on the WP-500. We also thank the California State University, Northridge, Foundation (E.R.), NATO (E.R. and L.M., Grant 1649/79), donors of the Petroleum Research Fund, administered by the American Chemical Society, and CNR (S.A., Grant 80.00311) for financial support and Johnson-Mathey for a generous loan of $RuCl_3 \cdot H_2O$.

Registry No. I, 56398-26-6; I-d_2, 91880-32-9; II, 91880-31-8; II-d_2, 91880-33-0; III, 41766-80-7; III-d_2, 80137-11-7; IV, 57673-31-1; IV′, 66973-03-3; V, 76721-83-0; V-d_2, 91897-70-0; V-d_3, 91880-34-1; $[(C_6H_5)_4As]^+[Ru_3(CO)_9(\mu_3\text{-}C_2\text{-}t\text{-}Bu)]^-$, 76741-75-8; CF_3COOD, 599-00-8.

Synthesis, Characterization, and Rearrangements of [(1-Methylcyclobutyl)methyl]platinum(II) Complexes. Very Mild Ring-Strain-Induced Carbon–Carbon Activation

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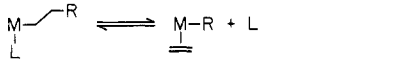
Complexes *trans*-$Pt(PMe_3)_2ClR$, where R = (1-methylcyclobutyl)methyl (mcbm, **1**), (adamantyl)methyl (adm, **8**), 4-methylpentyl-*1,1*-d_2 (**9**), and 4-methyl-4-pentenyl (**10**), and also PtCl(dmpe)(mcbm) [dmpe = 1,2-bis(dimethylphosphino)ethane] (**2**) have been prepared. Pyrolysis of **1** or **2** at 140 °C yields 2-methyl-1,4-pentadiene (**12**) as the only organic product, and *trans*-$HPt(PMe_3)_2Cl$ (**13**) is isolated in high yield in the case of **1**. Added PMe_3 retards the pyrolysis of **1**, leading to formation of $[HPt(PMe_3)_3]Cl$ (**14**) and exhibiting kinetics consistent with initial PMe_3 dissociation. Decomposition of **8** requires heating at 240 °C for hours. Pyrolysis of **9** at 140 °C forms **13** and 4-methyl-1-pentene-*1,1*-d_2 with very little rearrangement of the deuterium label. Treatment of **1** with Ag^+ in acetone at −80 °C forms [*trans*-$Pt(PMe_3)_2$(mcbm)(acetone)]$^+$ (**15**) that rearranges above −40 °C to {*cis*-$Pt(PMe_3)_2[1,4,5\text{-}\eta\text{-}(CH_2)_3C(Me)\!=\!CH_2]\}^+$ (**16**) and above −10 °C to a mixture of $[Pt(PMe_3)_2$(2–4-η-2-methylpentenyl)]$^+$ (**17a**) and $[Pt(PMe_3)_2$(1–3-η-2-methylpentenyl)]$^+$ (**17b**), which is isolated as the PF_6^- salt. Reaction of **1** with Ag^+ in CD_2Cl_2 at −80 °C leads within 30 min to direct formation of **16**, representing an extremely mild C–C activation step. Reaction of **10** with Ag^+ at −80 °C followed by warming to −20 °C also generates **16**. In contrast, **8** and Ag^+ from $[Pt(PMe_3)_2$(adm)(acetone)]$^+$ which is isolable at ambient temperature. Mechanistic implications of these reactions are discussed.

Introduction

Formation and cleavage of carbon–carbon bonds mediated by transition-metal complexes is a central subject of organometallic chemistry. The activation of saturated hydrocarbons by heterogeneous metal-based catalysts has been a common practice for many years now and can be achieved under remarkably mild conditions in some cases.[1] However, heterogeneous reactions generally are not particularly mild, they are not very selective, and mechanistic details are not readily accessible. Homogeneous reactions hold the promise of being highly selective and of being amenable to testing for mechanistic information that may ultimately be valuable in helping to understand surface reactions.

In our search for homogeneous models for reactions which are components of hydrocarbon reformation, we have become particularly interested in possible carbon-carbon bond activation reactions. A priori, there are a number of C–C bond breaking/forming reactions that could participate in reformation such as α- or β-alkyl eliminations/insertions, α–γ twofold C–H activation followed by rearrangement or reversible fragmentation of the resulting metallacyclobutanes, and direct bimolecular insertion of an unsaturated metal fragment into a saturated C–C bond, among others. We consider the last of these to be the least likely. Instead, we make the assumption that successful C–C activation will be a property of already metal-bound alkyl groups. We have chosen to focus initially on β-alkyl insertion/elimination chemistry (eq 1).



(1)

Since unsupported Pt is a modest reformation catalyst,[4] and since the synthetic chemistry of Pt alkyls is relatively well worked-out, we have begun our investigation using this metal. In view of the fact that beta-alkyl eliminations are so rarely postulated, we have chosen to initially seek examples of the reaction in that direction.

There are two difficulties in particular that must be overcome to observe β-alkyl elimination. One problem is the propensity for metal alkyls to undergo very facile β-H eliminations, usually irreversibly. In a system which would be catalytically active, the β-H elimination must necessarily

(1) A Ni film is reported[2] to catalyze the H/D exchange of propane with D_2 at −47 °C, and heptane is hydrogenolyzed to smaller hydrocarbons by Ru catalysts at 88 °C.[3]

(2) Kemball, C. *Proc. R. Soc. London, Ser. A* **1954**, *223*, 377–392.

(3) Carter, J. L.; Cusumano, J. A.; Sinfelt, J. H. *J. Catal.* **1971**, *20*, 223–229.

(4) Evidence suggests that in commercial "platforming" the metal component serves mainly to C–H activate, while the C–C rearrangements are largely carbonium ion chemistry catalyzed by acidic sites on the support.[5] Nevertheless, pure Pt will much more slowly catalyze reformation.[6]

(5) Sinfelt, J. H. In "Catalysis: Science and Technology"; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: New York, 1981; Vol. 1, pp 257–300.

(6) (a) Clark, J. K. S.; Rooney, J. J. *Adv. Catal.* **1976**, *25*, 125–183. (b) Anderson, J. R.; Baker, B. G. In "Chemisorption and Reactions on Metallic Films"; Anderson, J. R., Ed.; Academic Press: New York, 1971; Vol. II, pp 64–210. (c) Davis, S. C.; Klabunde, K. J. *Chem. Rev.* **1982**, *82*, 153–208. (d) Gault, F. G. *Adv. Catal.* **1981**, *30*, 1–95.

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be reversible. For the moment, however, we have chosen to circumvent this problem in our model studies by the exhaustive incorporation of β-alkyl groups.

A second problem that is anticipated to complicate the direct observation of β-alkyl elimination is the thermochemistry. The reaction of eq 1 is expected to have a heat of reaction of ca. +20 kcal/mol (C—C bond energy minus C=C π-bond energy) when L is alkene at an activity of ca. 1. Thus, to observe the elimination, one of three conditions must be met. (1) The bond strength of M–L must be extremely weak compared to that of M(alkene), or there must be no ligand L present. (2) If the alkene and L do not stably bind to the metal, as in a hypothetical unsaturated d^0 olefin polymerization catalyst, then the alkene must be removed in some way from the system to drive the equilibrium to the right. (3) Strain that would be relieved upon β-elimination must be incorporated into the alkyl group.

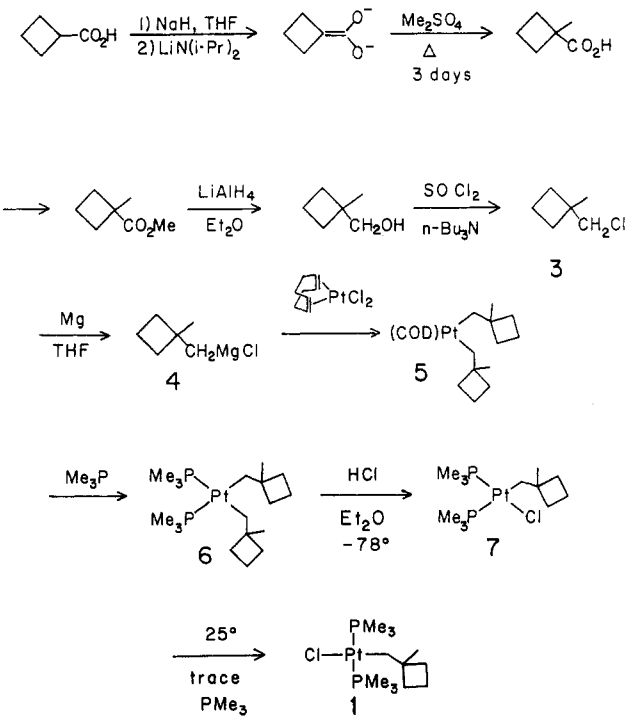
The second condition is probably responsible for the recently reported[7] β-alkyl elimination reaction of $(C_5Me_5)_2LuCH_2CHMe_2$. The complex is formally unsaturated, and the propene resulting from the β-methyl elimination is removed from the equilibrium by subsequent reactions. As expected for a d^0 complex, the M(alkene)R intermediate cannot be observed.

