nylidene plane should bisect the $[Fe(CO)_2(Cp)]$ symmetry plane (dihedral angle of 90°),[22] the observed dihedral angle in cation III is 130.3°. This orientation may be governed by both electronic and steric factors. Sterically, there are close intramolecular approaches between the methylated sulfur S1 and cyclopentadienyl carbon CP5 (3.31 Å) and phenyl carbon C22 (3.54 Å), between methyl carbon C3 and phenyl carbons C46 (3.47 Å) and C41 (3.67 Å), and between thione carbon C4 and phenyl carbon C21 (3.69 Å). Since these distances are close to the sums of the appropriate van der Waals radii (S, 1.85 Å; methyl, 2.0 Å, half-thickness of phenyl ring, 1.70 Å),[35] the vinylidene group may be "tilted" by steric contacts. On the other hand, Figure 2 emphasizes that the longer iron—phosphorus bond (Fe—P2) is nearly parallel to the plane of the vinylidene ligand, while the shorter iron—phosphorus bond (Fe—P1) is nearly perpendicular to it. The electron-withdrawing dithiocarbomethoxy group lies "trans" to the Fe—P2 bond across the vinylidene linkage. A similar orientation has been reported for the phenylvinylidene ligand in $[Mn(C{=}CHPh)(CO)_2(Cp)]$, in which the carbonyl ligand with a longer Mn—C bond lies nearly in the phenylvinylidene plane and is "trans" to the phenyl group, whereas the carbonyl with the shorter Mn—C bond lies perpendicular to the vinylidene plane.[32] Since there is no evidence for steric crowding in the manganese system, there may be an electronic component to the "unexpected" orientations of the vinylidene planes in both the manganese complex and III. Perhaps effects of ligand asymmetry, similar to those described by Hoffmann and co-workers for other [(Cp)MLL′] complexes, account for these orientations.[36] Further structural studies on metallacumulenes relevant to this problem are in progress.[37]

Acknowledgment. Thanks are due to the Research Corp., Sigma Xi, and the University of Kentucky's Research Foundation and Graduate School for financial support and to Dr. Phillip Fanwick for assistance with the crystallographic programs.

Registry No. I, 68866-84-2; II, 79792-47-5; III, 79792-49-7; CS_2, 75-15-0; ICH_3, 74-88-4.

Supplementary Material Available: Experimental parameters for data collection (Table V), positional and thermal parameters (Table VI), least-squares planes (Table VII), and observed and calculated structure factors (Table VIII) for the structure of III (21 pages). Ordering information is given on any current masthead page.

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Cyclometalation of Dialkylbis(triethylphosphine)platinum(II) Complexes: Formation of *Pt,Pt*-Bis(triethylphosphine)platinacycloalkanes[1]

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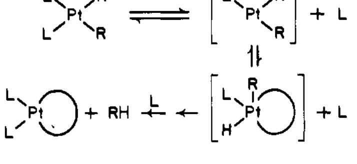
Abstract: The thermal decompositions of three analogues of bis(triethylphosphine)dineopentylplatinum(II) ($L_2Pt[CH_2C(CH_3)_3]_2$ (**1**))—$L_2Pt[CH_2C(CH_3)_2CH_2CH_3]_2$ (**3**), $L_2Pt[CH_2C(CH_3)_2CH_2CH_2CH_3]_2$ (**5**), and $L_2Pt[CH_2C(CH_3)_2CH_2C(CH_3)_3]_2$ (**7**)—have been examined. Compounds **3** and **7** decompose more rapidly than **1** by a factor of ca. 10^4 to give as products *Pt,Pt*-bis(triethylphosphine)-3,3-dimethylplatinacyclohexane (**4**) and *Pt,Pt*-bis(triethylphosphine)-3,3,5,5-tetramethylplatinacyclohexane (**8**), respectively, and 1 equiv of the corresponding alkane. Compound **5** decomposes at a rate ca. 50 times faster than **1** to yield *Pt,Pt*-bis(triethylphosphine)-2,4,4-trimethylplatinacyclopentane (**6a**), -3-methyl-3-*n*-propylplatinacyclobutane (**6b**), and -3,3-dimethylplatinacyclohexane (**6c**). The conversion of **3** to **4** and **5** to **6a** proceeds by dissociation of triethylphosphine, intramolecular oxidative addition of a δ carbon–hydrogen bond of one the alkyl groups to platinum, and reductive elimination of alkane. The decomposition of $L_2Pt[CH_2CH_2C(CH_3)_3]_2$ (**11**) proceeds by β-hydride elimination rather than cleavage of a carbon–hydrogen bond and formation of platinacycloalkane. The difference in the free energies of activation for reactions which form four- and five-membered platinacycloalkanes is small ($\Delta\Delta G^{\ddagger} \simeq 4$ kcal mol^{-1}); that for reactions which form four- and six-membered rings is smaller ($\Delta\Delta G^{\ddagger} \simeq 0$ kcal mol^{-1}). We identify these values of $\Delta\Delta G^{\ddagger}$ with estimates of the strain energies of these rings, assuming the strain energy of the platinacyclohexane is small. The important conclusion from these studies is that the strain energy of the platinacyclobutane studied here is small (<5 kcal mol^{-1}).

Homogeneous reactions which break unactivated aliphatic C–H bonds by oxidative addition to transition metals provide mechanistic information which is useful in understanding catalytic reactions of hydrocarbons.[4] Well-defined stoichiometric reactions which cleave C–H bonds include a group of facile intramolecular cyclizations involving a coordinated ligand.[5] Most reported

Scheme I. Mechanism of Formation of Metalacycloalkanes by Cyclometalation



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[2] Chevron Fellow, 1980–1982.

[3] NIH Postdoctoral Fellow, 1979–1981.

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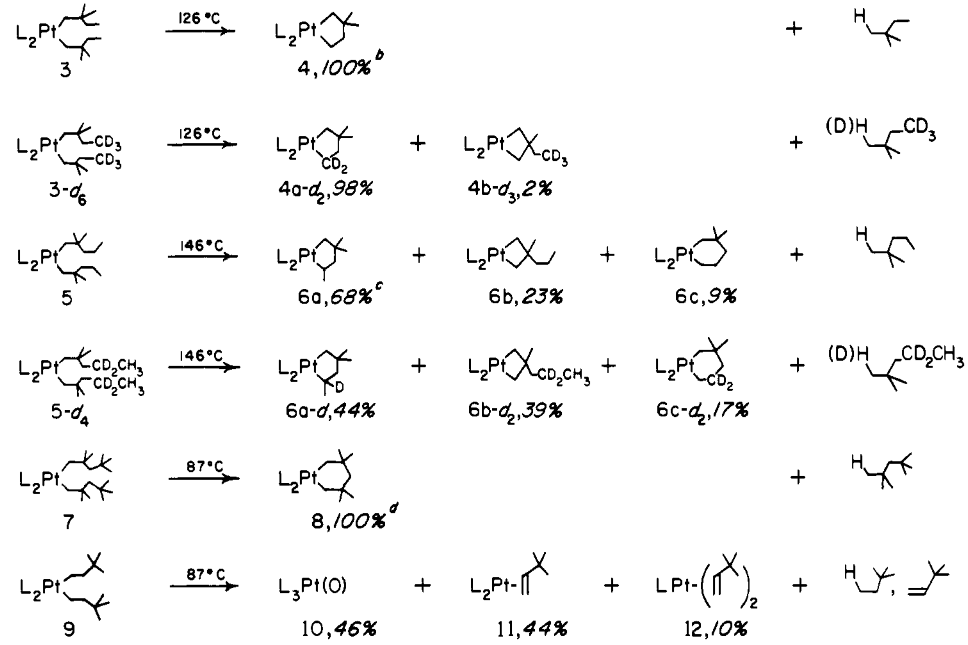
Table I. Formation of Platinacycloalkanes by Cyclometalation ($L = Et_3P$; Relative Yields)[a]



[a] Thermolyses were performed in cyclohexane. Except for **4**, **6a**, and **8**, the products of these reactions were not isolated but were identified by a combination of ^1H and ^{31}P $\{^1H\}$ NMR spectroscopy and chemical reactions. The relative yields of the products were calculated from the peak heights of their respective ^{31}P NMR signals. [b] Metallacycle **4** was the exclusive product by ^1H and ^{31}P NMR and was isolated in 78% following recrystallization. [c] Platinacyclopentane **6a** was isolated in 18% yield by preparative TLC and identified by comparison with an authentic sample. [d] Platinacyclohexane **8** was the exclusive product by ^1H and ^{31}P NMR and was isolated in 68% yield after recrystallization.

examples are of reactions which metalate a phenyl substituent on a ligand containing nitrogen, phosphorus, or arsenic donor atoms[4] and are considered to involve C–H bonds which are "activated" as a result of the adjacent unsaturation. Recently, however, a number of reactions involving cyclometalation of "unactivated" aliphatic C–H bonds have been reported.[6–8] Although the bonds cleaved in these reactions are "unactivated", in the sense that they are not immediately adjacent to unsaturation or heteroatoms, the reactions are undoubtedly facilitated by the energetic and entropic contributions of prior coordination. A well-characterized example of this type of reaction is the conversion of dineopentylbis(triethylphosphine)platinum(II) (**1**) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**2**).[8] The mechanism proposed for the formation of **2** involves the three following steps: (1) formation of a vacant coordination site on platinum by dissociation of phosphine, (2) intramolecular oxidative addition of the methyl C–H bond of a neopentyl moiety to platinum, and (3) reductive elimination of neopentane (Scheme I). A detailed kinetic analysis of the thermal decomposition of **1** and its deuterated analogues suggest that the third step (reductive elimination of alkane) is rate limiting.

This paper summarizes studies of mechanistically related cyclometalation reactions which form four-, five-, and six-membered platinacycloalkanes. These studies clarify the factors (especially the ring strain) which determine the relative energetics of these cyclometalation reactions and which contribute to the differences in the energetics of intramolecular and intermolecular reactions resulting in cleavage of unactivated C–H bonds.

Scheme II. Synthesis of **5-d_4**

$$(CH_3)_2CHCH(N\text{-}t\text{-}C_4H_9) \xrightarrow[\text{(3) 6 N HCl, 70\%}]{\text{(1) LDA/THF}\quad\text{(2) }CH_3CD_2CH_2Br}$$

$$CH_3CD_2CH_2C(CH_3)_2CHO \xrightarrow{\text{(1) LAH/}Et_2O\text{, 94\%}\quad\text{(2) TsCl/pyridine, 97\%}\quad\text{(3) LiBr/HMPA, 88\%}}$$

$$CH_3CD_2CH_2C(CH_3)_2CH_2Br \xrightarrow[\text{(3) }Et_3P\text{, 24\%}]{\text{(1) Mg/THF}\quad\text{(2) CODPtCl}_2/Et_2O}$$

$$\underset{\mathbf{5\text{-}}d_4}{(CH_3CD_2CH_2C(CH_3)_2CH_2)_2Pt(Et_3P)_2}$$

Results

Synthesis of Dialkylbis(triethylphosphine)platinum(II) Compounds. The dialkylbis(triethylphosphine)platinum(II) complexes were prepared by the reaction of dichloro(1,5-cyclooctadiene)platinum(II) with an excess of alkylmagnesium halide, followed by displacement of the 1,5-COD ligand with 2 equiv of triethylphosphine. A representative synthesis of L_2PtR_2 is described in Scheme II for bis(2,2-dimethyl-*n*-pentyl-*4,4*-d_2)bis(triethylphosphine)platinum(II) (**5-d_4**); a similar procedure was used to prepare bis(2,2-dimethyl-*n*-butyl-*4,4,4*-d_3)bis(triethylphosphine)platinum(II) (**3-d_6**) by substituting CD_3CH_2Br for $CH_3CD_2CH_2Br$.

