Conclusions

The following conclusions may be derived from this study:

(1) X-ray crystallographic work indicates that 1,2-diphenyl-3-nitrocyclopropene exists as the bisected conformer in the solid state. Ab initio calculations on 3-nitrocyclopropene indicate that this is true for the gas phase as well.

(2) The ring bond lengths (long C(1)–C(2), short C(1)–C(3)) and especially the long C–N bond length are anomalous for a strong π-acceptor such as NO_2 attached to the ring. Part of this is due to a natural tendency toward longer C substituent bonds at C(3) relative to cyclopropane, perhaps due to a "trace" of cyclopropenium character.[22] These effects are seen in the calculational results that represent gas-phase molecules. Most striking is the very large lengthening of the C–N bond in the solid state, which seems to indicate considerable zwitterionic character. There is precedent for favoring a zwitterionic structure in the crystalline state. Additionally, examination of the 3-21G optimized structure of 1,2-dimethyl-3-nitrocyclopropene indicated no significant structural change relative to 3-nitrocyclopropene. The methyl groups should mimic phenyl substituents, which should also stabilize a zwitterion by stabilizing cyclopropenium cation. The calculated result indicates very little zwitterionic character for the dimethyl and probably the diphenyl derivatives in the gas phase.

(3) The results indicate, along with the previously reported experiments of Jones and Kobzina,[1] that the title compound readily ionizes to nitrite and a carbocation, representing the first documented case for a $C–NO_2$ compound. The long $C–NO_2$ bond in the crystalline state exemplifies the Bürgi–Dunitz concept of predicting molecular dynamics from statics.[29,30] Thus, in principle, the X-ray structure could have been a predictor for the observed ionization.

(4) Electronegative substituents appear to be more stable thermodynamically at C(3) in cyclopropene than at a cyclopropane carbon.

Acknowledgment. We are grateful to acknowledge informative discussions with Professors William P. Dailey III, Joel F. Liebman, Stuart W. Staley, Peter A. Wade, and Kenneth B. Wiberg, some of whom have provided us with unpublished data. Generous support to C.J.C. from the Fulbright Program is gratefully acknowledged as is Professor P. J. Rentzeperis for graciously providing research space and facilities. We gratefully acknowledge the reviewer who pointed out published radical-anion reactions of 2,4-dinitrocumene.

Supplementary Material Available: Listings of bond lengths and angles (Table S1), torsion angles (Table S2), and anisotropic temperature factors (Table S3) (3 pages); observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

---

(29) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153–161.

(30) Bürgi, H. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 2924.

An Experimental and Computational Study of the Formation of (π-Allyl)palladium Complexes from Olefins and Palladium(II) Salts

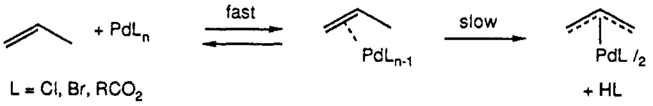
Douglas R. Chrisope,[†] Peter Beak,*[†] and William H. Saunders, Jr.*[‡]

Contribution from the School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, and the Department of Chemistry, The University of Rochester, Rochester, New York 14627. Received June 18, 1987

Abstract: Three general mechanisms are considered for the conversion of methylenecyclohexene by Pd(II) salts to the corresponding (π-allyl)palladium complex. All involve rapid equilibrium formation of a π-olefin complex followed by (A) insertion of the palladium into the carbon–hydrogen bond, (B) removal of allylic hydrogen by a ligand on palladium, or (C) removal of allylic hydrogen by an external base. Kinetic studies with Na_2PdCl_4 in AcOH which show first-order dependence on the concentrations of both the olefin and $PdCl_4^{2-}$, but no dependence on acetate, are taken to be inconsistent with mechanisms involving allylic proton abstraction by external acetate. Product isotope effects for reactions of 2,2-dideuteriomethylenecyclohexane of 4.55 ± 0.1 in DMF and ca. 3.5 in AcOH at 60 °C are considered inconsistent with mechanisms involving Pd insertion into the allylic C–H bond. Literature crystal structures for 21 Pt–olefin complexes were found to possess close contacts between chloride ligands and allylic hydrogens, usually less than the sum of the van der Waals radii. These findings are taken to support a mechanism in which chloride ligand in the intermediate π-olefin complex abstracts an allylic proton to give the π-allyl complex. Calculations of deuterium isotope effects based on transition-state structures for the three mechanisms considered are also most consistent with the intramolecular proton removal by a chloride ligand.

The use of transition-metal complexes to cleave and functionalize C–H bonds is a mechanistically interesting and synthetically attractive process which has received considerable attention in recent years.[1] An early example of a useful C–H bond cleavage by a transition-metal complex is removal of an allylic hydrogen from an olefin on reaction with a Pd(II) salt to provide a (π-allyl)palladium complex, as shown in Scheme I. While general preparative procedures have been developed, few details of the

Scheme I. Formation of (π-Allyl)palladium Complexes from Olefins and Palladium(II) Salts

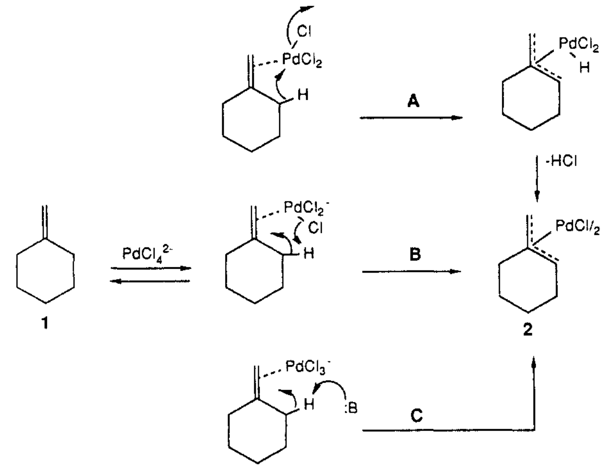


[†] University of Illinois at Urbana–Champaign.