The third condition, ring strain, is clearly responsible for the very facile ring opening observed in the case of certain methylenecyclopropanes induced by Ni,[8] Pd,[9] Pt,[10] and Fe.[11] One particularly well-defined example is the reversible acid-catalyzed interconversion of certain butenyl- and (cyclopropylcarbinyl)(pyridine)cobaloxime complexes.[12] In most cases, however, the presumably initially formed (cyclopropylmethyl)metal complex is not observable. It is also to be noted that cyclopropanes are themselves sufficiently strained for their rings to be cleaved by certain metals.[13]

Two other examples of homogeneous reformation that appear to proceed via mechanisms formally related to a β-alkyl elimination are a set of rearrangements of dienes catalyzed by Ni hydrides[14] and alkyl migrations from carbon to iron in certain (5,5-dialkyl-cyclopentadiene)iron complexes catalyzed by $Fe_2(CO)_9$.[15]

In our initial work, we have operated on the obvious premise that in order to study β-alkyl elimination, one must first observe it. To do this, one may have to settle at first for some alkyl ligands that are not entirely typical. Then, observing the reaction, one can optimize conditions and reagents, subsequently using these to achieve activation of more typical alkyl substrates. We have attempted to favor β-elimination by the incorporation of ring strain.

Scheme I



β-Hydride elimination has been blocked, as mentioned above, by exhaustive alkylation. The contribution of this work beyond the studies of cyclopropylcarbinyl and methylenecyclopane complexes mentioned above is the use of the somewhat less strained (per C–C bond) and therefore somewhat more typical cyclobutylcarbinyl system, the characterization of the starting alkyl complexes, and the achievement of the ring opening in these complexes under very mild conditions. The following describes some of this initial work, including the preparation of **1** and **2** and some analogous complexes, and some of the chemistry of these relevant to carbon–carbon activation.[16]

Results

Preparations. Complex **1** was prepared as shown in Scheme I and complex **2** by a completely analogous procedure.[17]

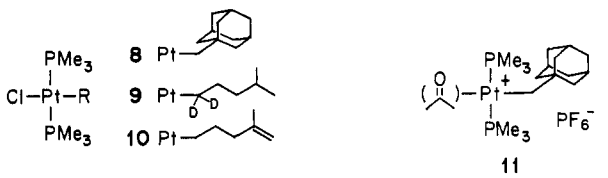
(Cyclobutylmethyl)lithium is known to ring open during preparation,[18a] but the Grignard reagent opens much more slowly.[18b] We saw no evidence of ring opening in **4** when the reagent was stored at −20 °C. It is well-known that monoalkylation of $Pt(COD)Cl_2$ (COD = 1,5-cyclooctadiene) is not practicable, so that it was necessary to dialkylate this material using the detailed and effective procedures of Whitesides and of Wilkinson[19] to produce **5**. The HCl

(7) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471–73.
(8) (a) Lehmkuhl, H.; Naydowski, C.; Benn, R.; Rufinska, A.; Schroth, G. *J. Organomet. Chem.* **1983**, *246*, C9–C12. (b) Binger, P.; Binkmann, A.; Wedemann, P. *Chem. Ber.* **1983**, *116*, 2920–30 and references therein. (c) Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780–81. (d) Noyori, R.; Ishigami, T.; Hayashi, N.; Takaya, H. *J. Am. Chem. Soc.* **1973**, *95*, 1674–76.
(9) (a) Noyori, R.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1969**, 525. (b) Green, M.; Hughes, R. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1880–89.
(10) (a) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1736–39. (b) Attig, T. G. *Inorg. Chem.* **1978**, *17*, 3097–3102.
(11) (a) Whitesides, T. H.; Slaven, R. W. *J. Organomet. Chem.* **1974**, *67*, 99–108. (b) Pinhas, A. R.; Samuelson, A. G.; Risemberg, R.; Arnold, E. V.; Clardy, J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 1668–75.
(12) Atkins, M. P.; Golding, B. T.; Bury, A.; Johnson, M. D.; Sellars, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3630–32.
(13) (a) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461–486. (b) Halpern, J. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II, pp 705–730.
(14) Miller, R. G., et al. *J. Am. Chem. Soc.* **1974**, *96*, 4211–20, 4221–29, 4229–34, 4235–43.
(15) Eilbracht, P.; Dahler, P. *Chem. Ber.* **1980**, *113*, 542–554.
(16) This work is taken from the Doctoral Dissertation of John A. Statler, University of Southern California, July 1982.
(17) An alternate preparation of ethyl 1-methylcyclobutanecarboxylate that employs hazardous $Ni(CO)_4$ has been reported: Diversi, P.; Rossi, R. *Synthesis* **1971**, 258–259.
(18) (a) Hill, E. A.; Richey, H. G.; Rees, T. C. *J. Org. Chem.* **1963**, *28*, 2161–62. (b) Hill, E. A.; Davidson, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 4663–69.
(19) (a) Whitesides, G. M.; Young, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 5808–15. (b) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–25. (c) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–28. (d) Bochmann, M.; Wilkinson, G.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1980**, 1879–87.

cleavage of 6 to form 7 is quite solvent dependent, reliably affording 7 only in ether at −78 °C; use of benzene, for example, yielded largely 6 and PtL_2Cl_2. In the case of 6, most of the cleavage product was the cis material 7, but addition of traces of PMe_3 led to rapid isomerization to 1. While 7 was not isolated, its ^1H NMR spectrum clearly showed the two triplets of doublets for the PMe_3 resonances characteristic of a *cis*-$Pt(PMe_3)_2XY$ complex. The higher field set of resonances is probably that of the PMe_3 trans to Cl, in analogy with the assignments for *cis*-$PtMeCl(PMePh_2)_2$.[20] Complex 2 exhibited a very similar pattern. The resonance of the platinum-bonded methylene group of the organic ligand in both 2 and 7 comprised a doublet of doublets of triplets, from coupling to two different phosphines and to platinum. Coupling to the trans phosphine was stronger than to the cis in each case, as observed, for example, in $Pt(NO_3)Me(diphos)$.[21]

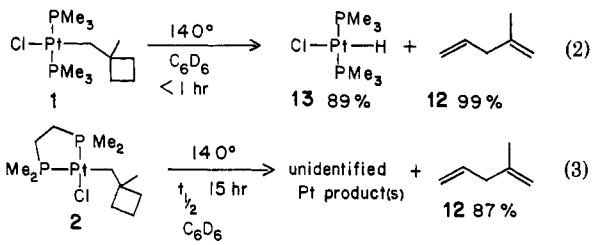
The ^1H NMR spectrum of complex 1 contained the PMe_3 resonance pattern of a 1:4:1 platinum-coupled triplet of phosphorus coupled virtual triplets. The chemical shift of the alkyl methyl group resonance was highly solvent dependent, appearing at δ 1.76 in benzene-d_6 and at δ 1.2 in acetone-d_6.

Additionally, *trans*-$PtRCl(PMe_3)_2$ complexes 8–10 were prepared in an analogous manner. The cationic acetone complex 11 was prepared by treatment of 8 with $AgPF_6$, much as has been done for other Pt complexes.[22] This could be isolated as a crystalline solid at ambient temperature but suffered slow decomposition in solution at that temperature.



11

High-Temperature Reactions. Complexes 1 and 2 were pyrolized at 140 °C in benzene-d_6 solvent and in toluene-d_8 with the same results. The outcome of these reactions is shown in eq 2 and 3. The only identifiable



organic product in either case was 2-methyl-1,4-pentadiene, 12, formed in high yield. Within the limits of ^1H NMR integration, 12 had not undergone any deuterium incorporation. Also formed in high yield in the case of 1 was *trans*-$PtClH(PMe_3)_2$, 13. No platinum hydride could be isolated from reaction of 2, but *cis*-PtClH(dmpe) would not be expected to be stable under such severe conditions.[23] The kinetics of these reactions were not well behaved, although at least initially the reaction of 2 appeared to be first order. In both cases autocatalysis set in. Thermolysis

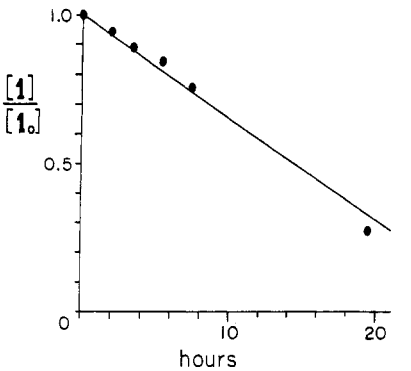
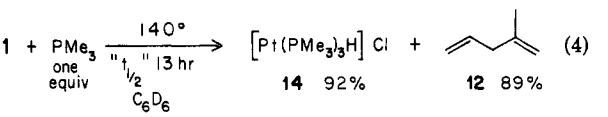


Figure 1. Plot of $[1]/[1_0]$ vs. time for the thermolysis of 1 as shown in eq 4.

of pure 1 always appeared homogeneous, and there was no effect of added Pt powder on either the nature of the products of the qualitative rate.