Characterization of the Products from the Thermal Decomposition of L_2PtR_2. The assignment of structures to the products of the thermolyses of the dialkylbis(triethylphosphine)platinum(II) complexes was based on a combination of chemical and spectroscopic evidence. $^{31}P\{^1H\}$ NMR was a particularly effective method for detecting and characterizing the organometallic products of these reactions. The ^{31}P chemical shifts of free phosphines and of phosphines complexed with platinum(0) and

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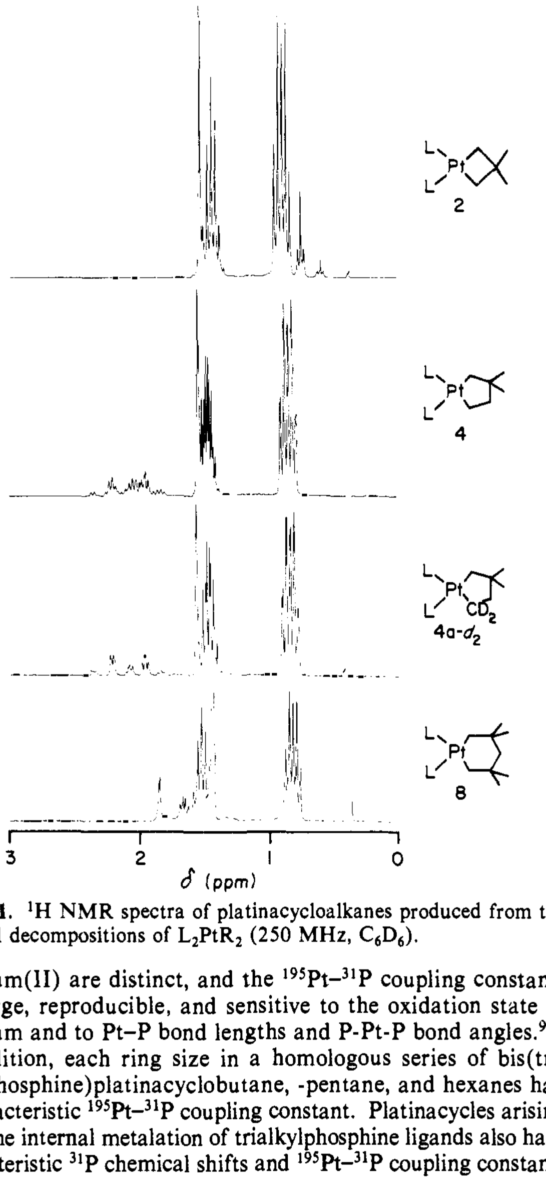

Figure 1. ^{1}H NMR spectra of platinacycloalkanes produced from the thermal decompositions of L_2PtR_2 (250 MHz, C_6D_6).

platinum(II) are distinct, and the ^{195}Pt–^{31}P coupling constants are large, reproducible, and sensitive to the oxidation state of platinum and to Pt–P bond lengths and P-Pt-P bond angles.[9,10] In addition, each ring size in a homologous series of bis(triethylphosphine)platinacyclobutane, -pentane, and hexanes had a characteristic ^{195}Pt–^{31}P coupling constant. Platinacycles arising from the internal metalation of trialkylphosphine ligands also have characteristic ^{31}P chemical shifts and ^{195}Pt–^{31}P coupling constants which depend on ring size.[11]

Heating a clear, colorless 0.1 M solution of **3**, **3**-d_6, **5**, **5**-d_4, or **7** in cyclohexane produced cleanly 1 equiv of alkane and one or more cyclometalated products (Table I); the reaction mixtures remained homogeneous throughout but turned from colorless to pale yellow. ^{1}H NMR spectra (250 MHz, C_6D_6) of the platinacycloalkanes isolated from the thermal decompositions of L_2PtR_2 are illustrated in Figure 1.

Bis(triethylphosphine)-3,3-dimethylplatinacyclopentane (**4**) was isolated as a white, air-stable crystalline solid from the thermal decomposition of **3**. The ^{31}P and ^{1}H NMR spectra of **4** (and **4a**-d_2 from **3**-d_6) permitted an unambiguous assignment of its structure. Although a DCl quench of a solution of **4** in cyclohexane gave a dideuterioalkane, the location of one of the two isotopic labels could not be inferred from the mass spectral fragmentation pattern. Thermal decomposition of **3**-d_6 produced bis(triethylphosphine)-3,3-(dimethyl-*5,5*-d_2)-platinacyclopentane (**4a**-d_2) and bis(triethylphosphine)-3-(ethyl-d_3)-3-methylplatinacyclobutane (**4b**-d_3) in 98% and 2% yields, respectively (based on relative ^{31}P NMR peak heights). One equivalent of alkane was also produced, and analysis by GC/MS indicated it to be predominantly 2,2-dimethylbutane-*1,4,4,4*-d_4 (≃90%) and 2,2-dimethylbutane-*4,4,4*-d_3 (≃ 10%) by comparison with authentic samples produced by the reaction of **3**-d_6 with DCl or HCl. An HCl quench of the platinacycles from the thermolysis of **3**-d_6 produced 1 equiv of hydrocarbon whose structure was inferred by GC/MS to be 2,2-dimethylbutane-*4,4*-d_2 (97%, from **4a**-d_2) and 2,2-dimethylbutane-*4,4,4*-d_3 (3%, from **4b**-d_3).

The formation of 2% of platinacyclobutane **4b**-d_3 from the thermal decomposition of **3**-d_6 was inferred from the ^{31}P and ^{1}H NMR spectra of the reaction mixture and from the reaction of bromine with the products of the thermolysis. The ^{31}P NMR spectrum revealed a 1:4:1 triplet with a chemical shift and ^{195}Pt–^{31}P coupling constant almost identical with that of bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**2**) and with those of platinacyclobutanes **6b** and **6b**-d_2 formed in the thermal decomposition of **5** and **5**-d_4 (vide infra).[12] The ^{1}H NMR spectrum (250 MHz, C_6D_6) showed a multiplet at δ 0.69 which is very similar to that observed for the $PtCH_2$ group of platinacyclobutanes **2** and **6b**. GC/MS analysis of the products from the reaction of bromine with the thermal decomposition products of **3**-d_6 revealed the formation of 1-(ethyl-d_3)-1-methylcyclopropane from **4b**-d_3.[13] Repeating this procedure with the reaction mixture from the thermal decomposition of **3**, the formation of 1-ethyl-1-methylcyclopropane was detected, suggesting the production of a small quantity of a platinacyclobutane from the thermolysis of **3** which was below the limits of detection of ^{31}P NMR spectroscopy (<2% yield).

The thermal decomposition of **5** produced bis(triethylphosphine)-2,4,4-trimethylplatinacyclopentane (**6a**), bis(triethylphosphine)-3-methyl-3-*n*-propylplatinacyclobutane (**6b**), and bis(triethylphosphine)-3,3-dimethylplatinacyclohexane (**6c**). The thermolysis of **5**-d_4 yielded the corresponding deuterated analogues **6a**-d_1, **6b**-d_2, and **6c**-d_2 (Table I). Preparative thin-layer chromatography of a preparative scale (2.2 mmol) thermal decomposition of **5** afforded **6a** as a pale yellow oil whose ^{31}P{^{1}H} and ^{1}H NMR spectra were indistinguishable from those of a sample of **6a** prepared by the reaction of 1,4-dilithio-2,2-dimethylpentane and dichlorobis(triethylphosphine)platinum(II); **6b** and **6c** could not be isolated cleanly from the reaction mixture. The presence of **6b** was confirmed by allowing the thermal decomposition products of **5** and **5**-d_4 to react with bromine and detecting 1-methyl-1-*n*-propylcyclopropane and 1-methyl-1-(*n*-propyl-*2,2*-d_2)-cyclopropane, respectively.[13] The ^{31}P NMR spectra of one of the products derived from **5** and **5**-d_4 yielded a 1:4:1 triplet with a ^{31}P NMR chemical shift and ^{195}Pt–^{31}P coupling constant indicative of a platinacyclobutane. The ^{1}H NMR spectrum (C_6D_6) of the mixture of products revealed a multiplet at δ 0.69 ($J_{Pt\text{-}H}$ = 76.0 Hz) which is also indicative of the Pt–CH_2 group of a platinacyclobutane.[14] Confirmation of the identity of **6c** was obtained by the preparation of authentic **6c** from the reaction of the corresponding Grignard reagent with dichloro(1,5-cyclooctadiene)platinum(II) and subsequently with triethylphosphine. The product of these reactions had a ^{31}P NMR spectrum indistinguishable from that of the **6c** observed in the thermolysis of **5**.

Bis(triethylphosphine)-3,3,5,5-tetramethylplatinacyclohexane (**8**) was isolated as a white, air-stable crystalline solid from the thermal decomposition of **7**. Its ^{31}P NMR and ^{1}H NMR spectra

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(12) ^{31}P{^{1}H} NMR (C_6H_{12}): **2**, δ 9.6 (t, $J_{Pt\text{-}P}$ = 1860 Hz);[8] **4b**-d_2, δ 9.5 (t, $J_{Pt\text{-}P}$ = 1850 Hz); **6b** and **6b**-d_2, δ 9.6 (t, $J_{Pt\text{-}P}$ = 1850 Hz).

(13) The reaction of platinacyclobutanes, but not platinacyclopentanes or platinacyclohexanes, with bromine results in the reductive elimination of a carbon–carbon bond; see ref 8. The yield of 1,1-dimethylcyclopropane is not a quantitative measure of the amount of platinacyclobutane present in the reaction mixtures because of the subsequent reaction of bromine with the liberated cyclopropane to produce dibromoalkanes.

(14) For **2**, ^{1}H NMR (C_6D_6): δ 0.76 ($J_{Pt\text{-}H}$ = 75.5 Hz). The $PtCH_2$ group for platinacyclopentanes and -hexanes generally occurs at δ 1.95–2.22 ($J_{Pt\text{-}H}$ ≃ 60 Hz).

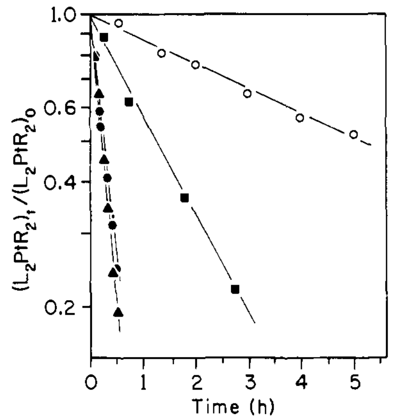

Figure 2. First-order plots of the disappearance of **3** (▲, $k = 9.81 \times 10^{-4}$ s^{-1}), **7** (●, $k = 8.62 \times 10^{-4}$ s^{-1}), **9** (■, $k = 1.55 \times 10^{-4}$ s^{-1}), and **5** (○, $k = 3.88 \times 10^{-5}$ s^{-1}) in cyclohexane at 87 °C (**3**, **7**, **9**) and 99 °C (**5**).

were consistent with platinacyclohexane **8**. A DCl quench of a solution of **8** in cyclohexane gave a compound inferred by GC/MS to have the structure 2,2,4,4-tetramethyl-*n*-pentane-*1*,*5*-d_2.

