30 on Chromosorb P column, which indicated the formation of 1,1-dimethylcyclopropane (99%) and neopentane (2%).

Repeating the above procedure with 30 mg (0.036 mmol) of 3 produced bis(tricyclohexylphosphine)platinum(0) as the sole product by ${}^{31}P{}^{1}H{}$ NMR: $\delta 62.5$ (t, 1:4:1, $J_{Pt-P} = 4229$ Hz) (lit.³⁴ (heptane) $\delta 63.8$ ($J_{Pt-P} = 4227$ Hz)). Analysis of the pale yellow, homogeneous mixture by GLC indicated the formation of 1,1-dimethylcyclopropane (94%) and neopentane (7%).

Kinetics of Thermal Decomposition of 2, 2-(L^D)₂, and 3. Into each of eight flame-dried, argon-filled 5-mm NMR tubes was weighed 23.0 mg (0.040 mmol) of freshly recrystallized 2. The tubes were capped with rubber septa and flushed with argon. To each tube was added by syringe 0.50 mL of a 0.16 M solution of triethyl phosphate in cyclohexane; the tubes were degassed by three freeze-pump-thaw cycles and sealed under vacuum (0.01 torr). Duplicate thermolyses at four different temperatures were performed simultaneously, following the disappearance of starting material by ³¹Pl⁴H NMR spectroscopy through at least 2 half-lives. The observed rate constants (average of two runs) for thermolyses of 2 at 98.5, 111.0, 116.5, and 125.0 °C were $k^{obsd} = 5.70, 39.4, 84.6, and 401 \times 10^{-5}$ s⁻¹, respectively.

Repeating the above procedure using 10.0 mg (0.0121 mmol) of 3 in each tube, and heating the tubes at 50 °C for 5 min to completely dissolve the platinum complex before beginning the kinetic runs, gave the following rate constants (average of two runs) at 90.5, 98.0, 109.5, and 116.0 °C: $k^{obsd} = 2.41, 7.71, 44.8$, and $105 \times 10^{-5} \text{ s}^{-1}$, respectively.

The rate of production of 1,1-dimethylcyclopropane from the thermal decomposition of 2, $2 \cdot (L^D)_2$, and 3 was measured by GLC. In a typical procedure, 93.6 mg (0.160 mmol) of 2 was dissolved in 1.0 mL of a 0.102 M solution of cyclopentane in cyclohexane and the resulting solution diluted to 2.0 mL with cyclohexane in a 2.0-mL volumetric flask. To each of nine 0.5-mL medium-wall thermal decomposition tubes was added 0.20 mL of this standard solution, and the walls of the tubes were washed down with an additional 0.10 mL of cyclohexane. The tubes were degassed three times and sealed under vacuum (0.01 torr), then heated at 116.5 °C for predetermined intervals, and opened, and the yield of 1,1-dimethylcyclopropane was determined. The observed rate constants for 2 and $2 \cdot (L^D)_2$ at 116.5 °C were $k^{obsd} = 8.20$ and $8.39 \times 10^{-4} \text{ s}^{-1}$, respectively, and the rate constant for 3 at 116.0 °C was $k^{obsd} = 9.88 \times 10^{-4} \text{ s}^{-1}$.

Thermal Decomposition of 2 and 3 in the Presence of Added Trialkylphosphine. Cyclohexane solutions 0.0075, 0.0125, 0.025, 0.050, and 0.10 M in triisopropylphosphine were prepared by diluting 0.075, 0.125, 0.25, 0.50, and 1.0 mL of a 0.20 M stock solution of the phosphine in cyclohexane to 2.0 mL in volumetric flasks under argon, and then 0.20 mL of each of these solutions was added by syringe to a 5-mm NMR tube containing 0.30 mL of a cyclohexane solution 0.133 M in 2 and 0.16 M in triethyl phosphate. The tubes were degassed and sealed under vacuum and then heated at 126.5 °C, and the rate of disappearance of 2 was measured relative to triethyl phosphate internal standard by ³¹P[¹H] NMR spectroscopy. The observed rate constants for reaction mixtures 80 mM in 2 and 3.0, 5.0, 10, 20, and 40 mM in triisopropylphosphine were $k^{obsd} = 119, 67.2, 33.4, 21.8, and 8.79 \times 10^{-5} s^{-1}$, respectively.