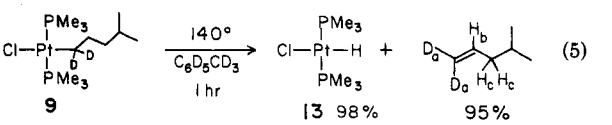
In an attempt to obtain better behaved kinetics and to examine the dependence of the rate on the presence of excess phosphine, the reaction of eq 4 was carried out by



using 1:1 $1/PMe_3$. Again, diene 12 was formed in high yield. The inorganic product in this case, however, was the white salt 14 that precipitated from solution as the reaction progressed. Its structure is presumably analogous to other known $HPtL_3^+$.[23,24] A good elemental analysis of this material could not be obtained, and the ^1H NMR spectrum varied considerably with solvent and temperature. A hydride resonance was visible in CD_3CN at 25 °C as a broad triplet with J_{PtH} = 623 Hz. The identity of this material was confirmed by independent synthesis from the instantaneous reaction of 13 and PMe_3 in benzene.

As indicated in eq 4, the pyrolysis of 1 is significantly inhibited by excess PMe_3. Progress of the reaction of eq 4 was followed by ^1H NMR, and a plot of $[PtR]/[PtR]_0$ vs. time was essentially linear, as shown in Figure 1. These results are interpreted in the Discussion. The ^1H NMR spectrum of a homogeneous solution of 1 and PMe_3 in toluene-d_8 at ambient temperature exhibits line broadening of the complexed PMe_3 and disappearance of the free ligand, indicating rapid ligand exchange. At −35 °C the ^{31}P NMR spectrum shows only resonances for starting materials; no trace of PtL_3RCl is visible. Inhibition of the pyrolysis reaction by association of PMe_3 would require that ca. 90% of such a material be present at 140 °C.

Attempts to pyrolize complex 8 in toluene-d_8 demonstrated its remarkable thermal stability. No reaction was observed after the mixture was heated for 35 h at 200 °C. Only after 24 h at 240 °C was the entire sample consumed. No attempt was made to determine the products. Pyrolysis of 9 yielded the results shown in eq 5. The relative ^1H NMR integrals of sites a:b:c in 4-methyl-1-pentene were 0.14:0.97:2.0, indicating very little scrambling during the β-hydride elimination.



Low-Temperature Reactions. We sought to generate species unsaturated, or at least very weakly coordinated

(20) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439.

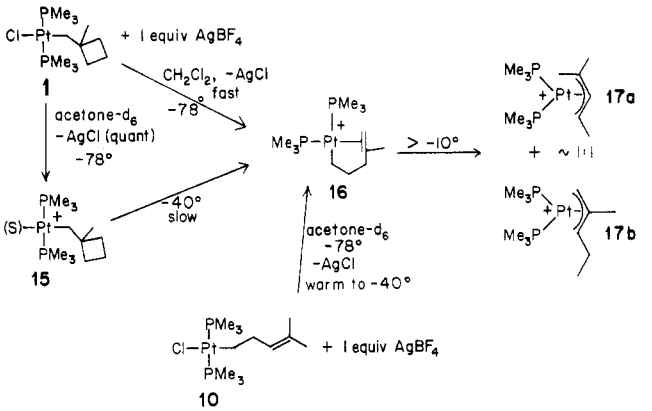
(21) Bennett, M. A.; Bramley, R.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1973**, 166–168.

(22) Chisholm, M. H.; Clark, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 1532–39.

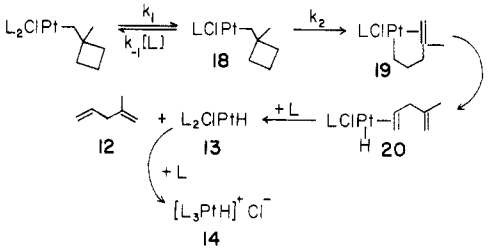
(23) (a) Clemmit, A. F.; Glockling, F. *J. Chem. Soc. A* **1969**, 2163–65. (b) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1976**, 365–366.

(24) (a) Clark, H. C., Dixon, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 596–599. (b) Roundhill, D. M. *Adv. Organomet. Chem.* **1975**, *13*, 273–361.

Scheme II



Scheme III



at Pt by abstraction of Cl^- by Ag^+, as has been done by others.[22] The first attempt was with **1** in acetone-d_6 at −78 °C (Scheme II). A gray precipitate of AgCl formed quantitatively over a period of several hours. ^1H NMR spectra were generally broad at −80 °C but clearly contained only the *trans*-$Pt(PMe_3)_2XY$ pattern and included a shoulder for the aliphatic methyl group. Warming to ca. −50 °C sharpened the spectrum to reveal the distinct triplet-of-triplet PMe_3 pattern. Also evident was the continued presence of the CH_3 resonance of the organic ligand. The AgCl precipitate could be separated at low temperature with only minor rearrangement of the complex. We assign this complex the structure **15**, wherein the bonding mode of the acetone ligand is not certain. Confidence in this assignment is enhanced by previous reports of analogous acetone complexes such as [*trans*-$PtMe(PMe_2Ph)_2(acetone)]^+ PF_6^-$[22] and by the fact that we were able to convert **8** into the stable isolable **11** in a completely analogous way.

Warming **15** to ca. −40 °C resulted in its slow rearrangement to a material that appeared to possess the doublet-of-doublets in its ^1H NMR spectrum expected for a *cis*-$Pt(PMe_3)_2XY$ species, but the platinum coupling patterns were obscured by the broad nature of the spectrum and by residual **15**. Also evident were resonances in the olefinic region. This material was tentatively assigned the structure of the chelated olefin complex **16**, the presumed ring-opened intermediate. This assignment was later confirmed by preparation of the complex from **1** in CD_2Cl_2 and from **10** in acetone. Further warming to −10 °C led to formation of material that was purified with some effort and was determined to be an approximately 1:1 mixture of two isomeric cationic platinum allyl complexes **17a** and **17b** (see Experimental Section) that we were unable to separate. Heating the sample to 40 °C did not change the a-to-b ratio.

In a similar experiment, **1** was treated with $AgPF_6$ in CD_2Cl_2 at −78 °C. AgCl precipitation appeared to be complete within 15 min, immediately after which the first ^1H NMR spectrum was recorded. The PMe_3 region was broad and difficult to interpret, but olefinic resonances centered at δ 4.75 were apparent. These resonances persisted as the temperature was increased to ca. −20 °C. At −20 °C the spectrum clearly showed a *cis*-$Pt(PMe_3)_2XY$ pattern for the PMe_3 resonances (see Experimental Section). The olefinic region was consistent with the spectral assignments for **16** but was not completely resolved. At ambient temperature the sample showed only resonances for the **17a,b** mixture.

One final experiment involved treatment of the open-chain alkenyl-ligated complex **10** with $AgPF_6$ in acetone-d_6 at −78 °C. The proton spectrum was too broad to interpret at this temperature, but by −40 °C the spectrum of **16** was evident. The olefinic region was relatively well resolved in this sample, and assignments were consistent with this structure. Confidence in these assignments comes from the similarity of the spectrum of **16** to the very well-resolved olefinic resonances of [Pt(dmpe)(1,4,5-η-$CH_2C(Me_2)CH_2C(Me)=CH_2$]$^+$ that is chelated via olefin coordination to Pt.[25] Nevertheless, there was sufficient noise and overlapping of the resonances at δ 4.6 and 4.9 that J_{PtH} for the resonance at δ 4.9 could not be reliably assigned. Subsequent warming of the sample above −20 °C formed **17a** and **17b**.

Discussion

As mentioned in the Introduction, a clean acid-catalyzed rearrangement of a (cyclopropylcarbinyl)bis(dimethylglyoximato)(pyridine)cobalt(III) system to the butenyl complex has been reported[12] which is analogous to that presented herein. In addition, numerous examples where methylenecyclopropanes, including substituted ones such as Feist's esters, are rapidly ring opened upon interaction with complexes of Ni,[8] Pd,[9] Pt,[10] and Fe[11] have appeared. However, in none of these latter cases was a (cyclopropylmethyl)metal complex detected. Generally the $M(CH_2CH_2CH=CH_2)$ intermediates expected from most of the above reactions are also not observable. They tend to isomerize directly to π-allyl species or to proceed to other products.

Nevertheless, it is important to point out that interaction of a strained hydrocarbon with a metal center does not guarantee that ring opening will occur.[26] Often the major products of Ni-catalyzed reactions that incorporate methylenecyclopropanes contain intact cyclopropyl groups.[8] Also, a number of stable methylenecyclopropane complexes of Pt, Ir, and Rh have been reported,[27] as have stable π-cyclopropene,[28] σ-cyclopropyl,[29,32] π-cyclobutene,[30,31] and σ-cyclobutyl[30] complexes of these and other metals. A π-allyl complex has even been isolated from the interaction of $PdCl_2$ with Dewar benzene without ring opening.[32] In

(25) This material has been synthesized and characterized in our laboratories: Steven P. Bitler, Doctoral Dissertation, University of Southern California, Jan 1984.