The thermal decomposition of **9** did not proceed as cleanly as the other dialkylbis(triethylphosphine)platinum(II) complexes but instead turned dark brown-black with the precipitation of a small amount of solid. No cyclometalated products (<2%) were observed by ^{31}P NMR spectroscopy for thermolysis of **9**; the only products observed resulted from β-hydride elimination.[15] These products include tris(triethylphosphine)platinum(0) (**10**) and what have been tentatively identified as (3,3-dimethyl-1-butene)bis(triethylphosphine)platinum(0) (**11**) and bis(3,3-dimethyl-1-butene)(triethylphosphine)platinum(0) (**12**). None of the products were isolated, and assignment of their structures rests primarily on the ^{31}P NMR spectra of the reaction mixture. The observed signals for **10** were those reported.[16] Complex **11** gave an AB pattern with chemical shifts and ^{195}Pt–^{31}P coupling constants very similar to that reported for (propylene)bis(trimethylphosphine)platinum(0),[17] while **12** appeared as a 1:4:1 triplet with chemical shift and coupling constant indicative of bis(olefin)(phosphine)platinum(0) complexes.[18] Addition of triethylphosphine to the reaction mixture consumed **11** and **12** and yielded additional **10**. A separate experiment established that equimolar quantities of 2,2-dimethylbutane and 3,3-dimethyl-1-butene were produced throughout the course of the reaction, yielding a total of 1 equiv of each/equiv of **9**.

Kinetics of Cyclometalations. The rates of thermal decomposition of **3**, **5**, **7** and **9** were determined by following the disappearance of L_2PtR_2 by $^{31}P\{^1H\}$ NMR spectroscopy or by monitoring the appearance of hydrocarbons by GLC; indistinguishable results were obtained by using these different methods. Figure 2 summarizes representative data. The disapparance of L_2PtR_2 and the appearance of the corresponding hydrocarbon were first order in L_2PtR_2 to greater than 90% decomposition, both in the presence and absence of added phosphine, for all cases examined. Rate constants were independent of the initial concentration of L_2PtR_2 but were dependent on the concentration of added triethylphosphine in the solution. The rates of decomposition of **3**, **5**, **7** and **9** were slowed by added triethylphosphine, but the ultimate yields of hydrocarbons produced remained the same. Figure 3 summarizes rates of thermolysis of **3** in the presence of different concentrations of added triethylphosphine; plotting $(k^{obsd})^{-1}$ vs. concentration of added ligand yielded the linear relationship established previously for **1**[8] and $(Et_3P)_2Pt(CH_2CH_3)_2$ (**13**)[15] (eq 1). This observation suggests that phosphine dissociation occurs before the rate-limiting step.

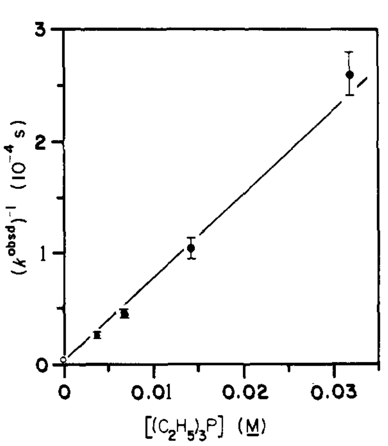

Figure 3. Plot of $(k^{obsd})^{-1}$ vs. the concentration of added $(CH_3CH_2)_3P$. Rate constants were obtained at 107 °C in decane solution by GLC.

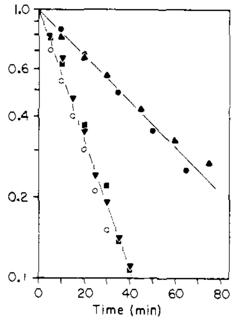

Figure 4. Plot of the thermal decomposition of **3** (○, ▼, ■; $k_H = 9.58 \times 10^{-4}$ s^{-1}) and **3**-d_6 (●, ▲; $k_D = 3.22 \times 10^{-4}$ s^{-1}) at 87 °C in the absence of added triethylphosphine; $k_H/k_D = 3.0 \pm 0.3$. Data indicated with filled symbols were collected by ^{31}P NMR; open symbols are based on GLC data.

$$-d[L_2PtR_2]/dt = k^{obsd}[L_2PtR_2][L]^{-1.0} \qquad (1)$$

Is phosphine dissociation (as in the case of **13**) or oxidative addition or reductive elimination of a C–H bond (as in the case of **1**) the rate-determining step in the thermal decomposition of these L_2PtR_2 complexes? Deuterated compounds **3**-d_6 and **5**-d_4 were prepared and their rates of decomposition compared to those of their nondeuterated analogues. In the absence of added triethylphosphine the kinetic deuterium isotope effect determined from the rates of decomposition of **3** and **3**-d_6 is $k_H/k_D = 3.0$ (Figure 4) and is indistinguishable from that observed in the presence of added triethylphosphine (Table II). Estimation of a kinetic deuterium isotope effect from the thermolyses of **5** and **5**-d_4 was complicated by the fact that both compounds decomposed to a mixture of four-, five-, and six-membered platinacycloalkanes with only the formation of the platinacyclopentane (**6a** and **6a**-*d*, respectively) subject to an isotope effect. The relative rates of formation of the four-, five- and six-membered platinacycloalkanes remain constant throughout the decomposition. This observation permits the calculation of the rates of formation of **6a** and **6a**-*d* from the rates of decomposition of **5** and **5**-d_4, respectively (Table II). These results establish that the thermolysis of **3** to **4** and **5** to **6a** do not involve rate-limiting loss of triethylphosphine but that either oxidative addition or reductive elimination of a C–H bond is rate determining.

Analysis of the temperature dependence of the rate of thermal decomposition of **3** to **4** at four different temperatures, both in the presence and absence of added triethylphosphine, gave linear Arrhenius plots. Rates of formation of platinacyclopentane **6a** (calculated from the rates of disappearance of **5** in a manner analogous to that used to estimate k_H/k_D for **5** → **6a**) also yielded linear Arrhenius plots for thermolyses performed under conditions

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(17) $^{31}P\{^1H\}$ NMR (C_6H_{12}): δ 18.5 (d of t, $J_{Pt-P} = 3279$ Hz, $J_{P-P} = 66$ Hz), 21.1 (d of t, $J_{Pt-P} = 3677$ Hz, $J_{P-P} = 66$ Hz).[15]

(18) This class of complexes is known for ethylene and a variety of phosphines other than triethylphosphine: Harrison, N. C.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, *1337*–1342.

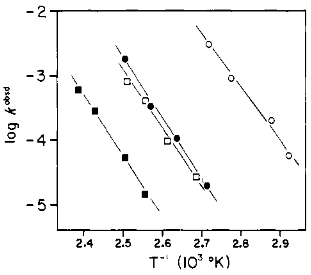

Figure 5. Arrhenius plots for the thermal decomposition of **3** (0.081 M) to yield **4** in the presence (●) and absence (○) of added Et_3P (0.019 M) and for the thermal decomposition of **5** (0.081 *M*) to yield **6a** in the presence (■) and absence (□) of added Et_3P (0.019 M) (calculated from corrected rate constants based on the amount of **5** which decomposed and yielded **6a**).

similar to those used for **3** (Table II and Figure 5). The close similarity between activation parameters for thermolyses run in the presence and absence of added triethylphosphine for each compound suggests that the same mechanism of decomposition is followed.

To determine whether the platinacycles **6a**, **6b**, and **6c** were kinetic or thermodynamic products, compounds **6a** and **6c** were each subjected to experimental conditions under which **5** decomposed to an extent greater than 90% (118 °C, 0.5 h in cyclohexane); no decomposition or isomerization of either **6a** or **6c** to other compounds were observed.[19] This result and the observation that the rates of production of **6a**, **6b**, and **6c** were constant during the thermolyses of **5** indicate that the observed products were kinetic in origin.[20]

Discussion

The transformation of **3** to **4**, of **5** to **6a** (and by analogy, **6b** and **6c**), and of **7** to **8** follow mechanisms similar to that established previously for the conversion of **1** to **2** (Scheme I). In each, 1 equiv of alkane is released, and a platinacycloalkane is the major or exclusive platinum-containing product. Added triethylphosphine slows the decomposition; this observation indicates that the reaction proceeds by initial formation of a vacant coordination site on platinum by dissociation of a triethylphosphine ligand. Comparison of the Arrhenius activation parameters and deuterium kinetic isotope effects for **3** and **5** with that of **1**, both in the presence and absence of added ligand, indicates that a similar reaction mechanism operates for all three compounds. The observed deuterium kinetic isotope effect ($k_H/k_D \simeq 3.0$) together with a large Arrhenius preexponential factor ($\log A \simeq 20$) is most consistent with a mechanism in which reductive elimination is overall rate limiting.

Two conclusions follow from the similarity in these reactions. First, it is unlikely that the driving force for conversion of **1** to **2** is any special stability associated with the platinacyclobutane ring, since other rings form at comparable rates. Second, since the platinacycloalkanes seem to be fully formed *before* the rate-limiting transition states for all of these decompositions and since each reaction expels a similar alkane moiety in the transition state, the relative *rates* of formation of the metallacycles should reflect directly their relative strain energies. That is, to a first approximation, $\Delta\Delta G^{\ddagger} \simeq \Delta\Delta G$, where $\Delta\Delta G^{\ddagger}$ is the difference in activation free energy for two reactions forming platinacycles and $\Delta\Delta G$ is the difference in the strain energy of these rings.

A value of $\Delta\Delta G^{\ddagger}$ can be estimated for the formation of a platinacyclobutane and a platinacyclopentane from the 98:2 ratio of **4a**-d_2 and **4b**-d_3 observed in the thermal decomposition of **3**-d_6

Table II. Arrhenius Activation Parameters, Enthalpy and Entropy of Activation, Kinetic Deuterium Isotope Effect, and Relative Rates of Decomposition for Bis(triethylphosphine)dialkylplatinum(II) Complexes ($L = Et_3P$)[a]

	no added L					added L[b]					
	E_a	$\log A$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	k_H/k_D	E_a	$\log A$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	k_H/k_D	$^{87\,°C}k_{rel}$[c]
1[d] $L_2Pt[CH_2C(C\mathit{H}_3)_3]_2$	46 ± 5	21 ± 3	45 ± 5	35 ± 14	2.9 ± 0.1	49 ± 4	20 ± 2	48 ± 4	30 ± 9	3.0	1
3 $L_2Pt[CH_2C(CH_3)_2CH_2C\mathit{H}_3]_2$	38 ± 3	20 ± 2	37 ± 3	30 ± 9	3.0 ± 0.3	42 ± 2	20 ± 1	41 ± 2	30 ± 5	3.2 ± 0.1	9500
5[e] $L_2Pt[CH_2C(CH_3)_2CH_2C\mathit{H}_2CH_3]_2$	40 ± 3	19 ± 3	39 ± 3	26 ± 14	4.1 ± 0.4[f]	43 ± 2	20 ± 2	42 ± 2	30 ± 9	2.8 ± 0.2	50
7 $L_2Pt[CH_2C(CH_3)_2CH_2C(CH_3)_3]_2$											8000
9 $L_2Pt[CH_2CH_2C(CH_3)_3]_2$											1200
13[g] $L_2Pt[C\mathit{H}_2C\mathit{H}_3]_2$	29 ± 2	14 ± 1	28 ± 2	3 ± 5	1.0 ± 0.3	46 ± 3	22 ± 2	45 ± 3	35 ± 5	3.3 ± 0.5	1600

[a] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for cyclometalations of 1, 3, 5, and 13 are reported for reactions at 157, 126, 146, and 118 °C, respectively. E_a and $\Delta H^{\ddagger}$ are expressed in kcal mol^{-1}, $\Delta S^{\ddagger}$ in eu. Isotope effects are those observed for the deuterium substitution indicated. Positions deuterated in obtaining isotope effects are indicated in italics. [b] For 1, 3, 5, and 13 [L] = 0.022, 0.019, 0.019, and 0.30 M, respectively. [c] Relative rates for thermolyses of 1 and 5 at 87 °C were extrapolated from Arrhenius plots, and all are for decompositions run in the absence of added phosphine. [d] Data obtained from ref 8. [e] Data calcualted for the conversion of 5 to 6a. [f] Measurement of k_H/k_D for 5 in the absence of added phosphine was difficult due to a rapid increase in the rate of decomposition after 1-2 half-lives. This rate increase was not observed in the presence of added phosphine. [g] Data obtained from ref 15.

