# Kinetics and Conformation in the Reversible Insertion of an Alkene into a Platinum–Carbon Bond in a Chelated (Pentenyl)platinum Complex

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The synthesis and characterization, including detailed $^1$H, $^2$H, $^{31}$P, and $^{13}$C NMR analysis of [(1,1-dideuterio-2,2-dimethyl-4-penten-1-yl-$\kappa^3C^{1,4,5}$)(dmpe)Pt$^{II}$]BF$_4$, 1-$\alpha$-$d_2$, and its 3,3-dideuterio isotopomer, 1-$\gamma$-$d_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane), are described. Thermolysis of each 1-$\alpha$-$d_2$ and 1-$\gamma$-$d_2$ was carried out at 125 °C in several solvents to yield a 1/1 mixture of 1-$\alpha$-$d_2$ and 1-$\gamma$-$d_2$. The rate of rearrangement is cleanly first order. Thermolysis of 1-$\alpha$-$d_2$ between 81 and 125 °C in methylene chloride led to determinations of activation parameters, $E_a$ = 31.8(0.6) kcal/mol and $\Delta S^{\ddagger}$ = -0.5(1.6) eu (100 °C). An X-ray crystal structure determination was carried out on the compound. It crystallizes in the monoclinic space group $P2_1/n$ (No. 14), with $a$ = 19.337(11) Å, $b$ = 6.948(4) Å, $c$ = 17.260(9) Å, $\beta$ = 122.34(6)°, $V$ = 1959.3 Å$^3$, and $Z$ = 4. The structure was solved with heavy atom techniques and refined to a final $R$ factor of 4.18%. In the solid state, the coordinated vinyl group is slipped slightly out the plane of the molecule and is canted at a dihedral angle of 52° from the molecular plane. The chelate ring shows only very slight distortions from a presumed strain-free shape. 2D NOESY spectra suggest that the in-plane conformation of the pentenyl chelate is at least partly populated in solution. (dmpe)Pt(CH$_2$-c-C$_4$H$_7$)Cl, 11, was prepared. Thermolysis of 11 at 110 °C yielded intractable metal-containing materials along with methylenecyclobutane and methylcyclobutane together in *ca.* 60% yield as the only identifiable organic products. Treatment of 11 with silver ion at low temperatures in acetone or methylene chloride yielded two products in a 1:7 (NMR) ratio, methylenecyclobutane and a material stable only below 0 °C that is assigned the structure [(4-penten-1-yl-$\kappa^3C^{1,4,5}$)(dmpe)Pt$^{II}$]BF$_4$ on the basis of its NMR spectrum.

## Introduction

Several years ago, we reported the equilibration of [(3,3-dideuterio-2,2-dimethyl-4-penten-1-yl-$\kappa^3C^{1,4,5}$)(dmpe)Pt$^{II}$]-BF$_4$, 1-$\gamma$-$d_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) (Scheme I) to a mixture of 1-$\alpha$-$d_2$ and 1-$\gamma$-$d_2$.[1] This rearrangement was interpreted as proceeding through the reversible insertion of the coordinated alkene into the metal–carbon bond of 1 to form the (cyclobutylmethyl)-platinum intermediate 2-$d_2$. Precedent for the possible existence of a species such as 2 was provided by the synthesis and silver ion-induced ring opening of 3 to form 5 (Scheme II),[2] presumably through the intermediacy of structurally analogous 4.

We have continued to study the structure and chemistry of 1 with the intent of better establishing the energetics of the reaction and the role of conformation in the apparent insertion. We report here the synthesis of the other isotopomer, 1-$\alpha$-$d_2$, additional results on kinetic investigations, an X-ray crystal structure, and a solution phase NOESY study of 1-$\alpha$-$d_2$. In addition, we have carried out ring-opening reactions of a complex related to 3, (dmpe)-(cyclobutylmethyl)PtCl.

## Results

**Synthesis.** Complex 1 was prepared as shown in Scheme III. Preparation of 5-bromo-5,5-dideuterio-4,4-
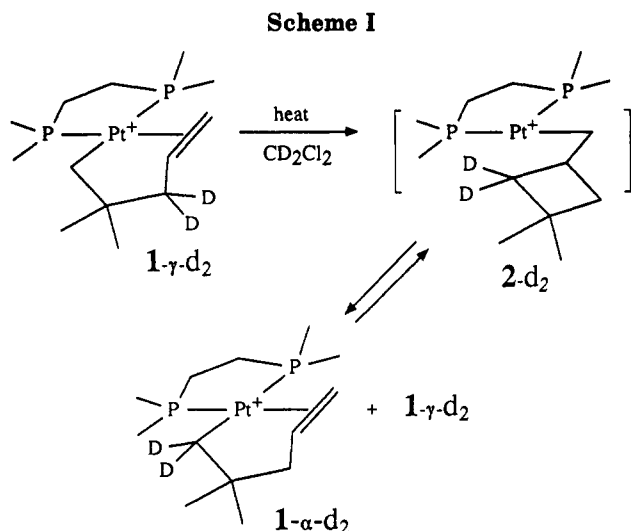
**Scheme I**



dimethyl-1-pentene (9-$\alpha$-$d_2$) is shown in Scheme IV. The isotopic purity of 9-$\alpha$-$d_2$ was such that no $^1$H NMR signal for the labeled $\alpha$-methylene could be detected. Preparation of 3,3-dideuterio-2,2-dimethyl-4-pentenal (10) was carried out as shown in Scheme V according to the procedure of House[3] for the unlabeled material. The allylic alkylation yielded 10 that was labeled 87% in the allylic position and 13% in the vinyl position, but the vinyl deuterium caused no problems in subsequent rearrange-

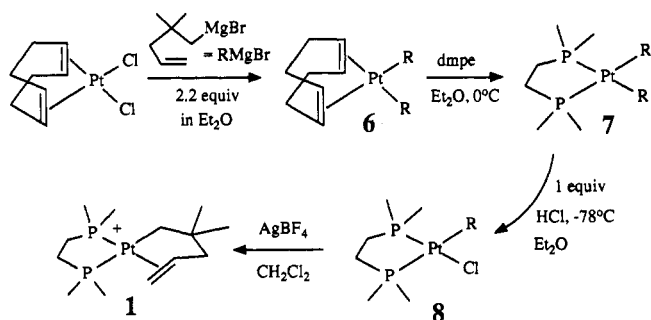(1) Flood, T. C.; Bitler, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6076.
(2) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795.

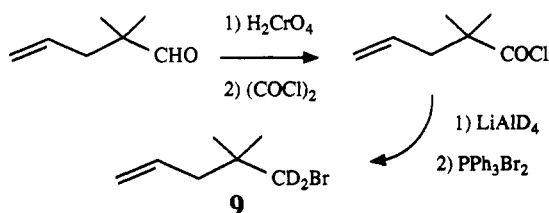(3) House, H. O.; Liang, W. C.; Weeks, P. D. *J. Org. Chem.* **1974**, *39*, 3102.
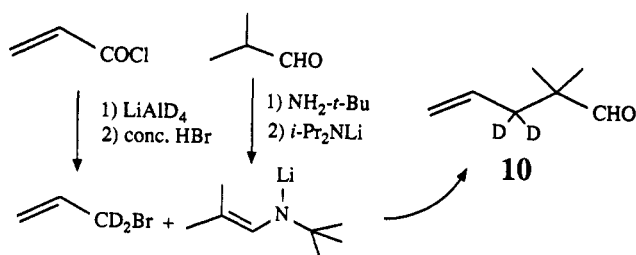
**Scheme II**
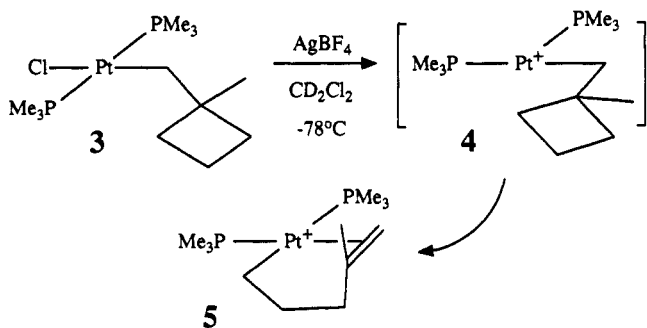
**Scheme III**

**Scheme IV**

**Scheme V**

ment experiments. Conversion of aldehyde 10 to 5-bromo-3,3-dideuterio-4,4-dimethyl-1-pentene (9-$\gamma$-$d_2$) was carried out in the same way as shown for 9-$\alpha$-$d_2$ in Scheme IV. To prepare 1, a solution of alkyl chloride 8 in methylene chloride was added to a suspension of silver fluoroborate in the same solvent at −78 °C, and the product was recrystallized from $CH_2Cl_2$/ether.