(26) Recently, transient "$(C_5Me_5)Ir(PMe_3)$" generated photochemically has been reported to insert only into the C–H bond of cyclopropane; no C–C insertion was observed: Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–39.

(27) Green, M.; Howard, J. A. K.; Hughes, R. P.; Kellett, S. C.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 2007–14.

(28) (a) Visser, J. P.; Schipperijn, A. T.; Lucas, J. *J. Organomet. Chem.* **1973**, *47*, 433–438. (b) Fredericks, S.; Thomas, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 350–351.

(29) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732–35.

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any event, there are clearly factors that determine the facility of ring opening in various systems, the precise nature of which remains to be delineated.

The present (cyclobutylcarbinyl)Pt system represents a compromise among the needs to incorporate the least possible strain, to keep the organic ligand as simple as possible, and to maximize the chances of *observing* the C–C activation. In connection to the need to minimize ring strain, we have been unable to find examples of any metal-mediated ring opening of a monocyclic cyclobutane or cyclobutene. This and other observations (see below) lead us to believe that the cyclobutylcarbinyl ligand is probably significantly closer to being a model for a normal alkyl ligand than is the cyclopropylcarbinyl group.

A reasonable path for the high-temperature reactions of eq 2–4 is exemplified for **1** in Scheme III. This scheme would yield a rate law as in eq 6. If the first step were

$$\frac{-d[1]}{dt} = \frac{k_1 k_2 [1]}{k_{-1}[L] + k_2} \qquad (6)$$

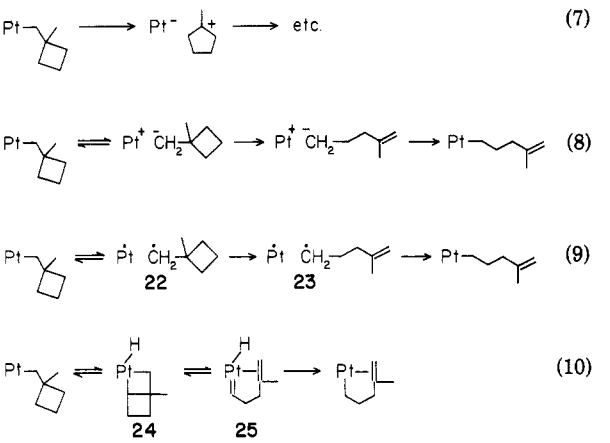
rapidly reversible, i.e., if $k_{-1}[L] >> k_2$, then the rate would be $(k_1k_2/k_{-1})([1]/[L])$. Thus, if ligand L were added so that $[1]_0 = [L]_0$, then product **13** would consume L to form **14** at the same rate that **1** would disappear, and [1] = [L] at all times. The rate would then be k_1k_2/k_{-1}, or zero order, as was observed in the experiment of eq 4.

The pyrolysis of eq 5 gives an indication of why the less stable unconjugated isomer of **12** is the only observed organic product. Very little reversible hydride addition in **20** to form a secondary Pt(alkyl) must be occurring since pyrolysis of **9** yields 4-methyl-1-pentene-*1,1-d*$_2$ with so little isotopic scrambling. Apparently, attack upon **20** by PMe_3 to form **12** and **13** must be quite rapid. This result is surprising in light of the observations of Whitesides and co-workers that pyrolysis of $Pt(PEt_3)_2(CD_2CH_2CH_2CH_3)_2$ resulted in formation of butane and butene in which the label was randomly distributed.[33]

Our low-temperature data are consistent with the sequence already presented in Scheme II. It seems unlikely that Ag^+ is playing any role in the ring opening of **15** to form **16**. Complex **1** was treated with 0.5 equiv of $AgPF_6$, followed by several hours at −78 °C to allow complete precipitation of AgCl, and then the solution of **15** was decanted from the precipitate at −78 °C. Subsequent warming of this solution revealed no change in the behavior of **15** compared to other reactions carried out in the continuous presence of stoichiometric amounts of Ag^+.

It is interesting to compare the fate of **19** with that of **16**. An intermediate such as **20** is presumably formed from **19**. The good nucleophile PMe_3, originally dissociated from **1**, probably displaces diene **12** from platinum in complex **20**. Complex **16** presumably leads to an intermediate such as $[Pt(PMe_3)_2(4,5\text{-}\eta\text{-}CH_2{=}CMeCH_2CH{=}CH_2)H]^+$, **21**. In this case there is no good nucleophile present, so **21** has time to rearrange to the mixture of π-allyl complexes **17a** and **17b**.

Rearrangements **18** to **19** and **15** to **16** are the key steps in this work. They appear to be β-alkyl eliminations, but other paths are possible. The most obvious alternative mechanisms are listed in eq 7–10. A carbonium ion dissociation might occur (eq 7), especially from cation **15**, but anchimeric assistance would clearly be expected.[34] In this



case, substantial quantities of products that are derivatives of cyclopentane should be observed. No such products can be detected.

A carbanion mechanism (eq 8) seems quite unreasonable since organoplatinum complexes do not react as carbanions. They are stable to water and relatively stable to air. Strong acid is required for protonolysis. This covalency is to be contrasted with the behavior of the highly ionic (cyclobutylcarbinyl)lithium reagent, which rapidly rearranges to pentenyllithium during its formation at ambient temperature.[18a]

A radical path (eq 9) is also possible, wherein complex **15** or **18** might suffer homolysis to form radical pair **22**. While the total ring strain of the cyclobutylcarbinyl radical is approximately the same as that of cyclopropylcarbinyl radical, the strain per ring–C–C bond is significantly less in the former. This difference in distribution of strain is reflected in the relative rate constants for ring opening/closing rearrangements; cyclopropylcarbinyl–butenyl radicals, k(opening, 25 °C) = 1.3×10^8 s^{-1}, irreversible under accessible conditions;[35] cyclobutylcarbinyl–pentenyl radicals, k(opening, 25 °C) = 5.0×10^2 s^{-1}, estimated k(cyclization, 60 °C) = ca. 10^{-1} s^{-1}.[36] These are to be compared with the "normal" hexenyl–cyclopentylcarbinyl radicals; k(cyclization, 25 °C) = 2.5×10^5 s^{-1}, irreversible under accessible conditions.[37] Parenthetically, this intermediate behavior of the cyclobutylcarbinyl–pentenyl radical suggests that this system is closer to being a reasonable model for a typical aliphatic group than is the cyclopropylcarbinyl group. In any event, because of the relatively slow rate of ring opening of the cyclobutylcarbinyl radical, it is highly unlikely that it would have a long enough lifetime to rearrange to pentenyl radical and then to quantitatively recombine with the Pt(I) fragment as required by the mechanism of eq 9 without suffering extensive coupling, disproportionation, and hydrogen transfer from solvent (particularly from toluene-d_8). These latter reactions are expected to be extremely fast,[38] and yet none of the corresponding products are observed.

The scheme of eq 9 is rendered even less likely by the results of the pyrolysis of **8** and by the isolation of **11**. Since cyclobutylcarbinyl radical is known to have a finite existence, its formation cannot be anchimerically assisted. The homolysis of **1** should have the same kinetic properties as that of any analogous alkyl complex, including **8**; i.e.,

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the rates of alkyl dissociation of 1 and 8 should be similar. In fact, the pyrolysis of 1 was complete in less than 1 h at 140 °C, while pyrolytic decomposition of 8 required a day at 240 °C. Similarly, rearrangement of 16 requires several hours at −40 °C, while 11 is isolable and reasonably stable at ambient temperature. It therefore seems highly unlikely that the reaction paths of 1 and 8 or of 16 and 11 would be same. We conclude that while homolysis may or may not operate for 8 or 11, it does not operate in the case of 1 or 16.

One other possible path is that proceeding via γ-C–H activation (eq 10). The ability of coordinatively unsaturated Pt(II) to undergo intramolecular oxidative addition of C–H bonds in the 3-, 4-, or 5-position of alkyl ligands has been meticulously documented by Whitesides and his co-workers.[19b,39] Intermediate 24 would result if 18, for example, were to undergo such activation. While platinacyclobutanes are generally very resistant to ring cleavage,[40] rearrangement to 25 might be quite facile because of the additional strain of the cyclobutane moiety. Subsequent hydride migration would complete a plausible path. While 24 at first glance looks too strained to be accessible, it probably is energetically feasible. Whitesides and co-workers have demonstrated that platinacyclobutane possesses less than 5 kcal/mol of strain energy,[39] and best estimates place the excess strain in bicyclo[2.2.0]hexane (that in excess of twice the strain energy of cyclobutane) to be only ca. 1 or 2 kcal/mol.[41] The excess strain of bicyclo[3.2.0]heptane, probably a better model for 24, is nil. Thus, the ring strain that would accrue in the formation of 24 from 18 should be significantly less than 6 or 7 kcal/mol. At this time, we cannot distinguish between the β-alkyl elimination and the γ-C–H activation paths.