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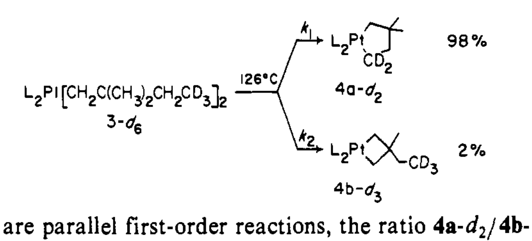
(19) Platinum metallacycles are more stable toward β-hydride elimination reactions than acylic analogues by a factor of 10^4: McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528. Young, G. B.; Whitesides, G. M *Ibid.* **1978**, *100*, 5808–5815.

(20) If either **6a** or **6c** is thermally decomposed under more arduous conditions (146 °C, 40 h), **6a**, **6b**, **6c** and (ethylene)bis(triethylphosphine)platinum(0) are observed in the resulting heterogeneous reaction mixtures by ^{31}P NMR spectroscopy: the mechanism of the decomposition has not been determined.

(eq 2). With the assumption that the formation of **4a**-d_2 and **4b**-d_3 are parallel first-order reactions, the ratio **4a**-d_2/**4b**-d_3 is equal to k_1/k_2. The difference in the free energies of activation, $\Delta\Delta G^\ddagger$, for the formation of **4a**-d_2 and **4b**-d_3 is then calculated to be 3 kcal mol^{-1} at 126 °C (Figure 6).[21] This value of $\Delta\Delta G^\ddagger$ neglects the effect of the deuterium isotope effect on the rate of formation of **4a**-d_2 relative to **4**. The isotope effect $k_H/k_D \simeq 3.0$ corresponds to a difference of 0.9 kcal mol^{-1} at 126 °C in the free energies of activation for formation of **4** and **4a**-d_2.[22] The free energy of activation for the formation of platinacyclobutane **4b**-d_3 is therefore approximately 4 kcal mol^{-1} greater than for the formation of platinacyclopentane **4**. Finally, statistical correction for the presence of two neopentyl methyl groups and one terminal methyl group suggests that $\Delta\Delta G^\ddagger$ for reactions leading to the four- and five-membered metallacycles is approximately 4.6 kcal mol^{-1}. We suggest that this value is also an approximate measure of the difference in strain energies between these two rings.



(2)

We make the tacit assumptions in reaching this estimate that steric effects between the two metallacyclic rings and other groups present in the transition states are equal and that at these transition states the reactions have progressed to the same extent along the reaction coordinate leading to expulsion of the alkyl group by reductive elimination. Moreover, "ring strain" in this context is intrinsically an imprecise concept, since it includes (in principle) contributions to energy arising from parts of the molecule not directly related to the rings (for example, the $(Et_3P)_2Pt$ moieties). In addition, a contribution to $\Delta\Delta G^\ddagger$ due to differences in $\Delta\Delta S^\ddagger$ for the formation of four- and five-membered metallacycles is possible, but we have no way of estimating the magnitudes of such differences. Nonetheless, it is evident that the difference in the intrinsic strain energy in four- and five-membered platinacycloalkanes is much smaller than the corresponding difference between cycloalkanes ($\Delta\Delta G^\circ \approx 20$ kcal/mol[23]). Ambiguities in the interpretation of the metallacyclic strain notwithstanding, this qualitative difference is useful in rationalizing the apparently common occurrence of metallacyclobutanes as intermediates in organometallic reactions.[24]

The decomposition of **5** to five-, four- and six-membered platinacycloalkanes (**6a**, **6b**, and **6c**, respectively) provides further evidence that the differences between the free energies of activation for the formation of platinacycles of different sizes must be small. The decomposition of **5** affords a substantial amount of platinacycles **6b** and **6c**, in contrast to the decomposition of **3**, which affords platinacyclopentane **4** exclusively.[25] Platinacyclopentane **6a** has a methyl substituent on an α-methylene group of the platinacycle. This substitution introduces unfavorable interactions (whether steric or electronic is unknown) in the transition state leading to the platinacyclopentane and permits the processes leading to **6b** and **6c** to become competitive with platinacyclopentane formation.[26] Deuterium substitution of the δ-position of the alkyl groups of **5** (**5**-d_4) results in a decrease in the yield of platinacyclopentane **6a**-*d* with a concomitant increase in the yields of both **6b**-d_2 and **6c**-d_2 (Table I). The yields of platinacyclobutane and platinacyclohexane increase by roughly a factor of 2 as a result of the kinetic deuterium isotope effect, $k_H/k_D \approx$ 3–4 ($\Delta\Delta G^\ddagger \simeq 1$ kcal mol^{-1}), observed for the formation of platinacyclopentane. Collecting these terms and again including statistical corrections, we estimate that $\Delta G^\ddagger_{5\to 6b} - \Delta G^\ddagger_{5\to 6c} = -0.24$ kcal mol^{-1} and $\Delta G^\ddagger_{5\to 6a} = 1.8$ kcal mol^{-1}.[27]

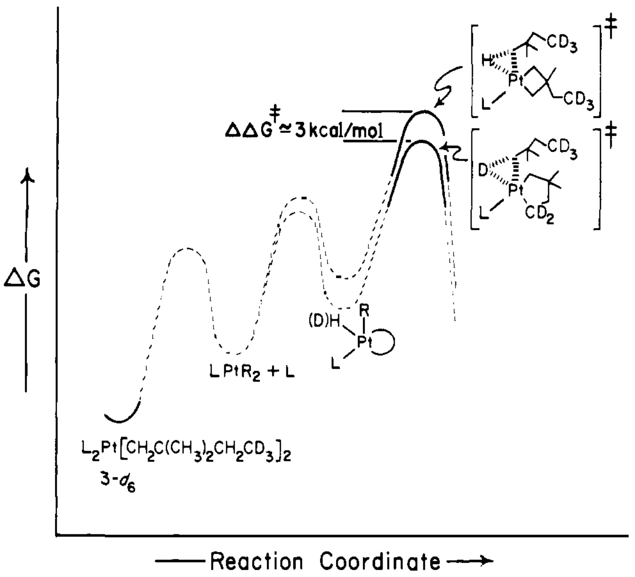


Figure 6. Gibbs free energy–reaction coordinate diagram illustrating the difference in the free energies of activation for the formation of **4a**-d_2 and **4b**-d_3 calculated from their relative rates of production from **3**-d_6 at 126 °C.

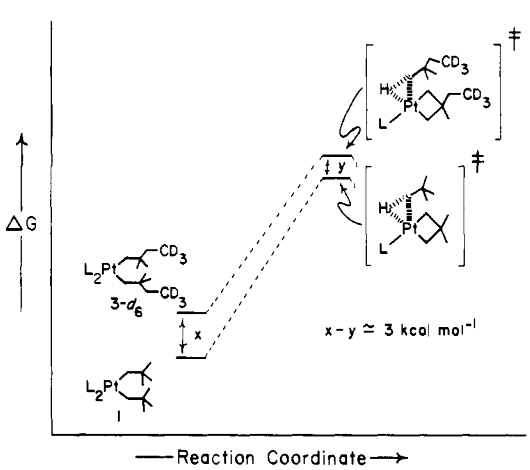


Figure 7. Gibbs free energy–reaction coordinate diagram depicting the relative ground- and transition-state energies for the reactions **1** → **2** and **3**-d_6 → **4b**-d_3 at 126 °C.

In all of these discussions, we have neglected contributions from effects not included in the category of "ring strain", because we have no way of estimating the details of these effects. In one

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[21] $\Delta\Delta G^\ddagger = RT \ln (k_1/k_2)$; see: Bunnett, J. F. In "Investigation of Rates and Mechanisms of Reactions", Part 1, 3rd ed.; Lewis E. S., Ed.; Wiley-Interscience: New York, 1974, p 468.

[22] $\Delta\Delta G^\ddagger$ at 126 °C was calculated by using a k_H/k_D measured at 87 °C; we assume that k_H/k_D does not change appreciably over this range of temperatures.

[23] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 273.

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[25] Within detectable limits by ^{31}P NMR spectroscopy (1–2%).

[26] A similar effect has been observed in formation of α-methylphosphairidicycles. Treatment of $[(COT)_2IrCl]_2$ with $(t\text{-Bu})_2P(n\text{-Pr})$ in the presence of γ-picoline (pic) afforded $[(t\text{-Bu})_2\overline{PCH_2CH_2CH_2Ir}(H)Cl\{(t\text{-Bu})_2P(n\text{-Pr})\}(pic)]$ (55%) and $[(t\text{-Bu})(n\text{-Pr})\overline{PC(CH_3)_2CH_2Ir}(H)Cl\{(t\text{-Bu})_2P(n\text{-Pr})\}(pic)]$ (20%). Similar treatment of $[(COT)_2IrCl]_2$ with $(t\text{-Bu})_2P(n\text{-Bu})$ gave $[(t\text{-Bu})(n\text{-Bu})\overline{PC(CH_3)_2CH_2Ir}(H)Cl\{(t\text{-Bu})_2P(n\text{-Bu})\}(pic)]$ (20%) and only a trace of $(t\text{-Bu})_2\overline{PCH_2CH_2(CH_3)CHIr}(H)Cl\{(t\text{-Bu})_2P(n\text{-Bu})\}(pic)]$. The decrease in the yield of phospharidacyclopentane in the latter reaction is ascribed to increased steric interactions about the central metal atom due to the α-methyl substituent. Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1977**, *139*, 189–198.

[27] At 125 °C, $\Delta G^\ddagger_{5\to 6a} = 29$ kcal mol^{-1}, $\Delta G^\ddagger_{5\to 6b} = 31$ kcal mol^{-1}, and $\Delta G^\ddagger_{5\to 6c} = 31$ kcal mol^{-1}.

instance we can, however, estimate their aggregate magnitude. Decomposition of **1** yields platinacyclobutane **2**; decomposition of **3**-d_6 yields platinacyclobutane **4b**-d_3. At 126 °C, the relative rates of these reactions are approximately 1:20.[28] Thus, for the ground and transition states summarized in Figure 7, $x - y \approx 3$ kcal/mol. The importance of this estimate is that two similar processes which form two similar platinacyclobutanes differ in $\Delta\Delta G^{\ddagger}$ by ~3 kcal/mol. This value is not far from that estimated for the difference in ring strain between platinacyclobutane and platinacyclopentane rings. Thus, the *uncertainties* in the estimate of the strains reflecting the small difference in the systems not considered when calculating the strains is probably similar to the estimates of the strains themselves. The *qualitative* conclusion that ring strain in a platinacyclobutane is small is very probably correct. The numerical estimate of this strain derived from this work is not highly accurate. The observed yields reinforce the qualitative character of these estimates. Within the limited range of compounds that have been examined, production of five-membered rings seems to be more facile than that of either four- or six-membered rings. Complex **3** decomposes to yield only platinacyclopentane **4**, and **5** yields three platinacycles of which the major product is a 2-methylplatinacyclopentane (**6a**). The question of whether four- or six-membered platinacycle formation occurs more readily can only be answered by considering each reaction individually. Complex **5** affords more platinacyclobutane (23%) than platinacyclohexane (9%), while the thermal decomposition of **7** yields only platinacyclohexane **8** and none of the corresponding platinacyclobutane. The rate of formation of platinacyclohexane **8** from **7** is approximately a factor of 10 greater than for the formation of **6c** from **5**. This observation is consistent with the "*gem*-dimethyl effect",[29] which predicts that the formation of the more highly substituted platinacycle, by analogy with carbocyclic systems, should be favored with respect to that of a less substituted one.