$^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} spectra of 1 are summarized in Table I, with the assignments being confirmed by $^{13}$C–$^1$H DEPT and 2D $^1$H–$^1$H and $^{13}$C–$^1$H correlation NMR spectra. The coordinated alkene $CH_2$ exhibits a $^{13}$C chemical shift that is normal (83 ppm), while the internal CH group (121 ppm) is at the low-field end of the range for coordinated alkenes.[4] The $^1J_{PtC}$ is the same for each of these (ca. 40 Hz) and is typical of a platinum alkene trans to a strong trans-influence ligand. We assign the $^{31}$P resonance at $\delta$ 35.65, having the smaller $^1J_{PtP}$ = 1545

Hz, to P2 (see the atom numbering in the X-ray structure in Figure 1) trans to the strong-field alkyl ligand. The resonance at $\delta$ 36.50 with $^1J_{PtP}$ = 3663 is attributed to P3 trans to the weaker-field coordinated alkene. For comparison, the latter coupling constant is typical for phosphines trans to pyridines.[5]

The cationic chelate 1 could be treated with nucleophiles to regenerate neutral analogs of 8. Treatment of 1 with KI in acetone or with KCN in ethanol gave low yields of (dmpe)Pt(I)($CH_2CMe_2CH_2CH=CH_2$) or (dmpe)Pt-(CN)($CH_2CMe_2CH_2CH=CH_2$), respectively.

**Thermolysis of 1-$\alpha$-$d_2$.** Heating of solutions of 1-$\alpha$-$d_2$ above 80 °C in sealed NMR tubes in any of several solvents results in rearrangement to a mixture of 1-$\alpha$-$d_2$ and 1-$\gamma$-$d_2$. Attempts to follow the rearrangement by $^1$H NMR spectroscopy met with difficulties: in all of the common deuterated solvents, peaks of interest are obscured by either residual protium in the solvent or by phosphine alkyl groups. Alternatively, the reaction mixture was quenched with potassium iodide to generate (dmpe)Pt-(I)($CH_2CMe_2CH_2CH=CH_2$)-$d_2$ for proton NMR analysis, but this would require large amounts of material for aliquots for kinetics and it met with problems in material balance. It was decided to monitor the rearrangement by deuterium NMR. This technique has several advantages: it requires only a small amount of sample, there are no other peaks blocking the resonances of interest, it allows for the general use of protio solvents, and material balance can be followed by comparison to the intensity of the natural abundance deuterium peak in the solvent. The $^{13}$P{$^1$H} NMR spectrum was also monitored as an explicit measure of the structural integrity of the complex.

The $^2$H spectrum shows two peaks corresponding to the two diastereotopic deuteriums on the $\alpha$-methylene of 1-$\alpha$-$d_2$ at $\delta$ 1.4 and 2.0. The low-field resonance is seen as a broad singlet ($w_{1/2}$ ca. 5 Hz) while the high-field resonance, although also broad, shows a 1:4:1 "triplet" (s + d, $J_{PtD}$ = 11 Hz for the doublet) due to coupling with 34% of platinum-195. A similar pattern is seen for the diastereotopic allylic ($\gamma$) methylene deuteriums in 1-$\gamma$-$d_2$, with resonances at $\delta$ 1.8 (s) and 2.6 (s + d, $J_{PtD}$ = 8 Hz). In mixtures of 1-$\alpha$-$d_2$ and 1-$\gamma$-$d_2$, there is overlap between the $\delta$ 1.8 and 2.0 peaks, but the other two peaks exhibit baseline separation from the overlapping pair, allowing quantitative monitoring of the reaction. As the thermolysis progresses, starting with 1-$\alpha$-$d_2$, the two peaks for the $\alpha$ deuteriums gradually diminish and those of the 1-$\gamma$-$d_2$ isomer gradually increase until they are one-to-one. The proton ($^1$H) signal for the one $\gamma$-hydrogen of 1-$\alpha$-$d_2$ at $\delta$ 2.6 remains clearly visible as the reaction progresses, although it does diminish to 50% intensity. Its geminal H–H coupling of 11 Hz remains clear even after prolonged heating of the sample, indicating that the $\alpha$–$\gamma$ exchange remains pairwise: there is no indication of single atom H–D exchange between these sites. We also do not see any evidence of exchange of deuterium from 1 into the protio solvent or from the deuterated solvent into any position of 1. When the reaction is begun with 1-$\gamma$-$d_2$, all of the same resonances are seen, as equilibrium is reached at the same rate.

A small amount of a sharp singlet at $\delta$ 0.9 in the $^2$H spectrum appears (presumably free $CH_2=CHCH_2CMe_2$-

(4) Mann, B. E.; Taylor, B. F. *$^{13}$C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; pp 192–198.

(5) Crumbliss, A. L.; Topping, R. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; p 531.

**Table I. NMR Spectral Assignments ($\delta$ in ppm, $J$ in Hz) of 1-$\alpha$-$d_2$ in CD$_2$Cl$_2$[a]**

| proton | $\delta(^1H)$ | $J_{PtH}$ | $J_{HH}$ | $J_{PH}$ | $\delta(^{13}C)$ | $J_{PtC}$ | $J_{PC}$ | other |
|---|---|---|---|---|---|---|---|---|
| a | 5.25 | 40 | 9, 3 | 13, 2 | | | | |
| b | 3.95 | 42 | 17, 3 | | 82.97 | 40.4 | 11.8 | |
| c | 5.60 | 55 | m | | 121.36 | 41.0 | 9.7, 1.4 | |
| d | 2.63 | 52 | 12 | | | | | |
| e | 1.82 | | obscured | | 48.15 | | | |
| f | 1.13 | | s | | 33.9 | 52.2 | 9.8 | $\delta(^{13}C)$ 57.77, 4° carbon to which methyls attach |
| g | 1.18 | | s | | 29.8 | 15.0 | | |
| h | 1.72 | 16 | | 10 | 12.76 | 18.1 | 28.5 | $\delta(^{31}P)$ 35.65, $J_{PtP}$ 1545, $J_{PP}$ 7 |
| i | 1.59 | 16 | | 10 | 12.14 | 21.4 | 28.7 | |
| j, k | 1.71 | 11 | | 12 | 11.06 | 41.2 | 41.1 | $\delta(^{31}P)$ 36.55, $J_{PtP}$ 3663 |
| | 1.77 | 11 | | 12 | 14.10 | 63.3 | 40.7 | |
| $\alpha$[b] | 1.4 | 11 | | | | | | |
| | 2.0 | <5 | | | | | | |

[a] Label designations are as in Figure 2. [b] Methylene $\alpha$ to Pt, from $^2$H{$^1$H} NMR; couplings are Pt–D.
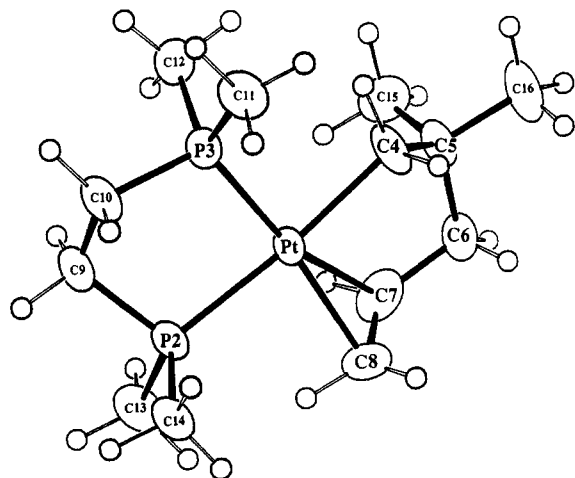


**Figure 1.** ORTEP diagram of the molecular structure of cation 1, excluding the BF$_4^-$ counterion for clarity. The atom numbering is that used in Table II and in the text. Hydrogen positions were not located crystallographically but are those calculated from standard distances and angles, including an assumption of maximum staggering of the methyl group hydrogens.