⁽³³⁾ Reaction of the remaining bis(triisopropylphosphine)platinum(0) with 1 equiv of methyl iodide resulted in the immediate production of *trans-(i*- $Pr_3P_2Pt(I)CH_3$: mp 178-180 °C dec; ³¹P{¹H} NMR (C₆D₆) δ 28 (t, J_{P_1-P} = 2801 Hz); ¹H NMR (C₄D₆) δ 0.77 (3 H, t J_{P_1-H} = 88.9 Hz, PtCH₃), 1.23 (36 H, d of d, J_{P-H} = 13.7 Hz, J = 6.8 Hz, (CH₃)₂CHP), 2.95 (6 H, m, (CH₃)₂CHP). Anal. (C₁₉H₄₅IP₂Pt) C, H, I. (34) Marce B. E. Murso, J. Chur, Soc. Deltage Taxon 1980, 727 (26)

⁽³⁴⁾ Mann, B. E.; Musco, A. J. Chem. Soc., Dalton Trans. 1980, 776-785.

Thermal decomposition of a cyclohexane solution of 3 (0.024 M) and tricyclohexylphosphine (0.028 M) at 116 °C as described above yielded $k^{obsd} = 5.93 \times 10^{-5} \text{ s}^{-1}$, compared to $k^{obsd} = 105 \times 10^{-5} \text{ s}^{-1}$ in the absence of added phosphine.

Phosphine Exchange of 2 with 2-(L^D)₂. A degassed cyclohexane solution of **2** (86 mM), **2-(L^D)**₂ (86 mM), and triethyl phosphate (16 mM) was heated for 8 h at 50 °C in a 5-mm NMR tube. Examination of the resulting solution by ³¹P{¹H} NMR (C₆H₁₂, 101.28 MHz) revealed the presence of the following compounds: **2**, δ 33.45 (t, 1:4:1, J_{PL-P} = 1816 Hz); **2-(L^D)**₂, δ 32.16 (t, 1:4:1, J_{PL-P} = 1820 Hz); **2-L^HL^D**, δ 33.54 (d of t, J_{PL-P} = 1818 Hz, J_{P-P} = 4 Hz). The doublet of triplets for L^D of **2-L^HL^D** could not be resolved from the signal for **2-(L^D)**₂ due to the

broadness of the peak. No bis(triisopropylphosphine)platinum(0) was observed, and heating the solution for an additional 16 h at 50 °C produced no change in the distribution of products.

Registry No. 1, 70620-74-5; **2**, 81602-78-0; **2**- $(L^{D})_{2}$, 81602-79-1; **3**, 81602-80-4; tris(isopropyl)phosphine, 6476-36-4; 1,1-dimethylcyclopropane, 1630-94-0; neopentane, 463-83-1; 2,2,5,5-tetramethylhexane, 1071-81-4; 1,3,5-cyclooctatriene, 1871-52-9; tris(isopropyl- d_{21})phosphine, 81583-58-6; isopropyl- d_{7} promide, 39091-63-9; 1,5-COD, 111-78-4; [(*i*-Pr)₃P]₂Pt, 60648-71-7; (1,5-COD)Pt[CH₂C(CH₃)₃]₂, 75101-19-8; (CH₃)₂C(CH₂D)₂, 72110-09-9; (CH₃)₃C(CH₂D), 4741-94-0; Cy₃P, 2622-14-2; (Cy₃P)₂Pt, 55664-33-0.