Puddephatt has estimated that the ring strain in the platinacyclobutane moiety of platinum(IV) complexes (e.g., $PtCl_2(C_3H_6)(bpy)$) is ~12 kcal/mol by comparisons of heats of decomposition measured by using differential scanning calorimetry.[24] It is difficult to judge the accuracy of this estimate, but even assuming it is correct, it is not necessarily incompatible with our smaller estimate since the degree of steric crowding around the platinum(II) and platinum(IV) complexes is quite different.

Experimental Section

General Remarks. All reactions involving organometallic compounds were carried out under argon or prepurified dinitrogen by using standard anaerobic techniques.[30] Diethyl ether and tetrahydrofuran were distilled from disodium benzophenone dianion under argon. Olefins were removed from pentanes, hexane, cyclohexane, and decane by stirring over concentrated sulfuric acid for 48 h, washing with saturated sodium bicarbonate solution, washing with water, drying with phosphorus pentoxide, and distilling under argon. HMPA was distilled from calcium hydride at reduced pressure. Cyclohexane-d_{12} (Stohler) was distilled from phosphorus pentoxide under argon. DCl (38% in D_2O, 99% D, Stohler) was used as received. All other compounds were reagent grade and were used without further purification unless otherwise noted. Boiling points are uncorrected. Melting points were determined in open capillary tubes on a Thomas Hoover Apparatus and are uncorrected. Proton-decoupled ^{31}P NMR spectra were recorded at 36.4, 36.2, and 101.3 MHz on Bruker HFX-90, Jeol FX-90Q, and Bruker WP-250 spectrometers, respectively. Spectra are reported at 101.3 MHz unless otherwise noted, and chemical shifts, in parts per million, are reported relative to external 85% phosphoric acid (downfield shifts positive). ^1H NMR spectra were recorded at 60 and 250 MHz on Varian T-60 and Bruker WP-250 spectrometers, respectively. ^1H NMR spectra are reported at 250 MHz, unless otherwise specified, and 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. Yields of Grignard and lithium reagents were determined by using the procedure of Eastham.[31] Organoplatinum compounds were stored in tightly sealed vials in the dark at −15 °C and were recrystallized immediately before performing thermolyses. Thermal decompositions were performed in constant temperature baths according to previously described procedures.[8] Bis(triethylphosphine)platinum(II) dichloride,[32] dichloro(1,5-cyclooctadiene)platinum(II) ($(COD)PtCl_2$),[19] 2-methyl-*N*-(2-methylpropylidene)-2-propanamine,[33] 1-bromoethane-*2,2,2-d$_3$*,[34] and 1-bromopropane-*2,2-d$_2$*[35] were prepared according to literature procedures.

2,2-Dimethyl-1-pentanol. Treatment of the lithium salt of 2-methyl-*N*-(2-methylpropylidene)-2-propanamine with 1-bromopropane in ether and hydrolysis of the resulting imine[33] afforded 2,2-dimethylpentanal, which was reduced directly to the alcohol with $LiAlH_4$ in ethyl ether in 76% yield; bp 155–156 °C (lit.[36] bp 155.6–157.6 °C). 2,2-Dimethyl-1-pentyl *p*-toluenesulfonate was prepared in 86% yield from the alcohol upon treatment with *p*-toluenesulfonyl chloride in pyridine.[37] 1-Bromo-2,2-dimethylpentane was obtained in 75% yield by reaction of the 2,2-dimethyl-1-pentyl tosylate with lithium bromide in HMPA:[38] bp 153–156 °C; ^1H NMR (C_6D_6) δ 0.88–0.99 (5 H, m, CH_3CH_2), 0.99 (6 H, s, $C(CH_3)_2$), 1.29 (2 H, m, $CH_2C(CH_3)_2$), 3.28 (2 H, s, CH_2Br).

Bis(2,2-dimethyl-*n*-pentyl)bis(triethylphosphine)platinum(II) (5). In a flame-dried, argon-filled 500-mL round-bottomed flask equipped with magnetic stirring bar, reflux condenser, and addition funnel was placed 3.9 g (0.16 mmol) of magnesium turnings and 200 mL of dry THF. A solution of 26 g (0.15 mol) of 1-bromo-2,2-dimethylpentane in 60 mL of THF was added dropwise with stirring at reflux. The mixture was heated at reflux for 3 h after the addition was complete. The resulting Grignard reagent (ca. 0.075 mol) was added dropwise to a stirred suspension of 9.2 g (0.025 mol) of dichloro(1,5-cyclooctadiene)platinum(II) in 300 mL of ether at −78 °C. The mixture was allowed to warm slowly to 25 °C and filtered. The filtrate was washed with three 500-mL portions of water, and the combined aqueous washings were extracted with 250 mL of ether. The combined organic extracts were dried over $MgSO_4$, stirred with 2 g of carbon black, and filtered, and the solvent was removed by rotary evaporation at reduced pressure. The remaining dark brown oil was redissolved in 500 mL of dry ether to which was added, by syringe, 5.8 g (0.049 mol) of triethylphosphine. After being stirred for 3 h at 25 °C, the solution was filtered through a 6.0 × 0.5-cm column of activated alumina (Alcoa Type F-20) and the solvent removed by using a rotary evaporator to yield a light brown oil. The oil was dissolved in 30 mL of acetone and transferred to a 40-mL centrifuge tube which was capped with a rubber septum. After the solution was cooled to −78 °C, the volume of the solution was reduced to ca. 25 mL by rapidly flowing argon over the top of the solution as a white emulsion formed. After the emulsion was allowed to settle to the bottom of the solution, the yellow supernatant was removed via cannula and the volume of the solution returned to 30 mL with fresh acetone. This procedure was repeated three more times, at which point the product precipitated as a white, crystalline solid. The solution was filtered at −78 °C and remaining solvent removed under vacuum (0.01 torr) to yield 5.1 g (33% yield from $(COD)PtCl_2$) of **5**: mp 46.0–47.5 °C; $^{31}P\{^1H\}$ NMR (C_6H_{12}) δ −1.4 (t, J_{Pt-P} = 1616 Hz); ^1H NMR (C_6D_6) δ 0.91 (18 H, d of t, J = 8 Hz, J_{P-H} = 15 Hz, CH_2CH_2P), 1.08 (6 H, m, $-CH_2CH_2CH_3$), 1.35 (12 H, br s, $C(CH_3)_2$), 1.56–1.64 (20 H, m, CH_2P and $CH_2CH_2CH_3$), 2.00 (4 H, m, J_{Pt-H} = 73 Hz, Pt–CH_2); IR (KBr) 2980–2800 (vs), 1470–1440 (m), 1420 (m), 1350 (m), 760 (s), 710 (s), 620 (m) cm^{-1}. Anal. ($C_{26}H_{60}P_2Pt$): C, H.

Bis(2,2-dimethyl-*n*-pentyl-*4,4-d$_2$*)bis(triethylphosphine)platinum(II) (5-*d$_4$*) was prepared in 24% yield (from $(COD)PtCl_2$) by a procedure analogous to that described for **5**, substituting $CH_3CD_2CH_2Br$ for 1-bromopropane (Scheme II): mp 45.5–46.5 °C; $^{31}P\{^1H\}$ NMR (C_6H_{12}) δ −1.5 (t, J_{Pt-P} = 1614 Hz); ^1H NMR (C_6D_6) δ 0.91 (18 H, d of t, J =

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(28) The rate constant at 126 °C for the formation of **2** was extrapolated from the Arrhenius plot for decomposition of **1** and the rate of formation of **4b-d$_3$** from **3**-d_6 calculated from the Arrhenius plot for **3**, using $k_H/k_D = 3$ and $k_{4b\text{-}d_3}/k_{4a\text{-}d_2} = 2/98$.

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8 Hz, $J_{\mathrm{P-H}}$ = 14 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 1.07 (6 H, s, $\mathrm{C}\mathit{H}_3\mathrm{CD_2CH_2}$–), 1.37 (12 H, s, $\mathrm{C(CH_3)_2}$), 1.55–1.66 (16 H, m, $\mathrm{CH_2P}$ and $\mathrm{CH_3CD_2C}\mathit{H}_2$), 2.01 (4 H, m, $J_{\mathrm{Pt-H}}$ = 72 Hz, $\mathrm{PtCH_2}$); IR (KBr) 2990–2790 (vs), 2200–2180 (w), 2120–2100 (w), 1470 (m), 1370 (m), 1350 (m), 760 (s), 710 (s), 620 (m) cm^{-1}. Anal. ($\mathrm{C_{26}H_{56}D_4P_2Pt}$): C, P.

Bis(2,2-dimethyl-*n*-butyl)bis(triethylphosphine)platinum(II) (3) was prepared in 52% yield (from $\mathrm{(COD)PtCl_2}$) by a procedure analogous to that described for **5**, substituting 1-bromoethane for 1-bromopropane: mp 86.0–88.0 °C; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6H_{12}}$) δ −1.5 (t, $J_{\mathrm{Pt-P}}$ = 1615 Hz); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.88 (18 H, d of t, J = 8 Hz, $J_{\mathrm{P-H}}$ = 14 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 1.21 (6 H, t, J = 8 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2C(CH_3)_2}$), 1.36 (12 H, s, $\mathrm{C(CH_3)_2}$), 1.54–1.65 (12 H, m, $\mathrm{CH_2P}$), 1.74 (4 H, m, $\mathrm{CH_3C}\mathit{H}_2\mathrm{C(CH_3)_2}$), 2.00 (4 H, m, $J_{\mathrm{Pt-H}}$ = 73 Hz, $\mathrm{PtCH_2}$); IR (KBr) 2990–2880 (vs), 1460 (s), 1435 (m), 1372 (m), 1355 (m), 1265 w, 1136 m, 1035 (s), 996 (m), 759 (vs), 715 (s), 620 m cm^{-1}. Anal. ($\mathrm{C_{24}H_{56}P_2Pt}$): C, H.

Bis(2,2-dimethyl-*n*-butyl-*4,4,4-d*$_3$)bis(triethylphosphine)platinum(II) (**3**-d_6) was prepared in 32% yield (from $\mathrm{(COD)PtCl_2}$) by a procedure analogous to that described for **5**, substituting $\mathrm{CD_3CH_2Br}$ for 1-bromopropane: mp 86.0–87.5 °C; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6H_{12}}$) δ −1.5 (t, $J_{\mathrm{Pt-P}}$ = 1615 Hz); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.88 (18 H, d of t, J = 8 Hz, $J_{\mathrm{P-H}}$ = 14 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 1.36 (12 H, s, $\mathrm{C(CH_3)_2}$), 1.54–1.65 (12 H, m, $\mathrm{CH_2P}$), 1.74 (4 H, br s, $\mathrm{CD_3C}\mathit{H}_2$), 2.00 (4 H, m, $J_{\mathrm{Pt-H}}$ = 73 Hz, $\mathrm{PtCH_2}$); IR (KBr) 2960–2720 (vs), 2200 (m), 2120 (w), 2080 (w), 1480–1450 (m), 1370 (m), 1350 (m), 750 (s), 710 (s), 620 (m) cm^{-1}. Anal. ($\mathrm{C_{24}H_{50}D_6P_2Pt}$): C, P.