(CD$_2$H)), but this amounts to less than 10% after *ca.* 4 rearrangement half-lives in CH$_2$Cl$_2$ solvent. At this point there is also a very small amount of solid material in the NMR tube, but overall there is very little indication of decomposition for several half-lives of the rearrangement. The rate of decomposition is a function of the solvent. Heating 1-$\alpha$-$d_2$ in acetone solvent, for example, leads to comparatively rapid generation of the $\delta$ 0.9 peak. Thermolysis in CH$_2$Cl$_2$ at 110 °C leads to a very slow decomposition over a period of *ca.* 10 days. After complete decomposition in CH$_2$Cl$_2$, the $^2$H NMR spectrum shows peaks at $\delta$ 0.9 (CH$_2$=CHCH$_2$CMe$_2$(CD$_2$H)), 1.9 (CH$_2$=CHCD$_2$CMe$_3$), and 2.4. The last peak, which amounts to *ca.* 6% of the material, is assigned to 2,2-dideuterio-3,3-dimethyl(methylene)cyclobutane, CH$_2$=$\overline{\text{CCD}_2\text{CMe}_2\text{CH}_2}$. All of these assignments are made in comparison to the chemical shift of the analogous proton resonances of standard samples of 4,4-dimethyl-1-pentene and methylenecyclobutane. The insoluble, presumably platinum-containing product was intractable.

**Kinetics.** Samples of 1-$d_2$ in CH$_2$Cl$_2$ or CH$_3$NO$_2$ solvent in sealed NMR tubes were heated in a constant temperature bath with periodic measurement of the $^2$H{$^1$H} NMR spectrum. The small amount of decomposition during the rearrangement did not seem to have any influence on

**Table II. Selected Bond Lengths (Å) and Bond Angles (deg) from the X-ray Structure Determination of 1[a]**

| | | | |
|---|---|---|---|
| Pt–P2 | 2.328(5) | P2–Pt–P3 | 85.7(2) |
| Pt–P3 | 2.232(6) | P2–Pt–C4 | 172.9(6) |
| Pt–C4 | 2.164 | P3–Pt–C4 | 87.4(7) |
| Pt–C7 | 2.219(22) | Pt–C4–C5 | 110.8(14) |
| Pt–C8 | 2.248(25) | C4–C5–C6 | 104.5(21) |
| C4–C5 | 1.548(33) | C5–C6–C7 | 110.0(19) |
| C5–C6 | 1.515(33) | | |
| C6–C7 | 1.565(35) | | |
| C7–C8 | 1.359(36) | | |

[a] Atoms are numbered as in Figure 1.

the kinetics. The rates were essentially the same in CH$_3$-NO$_2$ or CH$_2$Cl$_2$.

Since the forward ($k_1$) and reverse ($k_{-1}$) rate constants for the 1-$\alpha$-$d_2$ $\rightleftarrows$ 1-$\gamma$-$d_2$ isomerization were identical (we did not detect any equilibrium isotope effect), the forward rate constant is half of the observed rate constant for the approach to equilibrium. The measured rate constants in methylene chloride solvent were as follows: 81 °C, $k_1$ = 4.02(0.18) × 10$^{-7}$; 100 °C, $k_1$ = 3.84(0.30) × 10$^{-6}$; 110 °C, $k_1$ = 1.32(0.13) × 10$^{-5}$; 125 °C, $k_1$ = 5.73(0.31) × 10$^{-5}$. An Arrhenius plot of these data yielded $E_a$ = 31.8(0.6) kcal/mol and $\Delta S^{\ddagger}$ = -0.5(1.6) eu (100 °C).

**Crystal Structure.** Crystals of 1 were grown from methylene chloride/ether by vapor diffusion, and an X-ray crystal structure was obtained. The BF$_4^-$ anion was slightly disordered, but the final agreement factor was nonetheless 4.2%. One perspective of the structure is shown in Figure 1. Selected bond lengths and angles are shown in Table II. As expected, judging from the Pt–P bond lengths (with atom numbering as in Figure 1), the alkyl group exercises a larger trans influence (Pt–P2 2.328 Å) than does the alkene (Pt–P3 2.232 Å). This structural information is consistent with the interpretation of the platinum-phosphorus NMR coupling constants discussed above. The P–Pt–P angle is 86°, as expected from the constraints of the chelate.

Of greatest interest, of course, is the conformation of the pentenyl ligand. There are three notable features of the pentenyl chelate that deviate somewhat from an ideal geometry. First, two of the three C—C—C angles are normal, but the C4—C5—C6 angle is slightly pinched at 104.5°.[6] Second, if we define the molecular plane by the atoms Pt, P2, and P3, then (looking down from above the

(6) This angle may not be particularly abnormal. Thorpe and Ingold 70 years ago postulated that the so-called geminal dimethyl effect could arise from a natural compression of the interior angle of a quaternary carbon center in a chain. Structural data exist that this angle compression does occur. See, for example: Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.
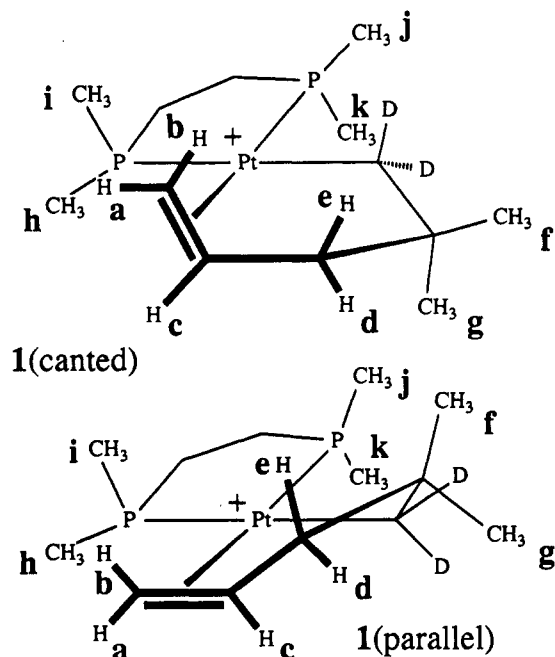
**Figure 2.** Conformations of 1-α-$d_2$.



**Figure 3.** Partial NOESY spectrum of 1-α-$d_2$ in $CD_2Cl_2$ at 25 °C with mixing time = 4 s. Cross-peak assignments are indicated by pairs of letters corresponding to labeling in Figure 2 for the parallel conformation.

molecule as in Figure 1) the alkyl carbon, C4, is slightly above the plane (0.065 Å) and the centroid of the alkene C=C bond is slipped slightly below the plane (toward C6) by ca. 0.20 Å. The third distortion arising as a consequence of the chelation is the dihedral angle between the P—Pt—P plane and the C7—Pt—C8 plane which is 51.9°; *i.e.*, the alkene is canted ca. 38° away from being perpendicular to the plane of the molecule, the conformation that is generally most stable for Pt(alkene) complexes.[7a] The angle at platinum between the alkyl carbon (C4) and the alkene centroid is normal 89.4°.

**Solution Conformations.** 2D NOESY NMR spectra[8a] were obtained in an attempt to gain information regarding the conformation of 1 in solution. Longitudinal relaxation times were measured for 1 using the inversion-recovery method; all $T_1$'s are in the range 1–3.2 s. The NOESY spectra were collected with mixing times, $\tau_m$, of 1–5 s with the result that cross peak intensities of the olefin protons with phosphine methyl groups h and i (for proton labeling see Figure 2) are most clear at ca. 4 s (Figure 3). As expected for either conformation shown in Figure 2, the resonance for proton a exhibits strong cross peaks with both resonances h and i. The resonance for proton b shows a significant cross peak with resonance i (assigned δ 1.59), but apparently not with h. There is no evidence of any NOE interaction between c and either h or i at any mixing time from 1 to 5 s.

Hydrogen–hydrogen distances were calculated from the X-ray data for the structure designated 1(canted) in Figure 2. Since hydrogens had not been located in the refinement, they were placed at standard positions. Distances to the methyl groups were taken to be to the closest hydrogen in the presumed most stable (staggered) conformation. For the canted structure, the closest vinyl-to-PMe H–H distances (Å) were as follows: a–h, 2.17; a–i, 2.62; b–i, 3.52; c–h, 3.21. Recall, there is a significant NOE
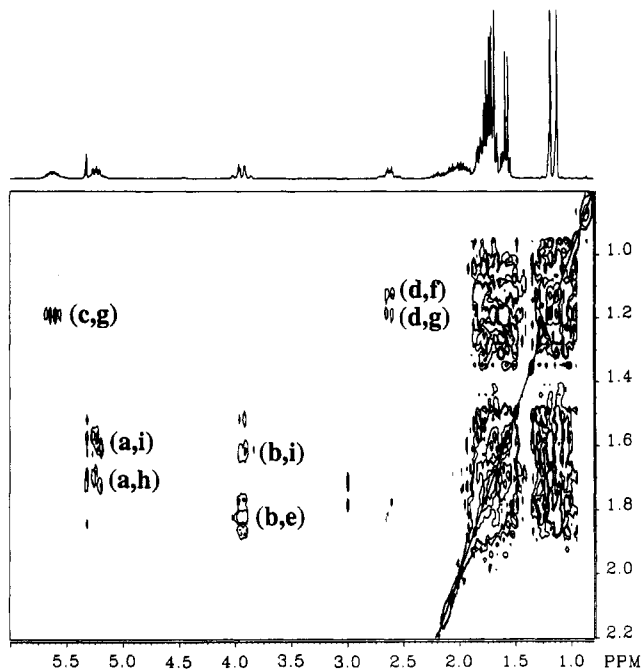
interaction observed between b and i. Since the b–i distance in the canted structure is slightly larger than the c–h distance, one would expect to observe an NOE cross peak for the c–h interaction as well. That the last assertion is contrary to fact suggests that the dominant conformation in solution is closer to 1(parallel) than to the solid state structure, 1(canted).