[‡] The University of Rochester.

0002-7863/88/1510-0230$01.50/0

Scheme II. Proposed Mechanisms for (π-Allyl)palladium Complex Formation from Olefins



C–H bond breaking step are known.[2]

It is generally accepted that the reaction of olefins with $PdCl_2$ or ionic equivalents such as $PdCl_4^{2-}$ to give π-allyl complexes proceeds via initial fast π-complexation of the olefin to Pd,[3] as shown in Scheme I. These intermediate π-olefin complexes of $PdCl_2$ are sufficiently stable to isolate and characterize in some cases.[4,5] The allylic hydrogen is removed in a subsequent step which is considered to be slower than π-complexation.

Three mechanisms proposed for the hydrogen removal step are shown in Scheme II for methylenecyclohexane and tetrachloropalladate. Mechanism A, a Pd insertion into the allylic carbon–hydrogen bond, is the most popular and is apparently favored by analogy to similar reactions of other transition-metal complexes.[6,7] The (π-allyl)palladium hydride intermediate could react with oxidants or base to produce the final product.[8b]

The second mechanism, shown as B, involves intramolecular removal of an allylic proton by a chloride ligand. This process was initially suggested by Lukas to explain a striking stereochemical result in the reaction of a sterically hindered olefin, 2,4,4-trimethyl-2-pentene, to give the thermodynamically less stable *anti*-di(μ-chloro)bis(1-*tert*-butyl-2-methyl-π-allyl)dipalladium.[9] McQuillin proposed a similar mechanism to explain the stereochemistry and deuterium isotope effect in the reaction of cholest-4-ene with $PdCl_2(PhCN)_2$ to give the π-allyl complex with η^3-bonding at C4–C6.[10a] This mechanism is also consistent with the recent stereochemical and isotopic studies of Stephenson.[10b]

The final mechanism, C, is proton abstraction by a base external to the intermediate π-olefin–Pd complex. This mechanism was proposed by Ketley and Braatz, who demonstrated that treatment of π-olefin complexes with inorganic and organic bases results in π-allyl complex formation.[11] Cases which do[7] and do not[12] require an added base are known.

Table I. Rate Constants for the Reaction of Methylenecyclohexane with Na_2PdCl_4 in Acetic Acid-d_4[a]

temp, °C	k_{obsd}, M^{-1} s^{-1}	no. of pts	r	av k_{obsd}
59.5	1.60×10^{-3}	8	0.949	
68.2	2.86×10^{-3}	7	0.997	2.80×10^{-3}
68.2	2.74×10^{-3}	9	0.991	$\pm 0.09 \times 10^{-3}$
78.2	5.48×10^{-3}	10	0.993	5.77×10^{-3}
78.2	6.06×10^{-3}	8	0.988	$\pm 0.41 \times 10^{-3}$
87.6	1.01×10^{-2}	9	0.996	1.04×10^{-2}
87.6	1.07×10^{-2}	10	0.993	$\pm 0.04 \times 10^{-2}$

[a] The accuracy of rate constants is estimated at ±20%; the precision of duplicate determinations is shown. $[\text{Olefin}]_{22\,°C} = 0.1051$ M, $[PdCl_4^{2-}]_{22\,°C} = 0.03882$ M.

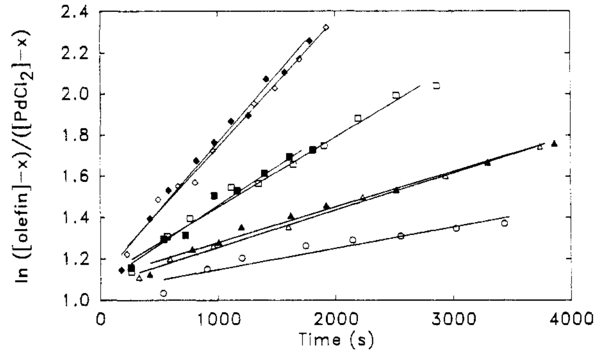


Figure 1. Kinetic plots for reaction of methylenecyclohexane with Na_2PdCl_4 in AcOH at 60 (○), 70 (△), 80 (□), and 90 °C (◇).

In this paper we report kinetic and isotope effect data for the reaction of methylenecyclohexane and calculations of isotope effects which are most consistent with mechanism B. An attractive interaction between chloride ligands and allylic hydrogens in crystalline Pt–olefin complexes is indicated in published structures of complexes and offered as further support for this mechanism. In addition, we provide an isotope effect for the isomerization of methylenecyclohexane to 1-methylcyclohexene, which is consistent with a palladium hydride addition–elimination mechanism for that reaction. A preliminary report of our isotope effect work has appeared.[13]

Results and Discussion

Kinetics. The mechanisms of Scheme II might be distinguished by reaction order. Pathways A and B should be first order in the intermediate π-olefin complex. Mechanism C, on the other hand, would be first order in π-olefin complex and first order in the external base.