2,2,4,4-Tetramethyl-1-pentanol was prepared by refluxing a mixture of 47 g (0.30 mol) of 2,2,4,4-tetramethylpentanoic acid[39] and 400 mL of 1 M $\mathrm{BH_3{\cdot}THF}$ (Aldrich) for 3 h, then carefully quenching the resulting mixture with 300 mL of water, and stirring for 2 h. The organic phase was separated, the aqueous phase was extracted with pentane, and the combined organic fractions were dried over magnesium sulfate. Pentane and THF were removed by distillation, and the residue was fractionally distilled to yield 38 g (87%) of the alcohol: bp 88–91 °C (23 torr); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.98 (6 H, s, $\mathrm{C(C}\mathit{H}_3\mathrm{)_2CH_2OH}$), 1.02 (9 H, s, $\mathrm{(CH_3)_3C}$), 1.24 (2 H, s, $\mathrm{(CH_3)_3CC}\mathit{H}_2$), 3.30 (2 H, s, $-\mathrm{C}\mathit{H}_2\mathrm{OH}$); IR (neat) 3600–3100 (vs), 3050–2750 (vs), 1480 (s), 1390 (m), 1370 (s), 1250 (m), 1040 (m) cm^{-1}.

Bis(2,2,4,4-tetramethyl-*n*-pentyl)bis(triethylphosphine)platinum(II) (7) was prepared from 2,2,4,4-tetramethyl-1-pentanol by a procedure analogous to the preparation of **5** from 2,2-dimethyl-1-pentanol. Complex **7** was obtained in 25% yield from $\mathrm{(COD)PtCl_2}$ as a viscous, brown oil which could not be induced to crystallize. The oil was purified by repeated cooling of a solution of the oil in acetone to −78 °C, centrifugation at −78 °C, and removal of the supernatant. This procedure was repeated until the supernatant was colorless. The residual solvent was removed under vacuum as the white solid was allowed to warm to room temperature; at ca −20 °C the solid melted to a pale yellow oil: $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6H_{12}}$) δ −1.6 (t, $J_{\mathrm{Pt-P}}$ = 1607 Hz); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.85–1.00 (18 H, m, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 1.00 (18 H, s, $\mathrm{C(CH_3)_3}$), 1.1 (12 H, s, $\mathrm{C(CH_3)_2}$), 1.40–2.20 (20 H, m, $\mathrm{CH_2P}$, $\mathrm{C}\mathit{H}_2$, $\mathrm{PtCH_2}$); IR (neat) 2960–2890 (s), 1468 (m), 1395 (w), 1378 (m), 1367 (m), 1250 (w), 1240 (w), 1135 (w), 1040 (m), 770 (m), 713 (m) cm^{-1}. Anal. ($\mathrm{C_{30}H_{68}P_2Pt}$): C, H.

Bis(3,3-dimethyl-*n*-butyl)bis(triethylphosphine)platinum(II) (9) was prepared from 3,3-dimethyl-1-butanol (Aldrich) by a procedure analogous to the preparation of **5** from 2,2-dimethyl-1-pentanol. Complex **9** was obtained as colorless needles by crystallization from ether/acetonitrile in 23% yield (from $\mathrm{(COD)PtCl_2}$): mp 70.5–71.1 °C; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6H_{12}}$) δ 8.9 (t, $J_{\mathrm{Pt-P}}$ = 1726 Hz); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.90 (18 H, d of t, J = 8 Hz, $J_{\mathrm{P-H}}$ = 15 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 1.22 (18 H, s, $\mathrm{C(CH_3)_3}$), 1.29–1.74 (20 H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2}$, $\mathrm{CH_2P}$); IR (KBr) 2950–2790 (s), 1479 (m), 1462 (m), 1390 (m), 1242 (m), 1038 (s), 1025 (m), 768 (s), 718 (m) cm^{-1}. Anal. ($\mathrm{C_{24}H_{56}P_2Pt}$): C, H.

1,5-Dichloro-2,2-dimethylpentane was prepared in 57% yield by the reaction of 2,2-dimethyl-1,5-pentyl di-*p*-toluenesulfonate[40] with lithium chloride in HMPA:[37] bp 104–107 °C (54 torr); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.99 (6 H, s, $\mathrm{(CH_3)_2C}$), 1.41–1.48 (2 H, m, $\mathrm{CH_2}$), 1.69–1.78 (2 H, m, $\mathrm{CH_2}$), 3.34 (2 H, t, J = 6.7 Hz, $\mathrm{CH_2C}\mathit{H}_2\mathrm{Cl}$), 3.35 (2 H, s, $\mathrm{C(CH_3)_2C}\mathit{H}_2\mathrm{Cl}$); IR (neat) 3050–2890 (s), 2880 (m), 1740 (w), 1550 (s), 1480 (s), 1440 (s), 1340 (m), 1290 (s), 775 (s), 730 (s), 630 (m) cm^{-1}. Anal. ($\mathrm{C_7H_{14}Cl_2}$): C, H.

Bis(triethylphosphine)-3,3-dimethylplatinacyclohexane (6c) was prepared by first treating 1,5-dichloro-2,2-dimethylpentane with magnesium metal[41] in THF and then reacting 1.5 equiv of the resulting Grignard reagent first with $\mathrm{(COD)PtCl_2}$ and then with triethylphosphine as previously described for **5**: mp 49.5–51.3 °C; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6H_{12}}$) δ 10.4 (d of t, $J_{\mathrm{Pt-P}}$ = 1714 Hz $J_{\mathrm{P-P}}$ = 8 Hz), 12.8 (d of t, $J_{\mathrm{Pt-P}}$ = 1734 Hz, $J_{\mathrm{P-P}}$ = 8 Hz); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.88 (18 H, m, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 1.40 (6 H, t, J = 6.8 Hz, $\mathrm{C(CH_3)_2}$), 1.39–1.82 (16 H, m, $\mathrm{PtC}\mathit{H}_2\mathrm{C(CH_3)_2C}\mathit{H}_2$, and a δ 1.51, $\mathrm{CH_2P}$), 2.02 (2 H, m, $\mathrm{(CH_3)_2CC}\mathit{H}_2$), 2.28 (2 H, m, $J_{\mathrm{Pt-H}}$ = 75 Hz, $\mathrm{PtC}\mathit{H}_2\mathrm{CH_2}$); IR (KBr) 2970–2875 (vs), 1462 (m), 1455 (m), 1430 (m), 1375 (m), 1352 (w), 1338 (w), 1250 (w), 1037 (s), 1029 (s), 770 (vs), 705 (s), 630 (m) cm^{-1}. Anal. ($\mathrm{C_{19}H_{44}P_2Pt}$): C, H.

5-Chloro-4,4-dimethyl-1-pentene. Claisen rearrangement of the allyl enol ether of the isobutyraldehyde gave 2,2-dimethyl-3-pentenal in 59% yield.[42] Sodium borohydride reduction of this aldehyde afforded 4,4-dimethyl-1-penten-5-ol in 78% yield.[43] Treatment of this alcohol with tosyl chloride afforded the tosylate, in 98% yield, as a viscous oil. Reaction of 113 g (0.42 mol) of the tosylate with 29 g (0.69 mole of lithium chloride in HMPA[38] yielded 49 g (88%) of 5-chloro-4,4-dimethyl-1-pentene: bp 74–75 °C (104 torr); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.98 (6 H, s, $\mathrm{C(CH_3)_2}$), 2.08 (2 H, br d, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$), 3.34 (2 H, s, $\mathrm{CH_2Cl}$), 5.04–5.11 (2 H, m, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH}$), 5.78 (1 H, m, $\mathrm{CH_2{=}C}\mathit{H}$); IR (neat) 3065 (m), 2960 (br s), 1875 (w), 1638 (m), 1468 (s), 1432 (m), 1382 (m), 1365 (m), 998 (m), 918 (s), 780 (m), 732 s). Anal. ($\mathrm{C_7H_{13}Cl}$): C, H.

1,4-Dichloro-2,2-dimethylpentane. To 100 mL of glacial acetic acid was added 20 g (0.15 mol) of 5-chloro-4,4-dimethyl-1-pentene. To the resulting solution was added 1 mL of $\mathrm{SnCl_4}$. The resulting solution was heated at 65–70 °C for 48 h as gaseous HCl was bubbled into the mixture. The reaction mixture was decanted into water and extracted with pentane. The combined organic extracts were washed with water and saturated aqueous $\mathrm{NaHCO_3}$ and dried over sodium sulfate. The solvent was removed by distillation at atmospheric pressure and the residue distilled in vacuo to give 17.6 g (69%) of the chloride: bp 96–98 °C (37 torr); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.08 (3 H, s, $\mathrm{CH_3}$), 1.09 (3 H, s, $\mathrm{CH_3}$), 1.55 (3 H, d, J = 6.7 Hz, $\mathrm{CH_3}$), 1.79 (1 H, J_{AB} = 15.2 Hz, ^3J = 3.3 Hz, $\mathrm{(CH_3)_2CC}\mathit{H}_\mathrm{A}\mathrm{H_B}$), 1.91 (1 H, J_{AB} = 15.2 Hz, J = 9.0 Hz, $\mathrm{(CH_3)_2CCH_A}\mathit{H}_\mathrm{B}$), 3.45 (2 H, s, $\mathrm{CH_2Cl}$), 4.12 (1 H, s, CHCl); IR (neat) 2960 (br s), 1730 (s), 1466 (br s), 1368 (s), 1240 (s), 1122 (m), 1044 (m), 1018 (m), 768 (m), 728 (m), 624 (m) cm^{-1}. Anal. ($\mathrm{C_7H_{14}Cl_2}$): C, H.

Bis(triethylphosphine)-2,4,4-trimethylplatinacyclopentane (6a). 1,4-Dichloro-2,2-dimethylpentane (1.2 g, 7.1 mmol) was reacted with 0.60 g (0.086 mol) of lithium metal (Alfa) in 30 mL of dry, deolefinated hexane for 12 h at 25 °C. The resulting lithium reagent was filtered and allowed to react with 1.2 g (2.3 mmol) of bis(triethylphosphine)platinum(II) dichloride in hexane for 7 h at 0 °C. The resulting mixture was quenched with 0.1 mL of water and filtered through a 2.0 × 0.5-cm column of activated alumina (Alcoa Type F-20) and the solvent removed by rotary evaporation to yield 200 mg of a yellow oil. The oil was purified by preparative layer chromatography on a 1000-μm alumina preparative TLC plate (Analtech) using pentane as eluant to yield 32 mg (2%) of **6a** as a pale yellow oil: $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6H_{12}}$) δ 9.5 (d of t, $J_{\mathrm{Pt-P}}$ = 1890 Hz, $J_{\mathrm{P-P}}$ = 9 Hz), 10.8 (d of t, $J_{\mathrm{Pt-P}}$ = 1527, $J_{\mathrm{P-P}}$ = 9 Hz); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.87 (9 H, d of t, J = 8 Hz, $J_{\mathrm{P-H}}$ = 15 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 0.90 (9 H, d of t, J = 8 Hz, $J_{\mathrm{P-H}}$ = 15 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 1.41–1.69 (21 H, m, $\mathrm{CH_2P}$, $\mathrm{C(CH_3)_2}$, $\mathrm{PtCH(C}\mathit{H}_3\mathrm{)}$), 1.75–2.10 (4 H, m, $\mathrm{PtC}\mathit{H}_2\mathrm{C(CH_3)_2C}\mathit{H}_2$–), 2.34 (1 H, m, $J_{\mathrm{Pt-H}}$ = 81 Hz, $\mathrm{Pt(C}\mathit{H}\mathrm{(CH_3))}$).