We have employed molecular models and low-level molecular modeling to attempt to assess H–H distances in 1(parallel) and in both 1(canted) and 1(parallel) with the diphosphine chelate in a puckered conformation opposite to that in Figure 1. These suggest, first of all, that the NOE predictions are not very sensitive to the diphosphine chelate conformation. Secondly, the c–g distance should be slightly shorter in 1(canted) than in 1(parallel), but it appears that a c–g NOE effect is reasonable in either conformation. In addition, the d–f and d–g distances should be more nearly the same in 1(canted) than in 1(parallel). (The cross peaks for d–f and d–g appear to be of very similar intensity in the NOESY spectrum in Figure 3.) Given the crude nature of measurements on molecular models, we do not attach much significance to these observations. A point of greater contradiction to the conclusion of a dominant 1(parallel) conformation is as follows. According to Figure 3, vinyl proton c has a distinct NOE cross peak with methyl group g, but not f. This necessitates that in 1(parallel) g must be quasi equatorial while in 1(canted) g must be quasi axial. Note from Table I that $J_{PtC}$ for methyl f is 52 Hz, while for methyl g $J_{PtC}$ is 15 Hz. If one accepts the idea that through-bond coupling along Pt–C4–C5–Me should be greatest when the Pt–Me dihedral angle is 180° and smallest when this angle is 90°, then the observed coupling constants and c–g NOE are most consistent with 1(canted) and not 1(parallel). We find it difficult to reconcile this interpretation with the conclusion from the vinyl hydrogen NOE effects with phosphine methyls i and j. One possible resolution of this apparent contradiction is that geminal

(7) (a) See footnote 23 in the following reference for an extensive catalog of Pt(alkene) structures. (b) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801–3812.
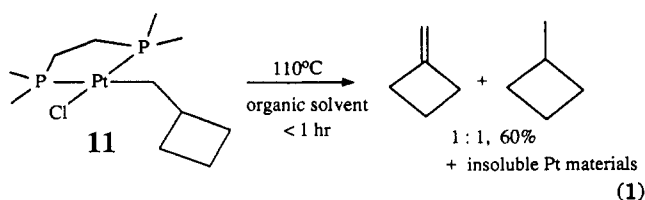
(8) (a) Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: New York, 1989. (b) *Ibid.*, Chapter 11.

methyl f in 1(parallel) extends over the metal close to its perpendicular molecular axis and so acquires an unusually large $J_{PtC}$ arising from direct steric interaction. These kinds of "through-space" couplings of hydrocarbon ligands to platinum are known,[9a] and they are well-known for H–F and F–F couplings.[9b] However, in known[9a] cases of through-space Pt–C coupling, the $J_{PtH}$ to hydrogen on that carbon is also very large. For example, in *trans*-PtCl₂-(8-methylquinoline)(PMe₃), for the 8-methyl group $J_{PtC}$ is 27 Hz and $J_{PtH}$ 12 Hz. In the case of 1, $J_{PtC}$ for methyl group f is 52 Hz, while $J_{PtH}$ is not detectable. Furthermore, models suggest that the distance between platinum and methyl group f in 1(parallel) is simply too great for through-space coupling.

Perhaps the best explanation is that the observed NOESY spectra reflect a much larger NOE effect from a minor conformation,[8b] while the coupling constants correspond to those of the major conformation. Models suggest that the distance from b to i in 1(parallel) might be as much as 1 Å shorter than the corresponding distance in 1(canted). However, a large NOE effect from a minor 1(parallel) conformer would still mean that the two conformers must be close in energy, and there would not be a large conformational contribution to the barrier for alkene insertion.

Incidentally, the NOESY spectra can be used to make specific assignments for several resonances, independent of the limited range of available conformations. Allylic proton d is expected to interact with both geminal methyls f and g, while e is expected to interact more strongly with one than the other. Vinyl proton b should also interact more strongly with allylic proton e than with d. Also, of course, the interactions with vinyl hydrogens a and b distinguish phosphine methyls h and i from j and k.

**Reactions of (dmpe)(cyclobutylcarbinyl)PtCl, 11.** A striking feature of the reaction of Scheme I is that β-hydrogen elimination in the unsaturated (or solvent coordinated) cyclobutylmethyl intermediate 2 does not appear to compete significantly with β-alkyl elimination. For this reason, we decided to check the chemistry of complex 11 in analogy to that of 3, which we have previously reported.[2] Complex 11 does not have the quaternary methyl group which blocks β elimination in 3. The preparation of 11 carried out in a way completely analogous to the sequence shown in Schemes III and IV. Its thermolysis was conducted at 110 °C in methylene chloride, acetonitrile, acetone, and benzene (deuterated solvents). In all cases, insoluble material was formed. ¹H NMR of the volatile fraction of the reaction showed methylenecyclobutane and methylcyclobutane, identified by comparison of their spectra with those of standard samples, as the only organic products (eq 1). Each was formed in ca.
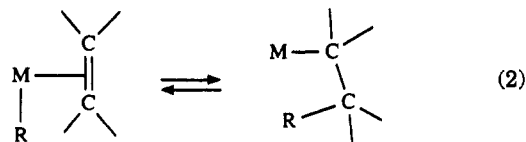


(1)

30% yield. No 1,4-pentadiene could be detected in the

(9) (a) Pregosin, P. S.; Wombacher, F. *Magn. Reson. Chem.* **1991**, *29*, S106 and references therein. (b) Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. *Organic Structural Analysis*; Macmillan Publishing Co.: New York, 1976; p 77.

**Scheme VI**



reaction mixtures. The sole organic product from thermolysis of 3 at 140 °C is 2-methyl-1,4-pentadiene.[2]

In order to generate an unsaturated intermediate like 2 or 4, low temperature chloride ion abstraction was carried out analogously to that reported earlier for 3 as shown in Scheme II.[2] Complex 11 was treated with silver fluoroborate at –78 °C in methylene chloride-$d_2$ (Scheme VI) and independently in acetone-$d_6$. Progress of the reaction was monitored by ¹H NMR beginning at –80 °C. The spectrum showed no vinyl resonances until the sample reached –25 °C, at which point resonances of a new platinum intermediate and of methylenecyclobutane were observed. Above 0 °C, decomposition of the intermediate slowly occurred, so no stable product could be isolated. Resonances of the intermediate include multiplets at δ 4.33 (ddt), 5.58 (dddt), and 5.90 (m). These closely parallel in chemical shift and coupling pattern the resonances for b, a, and c, respectively, in 1, and the a and b resonances reported for 5.[2] On this basis, we assign the intermediate species the structure 13. The spectral fingerprint for methylenecyclobutane is distinctive (see Experimental Section). Integrations indicated that 13 and methylenecyclobutane were formed in a 7:1 ratio.

**Discussion**

In the last decade, a number of well-defined examples of alkene insertions into and some β-alkyl eliminations from metal–alkyl(sp³-carbon) bonds as in eq 2 have appeared. Several examples of single-component ethylene



(2)

polymerization catalysis thought to proceed by this path have also appeared. This chemistry includes complexes of La,[10] Nd,[10] Lu,[10,11] Sc,[12] Zr,[13] Cr,[14] Co,[15,16] Rh,[17–19] and

(10) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103.

(11) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471–6473.

(12) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566–1577.

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Ni.[20] Still, the variables which determine the functioning of this path in general are not fully delineated, particularly for the late transition metals.