The kinetics for the conversion of methylenecyclohexane (**1**) to di(μ-chloro)bis(η^3-2-methylenecyclohexyl)dipalladium (**2**) were followed by ^1H NMR at 200 MHz. Solutions of Na_2PdCl_4, NaOAc-d_3, 1,4-benzoquinone, and **1** in acetic acid-d_4 provided kinetically well-behaved reactions from 59.5 to 87.6 °C. The 1,4-benzoquinone was the most convenient oxidant for inhibition of olefin isomerization and was quite effective at 20 mol %, relative to $PdCl_2$.[14] In its absence, **1** was rapidly isomerized to 1-methylcyclohexene, which gives a different π-allyl complex.[8a]

Separate NMR signals cannot be detected for the olefin and π-olefin complex due to fast exchange. The π-olefin complex of **1** was prepared and characterized but was not sufficiently soluble in AcOH for ^1H NMR determination of the equilibrium constant at low temperatures. Since the equilibrium constant is unknown,

---

(1) For recent examples of alkane C–H activation, see: (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (c) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (d) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (e) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (f) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448. (g) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243.

(2) Collman, J. P.; Hegedus, L. S. *Principles of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 680.

(3) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 38.7.

(4) Hüttel, R.; Kratzer, J.; Bechter, M. *Chem. Ber.* **1961**, *94*, 766.

(5) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

(6) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 736.

(7) Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1969**, *87*, 225.

(8) (a) Trost, B. M.; Strege, P. E. *Tetrahedron Lett.* **1974**, 2603. (b) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407.

(9) (a) Lukas, J.; Coren, S.; Blom, J. E. *J. Chem. Soc., Chem. Commun.* **1969**, 1303. (b) Lukas, J.; Ramakers-Blom, J. E.; Hewitt, T. G.; de Boer, J. J. *J. Organomet. Chem.* **1972**, *46*, 167.

(10) (a) Harvie, I. J.; McQuillin, F. J. *J. Chem. Soc., Chem. Commun.* **1978**, 747. (b) Stephenson, L. M., private communication, June 1984.

(11) Ketley, A. D.; Braatz, J. *J. Chem. Soc., Chem. Commun.* **1968**, 169.

(12) Hüttel, R.; Dietl, H.; Christ, H. *Chem. Ber.* **1964**, *97*, 2037.

(13) Chrisope, D. R.; Beak, P. *J. Am. Chem. Soc.* **1986**, *108*, 334.

(14) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 2, pp 128–142.

the reaction is best treated as first order in both olefin and $PdCl_4^{2-}$. The rate expression appropriate for mechanisms A and B, shown as eq 1, is a typical second-order equation.[15] Mechanism C requires a different expression, eq 2.[15]

$$kt = \frac{1}{[\text{olefin}] - [PdCl_4^{2-}]} \ln \frac{[PdCl_4^{2-}]([\text{olefin}] - x)}{[\text{olefin}]([PdCl_4^{2-}] - x)} \quad (1)$$

$$kt = \frac{1}{[\text{acetate}] - [\pi\text{-complex}]} \ln \frac{[\pi\text{-complex}]([\text{acetate}] - x)}{[\text{acetate}]([\pi\text{-complex}] - x)} \quad (2)$$

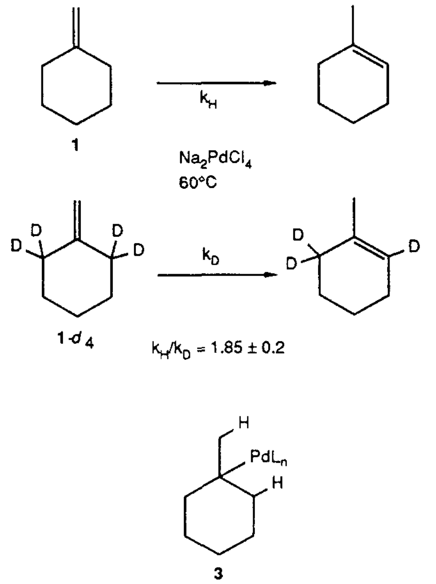
The disappearance of methylenecyclohexane was followed by integration of the ^1H NMR signal of the vinyl protons at δ 4.56. The (π-allyl)palladium complex product has singlets at δ 4.14, 3.60, and 2.60, corresponding to protons on the η^3-bonded carbons, and its appearance was followed directly.[8] The variable x in each equation represents the amount of either reagent consumed at a given time. Since, in the absence of side reactions, this is equivalent to the amount of product formed, x was determined from the ratio of the product integral to the sum of the integrals for product and starting material. Multiplication of this fraction by the initial olefin concentration provided x. The kinetic data fit eq 1 very well, while eq 2 was not appropriate. The calculated rate constants and statistical data are listed in Table I, while the corresponding kinetic plots are shown in Figure 1. The superimposed lines represent duplicate runs.

Due to solubility limits and instrumental sensitivity, only a threefold increase or reduction in the concentrations of olefin and Na_2PdCl_4 could be realized in our efforts to isolate each of the components of the rate expression. That the calculated rate constants were indeed constant over this range indicates agreement between the kinetic data and the rate expression.

The kinetic results favor mechanism A or B. Mechanism C with acetate as the base is not consistent with the kinetic data, although it is possible that chloride functions as the external base in mechanism C. No rate dependence on the oxidant was found, ruling out any mechanism involving this in the rate-determining step.[8b]

From the data in Table I, values of $\Delta H^{\ddagger}$ of 15.3 ± 2.3 kcal mol^{-1} and $\Delta S^{\ddagger}$ of −25 ± 7 cal deg^{-1} mol^{-1} can be calculated. Since k_{obsd} is the product of the complexation equilibrium constant and the first-order rate constant for the hydrogen removal step, the activation parameters reflect both steps. If the free energy and entropy for complexation in the first step are small and have a small temperature dependence, then the complexation would contribute little to the observed entropy of activation, and we suggest that this is likely.[16,17] For comparison, reported values for [3,3]-sigmatropic rearrangements and cyclic eliminations are E_a = 30–45 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −5 to −15 eu.[18] Consequently, the present values may be interpreted in terms of a highly ordered transition state in which significant bond making and bond breaking are occurring, consistent with mechanism A or B. Thus, the kinetic behavior of the reaction, while indicative, is not definitive as to the mechanism of (π-allyl)palladium complex formation.