Isolation of Bis(triethylphosphine)-3,3-dimethylplatinacyclopentane (4). A thermal decomposition tube constructed from medium-wall, 1.3-cm o.d. Pyrex tubing (15 cm from sealed end to constriction, ca. 12-mL volume) was charged with **3** (0.23 g, 0.38 mmol) and purged with nitrogen. Cyclohexane (6 mL) was added, the contents of the tube were degassed by three freeze–pump–thaw cycles at 0.01 torr, and the tube was sealed under vacuum. The solution was heated at 87 °C for 3 h. The resultant pale yellow-brown solution was treated with activated charcoal, filtered, and concentrated to an oil by rotary evaporation at reduced pressure. The oil was dissolved in diethyl ether (4 mL), and methanol (2.5 mL) was added. The volume of the solution was reduced by rapidly flowing nitrogen over the solution at 0 °C as granular, white crystals were precipitated. The product was collected by suction filtration, washed with cold (0 °C) methanol, and dried in vacuo to yield 0.16 g (78%) of **4**: mp 67.0–68.5 °C; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6H_{12}}$) δ 11.1 (t, $J_{\mathrm{Pt-P}}$ = 1775 Hz, $J_{\mathrm{P-P}}$ = 11 Hz), 13.5 (t, $J_{\mathrm{Pt-P}}$ = 1761 Hz, $J_{\mathrm{P-P}}$ = 11 Hz); ^{1}H NMR ($\mathrm{C_6D_6}$) 0.87 (9 H, d of t, J = 8 Hz, $J_{\mathrm{P-H}}$ = 15 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 0.88 (9 H, d of t, J = 8 Hz, $J_{\mathrm{P-H}}$ = 15 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2P}$), 1.44–1.56 (18 H, m with s at 1.56 ppm, $\mathrm{C(CH_3)_2}$, $\mathrm{CH_2P}$), 1.96 (2 H, m, $J_{\mathrm{Pt-H}}$ = 60.0 Hz, $\mathrm{PtC}\mathit{H}_2\mathrm{C(CH_3)_2}$); 2.06 (2 H, m, $\mathrm{PtC}\mathit{H}_2\mathrm{CH_2}$, absent in **4**-$d_2$), 2.21 (2 H, m, $J_{\mathrm{Pt-H}}$ = 70.5 Hz, $\mathrm{PtCH_2C}\mathit{H}_2$); IR (KBr) 2962 (s), 2940 (s), 2880 (s), 1462 (m), 1451 (m), 1430 (m), 1412 (m), 1375 (m), 1352 (m), 1240 (m), 1041 (m), 772

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(vs), 717 (vs), 672 cm^{-1}. Anal. ($C_{18}H_{42}P_2Pt$): C, H.

Isolation of Bis(triethylphosphine)-3,3,5,5-tetramethylplatinacyclohexane (8). A solution of **7** (0.44 g, 0.64 mmol) in cyclohexane (10 mL) was degassed and sealed under vacuum (0.01 torr) in a 20-mL thermal decomposition tube and the solution heated at 87 °C for 4 h. The resulting pale yellow solution was filtered through a 2.0-cm column of charcoal/silica-gel and the column washed with 50 mL of ether. The resulting solution was reduced to a yellow wax by rotary evaporation at reduced pressure followed by evacuation (0.01 torr). The product was recrystallized by slowly cooling a solution of the wax (0.25 g) in ether (2 mL) and methanol (5 mL) to −78 °C for 12 h and then drying in vacuo to yield 0.24 g (68%) of **8**: mp 91.0–94.5 °C; $^{31}P\{^1H\}$ NMR (C_6H_{12}) δ 9.7 (t, J_{Pt-P} = 1718 Hz); ^1H NMR (C_6D_6) δ 0.85 (18 H, d of t, J = 8 Hz, J_{P-H} = 15 Hz, CH_3CH_2P), 1.45 (12 H, t, "J" = 6 Hz, $C(CH_3)_2$), 1.55 (12 H, m, CH_2P), 1.67 (4 H, m, J_{Pt-H} = 73 Hz, Pt–CH_2), 1.85 (2 H, s, $CH_2C(CH_3)_2$); IR (KBr) 2970–2880 (s), 1456 (m), 1431 (w), 1380 (w), 1356 (m), 1238 (m), 1042 (s), 1028 (m), 772 (s), 714 (s), 631 (m) cm^{-1}. Anal. ($C_{21}H_{48}P_2Pt$): C, H.

Thermal Decomposition of 5 To Yield 6a, 6b, and 6c. Into a flame-dried, argon-filled 1 × 30-cm medium-wall decomposition tube was weighed 1.4 g (2.2 mmol) of **5**, and the tube was capped with a rubber septum and flushed with argon. Cyclohexane (10 mL) was added, the resulting solution degassed, the tube sealed under vacuum (0.01 torr), and the solution heated for 10 min at 146 °C. After being cooled to 25 °C, the tube was opened and the reaction mixture examined by $^{31}P\{^1H\}$ NMR (C_6H_{12}), which indicated the presence of three products: **6a** (68%), δ 9.5 (d of t, J_{Pt-P} = 1840 Hz, J_{P-P} = 9 Hz), 10.8 (d of t, J_{Pt-P} = 1577 Hz, J_{P-P} = 9 Hz); **6b** (23%), δ 9.6 (t, J_{Pt-P} = 1850 Hz); **6c** (9%), δ 10.4 (d of t, J_{Pt-P} = 1716 Hz, J_{P-P} = 8 Hz), 12.8 (d of t, J_{Pt-P} = 1735 Hz, J_{P-P} = 8 Hz).[44] The reaction mixture was concentrated to a brown oil by rotary evaporation at reduced pressure. Attempts to fractionally crystallize the crude reaction mixture were unsuccessful. Two successive preparative layer chromatographies of a 0.20-g portion of the oil on 1000-μm alumina preparative TLC plates (Analtech) using pentane as eluant gave 35 mg of **6a** (corresponding to an 18% isolated yield from **5**) as a pale yellow oil. The $^{31}P\{^1H\}$ and ^1H NMR spectra of the purified compound were identical with those of the authentic sample of **6a**.

The structure **6b** was verified in the following manner. Into a flame-dried 1.0-mL thermal decomposition tube prepared from 0.25-in. o.d. medium-wall Pyrex tubing was weighed 20 mg (0.032 mmol) of **5**, the tube flushed with argon, decane (0.25 mL) added, and the resulting solution degassed and sealed at 0.01 torr. After the tube was heated at 146 °C for 5 min and cooled to 25 °C, the tube was opened and the solvent removed under vacuum. The remaining oil was dissolved in 0.5 mL of decane and the volume of the resulting solution reduced to 0.20 mL under vacuum. To the tube was then added 2 μL (ca. 6 mg, 0.04 mmol) of bromine[13] and the resulting mixture shaken for 5 min. GC/MS analysis of the reaction mixture using a 10-ft, $^1/_8$-in. 20% SE-30 on Chromosorb P column indicated the presence of 1-methyl-1-*n*-propylcyclopropane (6% yield, identical with GC/MS of an authentic sample[45]): mass spectrum, *m/e* (%) 98 (8, M$^+$), 83 (7), 70 (41), 69 (64), 56 (49), 55 (80), 43 (12), 42 (17), 41 (100), 39 (38), 29 (22). A similar bromine quench of the thermal decomposition mixture from **5**-d_4 yielded 1-methyl-1-(*n*-propyl-*2,2*-d_2)-cyclopropane (10%) from **6b**-d_2: mass spectrum, *m/e* (%) 100 (12, M$^+$), 85 (9), 72 (22), 71 (51), 70 (44), 69 (45), 58 (12), 57 (72), 56 (43), 55 (60), 54 (11), 53 (11), 45 (10), 43 (25), 42 (42), 41 (100), 40 (17), 39 (42).

The presence of **6c** was verirfied by comparison of its $^{31}P\{^1H\}$ NMR spectrum to that of an authentic sample of **6c** prepared as described above.

Reaction of the Thermal Decomposition Products of 3 and 3-d_6 with Bromine. With use of a procedure analogous to that described for the reaction of the thermal decomposition products of **5** with bromine, 40 mg (0.067 mmol) of **3** was dissolved in 0.25 mL of decane and heated at 126 °C for 1.5 h. The solvent was then removed from the reaction mixture under vacuum and the remaining oil dissolved in 0.20 mL of decane. To the tube was then added 3.5 μL (11 mg, 0.066 mmol) of bromine,[13] and the resulting mixture was shaken for 5 min. GC/MS analysis of the resulting mixture using a 20-ft, $^1/_8$-in. 3% UCW-98 on Chromsorb P column indicated the formation of 1-ethyl-1-methylcyclopropane (<1% yield, MS in agreement with that reported[46]): mass spectrum, *m/e* (%) 84 (23, M$^+$), 69 (60), 56 (45), 55 (87), 53 (14), 42 (12), 41 (100), 40 (12), 39 (37), 29 (22), 27 (32). Repeating this procedure for **3**-d_6 produced 1-(ethyl-d_3)-1-methylcyclopropane (<1% yield) from **4b**-d_3: mass spectrum, *m/e* (%) 87 (49, M$^+$), 73 (12), 72 (84), 71 (12), 70 (14), 69 (36), 59 (36), 58 (30), 57 (26), 55 (86), 54 (12), 53 (16), 44 (24), 43 (54), 42 (60), 41 (100), 40 (25), 39 (49).

Thermal Decomposition of 3 in the Presence of Added Triethylphosphine. The thermolyses of four 30-mM solutions of **3** in decane and in the presence of added $(C_2H_5)_3P$ (concentrations 3.8, 6.9, 14, and 32 mM) were performed at 107 °C. Appearance of 2,2-dimethylbutane was followed by GLC on a 10-ft, $^1/_8$-in. 20% SE-30 on Chromosorb P column using cyclopentane as internal standard. The thermolyses were run in a 2.0-mL volumetric flask fitted with a Teflon stopcock; the flask was cooled to 25 °C at predetermined intervals, the stopcock opened under argon, and the solution sampled for analysis by syringe. The observed rate constants, $k^{obsd} = 42, 23, 9.5, \text{ and } 3.8 \times 10^{-5}\ s^{-1}$, respectively, were derived from data that extended through 2 half-lives.

Kinetics of Thermal Decomposition of 3 and 3-d_6 in the Presence and Absence of Added Ligand. Into each of eight flame-dried, argon-filled 5-mm NMR tubes was weighed 24.3 mg (0.0404 mmol) of freshly recrystallized **3**, and the tubes were capped with rubber septum and flushed with argon. To each of the tubes was then added by syringe 0.50 mL of either a 0.16 M solution of triethyl phosphate in cyclohexane or a cyclohexane solution 0.16 M in triethyl phosphate and 0.0185 M in triethylphosphine. The contents of the tubes were immediately degassed three times and the tubes sealed under vacuum (0.01 torr). Duplicate thermolyses at four different temperatures were performed simultaneously, following the decompositions by $^{31}P\{^1H\}$ NMR spectroscopy through at least 2 half-lives.