Several platinum complexes relevant to this work have been reported. Clark[21a] has prepared the *cis*-Pt(ethylene)-(methyl) complex 14, and commented on its facile decomposition, but no mention was made of the fate of the organic ligands. He and his co-workers have also prepared the trans complexes 15[21b] and 16,[21c] neither of which is
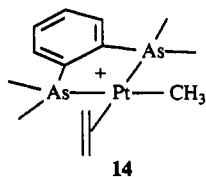


14
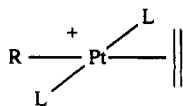
15, L = PPh₂Me, R = Et

16, L = PPhMe₂, R = Me

said to exhibit insertion chemistry. Mechanisms similar to the pentenyl–cyclobutylmethyl transformation proposed here have been invoked for carbon skeletal rearrangements during Ti-catalyzed codimerization of ethylene and butadiene,[22] for Ni/Al-based catalytic rearrangements of 1,4-dienes,[23] for reversible rearrangement of (3-buten-1-yl)Co to (cyclopropylmethyl)Co,[24] and for scandocene hydride catalyzed rearrangements of dienes.[25]

The ligand $-CD_2CMe_2CH_2CH=CH_2$ is well suited to observe reversible intramolecular alkene insertion–elimination into a metal—carbon $\sigma$ bond for a couple of reasons. First, the $\beta$-dimethyl substituents prevent the normally very facile $\beta$-hydride elimination. Second, coordination of the alkene should be aided by the chelate effect. There are now a number of systems known where simple nonchelated alkyl and alkene ligands are both present in the coordination sphere of isolable or spectroscopically well-characterized metal complexes,[15,16,18–21,26] but few of these[15,16,18–20] have been directly observed to undergo insertion chemistry. It may be that a significant increase in the barrier to insertion results from a larger enthalpy of metal—alkene bonding. In general, chelation should increase the probability of observing a M(alkene)R intermediate, allowing the direct study of the single-step insertion of such a species without needing the metal—

alkene bonding enthalpy to be strong enough that it becomes an impediment to insertion.

There are several important questions in trying to evaluate the usefulness of the pentenyl chelate as a model for the study of $\beta$-alkyl insertions. (1) How strained is the chelated pentenyl ligand? Ring strain could artificially raise the energy of the ground state and could draw the alkene carbon closer to the metal–alkyl bond, bypassing normal and possibly serious steric barriers to insertion. (2) Chelation could result in an artificially low barrier to rotation of the alkene group into the plane of the complex or could even render the in-plane conformation the ground state of the molecule. Intuitively, the planar conformation would be most favorable for the insertion reaction, and theoretical calculations support this notion.[27] Normally, in square-planar complexes of d⁸ metals, the lowest energy conformation is that where the alkene is perpendicular to the molecular plane or nearly so. The planar conformation is usually the energy maximum of a metal–alkene rotational barrier that theoretical considerations suggest is largely steric in origin in d⁸ complexes.[7b,28] Experimentally, barriers in platinum complexes are typically between 10 and 20 kcal/mol,[29] and such a barrier could represent a significant portion of the activation energy for insertion via a presumably planar transition state.

As to the first question regarding strain in the chelate ring of 1, it was noted above that three features of the X-ray structure deviate slightly from an ideal geometry. The C–C–C bond angle at one of the three saturated carbons of the chelate ring (C5) is distorted by *ca.* 5°. Bending force constants for methylene chains are small, and a 5° deformation would amount to less than 0.5 kcal/mol of strain.[6,30] Second, the alkyl carbon is 0.065 Å (*ca.* 1.7°) above the molecular plane, and the centroid of the alkene bond is slipped slightly below the plane (toward the alkyl chain) by ca. 0.02 Å (*ca.* 5.2°). Out-of-plane bending will have an even weaker force constant than methylene chain bending, so the total of these distortions will amount to very little strain energy. The third feature arising as a consequence of the chelation is the alkene being canted *ca.* 38° away from perpendicular to the plane of the molecule. As mentioned above, rotational barriers in (alkene)Pt^II complexes are thought to be steric in origin.[7b,28] Small deviations from perpendicularity are not likely to be high in energy, and there are examples of relatively unhindered complexes with angles up to 17° from upright in the solid state.[31]

Thus, the three distortions in the chelate ring do not represent any significant increase in the ground state energy of the alkene and alkyl reactant partners toward an incipient insertion reaction. Additionally, the platinum–alkyl bond and the vector from platinum to the center of the alkene bond form an angle of 89.4°, so there is no in-plane angle strain. The two potential reactants within the chelate are not artificially pulled together in such a way as to force them along the reaction coordinate toward

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(29) For experimental determinations of platinum–alkene rotational barriers, see footnote 25 in ref 7b.

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(31) For example, in dichloro(benzylamine)(3-methyl-1-pentene)platinum(II) the dihedral angle between the Pt–alkene plane and the plane of the molecule is 73°. Merlino, S.; Lazzaroni, R.; Montagnoli, G. *J. Organomet. Chem.* 1971, *30*, C93–C95.
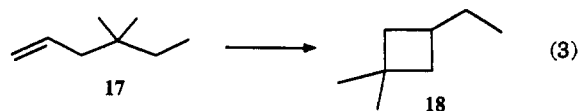
**Scheme VII**
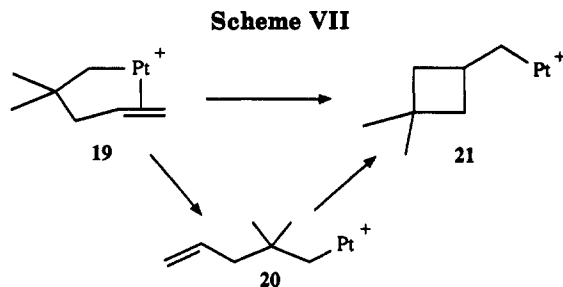


insertion. As far as we can tell, the chelated pentenyl ligand should be a reasonable model for a typical insertion substrate, at least in the ground state.

The second question raised above regards the rotational barrier of the alkene and its importance to the activation energy for insertion. The NOESY experiment discussed above suggests that the alkene-in-plane conformation, 1(parallel), is at least partially populated at room temperature. Although it is interesting that the solid phase and solution phase structures of 1 might be different, it is not surprising. Models indicate that the chelate would probably not be strained whether the alkene is parallel to the square plane of the molecule or canted as in the solid state, and as just mentioned, electronic effects on the conformation are thought to be minimal. This similarity in energy of the two conformations means that the accessibility of the in-plane conformation does not represent a raising of the ground state of the molecule by steric compression imposed by chelation (and so a diminution of the overall insertion barrier). Rather, it represents the removal of some of the steric compression and a lowering of the parallel conformer closer to the ground state perpendicular conformer's energy. Thus, the energy of the ground state of this chelated complex should be reasonably representative of that of a normal insertion substrate. Parenthetically, models suggest that the 90° perpendicular conformation of the alkene with respect to the molecular plane would be significantly more strained than the other two conformations considered here.

The issue that we still cannot address, of course, is just how atypical the transition state is for the insertion of 1 compared to an unconstrained system. Clearly, the incorporation of substantial ring strain and conformational restrictions of the Pt–CH$_2$ group in the transition state, especially the former, make the transition state potentially quite atypical.

One can draw some conclusions regarding the probable strength of the Pt($\pi$-alkene) bond from the insertion kinetic parameters. Using Benson's rules,[32] one can estimate that $\Delta H°$ for the transformation of 17 to 18 (eq 3) would be 4 kcal/mol. This should be a good analogy for



the cyclization of platinum complex 20 to 21 (Scheme VII)-since the Pt–CH$_2$ bonding in 20 and 21 should be essentially the same. To estimate $\Delta H°$ for the 19 to 21 insertion requires some information about the metal–alkene $\pi$-bond dissociation energy (BDE) in complex 19, but to our knowledge there are not extant experimental numbers for this kind of bond. Reported platinum–alkene rotational

barriers can be taken as lower limits for bond energies in the respective complexes, but variations in ligands, charge, etc. could cause large differences in specific BDEs. Hay[28] has calculated a dissociation energy of 28 kcal/mol for ethylene in Zeise's salt, [PtCL$_3$(C$_2$H$_4$)]$^-$, using ab initio methods with an extended basis set and a relativistic core potential. In any event, since the experimental $E_a$ for the 19 to 21 transformation (i.e. 1 to 2) is 32 kcal/mol, the BDE for 19 (i.e. 1) cannot be more than approximately 28 kcal/mol. Since it is unlikely that the reverse reaction would have an $E_a$ of 0, the alkene BDE is probably less than this. As discussed above, there should not be any substantial ring strain term for 19 in the enthalpy calculation.