Conclusions

We have found that [(1-methylcyclobutyl)methyl]-$PtCl(phosphine)_2$ complexes are stable materials that can readily be isolated and purified. If a vacant coordination site is generated by thermal dissociation of a phosphine or by Ag^+ abstraction of Cl^- at low temperature, carbon–carbon bond activation becomes very facile. If the chloride abstraction is carried out at −80 °C in CD_2Cl_2, the rearrangement is complete in less than 30 min. We cannot yet determine if the reaction is a direct β-alkyl elimination or whether it involves a γ-C–H activation. The facility of this reaction is to be contrasted with the rearrangements of (cyclobutylmethyl)MgX and (cyclobutylmethyl)BR_2 that have rate constants of 4.5×10^{-6} s^{-1} in THF at 61.6 °C[18b] and 4×10^{-6} s^{-1} in triglyme at 100 °C,[42] respectively. Since the boron center has a vacant coordination site and the Grignard reagent has an incipient acidic orbital present, additional factors must contribute to the especially high reactivity of the platinum complexes. One of these may be the relatively strong platinum–alkene bond that is presumably forming in the transition state, if the reaction is indeed a β-alkyl elimination.

Our efforts are continuing toward distinguishing between the two likely paths for this carbon–carbon activation and toward other examples of such activation of more representative alkyl ligands.

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Experimental Section

General Comments. NMR spectra were recorded on Varian T60, XL-100 FT, or XL-200 FT spectrometers or on Bruker 80- or 500-MHz spectrometers; chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane for both ^1H and ^{13}C spectra and from 80% H_3PO_4 for ^{31}P spectra; all coupling constants are apparent, not calculated, with absolute values reported in hertz. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer. Melting points were determined with a Thomas-Hoover apparatus and, unless otherwise noted, were for samples in evacuated, sealed tubes and are uncorrected. Gas chromatographic analyses were performed on a 0.5 m × $^1/_8$ in. 10% UCW982 column on a Hewlett-Packard 5730A GLC.

All reactions involving organometallic compounds were carried out under an atmosphere of nitrogen purified over reduced copper catalyst and in flamed-out glassware, using standard Schlenk techniques, or in a Vacuum Atmospheres dinitrogen atmosphere box. All metal-containing reactions and samples were shielded from direct light. THF, Et_2O, and toluene were distilled from purple solutions of sodium/benzophenone. Hexane was distilled from sodium/potassium/benzophenone. Deuterated solvents and phosphines were obtained commercially. $PtCl_2(COD)$[19c] and *cis*-$(adamantylmethyl)_2Pt(PMe_3)_2$[19d] were prepared by literature methods.

[(1-Methylcyclobutyl)methyl]magnesium Chloride (4). 1-Methylcyclobutanecarboxylic acid was prepared by a procedure developed by Mrs. Liung-Chu Lee Bao in our laboratories. Diisopropylamine (distilled under N_2 from KOH, 43 mL, 0.31 mol) was added dropwise to a suspension of NaH (13.0 g, 0.33 mol) in 300 mL of THF. Cyclobutanecarboxylic acid (27.4 g, 0.27 mol) was added, and the slurry was cooled to 0 °C. A 2.45 M solution of *n*-BuLi in hexane (140 mL, 0.34 mol) was added dropwise with mechanical stirring, followed by gradual warming to ambient temperature. After cessation of gas evolution, the mixture was heated at reflux for 2 h, and then Me_2SO_4 (37 mL, 0.39 mol) was added dropwise at 0 °C. This mixture was heated at reflux for 3 days and cooled to 0 °C, and H_2O was added dropwise until no solid remained (ca. 250 mL). Et_2O (150 mL) was added to the separated organic layer, and this was washed with H_2O (3 × 50 mL). The combined aqueous layers were washed with Et_2O (3 × 50 mL). The aqueous phase was acidified to pH 2 with concentrated HCl and extracted with Et_2O (4 × 50 mL). The combined Et_2O fractions were dried ($MgSO_4$) overnight, the solvent was removed, and the crude product was trap-to-trap distilled at ca. 50 °C. The product (20.9 g) contained ca. 10% starting acid (subsequent GLC analysis of the esters). ^1H NMR spectrum agreed well with that reported in the literature.[17]

The mixture of the two acids was converted to the methyl esters by the standard Fischer esterification, and this mixture was separated by distillation through a Teflon annular spinning band column, using decane as a chaser. The product, bp 129–133 °C (758 mm), amounted to 6.5 g (51 mmol, 19%) and contained no GLC-detectable methyl cyclobutanecarboxylate: ^1H NMR (C_6D_6) δ 1.36 (s, 3 H), 1.6–1.9 (complex, 4 H), 2.3–2.7 (complex, 2 H), 3.40 (s, 3 H).

A standard $LiAlH_4$ reduction of methyl 1-methylcyclobutanecarboxylate (33.8 g, 0.26 mol) in Et_2O resulted in formation of 19.2 g (0.19 mol, 73%) of (1-methylcyclobutyl)methanol: bp 74–77 °C (43 mm), >99% pure by GLC; ^1H NMR spectrum agreed well with that reported in the literature.[43]

Preparation of 1-methyl(chloromethyl)cyclobutane, 3, was similar to literature procedures.[44] Product amounted to 4.1 g (61%): bp 38–40 °C (45 mm); 97% pure (GLC); ^1H NMR agreed well with that reported in the literature.[43]

Approximately 3 mL of a solution of alkyl chloride 3 (6.1 g, 52 mmol in 5 mL of THF) was added to 1.98 g of Mg turnings, and reaction was initiated with 1,2-dibromomethane. An additional 6 mL of THF was added to the solution of 3, and this was added to the Mg over 30 min. After an additional 15 min at reflux, the THF was removed under vacuum, and the residue was dissolved in ca. 15 mL of benzene, producing 19 mL of a 0.87 M

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solution (32% yield) of **4**. If the residue is more thoroughly dried, it is soluble in Et_2O. This reagent is a disolvate: ^1H NMR (C_6D_6) δ 0.50 (s, 2 H), 1.28 (br, 8 H, THF), 1.60 (s, 3 H), 1.6–2.1 (complex, 2 H), 2.16 (br, 4 H), 3.71 (br, 8 H, THF).

(1,5-Cyclooctadiene)bis[(1-methylcyclobutyl)methyl]-platinum(II) (5). In analogy with published procedures,[19] a suspension of $PtCl_2$(COD) (1.10 g, 2.94 mmol) in 50 mL of Et_2O was cooled to −78 °C, and 31.2 mL of a 0.20 M solution of **4** was added. This was stirred at −78 °C for 15 min and then at 0 °C for 6 h. Grignard reagent in benzene is also adequate but requires longer reaction times. The brown solution was chromatographed through a column composed of a 5-cm layer of silica gel, a 15-cm layer of 1:3 charcoal/silica gel (by weight), and another 5-cm layer of silica gel, with the column cooled to 0 °C. Elution with Et_2O, solvent removal, and vacuum drying afforded **5** as a yellow oil that crystallized as a pale yellow solid from Et_2O/MeOH in 54% yield (0.75 g, 1.6 mmol): mp 58–59 °C ^1H NMR (C_6D_6) δ 1.52 (s, 6 H), 1.66–2.20 (complex, 20 H), 2.28 (t, 4 H, J_{PtH} = 92 Hz), 4.78 (t, 4 H, J_{PtH} = 38 Hz).

***cis*-Bis[(1-methylcyclobutyl)methyl]bis(trimethylphosphine)platinum(II) (6).** In analogy with a published procedure,[19] PMe_3 (0.35 mL, 3.6 mmol) was added dropwise to a solution of **5** (0.75 g, 1.6 mmol) in 15 mL of Et_2O at 0 °C. The solution was stirred for 6 h at 0 °C, and then the solvent was removed. The solid was washed with MeOH and crystallized from Et_2O/MeOH producing 0.65 g of **6** (1.14 mmol, 72%): mp 53 °C; ^1H NMR (C_6D_6) δ 1.02 (dt, 18 H, J_{PtH} = 18, J_{PH} = 7 Hz), 1.64 (t, 6 H, J_{PtH} = 6 Hz), 1.7–2.2 (complex, 12 H, $PtCH_2$ obscured), 2.3–2.6 (complex, 4 H).