Scheme III. Kinetic Isotope Effect in Pd-Promoted Isomerization of Methylenecyclohexane



Hydrogen–Deuterium Isotope Effects. The magnitudes of hydrogen–deuterium isotope effects in the formation of the (π-allyl)palladium complex could provide information about transition-state geometry which might be used to distinguish the three mechanisms of Scheme II. Calculations of More O'Ferrall[19] suggest the isotope effect is related to the endocyclic transfer angle. More detailed calculations of deuterium isotope effects for models of the three transition states can also be performed and compared to the experimental results.

Mechanism A in Scheme II could take place most directly via a four-center cyclic transition state, with a hydrogen transfer angle of ca. 90°. The model calculations by More O'Ferrall indicate k_H/k_D = 1.7–2.3 would be expected for such a transfer angle at 25 °C. Mechanism B appears to require a five-center transition state with a larger hydrogen transfer angle of ca. 120°. The More O'Ferrall calculations give k_H/k_D = 3.0–3.9 in this case. The external base mechanism C is presumably a linear process leading to the maximum semiclassical isotope effect of ca. 7 at 25 °C unless reduced by transition-state asymmetry.[20]

In order to provide better estimates of transition-state geometry for mechanisms A and B, structural data for the intermediate π-olefin complex was sought. In the absence of X-ray structures for $PdCl_2$–olefin complexes bearing allylic hydrogens,[21] analogous $PtCl_2$ complexes were used as models. These differ from $PdCl_2$–olefin complexes by having stronger metal–olefin bonds which are ca. 5% shorter.[22] Crystal structures for 21 Pt–olefin complexes were examined for angles defined by the allylic carbon, allylic hydrogen, and the Pt or Cl atoms.[23-39] The C–H–Pt angle,

---

(15) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley: New York, 1981; p 23.

(16) Our suggestion that the ΔS° of complexation contributes little to the observed $\Delta S^{\ddagger}$ for the reaction is based on ΔS° values for olefin complexation to Pd(II), Pt(II), and Ag(I), which are reported to range from +10 to −15 eu: (a) Pestrikov, S. V.; Moiseev, I. I.; Romanova, T. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1965**, *10*, 1199. (b) Denning, R. G.; Hartley, F. R.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, 324. (c) Fueno, T.; Okuyama, T.; Deguchi, T.; Furukawa, J. *J. Am. Chem. Soc.* **1965**, *87*, 170. (d) Fueno, T.; Kajimoto, O.; Okuyama, J.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 785.

(17) The equilibrium constant for complexation of methylenecyclohexane to $AgNO_3$ is reported to be 6.0 at 40 °C: (a) Muhs, M. A.; Weiss, F. T. *J. Am. Chem. Soc.* **1962**, *84*, 4697. (b) An estimate based on molecular mechanics modeling of the methylenecyclohexane–$PdCl_3^-$ complex gives a value of ca. 1: Chrisope, D. R. Ph.D. Thesis, University of Illinois at Urbana–Champaign, 1987.

(18) (a) O'Connor, G. L.; Nace, H. R. *J. Am. Chem. Soc.* **1952**, *74*, 5454. (b) O'Connor, G. L.; Nace, H. R. *J. Am. Chem. Soc.* **1953**, *75*, 2118. (c) Blades, A. T. *Can. J. Chem.* **1954**, *32*, 366. (d) *J. Chem. Soc.* **1953**, 1715. (e) von E. Doering, W.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.

(19) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 785.

(20) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 154–156.

(21) A crystal structure of the π-olefin complex of 1,5-hexadiene with $PdCl_2$ has been reported: Zakharova, I. A.; Kukina, G. A.; Kuli-Zade, T. S.; Moiseev, I. I.; Pek, G. Yu.; Porai-Koshits, M. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1966**, *11*, 1364. This bidentate ligand has such atypical geometry that it may not be as informative as the monoolefin complexes studied.

(22) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, pp 614–680.

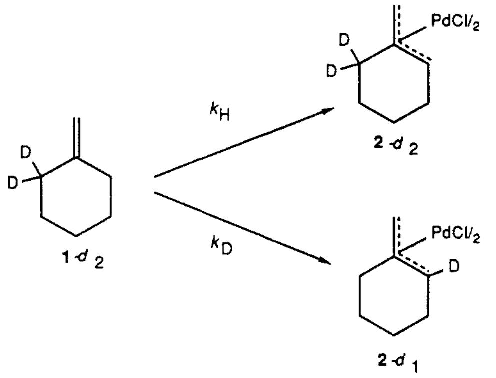
(23) Mura, P.; Spagna, R.; Zambonelli, L. *J. Organomet. Chem.* **1977**, *142*, 403.

(24) Pedone, C.; Benedetti, E. *J. Organomet. Chem.* **1971**, *29*, 443.

(25) Spagna, R.; Zambonelli, L. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2760.

(26) Spagna, R.; Ughetto, G.; Zambonelli, L. *Acta Crystallogr., Sect. B* **1973**, *B29*, 1151.