This discussion has made the assumption that there is no assistance to the insertion by solvent coordination to platinum in the transition state. To the extent that this assumption is incorrect, the transition state could lead to an already-solvated version of intermediate 21 (or 2) and the $\Delta H°$ for the insertion step could be smaller than the $\Delta H°$ for the insertion to an unsolvated 21. Thus, the upper limit for the Pt–alkene bond strength could be significantly greater than 28 kcal/mol. However, if an associative solvent interaction were involved, one would expect the $\Delta S^\ast$ for the insertion of 1 to 2 to be significantly negative rather than *ca*. 0 eu as is observed.

In addition, the observation that $\Delta S^\ast$ is *ca*. 0 eu for the insertion suggests that the counterion does not coordinate in the transition state, nor does any other kind of change in ion pairing or ion solvation occur compared to the ground state. The insertion seems to occur solely within the cationic complex.

It is reported above that thermolysis of 11 yields methylenecyclobutane and methylcyclobutane, while chloride abstraction from 11 by silver ion yields ring-opened product 13 and methylenecyclobutane in a 7:1 ratio. These results suggest that direct $\beta$ elimination from the square-planar complex, presumably via some five-coordinate intermediate, is much easier for elimination of hydrogen than of carbon. This is consistent with the observation that while formation of methylenecyclobutane from 11 requires less than 1 h at 110 °C, the thermolysis of (dmpe)-

Pt(CH$_2$CMeCH$_2$CH$_2$CH$_2$)Cl, has a half-life of 15 h at 140 °C to afford only 2-methyl-1,4-pentadiene.[2] It is likely that the methylcyclobutane also formed in the thermolysis of 11 arises from a rapid reaction of (dmpe)PtHCl or its decomposition products with another molecule of 11. The reason for the formation of some methylenecyclobutane during low temperature silver ion-induced chloride ion abstraction from 11, while only a very small amount is formed over long times in the thermolysis of 1, is unclear. Perhaps the answer may lie in intermediates 2 and 12 being formed in different states of solvation or different conformations during their brief lifetime.

The ground state properties of the chelated pentenyl ligand appear to be representative of a general *cis*-(alkyl)-(alkene)metal species and should be a reasonable approximation to an insertion substrate, whether or not the chelated form would be observable. Independent of whether the internal insertions of the pentenyl ligand proceed by a "typical" transition state, *trends* in rates of reversible alkene insertions as a function of selected variables may be informative concerning the general nature of the transition states of these important reactions.

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## Experimental Section

**General Information.** NMR spectra were recorded on Bruker WP-270-SY, AM-360, and AC-F250 spectrometers. Chemical shifts are expressed in ppm ($\delta$); $^1$H and $^2$H shifts are downfield from tetramethylsilane (TMS) and TMS-$d_9$, respectively. $^{31}$P chemical shifts are reported downfield from 80% H$_3$PO$_4$. Platinum-coupled resonances are referred to as "triplets"; coupling constants (Hz) are the separation of the first and third peak. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

All syntheses of metal complexes were performed in flame- or oven-dried apparatus under an inert atmosphere (either dinitrogen or argon), which had been passed through a column of Aquasorb (Mallinkrodt indicating P$_2$O$_5$) and then through a column of BASF R3-11 catalyst to remove any traces of oxygen. All "glovebox" manipulations were performed in a Vacuum Atmospheres Model HE43-2 inert atmosphere box under nitrogen. Reactions involving silver salts were shielded from direct light.

The following solvents were distilled under nitrogen immediately before use. Diethyl ether (Et$_2$O), benzene, toluene, pentane, hexane, and tetrahydrofuran (THF) were each distilled from sodium/benzophenone. Dichloromethane and dimethylformamide (DMF) were distilled from calcium hydride, and acetone was distilled from potassium carbonate. Deuterated solvents to be used with metal complexes (deuterated benzene, dichloromethane, acetone, and toluene) were freeze-thaw degassed, dried over calcium hydride, and trap-to-trap distilled. Bis(dimethylphosphino)ethane (dmpe) was used as purchased.

**CH$_2$=CHCH$_2$CMe$_2$CD$_2$MgBr.** 2,2-Dimethyl-4-pentenal[33] was oxidized to CH$_2$=CHCH$_2$CMe$_2$CO$_2$H using a standard Jones reagent[34] (CrO$_3$ in H$_2$SO$_4$) in acetone (89%). The carboxylic acid was converted to CH$_2$=CHCH$_2$CMe$_2$COCl using oxalyl chloride (75%),[35] and this was reduced to CH$_2$=CHCH$_2$CMe$_2$CD$_2$OH using LiAlD$_4$ in ether (94%).[36] Treatment of the alcohol with Ph$_3$PBr$_2$ in DMF (distilled from calcium hydride) yielded CH$_2$=CHCH$_2$CMe$_2$CD$_2$Br (74%).[37] The bromide was prepared for the Grignard reaction by passing it down a column of active alumina and drying it overnight over molecular sieves. The reaction was initiated in either with C$_2$H$_4$Br$_2$ and employed 1.5 equiv of Mg turnings. Yields of the Grignard reagent were between 55 and 73%.

**CH$_2$=CHCD$_2$CMe$_2$CH$_2$MgBr.** Allyl-1,1-$d_2$ bromide was prepared by reduction of acryloyl chloride by LiAlD$_4$ in ether[38] followed by treatment of the alcohol with concentrated HBr.[39] $^1$H NMR integration indicated that the allyl bromide was 87% deuterium labeled in the allylic position and 13% in the vinyl position. This bromide was used with the enolate anion of the *tert*-butylimine of isobutyraldehyde according to the procedure of House to produce CH$_2$=CHCD$_2$CMe$_2$CHO.[3] The aldehyde was converted to the Grignard, CH$_2$=CHCD$_2$CMe$_2$CH$_2$MgBr, as described above for its isotopomer.

**(COD)Pt(CD$_2$CMe$_2$CH$_2$CH=CH$_2$)$_2$ (6-$\alpha$-$d_2$).** Similarly to the literature,[40] PtCl$_2$(COD)[41] (2 g, 5.3 mmol) was suspended in 20 mL of ether and the suspension was cooled to −78 °C. Then 2.2 equiv of the freshly prepared Grignard solution was added with stirring. The temperature was allowed to gradually rise to

ambient temperature over 6 h. Solids were allowed to settle, and the light brown supernatant was transferred via syringe to an ice-jacketed column packed with the following: 5 cm of silica gel, 15 cm of 4:1 silica gel:carbon (by weight), 5 cm of silica gel (column diameter = 3 cm). The yellow product was eluted with ether and collected under dinitrogen. Ether was removed under vacuum leaving a bright yellow oil; 1.7 g, 4.2 mmol (79%).

**(dmpe)Pt(CD$_2$CMe$_2$CH$_2$CH=CH$_2$)$_2$ (7-$\alpha$-$d_2$).** All of dialkyl 6 from previous reaction was dissolved in 10 mL of ether, and the solution was cooled to 0 °C. With stirring, slightly more than 1 equiv of dmpe was added via syringe. After a few minutes, solvent was removed and the sample was left under vacuum overnight; 1.9 g, 3.5 mmol (85%). $^1$H NMR (C$_6$D$_6$): $\delta$ 0.79 (m, PCH$_2$), 0.97 (td, $J_{PtH}$ = 18, $J_{PH}$ = 7, PCH$_3$), 1.37 (s, gem CH$_3$), 2.48 (d, $J_{HH}$ = 7, allylic CH$_2$), 5.17 (m, =CH$_2$), 6.37 (m, =CH−). $^{31}$P{$^1$H} (C$_6$D$_6$): $\delta$ 20 (t, $J_{PtP}$ = 1559).