***trans*-Chloro[(1-methylcyclobutyl)methyl]bis(trimethylphosphine)platinum(II) (1).** Similar to a published procedure,[45] 4.70 mL of a 0.292 M solution of HCl in Et_2O (1.4 mmol) was added dropwise to a stirred solution of **6** (0.70 g, 1.4 mmol) in 20 mL of Et_2O at −78 °C, and this was stirred overnight at −78 °C. The mixture was warmed to ambient temperature, solvent was removed, and the solid was washed with 5 mL of Et_2O. The residue was extracted with benzene, and this solution was decanted from residual $PtCl_2(PMe_3)_2$. Some trans isomer could not be separated from the predominantly cis material: ^1H NMR (C_6D_6) δ 0.97 (dt, 9 H, J_{PtH} = 44, J_{PH} = 10 Hz), 1.09 (dt, 9 H, J_{PtH} = 15, J_{PH} = 9 Hz), 1.62 (s, 3 H), 2.0–2.4 (complex, 6 H, $PtCH_2$ obscured), 2.6–2.9 (complex, 2 H). Then 0.02 mL of PMe_3 was added to the benzene solution of the two isomers, and after 1 h, the solvent was removed under vacuum. The residue was washed with Et_2O (2 × 5 mL) and vacuum dried, yielding 0.52 g (1.1 mmol, 82%) of **1**: mp 168 °C; ^1H NMR (C_6D_6, 200 MHz) δ 1.29 (tt, 18 H, J_{PtH} = 28, J_{PH} = 4 Hz), 1.49 (t, 3 H, J_{PtH} = 11 Hz), 1.67 (br, 2 H), 1.76 (tt, 2 H, J_{PtH} = 103, J_{PH} = 9 Hz), 1.9–2.3 (complex, 4 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −14 (t, J_{PtP} = 2908 Hz). Anal. Calcd for $PtClP_2C_{12}H_{29}$: C, 30.94; H, 6.27. Found: C, 30.87; H, 6.59.

[1,2-Bis(dimethylphosphino)ethane]bis[(1-methylcyclobutyl)methyl]platinum(II). By the same procedure as used to prepare **6**, **5** was treated with a slight excess of dmpe. After solvent removal, the residue was crystallized from MeOH by cooling a saturated solution to 0 °C. Vacuum drying yielded 0.22 g (52%) of product: mp 65–66 °C; ^1H NMR (C_6D_6) δ 0.7–1.5 (complex, PCH_2), 1.08 (dt, 12 H, J_{PtH} = 20, J_{PH} = 8 Hz), 1.68 (s, 6 H), 2.0–2.6 (complex, ca. 12 H), 2.34 (ddt, ca. 4 H, J_{PtH} = 78, $J_{P(trans)H}$ = 11, $J_{P(cis)H}$ = 7 Hz).

Chloro[1,2-bis(dimethylphosphino)ethane][(1-methylcyclobutyl)methyl]platinum(II) (2). This was carried out as in the HCl cleavage of **6** to form **1**, except that Pt(mcbm)$_2$(dmpe) required only 6 h at −78 °C. Product was crystallized from benzene/Et_2O and dried under vacuum, yielding 0.15 g (76%) of **2**: mp 137–138 °C dec; ^1H NMR (C_6D_6) δ 0.4–1.0 (complex, PCH_2), 1.05 (dt, 6 H, J_{PtH} = 47, J_{PH} = 11 Hz), 1.16 (dt, 6 H, J_{PtH} = 15, J_{PH} = 10), 1.76 (s, 3 H), 2.1–2.3 (br, 4 H), 2.13 (ddt, 2 H, J_{PtH} = 59, $J_{P(trans)H}$ = 8, $J_{P(cis)H}$ = 5 Hz), 2.6–2.8 (complex, 2 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 33 (t, P cis to Cl, J_{PtP} = 1494 Hz), 15 (t, P trans to Cl, J_{PtP} = 4067 Hz). Anal. Calcd for $PtClP_2C_{12}H_{27}$: C, 31.07; H, 5.87. Found: C, 30.82; H, 5.78.

***trans*-Chloro(adamantylmethyl)bis(trimethylphosphine)platinum(II) (8).** By the same procedure as for **1**, 1.82 g (2.8 mmol) of *cis*-(adamantylmethyl)$_2$Pt(PMe$_3$)$_2$[19d] was cleaved with HCl in Et_2O. The precipitate was filtered in air and washed with 30 mL of Et_2O at 0 °C. Some cis isomer was present, so the sample was treated with 0.05 mL of PMe_3 in benzene. The supernatant was separated from some insoluble material, the solvent was removed, and the solid was vacuum dried to yield 1.09 g (2.1 mmol, 73%) of **8**: mp 260–262 °C; ^1H NMR (C_6D_6) δ 1.28 (tt, 18 H, J_{PtH} = 29, J_{PH} = 4 Hz), 1.53 (tt, 2 H, J_{PtH} = 85, J_{PH} = 9 Hz), 1.70–1.85 (br m, 12 H), 1.90–2.05 (br m, 3 H); $^{31}P\{^1H\}$ (C_6D_6) δ −14 (t, J_{PtP} = 2897 Hz). Anal. Calcd for $PtClP_2C_{17}H_{35}$: C, 38.38; H, 6.63. Found: C, 37.76; H, 6.67.

***trans*-Chloro(1,1-dideuterio-4-methylpentyl)bis(trimethylphosphine)platinum(II) (9).** Methyl 4-methylpentanoate was reduced in Et_2O by $LiAlD_4$ by standard techniques. The physical constants and spectra of 1,1-dideuterio-4-methylpentan-1-ol matched well with literature values[46] for the d_0 material, except that the δ 3.50 triplet was absent from the ^1H NMR. This alcohol was converted by reaction with PBr_3[47] to 1-bromo-1,1-dideuterio-4-methylpentane (lit.[48] for d_0 material): bp 34 °C (12 mm); ^1H NMR ($CDCl_3$) δ 0.94 (d, 6 H, J = 6 Hz), 1.2–1.7 (complex, 3 H), 1.90 (t, 2 H, J = 7 Hz); no resonance observable at lower field. A 0.86 M solution of Grignard reagent (80% yield) was prepared from the bromide in Et_2O.

The PtR_2(COD) derivative was prepared as for the others, from 1.03 g of $PtCl_2$(COD) and the above Grignard reagent. The product was an oil and so was treated directly with 0.75 mL (7.7 mmol) of PMe_3 in 20 mL of Et_2O at 0 °C for 4 h. Removal of solvent yielded a paste (0.46 g, ca. 0.88 mmol, 32% overall) that could not be crystallized but exhibited a ^1H NMR spectrum consistent with the structure *cis*-Pt[$CD_2CH_2CH_2CH(CH_3)_2$]$_2$-(PMe$_3$)$_2$: δ (C_6D_6) 1.12 (dt, J_{PtH} = 17, J_{PH} = 8 Hz), the remainder of the spectrum was broad and complex. This dialkyl (0.46 g, ca. 0.88 mmol) was cleaved just as in the preparation of **1** using etherial HCl. Recrystallization of the product from a saturated Et_2O solution by cooling to −78 °C yielded 0.23 g of **9** (0.49 mmol, 56%): mp 103–105 °C; ^1H NMR (C_6D_6) δ 1.07 (d, 6 H, J_{HH} = 6 Hz), 1.25 (tt, 18 H, J_{PtH} = 35, J_{PH} = 3 Hz), 1.33 (complex), 1.42 (br), 1.45–1.60 (complex). Anal. Calcd for $PtClP_2C_{12}H_{29}D_2$: C, 30.67; H, 6.22; D, 0.86. Found: C, 30.61; H, 6.08.

***trans*-Chloro(4-methylpent-4-enyl)bis(trimethylphosphine)platinum(II) (10).** Commercial 4-methylpent-4-en-1-ol was converted to the chloride by the method of Richey and Hill,[44] and this was converted to the Grignard reagent in THF as described above for **3**. Then 9 mL of this 0.26 M solution (2.3 mmol) was added dropwise to $PtCl_2$(COD) (0.346 g, 0.92 mmol) suspended in 10 mL of Et_2O at −78 °C. After 1 h, the mixture was warmed to 0 °C and stirred for 7 h. Product was isolated just as for **5**, and the resultant oil was immediately treated with 0.25 mL of PMe_3 in 8 mL of Et_2O for 5 h at 0 °C. This product could not be crystallized, so residual COD was removed by evacuation affording 0.23 g (0.44 mmol, 47%) of crude PtR_2L_2: ^1H NMR (C_6D_6) δ 1.10 (dt, 18 H, J_{PtH} = 18, J_{PH} = 7 Hz), 1.5–1.8 (complex, 4 H), 1.89 (s, 6 H), 1.9–2.2 (m, 4 H), 2.48 (t, 4 H, J_{HH} = 7 Hz), 4.98 (br d, 2 H, J_{HH} = 1 Hz), 5.00 (br d, 2 H, J_{HH} = 1 Hz).