The observed rate constants (average of two runs) for thermolysis of **3** in the absence of added triethylphosphine at 69, 74, 87, and 94.5 °C were $k^{obsd} = 5.77, 20.2, 98.1, \text{ and } 318 \times 10^{-5}\ s^{-1}$, respectively. The thermolysis of **3**-d_6 in the absence of added triethylphosphine at 87 °C yielded $k^{obsd} = 32.2 \times 10^{-5}\ s^{-1}$.

The observed rate constants (average of two runs) for thermolysis of **3** in the presence of added triethylphosphine at 95.5, 106, 116, and 126.5 °C were $k^{obsd} = 1.92, 10.4, 34.9, \text{ and } 181 \times 10^{-5}\ s^{-1}$, respectively. The thermolysis of **3**-d_6 in the presence of added triethylphosphine at 106 °C yielded $k^{obsd} = 3.27 \times 10^{-5}\ s^{-1}$.

Kinetics of Thermal Decomposition of 5 and 5-d_4 in the Presence and Absence of Added Ligand. Thermolyses of **5** and **5**-d_4 with and without added triethylphosphine were performed in the same manner as described for **3**. Rate constants for the reactions **5** → **6a** or **5**-d_4 → **6a**-*d* were calculated by multiplying the first-order rate constant determined for the disappearance of starting material by the fraction of the reaction attributed to the formation of **6a** or **6a**-*d* (68% and 44%, respectively).

The observed rate constants (average of two runs) for thermolysis of **5** and the calculated rate constants for appearance of **6a** in the absence of added triethylphosphine at 99, 109.5, 118, and 125 °C were $k^{obsd} = 3.88, 13.5, 60.2, \text{ and } 104 \times 10^{-5}\ s^{-1}$ and $k^{cald} = 2.64, 9.18, 40.9, \text{ and } 70.7 \times 10^{-5}\ s^{-1}$, respectively. The thermolysis of **5**-d_4 in the absence of added triethylphosphine at 125 °C yielded $k^{obsd} = 37.2 \times 10^{-5}\ s^{-1}$ and $k^{calcd} = 16.4 \times 10^{-5}\ s^{-1}$.

The observed rate constants (average of two runs) for thermolysis of **5** and the calculated rate constants for appearance of **6a** in the presence of added triethylphosphine at 118, 126, 138.5, and 146 °C were $k^{obsd} = 2.21, 7.66, 41.2, \text{ and } 86.7 \times 10^{-5}\ s^{-1}$ and $k^{calcd} = 1.50, 5.21, 28.0, \text{ and } 59.0 \times 10^{-5}\ s^{-1}$, respectively. The thermolysis of **5**-d_4 in the presence of added phosphine yielded $k^{obsd} = 49.9 \times 10^{-5}\ s^{-1}$ and $k^{calcd} = 21.9 \times 10^{-5}\ s^{-1}$.

Kinetics of the thermal decomposition of 7 were determined by dissolving 100 mg of freshly prepared **7** in 2.0 mL of a 0.16 M solution of triethyl phosphate in cyclohexane and then transferring 0.5 mL of the resulting solution into each of three 5-mm NMR tubes by syringe under argon. The solutions were degassed three times, the tubes sealed under vacuum (0.01 torr), and the rates of decomposition of **7** determined by $^{31}P\{^1H\}$ NMR spectroscopy at 87 °C: $k^{obsd} = 8.62 \times 10^{-4}\ s^{-1}$ (average of three runs).

Thermal Decompositions of 9. Heating a sealed 5-mm NMR tube containing a solution of 30 mg (0.050 mmol) of **9** dissolved in 0.5 mL of a 0.16 M solution of triethylphosphate in cyclohexane at 87 °C and following the thermolysis by $^{31}P\{^1H\}$ NMR yielded $k^{obsd} = 1.55 \times 10^{-4}\ s^{-1}$ (average of two runs). Three products were observed by $^{31}P\{^1H\}$ NMR

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(44) The corresponding yields of **6a**-d_1, **6b**-d_2, and **6c**-d_2 determined by relative peak heights of the three products by ^{31}P NMR spectroscopy were 44%, 39%, and 17%, respectively. The relative percent yields of the three products from the thermal decomposition of **5** or **5**-d_4 did not change within detectable limits (1–2%) over the limited range of temperatures employed for kinetics. Response factors for the different platinacycloalkanes were determined from authentic samples.

(45) 1,1-Dichloro-2-methyl-2-*n*-propylcyclopropane was prepared (Isagawa, K.; Kimura, Y.; Kwon, S. *J. Org. Chem.* **1974**, *39*, 3171–3172) and reduced to the cyclopropane (bp 82.5–83.0 °C) with sodium metal in wet ether (Kobayashi, K.; Lambert, J. B. *ibid.* **1977**, *42*, 1254–1256).

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spectroscopy: tris(triethylphosphine)platinum(0) (**10**), δ 41.7 (t, J_{Pt-P} = 4226 Hz; lit.[16] δ 42, J_{Pt-P} = 4220 Hz); (3,3-dimethyl-1-butene)bis(triethylphosphine)platinum(0) (**11**), δ 16.0 (d of t, J_{Pt-P} = 3159 Hz, J_{P-P} = 57 Hz), δ 20.9 (d of t, J_{Pt-P} = 3697 Hz, J_{P-P} = 57 Hz); bis(3,3-dimethyl-1-butene)(triethylphosphine)platinum(0) (**12**), δ 21.0 (t, J_{Pt-P} = 3552 Hz).[18] Addition of excess triethylphosphine to the reaction mixture consumed **11** and **12** and yielded **10**. The thermolysis of **9** was repeated in decane by using cyclopentane as internal standard and the decomposition followed by GLC using a 20-ft, $^1/_8$-in. 10% column of SE-30 on Anakrom; equimolar quantities of 2,2-dimethylbutane and 3,3-dimethyl-1-butene were produced throughout the course of reaction which at completion yielded 1 equiv of each/equiv of **9**.

Acknowledgment. Rates of decomposition of **9** were obtained by T. McCarthy and R. Nuzzo.

Registry No. **2**, 70620-74-5; **3**, 76722-29-7; **3**-d_6, 79827-23-9; **4**, 79816-36-7; **4a**-d_2, 79816-37-8; **4b**-d_3, 79816-38-9; **5**, 76722-30-0; **5**-d_4, 79816-39-0; **6a**, 79816-51-6; **6a**-*d*, 79816-52-7; **6b**, 79816-53-8; **6b**-d_2, 79816-54-9; **6c**, 79816-55-0; **6c**-d_2, 79816-56-1; **7**, 79816-57-2; **8**, 79816-58-3; **9**, 79816-59-4; **10**, 39045-37-9; **11**, 79816-60-7; **12**, 79816-61-8; dichloro(1,5-cyclooctadiene)platinum(II), 12080-32-9; 1-bromo-2,2-dimethylpentane, 79803-29-5; 2,2-dimethyl-1-pentanol, 2370-12-9; 2-methylpropanal-2-methyl-2-propanimine lithium salt, 52278-93-0; 1-bromopropane, 106-94-5; 1-bromoethane, 74-96-4; 2,2,4,4-tetramethyl-1-pentanol, 79803-30-8; 3,3-dimethyl-1-butanol, 624-95-3; 1,5-dichloro-2,2-dimethylpentane, 79803-31-9; 2,2-dimethyl-1,5-pentyl di-*p*-toluenesulfonate, 62718-14-3; 5-chloro-4,4-dimethyl-1-pentene, 79803-32-0; 4,4-dimethyl-1-penten-5-ol tosylate, 79803-33-1; 1,4-dichloro-2,2-dimethylpentane, 79803-34-2; bis(triethylphosphine)platinum(II) dichloride, 14177-93-6; 2,2,4,4-tetramethylpentanoic acid, 3302-12-3.

Crystal Structure of the Homoleptic Seven-Coordinate Complex Heptakis(*tert*-butyl isocyanide)chromium(II) Hexafluorophosphate, $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$[1,2]

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Abstract: The structural characterization of the first homoleptic seven-coordinate chromium complex, $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$, is reported. The geometry of the cation is close to that of the 4:3 (C_s) piano stool with Cr–C distances ranging from 1.966 (8) Å to 2.016 (6) Å. The chromium atom lies on a crystallographically required mirror plane that also contains three of the *tert*-butyl isocyanide ligands, one of which belongs to the trigonal face, the other two being in the tetragonal face of the 4:3 geometry. Crystal data are: a = 16.952 (3) Å, b = 20.795 (4) Å, c = 28.702 (6) Å, V = 10117.9 Å^3, Z = 8, orthorhombic, space group *Cmca*, final R = 0.069 for 2647 X-ray diffractometer data with $F_o > 6\sigma(F_o)$.

The complex $K_4[V(CN)_7]\cdot 2H_2O$ is thus far the only homoleptic seven-coordinate first-row transition-metal complex to have been structurally characterized by X-ray diffraction.[4] Recently, we described the synthesis of the title compound,[5] a homologue of the compounds $[M(CN\text{-}t\text{-}Bu)_7](PF_6)_2$ (M = Mo, W), the structures of which have been previously studied.[6,7] Although the molybdenum and tungsten analogues are isomorphous and have C_{2v} capped trigonal prismatic geometries, the chromium complex is shown here to crystallize in a different space group and to have a different solid state structure.

The number of structurally characterized homoleptic seven-coordinate complexes has recently seen considerable growth, the two largest groups being complexes with isocyanide and cyanide ligands. The isocyanide complexes are $[Mo(CN\text{-}t\text{-}Bu)_7](PF_6)_2$,[6] $[W(CN\text{-}t\text{-}Bu)_7](PF_6)_2$,[7] $[W(CN\text{-}t\text{-}Bu)_7](W_6O_{19})$,[8] $[Mo(CNCH_3)_7](BF_4)_2$,[9] and $[Mo(CNC_6H_{11})_7](PF_6)_2$,[7] while the cyanide complexes include $K_5[Mo(CN)_7]\cdot H_2O$,[10] $Na_5[Mo(CN)_7]\cdot 10H_2O$,[10] $NaK_3[Mo(CN)_7]\cdot 2H_2O$,[11] $K_4[Re(CN)_7]\cdot 2H_2O$,[12] and $K_4[V(CN)_7]\cdot 2H_2O$.[4] Other homoleptic seven-coordinate complexes for which structural information is available include the three fluoride compounds IF_7,[13] $(NH_4)_3[ZrF_7]$,[14] and $K_2[NbF_7]$,[15] and the complexes $[Ca(H_2O)_7](I_{10})$,[16] $[Sr(H_2O)_7](I_{12})$,[16] and $[Er(dmp)_7](ClO_4)_3$,[17] where dmp = 2,6-dimethyl-4-pyrone.

Seven-coordinate chromium compounds are not unknown although most examples contain multidentate ligands.[18,19] Two cases where all the ligands are unidentate are $Cr[P(OMe)_3]_5H_2$[20] and the present compound. Our previous studies[6,7] and those of others[8,9] on the stereochemistry of [metal(unidentate isocyanide)$_7]^{2+}$ complexes have revealed cations with geometries having C_{2v} (capped trigonal prismatic), C_{3v} (capped octahedral), and C_s (4:3 piano stool) symmetries. The present work shows that the title compound has a stereochemistry close to that of the 4:3 (C_s) piano stool geometry.

Experimental Section and Results

Collection and Reduction of X-ray Data. The synthesis of $[Cr(CN\text{-}t\text{-}Bu)_7](PF_6)_2$ has been described previously.[5] The orange crystal used in the diffraction study, grown from *tert*-butyl isocyanide, had approx-

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(1) Part 13 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 12 see ref 2.

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