Scheme IV. Determination of the Product Isotope Effect for Allylic Palladation of Methylenecyclohexane



used as a crude model of mechanism A, averaged 79 ± 10° for the 31 close contacts measured. The average C–H–Cl angle, measured as a model for mechanism B, was 112 ± 9°. These angles are close to those estimated from ring size considerations for cyclic transition states.[40]

The More O'Ferrall treatment predicting a low isotope effect of ca. 2 for a reaction involving a 90° hydrogen transfer is presumed to be little affected by the nature of the hydrogen acceptor atom, since C, Cl, O, and S give much the same results.[19] In order to demonstrate the applicability of the model to palladium, the isotope effect for palladium-catalyzed olefin isomerization was studied. This reaction is considered to be an addition–elimination process of unisolated palladium hydride species,[41,42] as shown in Scheme III. If the β-hydride elimination is rate determining, the roughly 90° transfer should lead to a kinetic isotope effect of ca. 2.

Scheme V. Amination of π-Allyl Complex **2**

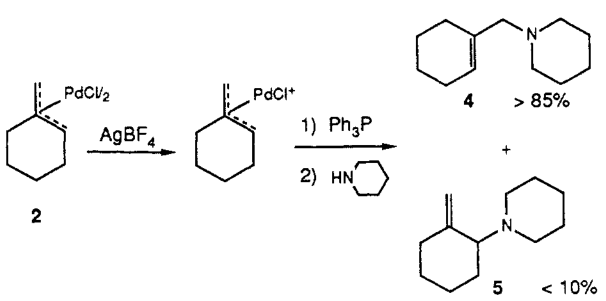


Table II. Product Isotope Effects in Formation of (π-Allyl)palladium Chloride Complexes **2**-d_1 and **2**-d_2 from **1**-d_2

no.	conditions[a] (solvent/reagents)	temp, °C	GC-MS k_H/k_D[b] ± 0.1
1	DMF/$PdCl_2$	21	5.19
2	DMF/$PdCl_2$	25	5.45[c]
3	DMF/$PdCl_2$	60	4.55[d]
4	DMF/$PdCl_2$	86	3.67
5	benzene/$PdCl_2$, 2 equiv of DMF	60	4.32
6	DMF/$PdBr_2$	60	4.64[c]
7	AcOH/$PdCl_2$, NaCl, NaOAc, $CuCl_2$[e]	60	3.44
8	90% aqueous AcOH/$PdCl_2$, NaCl, $CuCl_2$	60	3.58

[a] 1.5–3 equiv of olefin was used. [b] Determined from 70-eV capillary GC–EIMS of amine derivatives **4** and **4**-d_2 from duplicate palladations. [c] Single determination. [d] Analysis of acac complex **6** gave k_H/k_D = 4.56 and 4.57. [e] Conditions of Trost.[8]

The isotope effect for isomerization of **1** to 1-methylcyclohexene was determined for a mixture of **1** and **1**-d_4, as shown in Scheme III. The average kinetic isotope effect of two trials was 1.85 ± 0.2, the value expected for the addition–elimination mechanism via **3**. If a similar 90° transfer is occurring in mechanism A in π-allyl complex formation, a similar low isotope effect would be expected.

In the reaction of methylenecyclohexane with $PdCl_2$ to give **2**, a product isotope effect determination with **1**-d_2 was found to be more accurate and precise than the corresponding kinetic isotope effect with **1** and **1**-d_4. Determination of the product isotope effect is illustrated for the reaction of **1**-d_2 in Scheme IV. With this substrate, an intramolecular competition between chemically identical allylic sites in the molecule provides the isotopic discrimination, and the isotope effect is simply the ratio of **2**-d_2 to **2**-d_1 at any time during the reaction. The corresponding kinetic isotope effect was also determined by a competitive method requiring more measurements and providing greater error.

The present synthesis of 2,2-dideuteriomethylenecyclohexane (**1**-d_2) is a modification of a previously reported preparation.[43] The product of the new procedure was determined to contain >98.2% d_2 olefin by field ionization (FI) mass spectrometry, the remainder being d_1 material. Corrections for the residual protons would be small and were not applied to any isotope effects in this work.

The analysis of the isotopic mixture of complexes **2**-d_2 and **2**-d_1 required derivatization of the complexes, since direct analysis of the complexes by ^{1}H NMR or mass spectrometry presented difficulties. The amination procedure of Åkermark[44] gave high yields of isomeric amines **4** and **5** as shown in Scheme V. The minor isomer **5** was separable by capillary GC, and electron impact (EI) MS gave satisfactory analyses. The M – 1 peak was rather large, being 63 ± 1% of the M$^+$ signal, but identical relative intensities for M$^+$ and M – 1 with **4** and **4**-d_3 indicated that a deuteriated site was not involved. Control experiments demonstrated that isotopic fractionation during amination of the complexes was insignificant.

A second derivative was used for confirmation of the amine analysis. The reaction of **2** and sodium acetylacetonate in benzene or THF produced (η^3-2-methylenecyclohexyl)(2,4-pentanedionato-*O*,*O*′)palladium (**6**) in high yields. This acac complex was

---

(27) Ball, R. G.; Payne, N. C. *Inorg. Chem.* **1977**, *16*, 1871.

(28) Mura, P.; Spagna, R.; Zambonelli, L. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3745.

(29) Bordner, J.; Wertz, D. W. *Inorg. Chem.* **1974**, *13*, 1639.

(30) Colapietro, M.; Zambonelli, L. *Acta Crystallogr., Sect. B* **1971**, *B27*, 734.

(31) Mura, P.; Spagna, R.; Ughetto, G.; Zambonelli, L. *J. Cryst. Mol. Struct.* **1977**, *7*, 265.

(32) Mura, P.; Spagna, R.; Ughetto, G.; Zambonelli, L. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2532.

(33) Briggs, J. R.; Crocker, C.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 64.