The PtR_2L_2 (0.23 g, 0.44 mmol) was cleaved by HCl just as was **6**, and all but 2 mL of Et_2O was removed under vacuum. Benzene (0.8 mL) was added to dissolve all solid, and this was treated with 0.025 mL of PMe_3 for 5 min. Solvent removal afforded reasonably pure white solid (0.19 g, 0.41 mmol, 93%): mp 103–106 °C; ^1H NMR (C_6D_6) δ 1.22 (tt, 18 H, J_{PtH} = 29, J_{PH} = 7 Hz), 1.4–1.7 (complex, 2 H), 1.7–2.0 (complex, 2 H), 1.83 (s, 3 H), 2.23 (t, 2 H, J_{HH} = 7 Hz), 4.90 (br d, 1 H, J_{HH} = 1 Hz), 4.92 (br d, 1 H, J_{HH} = 1). Anal. (on material recrystallized from Et_2O). Calcd for $PtClP_2C_{12}H_{29}$: C, 30.94; H, 6.27. Found: C, 30.84; H, 6.44.

***trans*-[(Acetone)(adamantylmethyl)bis(trimethylphosphine)platinum(II)] Hexafluorophosphate (11).** Complex **8** (0.65 g, 1.23 mmol) suspended in 15 mL of acetone at 0 °C was treated with $AgPF_6$ (0.35 g, 1.4 mmol) in 1 mL of acetone.

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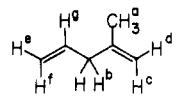
After 5 h at 0 °C, the solution was filtered and the solvent removed under vacuum. The solid was dissolved in acetone, Et_2O was added until a dark precipitate formed, and the solution was filtered and again taken to dryness. Recrystallization from MeOH/Et_2O yielded clear crystals and a dark powder. The physically separated crystalline material was extracted with acetone, and this solution was reduced in volume under vacuum until crystals began to form. Et_2O was added to complete the crystallization: 0.49 g (0.70 mmol, 57%); mp 205–206 °C dec; ^1H NMR (0 °C, $CDCl_3$) δ 1.45 (tt, J_{PtH} = 30, J_{PH} = 4 Hz), 1.5–1.7 (br), 1.8–2.0 (br), 2.46 (br, 1/7 of total integration, acetone); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ −22 (t, J_{PtP} = 2790 Hz), −144 (septet, J_{PF} = 700 Hz). Anal. Calcd for $PtP_3F_6OC_{20}H_{41}$: C, 34.34; H, 5.91. Found: C, 34.14; H, 6.06.

Pyrolyses. General Procedure. All pyrolyses were conducted in sealed NMR tubes at 140 °C, unless otherwise noted. Progress was monitored by ^1H NMR. The kinetics of the pyrolysis of **1**, **1** + PMe_3, and **2** were followed by using either the aromatic resonance of mesitylene, added for that purpose, or the resonance of C_6D_5H impurity in the solvent as internal standard. For quantitation of 2-methyl-1,4-pentadiene, the total integral of the four hydrogens on carbons 1 and 5 was used with respect to the internal standard.

Pyrolysis of 1. Complex **1** (0.192 g, 0.412 mmol), mesitylene (0.032 g, 0.27 mmol), and C_6D_6 (to a total volume of 4.0 mL) were sealed under vacuum in a 12-mm NMR tube of 1-mm wall thickness. The sample was heated for a total of 3.5 h. The rate of disappearance of starting material did not follow any common rate law; the reaction appeared to be autocatalytic. Peak integration indicated that the final yield of 2-methyl-1,4-pentadiene was 99%. The volatiles were separated by trap-to-trap distillation. The ^1H NMR spectrum was quite clean and revealed the diene to be the only olefinic product: (C_6D_6, see **12**) δ 1.68 (br s, 3 H_a),



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2.67 (br d, 2 H_b, J_{bg} = 6 Hz), 4.81 (m, 2 $H_{c,d}$, $J_{ac} \approx J_{bd} \approx$ 1 Hz), 4.90 (ddt, 1 H_e, J_{eg} = 9, J_{ef} = 3, $J_{be} \approx$ 1 Hz), 4.91 (ddt, 1 H_f, J_{fg} = 18, J_{ef} = 3, $J_{bf} m \approx$ 1 Hz), 5.78 (ddt, 1 H_g, J_{fg} = 18, J_{eg} = 9, J_{bg} = 7 Hz) (lit.[49] NMR).

The solid residue was recrystallized from benzene/hexane. *trans*-$PtClH(PMe_3)_2$: 0.141 g (0.37 mmol, 89%); mp 164–165 °C (open tube, 129–133 °C dec); IR (CCl_4) ν_{PtH} 2185 cm^{-1}; ^1H NMR (C_6D_6) δ −15.7 (tt, 1 H, J_{PtH} = 1294, J_{PH} = 16 Hz), 1.27 (tt, 18 H, J_{PtH} = 33, J_{PH} = 3 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −9 (t, J_{PtP} = 2600 Hz), (lit.[50] IR, mp).

Pyrolysis of 1 + PMe_3. Complex **1** (14.2 mg, 0.030 mmol), PMe_3 (2.3 mg, 0.030 mmol), and 0.3 mL of C_6D_6 were sealed in a 5-mm NMR tube under vacuum. The tube was heated for a total of 31 h. ^1H NMR spectra revealed the following: (time in hours/($[1]/[1]_0$)) 0.0/1.00, 2.0/0.93, 3.5/0.88, 4.5/0.83, 7.5/0.75, 19.5/0.27, 31/0; plotted in Figure 1. 2-Methyl-2,4-pentadiene was formed in 89% yield (by NMR integration). A white precipitate, later identified as $[PtH(PMe_3)_3]Cl$, was isolated in 92% yield (12.7 mg); mp 157–159 °C; ^1H NMR (acetone-d_6, −35 °C) δ 1.84 (tt, 18 H, J_{PtH} = 24, J_{PH} = 4 Hz), 2.06 (dt, 9 H, J_{PtH} = 42, J_{PH} = 11 Hz), PtH resonance not visible. This material was prepared independently by addition of PMe_3 (50 L, 0.37 mmol) to *trans*-$PtClH(PMe_3)_2$ (0.14 g, 0.37 mmol) in 5 mL of benzene. A white precipitate formed immediately. After 3 h, the benzene was removed under vacuum, and the $[PtH(PMe_3)_3]Cl$ was recrystallized twice from acetone in overall 55% yield: mp 158–159 °C; IR (mull) ν_{PtH} 2089 cm^{-1}; ^1H NMR (in acetone-d_6 at −35 °C, identical with that above; in CD_3CN at 25 °C) δ 1.58 (d, 27 H, J_{PH} = 9 Hz), −12.72 (t, 1 H, J_{PtH} = 623 Hz); $^{31}P\{^1H\}$ (CD_3CN) δ −37.8 (br s). Analytically pure material could not be obtained; attempted recrystallization led only to less pure material.

Pyrolysis of 2. A solution of **2** (11.1 mg, 0.024 mmol) in 0.5 mL of C_6D_6 in a sealed NMR tube was heated for a total of 61 h. 2-Methyl-1,4-pentadiene was formed in 87% yield. No other product could be identified. ^1H NMR revealed the following: (time in hours/($[2]/[2]_0$)) 0.0/1.00, 4.0/0.94, 7.0/0.85, 19.0/0.45, 31/0.22, 43/0.10.

Pyrolysis of 9. A solution of **9** (9.6 mg, 0.020 mmol) in 0.3 mL of toluene-d_8 was heated at 130 °C for 60 min. Heating a second hour did not change the ^1H NMR spectrum. 4-Methyl-1-pentene was formed in 95% yield as determined by NMR integration; ^1H NMR (toluene-d_8) δ 0.85 (d, 6 H, J = 6 Hz), 1.3–1.7 (m, 1 H), 1.85 (dd, 2 H, J = 7, 7 Hz), 5.66 (m, 1 H). This spectrum agreed well with the Sadtler spectrum (no. 26542) of the d_0 material. See Results for the analysis of deuterium labeling. Also, *trans*-$PtClH(PMe_3)_2$ was produced in 97% yield (7.6 mg).

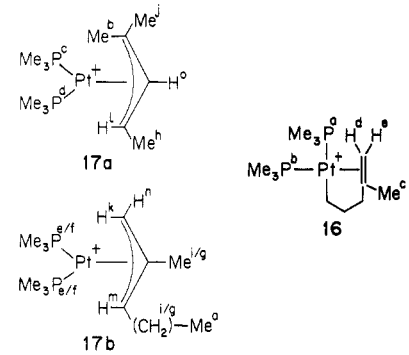
Reactions of Complex 1 with $AgPF_6$. (a) Preparative Scale. A solution of $AgPF_6$ (0.163 g, 0.645 mmol) in 2 mL of acetone was added dropwise to a stirred solution of **1** (0.300 g, 0.644 mmol) in 15 mL of acetone at −80 °C. AgCl precipitated over the next few hours, after which the solution was gradually allowed to warm to −15 °C overnight. The solution, separated from the black precipitate, was filtered and dried under vacuum. The solid was recrystallized from CH_2Cl_2/Et_2O and then acetone/Et_2O to yield an off-white solid, mp 185–187 °C dec, which was an approximately 1:1 mixture of the isomeric structures **17a** and **17b**.