**(dmpe)Pt(CD$_2$C(CH$_3$)$_2$CH$_2$CH=CH$_2$)Cl (8-$\alpha$-$d_2$).** Similar to a literature procedure,[42] a deficiency of anhydrous HCl in diethyl ether (12 mL of a 0.197 M solution; 2.4 mmol) was slowly added to a stirred solution of 7 (1.9 g, 3.5 mmol) in 20 mL of ether at −78 °C, and the mixture was allowed to warm to ambient temperature over 8 h. During this time, a white precipitate formed. The solvent was removed under vacuum, and unreacted dialkyl was removed by extraction of the residue with 3 × 20 mL of hexanes; yield (based on HCl) 1.1 g, 2.3 mmol (96%). $^1$H NMR (C$_6$D$_6$): $\delta$ 0.79 (m, PCH$_2$), 1.12 (td, $J_{PtH}$ = 50, $J_{PH}$ = 15, PCH$_3$), 1.23 (td, $J_{PtH}$ = 25, $J_{PH}$ = 15, PCH$_3$), 1.47 (s, gem CH$_3$), 2.57 (d, $J_{HH}$ = 7, allylic CH$_2$), 5.19 (m, =CH$_2$), 6.35 (m, =CH−). $^1$H NMR (acetone-$d_6$): $\delta$ 0.97 (s, CH$_3$), 1.37 (m, PCH$_2$), 1.53 (td, $J_{PtH}$ = 19, $J_{PH}$ = 10, PCH$_3$), 1.69 (td, $J_{PtH}$ = 47, $J_{PH}$ = 12, PCH$_3$), 2.15 (d, $J_{HH}$ = 7, allylic CH$_2$), 4.89 (m, =CH$_2$), 6.02 (m, =CH−). $^{31}$P{$^1$H} NMR: $\delta$ 15.2 (t, $J_{PtP}$ = 4148, P trans to Cl), 34.5 (t, $J_{PtP}$ = 1512, P trans to alkyl). Anal. Calcd for C$_{13}$H$_{29}$P$_2$ClPt: C, 32.67; H, 6.11. Found: C, 32.89; H, 6.21.

**[(dmpe)PtCD$_2$(CH$_3$)$_2$CH$_2$CH=CH$_2$]$^+$[BF$_4^-$] (1-$\alpha$-$d_2$).** A solution of 8 (480 mg, 1.0 mmol) in 10 mL of CH$_2$Cl$_2$ was cooled to −78 °C, and this was rapidly transferred by cannula to a solution of AgBF$_4$ (200 mg, 1.0 mmol) in 10 mL of CH$_2$Cl$_2$ also at −78 °C in a 40-mL centrifuge tube with a rubber septum and a magnetic stir bar. The mixture was stirred for 6 min, and then the tube was allowed to warm while being centrifuged for ca. $^1/_2$ h. The supernatant was cannulated into a Schlenk flask, and the solid residue was washed once with CH$_2$Cl$_2$. The solvent was removed from the combined organic phases under vacuum. The residue was crystallized from CH$_2$Cl$_2$/Et$_2$O to give an off-white solid: yield 394 mg, 0.75 mmol (75%). Vapor diffusion crystallization from CH$_2$Cl$_2$/ether resulted in the formation of small white needles, some of which were large enough for X-ray work. For $^1$H, $^{13}$C, and $^{31}$P NMR spectral assignments, see Table I. Assignments were made on the basis of $^{13}$C-DEPT, 2D-$^1$H,$^1$H-COSY, and $^{13}$C,$^1$H-HETCOR spectra. Anal. Calcd for C$_{13}$H$_{29}$F$_4$P$_2$BPt: C, 29.51; H, 5.52. Found: C, 29.79; H, 5.75.

**(dmpe)Pt(CH$_2$CMe$_2$CH$_2$CH=CH)I.** Complex 1 was treated with a 2-fold excess of KI in acetone at room temperature for 1 h. The solvent was evaporated, and the residual solid was extracted with benzene. The yield was generally ca. 25%. $^1$H NMR (C$_6$D$_6$): $\delta$ 1.05 (td, $J_{PtH}$ = 47, $J_{PH}$ = 11, PCH$_3$), 1.33 (td, $J_{PtH}$ = 18, $J_{PH}$ = 11, PCH$_3$), 1.43 (s, gem CH$_3$), 2.34 (tdd, $J_{PtH}$ = 70, $J_{PH}$ = 8 and 7, PCH$_2$), 2.51 (d, $J_{HH}$ = 7, allylic CH$_2$), 5.11 (m, =CH$_2$), 6.21 (m, =CH−), PCH$_2$ obscured. Anal. Calcd for C$_{13}$H$_{29}$P$_2$IPt: C, 27.43; H, 5.13. Found: C, 27.28; H, 5.19.

**X-ray Crystal Structure.** A crystal of the title compound was immersed in Paratone-N oil[43] in the glovebox, then brought out into air, and quickly mounted in a thin-walled glass capillary. Data were collected on a Siemens Ps$_1$ diffractometer at room temperature with graphite-monochromated molybdenum X-rays. The platinum atom was located from a Patterson map, and the rest of the non-hydrogen atoms were located from difference-

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Table III. Summary of Crystal Data and Refinement Results for 1

| space group | $P2_1/n$ (No. 14) |
|---|---|
| $a$ (Å) | 19.337(11) |
| $b$ (Å) | 6.948(4) |
| $c$ (Å) | 17.260(9) |
| $\beta$ (deg) | 122.34(6) |
| $V$ (Å$^3$) | 1959.3 |
| molecules/unit cell | 4 |
| fw | 529.2 |
| cryst dimens (mm) | 0.20 × 0.24 × 0.35 |
| calcd dens (g cm$^{-3}$) | 1.80 |
| abs coeff (mm$^{-1}$) | 70.5 |
| range in transm factor | 0.93–1.88 |
| wavelength (Å) used for data collcn | 0.710 69 |
| $(\sin\theta)/\lambda$ limit (Å$^{-1}$) | 0.6497 |
| total no. of reflns measd | 4445 |
| no. of ind reflns | 2495 |
| no. of reflns used in structural analysis $I > 3\sigma(I)$ | 1769 |
| no. of variable params | 190 |
| final agreement factor | $R(F) = 0.0418$ |

Table IV. Final Atomic Coordinates for 1

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Pt1 | 0.7383(1) | 0.2891(1) | 0.4724(1) |
| P2 | 0.6936(4) | 0.3299(9) | 0.5725(4) |
| P3 | 0.6251(4) | 0.1139(10) | 0.3881(4) |
| C4 | 0.7650(14) | 0.2380(44) | 0.3673(14) |
| C5 | 0.8559(15) | 0.1816(45) | 0.4105(18) |
| C6 | 0.9032(13) | 0.3349(41) | 0.4822(15) |
| C7 | 0.8717(14) | 0.3493(45) | 0.5487(20) |
| C8 | 0.8355(17) | 0.5080(42) | 0.5578(22) |
| C9 | 0.6164(19) | 0.1404(40) | 0.5420(20) |
| C10 | 0.5583(14) | 0.1292(43) | 0.4345(16) |
| C11 | 0.5573(13) | 0.1731(40) | 0.2686(13) |
| C12 | 0.6499(15) | −0.1380(36) | 0.3905(16) |
| C13 | 0.7681(15) | 0.3062(44) | 0.6993(15) |
| C14 | 0.6439(17) | 0.5547(36) | 0.5639(17) |
| C15 | 0.8717(15) | −0.0198(39) | 0.4467(19) |
| C16 | 0.8709(18) | 0.2086(54) | 0.3275(21) |
| F1 | 0.1664(12) | 0.1293(36) | 0.3217(16) |
| F2 | 0.0539(14) | 0.0214(37) | 0.1874(16) |
| F3 | 0.0426(15) | 0.1459(36) | 0.2995(16) |
| F4 | 0.0724(17) | 0.3203(39) | 0.2159(17) |
| B1 | 0.0896(42) | 0.1362(93) | 0.2622(44) |

Fourier maps.[44] The structure was subsequently refined by anisotropic full-matrix least squares to a final $R$ factor of 4.18%. Details of the structure analysis are summarized in Table III, atomic coordinates are listed in Table IV, and selected distances and angles are given in Table II. Other structural results are available as supplementary material.[45]

**Kinetics Experiments.** In the glovebox, solid 1-$\alpha$-$d_2$ (30–40 mg) was loaded into a 5-mm NMR tube with a glass joint. On the vacuum line, ca. 0.5 mL of solvent was condensed onto the sample. Thermolyses were conducted in nitromethane or methylene chloride; kinetic measurements were carried out in the latter solvent. The solution was degassed by three freeze/thaw cycles, and the tube was sealed by fusing the glass. The tube was fully immersed in an oil bath heated by refluxing solvent. Progress of the reaction was monitored by $^2$H NMR. After the label equilibration was complete (i.e. 1-$\alpha$-$d_2$:1-$\gamma$-$d_2$ was 50:50), the only insoluble solid in the tube was a very small amount of dark "dust". $^2$H NMR of 1-$\alpha$-$d_2$: $\delta$ 1.4 (t, $J_{PtD}$ = 11), 2.0 (s); both resonances due to diasteriotopic Pt–CD$_2$. $^2$H NMR of 1-$\gamma$-$d_2$: $\delta$ 1.8 (s), 2.6 (t, $J_{PtD}$ = 8); both resonances due to diastereotopic allylic CD$_2$. Rate constants and activation parameters are given in the Results.