(34) Spagna, R.; Zambonelli, L. *J. Chem. Soc. A* **1971**, 2544.

(35) Hewitt, T. G.; De Boer, J. J. *J. Chem. Soc. A* **1971**, 817.

(36) Spagna, R.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chim. Acta* **1970**, *4*, 475.

(37) Spagna, R.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chim. Acta* **1970**, *4*, 283.

(38) The reported Pt *y* coordinate is in error. The correct value of –0.2000 was retrieved from the Cambridge crystallographic database: Benedetti, E.; Corradini, P.; Pedone, C. *J. Organomet. Chem.* **1969**, *18*, 203.

(39) Baenziger, N. C.; Medrud, R. C.; Doyle, J. R. *Acta Crystallogr.* **1965**, *18*, 237.

(40) On the basis of the reasonable assumption that the transition-state structure contains C–H bonds longer than and H-acceptor bonds shorter than in the π-olefin complex, it seems likely the angles found in the X-ray structures are a few degrees smaller than in the transition states.

(41) (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985; Chapter 2. (b) Jira, R.; Freiesleben, W. In *Organometallic Reactions*; Becker, E. I., Tsutsui, M., Eds.; Wiley: New York, 1972; pp 133–148. (c) Cramer, R.; Lindsey, R. V., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 3534. (d) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, pp 677–679.

(42) Arguments for an alternative isomerization mechanism via (π-allyl)palladium hydride species have been presented: (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; pp 33–35. See also: (b) Hudson, B.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1972**, 1204.

(43) Beak, P.; Berger, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 3848.

(44) Åkermark, B.; Åkermark, G.; Hegedus, L. S.; Zetterberg, K. *J. Am. Chem. Soc.* **1981**, *103*, 3037.

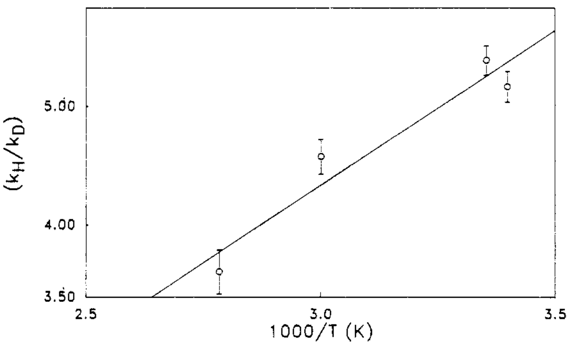


Figure 2. Temperature dependence of k_H/k_D for formation of **2** in DMF solvent. The *y* axis is ln scale.

easily analyzed by 70-eV EIMS.[45] Agreement was observed for the analyses of the amine and acac derivatives and provides confidence in both analyses.

Methylenecyclohexane-d_2 was allowed to react with $PdCl_2$ or $PdBr_2$ under various conditions to give the (π-allyl)palladium halide complexes. After amination, the ratio of **4**-d_2 to **4**-d_1 was determined by GC–MS. The resulting product isotope effects are listed in Table II. Entry 3 shows the isotope effect of 4.55 in dimethylformamide (DMF) at 60 °C is somewhat larger than that of ca. 3.5 in acetic acid, at the same temperature, entries 7 and 8. The isotope effect is also large, 4.32, when the reaction occurs in benzene solvent with 2 equiv of DMF per Pd, listed as entry 5. The use of $PdBr_2$ in DMF gives the same isotope effect as $PdCl_2$. The strong temperature dependence of the isotope effect in DMF solvent, giving $k_H/k_D = 5.45$ at 25 °C and 3.67 at 86 °C, is evident. The conditions in entry 7 are those of Trost[8] while in entry 8 the added acetate is omitted and less NaCl and $CuCl_2$ are used in aqueous AcOH. The corresponding isotope effects are identical within experimental error.

The intermolecular competition between **1** and **1**-d_4 was also examined. A mixture of the olefins was allowed to react with $PdCl_2$ in DMF at 60 °C. The product was isolated and converted to the amine derivative **4** whose isotope ratio was determined by GC–MS. From the isotopic ratios of the reagents and products and the extent of reaction, the isotope effect is calculated[46] as 5.4 ± 1, in agreement with the product isotope effect.

Mechanism. The equivalence of the kinetic and product isotope effects is consistent with a fast, reversible complexation prior to rate-determining C–H bond cleavage. The sizable effect of 5.4 ± 1 for the kinetic isotope effect confirms that C–H bond breaking is rate determining for the entire process. The identical product isotope effect indicates the ratio of products is established in the same elementary reaction.[43,47] We assume that all the product isotope effects we measured are accompanied by identical kinetic isotope effects.

The large product isotope effect of 5.45 at 25 °C in DMF solvent for allylic palladation implies a nearly linear and symmetrical transition state. This result appears to rule out mechanism A, as formulated, which is expected to display a small isotope effect of ca. 2. However, mechanism A could still be operative if the zero-point energy contribution to the isotope effect were augmented by a sizable tunneling correction.

Little or no tunneling is detectable, however, by the temperature dependence observed in DMF solvent. A plot of ln (k_H/k_D) vs $1/T$ is shown in Figure 2. Although the points are somewhat scattered, a line whose slope is proportional to $E_{aH} - E_{aD}$, the difference in barrier heights between the H and D species, is obtained. The slope gives a value of 1.15 ± 0.23 kcal mol^{-1}, fortuitously close to the value of 1.15 expected when the typical C–H(D) zero-point energy difference is responsible for the isotope effect.[48] Values larger than ca. 1.5 are acceptable evidence for tunneling. The *y* intercept represents A_H/A_D, the ratio of the Arrhenius preexponential factors. This parameter is indicative of tunneling when it is lower than ca. 0.7, but the present value of 0.76 ± 0.28 can be considered in the normal range of 0.7–1.4.[48,49] This normal temperature dependence of the isotope effect indicates that the zero-point energy factor is the major contributor to the observed isotope effect and strongly supports the nearly linear and symmetrical transition state suggested previously.