The ^1H NMR (acetone-d_6, 500 MHz) and $^{31}P\{^1H\}$ NMR (acetone-d_6, 500 MHz) spectra of **17a** and **17b** are listed in Table I with assignments corresponding to those shown in Figure 2. At 500 MHz, the ^{31}P NMR spectrum contained three resonances, but the more intense band possessed two pairs of Pt-coupled sidebands, indicating coincidence of two of four resonances. Selective irradiation of each of the three phosphorus resonances in turn and comparison with published spectral data for the

Table I. ^1H and ^{31}P NMR Data for **17a** and **17b**[a]

		coupling constants[b]				
assignt	^1H[c]	P_c[d]	$P_{e/f}$[e]	P_d[f]	Pt	^1H
a	0.98 (3)					7 (t)
b	1.32 (3)	4		2		
c	1.72 (9)			10	34	
d	1.79 (9)	10			38	
e	1.82 (9)		10		32	
f	1.83 (9)		10		32	
g	1.90[g]		*h*		*h*	*h*
h	1.95 (3)	4		9	28	6 (d)
i	2.06[g]		*h*		*h*	*h*
j	2.23 (3)	8		3	14	
k	2.88 (1)		8		39	2 (d)
l	3.17 (1)	*h*			*h*	10 (d), 6 (q)
m	3.82 (1)		6		19	3 (t)
n	4.01 (1)[i]		*h*		*h*	2 (d)
o	4.70 (1)				46	10 (d)

[a] Assignment as indicated in Figure 2. [b] Coupling constants in hertz; multiplicities of proton couplings caused by phosphorus is always doublet, by Pt is 1:4:1 triplet, and by other protons is indicated in parentheses. [c] Integrations given in parentheses. [d] P_c, δ −36.5 (J_{PtP} = 3787, $J_{P_cP_d}$ = 6 Hz). [e] $P_{e/f}$, δ −38.0 (J_{PtP} = 3604 and 3483, $J_{P_eP_f}$ = 8 Hz). [f] P_d, δ −38.2 (J_{PtP} = 3686 Hz). [g] Broad multiplet, precise intensity could not be determined. [h] Could not be determined. [i] Broad.



17a **16** **17b**

Figure 2. Labeling of structures for **16**, **17a**, and **17b** corresponding to the NMR spectral assignments in Tables I and II.

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Table II. ^{1}H NMR Data for 16[a]

assignt[b]	δ	J_{PtH}	J_{PH}
a	1.69	16	8
b	1.74	42	11
c	2.12	42	3
d	4.60	56	5
e	4.87	c	3

[a] Spectra taken at 100 MHz between −40 and 20 °C in acetone-d_6 or CD_2Cl_2 (only very slight differences in the chemical shifts of resonances d and e in these two solvents were observed). Coupling constants in hertz; multiplicity of proton couplings caused by phosphorus is doublet and by Pt is 1:4:1 triplet. [b] Assignments as indicated in Figure 2. [c] Could not be determined.

well-known (π-allyl)PtL_2 cations[29,51] allowed assignment of the proton spectrum as indicated in Figure 2 and Table I. Our inability to independently irradiate P_e and P_f precluded complete assignment of the stereochemical relationships in **17b**. An unexpected feature of the spectrum of **17a** are the relative sizes of the J_{PH} between H_L, Me_b, Me_h, and Me_j and P_c and P_d. Irradiation of P_d revealed no change in the resonance assigned to H_L. Irradiation of P_c led to a significant change in this resonance, although the precise magnitude of the coupling constant could not be determined. We therefore assign P_d and H_L a trans relationship, according to literature precedent.[29,51] At the same time, however, J_{PH} between P_c and Me_4 is 8 Hz, while that between P_c and Me_h in 4 Hz, indicating that the cis coupling is twice that of the trans. Similarly, J_{PH} of P_d and Me_h is 9 Hz, while that of P_d and Me_j is 3 Hz. We have been unable to find examples relevant to these couplings in the literature.

Anal. Calcd for $C_{12}H_{29}F_6P_3Pt$: C, 25.05; H, 5.08. Found: C, 24.92; H, 4.96.

(b) NMR Scale. A 0.106-mL aliquot of a solution of $AgPF_6$ (10.9 mg) in 0.200 mL of acetone-d_6 (0.027 mmol) was slowly added to a solution of **1** (13.1 mg, 0.027 mmol) in 0.35 mL of acetone-d_6 in an NMR tube at −80 °C. AgCl precipitation was complete in ca. 3 h, after which ^{1}H NMR spectra were recorded at the following temperatures: −80 °C, before addition of $AgPF_6$, δ 1.19 (s, Me), 1.43 (tt, PMe, J_{PtH} = 28, J_{PH} = 4 Hz); after precipitation of AgCl, δ 1.19 (sh, Me), 1.45 (br); −40 °C, initially, δ 1.29 (s, Me), 1.46 (tt, PMe, J_{PtH} = 28, J_{PH} = 4 Hz); after 3 h, the peaks at δ 1.29 and 1.46 overlapping with new multiplets centered at δ 1.74, 1.69, 2.12, 4.60, and 4.86 consistent with the assignments for structure **16** shown in Figure 2 and listed in Table II; at −10 °C the spectrum was identical with that of **17a** and **17b**. Warming the sample to 40 °C did not change the isomer ratio.

(c) Deficiency of $AgPF_6$. The reaction was repeated as in (b) by using 0.020 mmol of **1** and 0.010 mmol of $AgBF_6$ at −80 °C. After AgCl precipitation was complete (several hours), the supernatant was transferred to a cooled 5-mm NMR tube via cannula. Following transfer a few small new resonances appeared in the NMR spectrum, but no major changes were evident. Upon controlled warming no difference in behavior from (b) was noted.

(d) In CD_2Cl_2. This reaction was run as in part b using **1** (0.057 mmol) and $AgPF_6$ (0.057 mmol) in 0.24 mL of CD_2Cl_2 at −80 °C. AgCl precipitation appeared to be complete after 15 min. After 30 min the first NMR was taken. ^{1}H NMR of **1**: at −80 °C before $AgPF_6$ addition; δ 1.18 (s, Me), 1.47 (m, br, PMe); after AgCl precipitation at −80 °C, δ 1.54 (m, br, PMe), 2.06 (s, br), 4.2–4.9 (m, br); at −20 °C, the spectrum was that of **16** given in Table II; at ambient temperature the spectrum was that of **17a** and **17b**.

Reaction of 10 with $AgPF_6$. A 0.48-mL aliquot of a solution of $AgPF_6$ (63.3 mg) in 0.25 mL of acetone-d_6 (0.060 mmol) was added to a solution of **10** (23.6 mg, 0.051 mmol) in 0.35 mL of acetone-d_6 at −80 °C. After 9 h, ^{1}H NMR spectra were obtained; at −80 °C the spectrum in the PMe_3 region showed only broad features but showed a complex olefinic pattern at centered at δ 4.90; at −40 °C, the spectrum was that of **16** (Table II); at −10 °C the spectrum was that of **17a** and **17b**.

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Registry No. **1**, 91760-29-1; **2**, 91760-30-4; **3**, 38401-40-0; **4**, 91760-49-5; **5**, 91760-31-5; **6**, 91760-32-6; **7**, 91839-91-7; **8**, 91760-33-7; **9**, 91760-34-8; **10**, 91760-35-9; **11**, 91760-37-1; **12**, 763-30-4; **13**, 91760-38-2; **14**, 91760-39-3; **15**, 91760-48-4; **16**, 91760-40-6; **17a**, 91760-42-8; **17b**, 91760-44-0; $PtCl_2$(COD), 12080-32-9; *cis*-$R_2Pt(PMe_3)_2$ (R = adamantylmethyl), 76271-03-9; *cis*-$Pt[CD_2CH_2CH_2CH(CH_3)_2]_2(PMe_3)_2$, 91760-46-2; $PtR_2(PMe_3)_2$ (R = 4-methylpent-4-enyl), 91760-47-3; cyclobutanecarboxylic acid, 3721-95-7; 1-methylcyclobutanecarboxylic acid, 32936-76-8; methyl 1-methylcyclobutanecarboxylate, 75621-39-5; 1-methylcyclobutyl)methanol, 38401-41-1; [bis-1,2-(dimethylphosphino)ethane]bis[1-methylcyclobutylmethyl]platinum(II), 91760-45-1; *cis*-chloro(adamantylmethyl)bis(trimethyl phosphine)platinum(II), 91839-92-8; methyl 4-methylpentanoate, 2412-80-8; 1,1-dideuterio-4-methylpentan-1-ol, 35658-11-8; 1-bromo-1,1-dideuterio-4-methylpentane, 54498-76-9; 1-bromo-1,1-dideuterio-4-methylpentane Grignard reagent, 91760-50-8; 4-methylpent-4-en-1-ol, 22508-64-1; 4-methylpent-4-en-1-ol Grignard reagent, 30090-53-0; 4-methyl-1,1-dideuterio-1-pentene, 91760-51-9.

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