**(Cyclobutylmethyl)magnesium Chloride.** This compound was synthesized according to the literature for related com-

pounds.[46] Cyclobutylmethanol (10.0 g, 116 mmol) was dissolved in a mixture of 120 mL of ether and tri(n-butyl)amine (28 mL, 140 mmol, dried over KOH). A solution of thionyl chloride (8.4 mL, 120 mmol) in 60 mL of ether was added dropwise to the cooled (0 °C) solution of alcohol over 1.5 h. After additional 1 h at 0 °C, the ether was removed by trap-to-trap distillation and the product was fractionally distilled through a 30-cm Vigreux column at reduced pressure; bp 40–43 °C (60 mmHg); yield 6.06 g, 58 mmol (50%). $^1$H NMR (CDCl$_3$): $\delta$ 1.7–2.2 (m, ring CH$_2$), 2.60 (m, ring CH), 3.51 (d, $J$ = 7, CH$_2$Cl). The Grignard reagent was prepared from the cyclobutylmethyl chloride in ether with iodine initiation. The mixture was filtered to yield 69 mL of a 0.52 M solution (62% yield).

**(COD)Pt(CH$_2$-c-C$_4$H$_7$)$_2$.** Freshly prepared (cyclobutyl-methyl)magnesium chloride (34 mmol in 65 mL of ether) was added to a stirred suspension of PtCl$_2$(COD)[41] in 200 mL of ether at –78 °C. After 30 min, the solution was warmed to 0 °C and stirred for 4 h. The dark amber solution was filtered and stored for 15 h over decolorizing carbon. The solution was concentrated under vacuum to a pale yellow oil which was crystallized by cooling to –20 °C; mp 42–44 °C; yield 3.9 g, 8.8 mmol (55%). $^1$H NMR (C$_6$D$_6$): $\delta$ 1.2–2.4 (m, COD allylic and ring CH$_2$), 2.80 (m, ring CH), 4.67 (t, $J$ = 40, =CH–).

**(dmpe)Pt(CH$_2$-c-C$_4$H$_7$)$_2$.** (COD)Pt(CH$_2$-c-C$_4$H$_7$)$_2$ (3.9 g, 8.8 mmol) was dissolved in 60 mL of ether at 0 °C, and a slight excess of dmpe was added by syringe. The mixture was stirred at 0 °C for 2 h and filtered. The filtrate was concentrated to ca. 10 mL and crystallized at –20 °C by addition of methanol to a point just short of turbidity (ca. 20 mL); mp 107–109 °C; yield 0.90 g, 1.9 mmol (21%). $^1$H NMR (C$_6$D$_6$): $\delta$ 1.03 (td, $J_{PtH}$ = 18, $J_{PH}$ = 8, PCH$_3$), 1.8–2.2 (m, ring CH$_2$), 2.42 (m, PtCH$_2$), 3.06 (m, ring CH). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 20.5 (t, $J_{PtP}$ = 1599). Anal. Calcd for C$_{16}$H$_{34}$P$_2$Pt: C, 39.73; H, 7.09. Found: C, 39.22; H, 6.78.

**(dmpe)Pt(CH$_2$-c-C$_4$H$_7$)Cl (11).** To a stirred solution of (dmpe)Pt(CH$_2$-c-C$_4$H$_7$)$_2$ (0.9 g, 1.9 mmol) in 80 mL of ether at –78 °C was added dropwise a 0.42 M ether solution of HCl (4.4 mL, 1.8 mmol). The mixture was allowed to warm slowly to ambient temperature over 15 h. The supernatant was decanted, and the white solid was washed (2 × 5 mL) with ether and then dried under vacuum; mp 101–104 °C; yield 0.59 g, 1.3 mmol (69%). $^1$H NMR (acetone-$d_6$): $\delta$ 1.31 (dtt, $J$ = 4.5, 7.7, $J_{PtH}$ = 55.4, Pt–CH$_2$), 1.45 (dt, $J_{PH}$ = 9.8, $J_{PtH}$ = 15, P–CH$_3$), 1.64 (dt, $J_{PH}$ = 11.3, $J_{PtH}$ = 49, P–CH$_3$), 1.52–1.70 (m, PCH$_2$), 1.88–2.03 (m, ring CH$_2$), 2.8–2.9 (m, ring CH). $^{31}$P{$^1$H} NMR: $\delta$ 15.7 (t, $J_{PtP}$ = 4112 Hz, P trans to Cl), 32.2 (t, $J_{PtP}$ = 1539 Hz, P trans to alkyl). Anal. Calcd for C$_{11}$H$_{25}$P$_2$ClPt: C, 29.35; H, 5.60. Found: C, 29.11; H, 5.51.

**Thermolysis of 11.** In the glovebox, solid 11 (15–25 mg) was loaded into an NMR tube, solvent was condensed onto the sample on the vacuum line, and the tube was sealed under vacuum. The tube was placed in an oil bath heated to 110 °C by refluxing toluene. The thermolyses were performed in acetonitrile, methylene chloride, acetone, and benzene, and were all complete in less than 1 h. In all cases substantial precipitate formed. The $^1$H NMR spectrum showed the presence of methylenecyclobutane and methylcyclobutane, which were identified by comparison with spectra of authentic materials. Standard methylenecyclobutane was a commercial sample. $^1$H NMR (CDCl$_3$): $\delta$ 1.91 (pentet, 2H, $J$ = 7.5, CH$_2$), 2.67 (tt, 4H, CH$_2$), 4.67 (pentet, $J$ = 2.5, =CH$_2$). Standard methylcyclobutane was prepared by conversion of commercial cyclobutylmethanol to its tosylate which was in turn reduced by LiAlH$_4$ in diglyme at 50 °C, with the volatile product collected in a –78 °C trap. $^1$H NMR (acetone): $\delta$ 1.00 (d, $J$ = 6.7, CH$_3$), 1.53 (m, 2H), 1.78 (m, 2H), 2.03 (m, 1H), 2.37 (m, 1H). No 1,4-pentadiene was seen in any of the thermolyses. The solid residue was intractable.

**Low Temperature Reaction.** In the glove box, a sample of 11 (30 mg, 6.7 mmol) and a slight deficiency of AgBF$_4$ were placed in a 5-mm amber NMR tube with an attached joint. The tube

(44) Most of the crystallographic computations were carried out using SHELX-76, an amalgamated set of crystallographic programs written by G. M. Sheldrick, Univeristy of Cambridge, U.K., 1976.

(45) See the paragraph at the end of this paper for a description of the supplementary material.

(46) Richey, H. G.; Hill, E. A. *J. Org. Chem.* 1964, 29, 421–423. Caserio, M. C.; Graham, W. H.; Roberts, J. D. *Tetrahedron* 1960, 11, 171–182.

was placed on the vacuum line, and 0.5 mL of $CD_2Cl_2$ was transferred by trap-to-trap distillation. The sample was shielded from direct light and kept in a bath of liquid nitrogen during the transfer. The tube was then sealed and placed in a –78 °C bath. After equilibration at –78 °C, the tube was shaken and was placed in the NMR probe which had been cooled to –80 °C. Spectra were taken periodically as the temperature of the NMR probe was slowly raised. There was no change seen until the probe temperature reached –25 °C, at which point resonances of an intermediate as well as those of methylenecyclobutane appeared. The alkyl region of the spectrum was very crowded, but the intermediate was assigned structure 13 on the basis of the comparison to resonances of closely parallel chemical shifts and coupling patterns for b, a, and c in 1 and the a and b resonances reported for 5.[2] The spectral fingerprint for methylenecyclobutane is distinctive (see Thermolysis of 11 above). Integrations indicated that 13 and methylenecyclobutane were formed in a 7:1 ratio. The phosphorus spectrum of 13 is also very similar to that for 1: $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 38 (td, $J_{PtP}$ = 1540, $J_{PP}$ = 7, P trans to alkyl), 37 (td, $J_{PtP}$ = 3682, P trans to alkene). This experiment was also done in acetone-$d_6$, but the sample was allowed to warm to 0 °C before the products were observed.

Methylenecyclobutane and 13 were seen in this solvent also. When the samples were allowed to warm to room temperature, they became very dark and murky and their spectra were ill-defined. Attempted transfer and cleanup of the solutions and attempted isolation of products met with no success. At no point was any 1,4-pentadiene detected.

**Supplementary Material Available:** A table of the final temperature factors (Table S1), complete listings of distances (Table S2) and angles (Table S3), and a table of calculated hydrogen positions (Table S4) for 1 (4 pages). Ordering information is given on any current masthead page.

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