The influence of DMF and other amides on the reaction is marked, even when present in stoichiometric amounts. The yield of π-allyl complex is the same, 30–45%, whether the reaction occurs in benzene solvent with 2, 5, or 50 equiv of DMF per Pd added as when in DMF solvent. Under these conditions the yields are limited to 50% with limiting $PdCl_2$, due to concurrent formation of $[DMF_2H]_2[Pd_2Cl_6]$.[50] The reaction in benzene does not proceed in the absence of DMF, probably because $PdCl_2$ is insoluble in benzene. Olefin isomerization is greatly reduced in the presence of DMF. This can be rationalized as the result of strong complexation of DMF, discouraging formation of the catalytic Pd hydride complex. Other side reactions, such as formation of allylic acetates, were absent in DMF solvent, and the crude product was sufficiently pure that it crystallized spontaneously in every preparation.

Several other tertiary amides showed the same behavior as DMF. The palladation reaction was performed in benzene solvent with 5 equiv of several amide auxiliaries, including 1,3-dimethyl-2-imidazolidinone, tetramethylurea, and *N,N*-diisopropyl-2-methylpropionamide. The yields, which ranged from 19 to 37%, were roughly the same as those with DMF. Conti et al. noted that reaction of 1-pentene with $PdCl_2$ in dimethylacetamide solvent gave the same results as DMF.[50] A reasonable conclusion is that the binding of the amide moiety to Pd(II) has some influence in π-allyl complex formation in the presence of DMF and other amides, and moderate structural changes in the amide have little or no effect.

The observation that the yields and isotope effects are about the same whether DMF is the solvent or present as a stoichiometric ligand in a nonpolar solvent also can be interpreted as disfavoring mechanism C. It appears that the same mechanism is operative in these rather different environments, suggesting reaction within the coordination sphere, i.e., mechanism B, with DMF or chloride ligands acting as the base.

The identical isotope effects in the presence and absence of added acetate, along with the kinetics, show this reagent to have no role in the hydrogen removal step. Mechanism C with acetate as the base is again ruled out. Neither the isotope effects or the kinetic results preclude the operation of this mechanism with chloride as the base, although little evidence supports such a pathway.

The moderate isotope effects for the allylic palladation of **1**-d_2 in AcOH are also inconsistent with mechanism A. The values of ca. 3.5 are in the range expected for mechanism B, but could be consistent with mechanism C. An example of an isotope effect of this magnitude, 3.0–3.5, although at a higher temperature, for a C–H bond cleavage in a Pt complex has been reported.[51] That mechanism is thought to involve Pt insertion into the C–H bond of a neopentyl methyl in a five-center cyclic transition state. The similarity of the isotope effects and the assumed geometry lends

---

(45) The 70-eV MS of **5** agreed with the 11-line molecular ion cluster calculated from natural isotopic abundances. Since the corresponding d_1 and d_2 complexes should also have the same pattern, differing only in mass, the appearance of the M^+ region of mixtures of these two species could be calculated. The ratio of these species was varied until the pattern matched the experimental molecular ion region. Minimization of the sum of the squares of the differences of the calculated and actual patterns established the experimental ratio.

(46) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 95–102.

(47) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419.

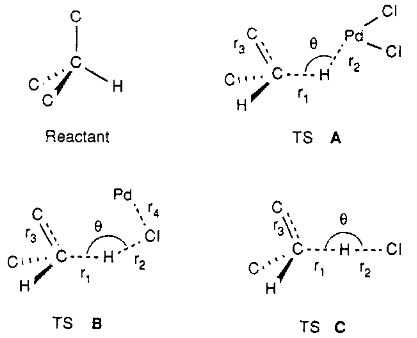
(48) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 140–144.

(49) Schneider, M. E.; Stern, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 1517.

(50) (a) Morelli, D.; Ugo, R.; Conti, F.; Donati, M. *J. Chem. Soc., Chem. Commun.* **1967**, 801. (b) Conti, F.; Donati, M.; Pregaglia, G. F. *J. Organomet. Chem.* **1971**, *30*, 421.

(51) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732.

Scheme VI. Cutoff Models of Reactant and Transition States for Isotope Effect Calculations



support to the semiquantitative use of the More O'Ferrall model.

Mechanism B has independent support from the results of Lukas and from X-ray structure data. In the reaction of 2,4,4-trimethyl-2-pentene with $PdCl_2$ to give the corresponding syn and anti (π-allyl) palladium complexes, Lukas found the formation of the anti isomer to be kinetically favored, suggesting a specific intramolecular interaction between a chloride ligand and an allylic hydrogen.[9] That this behavior might be more general is supported by X-ray structures of Pt–olefin complexes[23-39] which show that chloride ligands in these complexes are unusually close to the allylic protons. Although the Pt–olefin complexes are less prone to proceed to π-allyl complexes than the Pd–olefin compounds,[22] their structures are taken as good models of the corresponding Pd complexes. The average H–Cl distance is 2.73 ± 0.16 Å, while the sum of the van der Waals radii is 3.0 Å.[52] Such close contacts involving Pt and allylic H are not evident in any complex, with the average H–Pt distance being 1 Å greater than the sum of the van der Waals radii.[52]

In the context of mechanism B, the donor and acceptor atoms seem favorably positioned by geometrical constraints so that reactivity is enhanced, a proximity effect. Parshall has attributed some kinds of C–H activation to proximity of the reactive sites,[53] and other apparent examples exist.[51,54] While no definitive evidence has been produced to allow distinction between mechanisms B and C, the available evidence is most consistent with mechanism B, intramolecular proton abstraction by chloride ligand, which appears to be a simple consequence of the geometry of the intermediate complexes.

Calculations. The conclusions reached above by comparing our isotope effects to the predictions of the More O'Ferrall model[19] are reasonable and in accord with other evidence. There remains, however, the possibility that a model closer to the real system might lead to significantly different predictions. Consequently, we undertook calculations on models based on mechanisms A, B, and C of Scheme II.

Table III

Off-Diagonal Force Constant Elements Linking r_m and r_n and Hydrogen-Transfer Angles for Cutoff Models A, B, and C[a]

	model					
	A	A	B	B	B	C
a_{12}[b]	1.05	1.05	1.05	1.05	1.05	1.05
a_{13}[b]	0.31	0.31	0.22	0.22	0.22	0.31
a_{24}[b]			0.22	0.22	0.22	
θ[c]	100	110	120	135	140	180

Calculated Isotope Effects k_H/k_D[e] at 60 °C for Cutoff Models A, B, and C[a]

	model					
n_{CH}[d]	A	A	B	B	B	C
0.9	1.41	1.54	1.55	1.69	1.71	2.24
0.7	1.89	2.20	2.48	3.09	3.26	5.78
0.5	2.62	3.18	3.39	4.37	4.66	8.11
0.3	3.21	3.87	3.56	4.23	4.37	6.21
0.1	3.04	3.35	3.01	3.05	2.99	3.64

[a] See text and Scheme VI for models. [b] Off-diagonal force constant elements, a_{mn}, linking r_m and r_n. [c] Hydrogen-transfer angle C–H–Pd in model A, and C–H–Cl in models B and C. [d] Bond order of breaking bond (see r in Scheme VI). [e] Intermolecular isotope effect for reactant C_2CH_2 vs C_2CD_2.

Table IV. Temperature Dependences of Calculated Isotope Effects for Models A, B, and C[a,b]

model	n_{CH}[c]	θ[b]	k_H/k_D (60 °C)[d]	$E_a^D - E_a^H$	A_{aH}/A_{aD}
A	0.3	100	3.21	0.81	0.94
A	0.3	110	3.87	0.93	0.95
B	0.3	120	3.56	0.94	0.86
B	0.3	135	4.23	1.05	0.86
B	0.5	135	4.37	1.12	0.81
B	0.3	140	4.37	1.07	0.87
B	0.5	140	4.66	1.18	0.79
C	0.1	180	3.64	1.03	0.77
exptl			4.55[f]	1.15[g]	0.76[h]

[a] See text, Scheme VI, and Table III for models. Arrhenius parameters are from a least-squares fit of isotope effects calculated at 20, 40, 60, and 80 °C. [b] See note *c*, Table III. [c] See note *d*, Table III. [d] See note *e*, Table III. [f] ±0.1. [g] ±0.23. [h] ±0.28.

The reactant and transition-state models are shown in Scheme VI. The models omit atoms more than two bonds removed from the isotopically substituted atom, because Wolfsberg and Stern[63,64] have shown that such omissions make little difference in the calculated isotope effect. We omitted explicit Pd–C bonds in model A (the one case where the omission is not justified by the Wolfsberg–Stern cutoff procedure) in order to avoid the problems with cyclic transition states that Keller and Yankwich[65] describe. The reactant is assumed to be precisely tetrahedral, and standard C–H (1.09 Å) and C–C (1.54 Å) bond lengths are used. Force constants involving C–H, C–C, and H–Cl bonds are taken from standard compilations.[66-68] Bond lengths and stretching force constants involving the palladium atom are taken from Bäckvall et al.;[69] bending force constants for H–Pd–Cl (0.5 mdyn/Å) and C–H–Pd (0.3 mdyn/Å) are simply guessed.

Calculations were performed with the BEBOVIB-IV program,[70,71]

---

(52) The van der Waals radii of H (1.2 Å) and Cl (1.8 Å) are taken from: (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260. The values for Pt and Pd are nearly identical, 0.8 Å, and are given by: (b) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *B25*, 925. (c) Ahrens, L. H. *Geochim. Cosmochim. Acta* **1952**, *2*, 155.

(53) Parshall, G. W. *Catalysis* **1977**, *1*, 335.

(54) (a) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272. (b) Karsch, H. H.; Klein, H.-F.; Schmidbauer, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637. (c) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* **1971**, 3833. (d) Cheney, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 751, 860. (e) Bennett, M. A.; Longstaff, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 6266. (f) Bennett, M. A.; Clark, P. W. *J. Organomet. Chem.* **1976**, *110*, 367. (g) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356.

(55) Wittig, G.; Schöllkopf, U. *Org. Synth.* **1973**, *Collect Vol. 5*, 751.

(56) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.

(57) Atkinson, J. G.; Fisher, M. H.; Horley, D.; Morse, A. T.; Stuart, R. S.; Synnes, E. *Can. J. Chem.* **1965**, *43*, 1614.

(58) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264.

(59) Masilamani, D.; Rogić, M. M. *J. Org. Chem.* **1981**, *46*, 4486.

(60) Gutsche, C. D. *J. Am. Chem. Soc.* **1949**, *71*, 3513.

(61) Cope, A. C.; Ciganek, E. *Org. Synth.* **1963**, *Collect. Vol. 4*, 339.

(62) Cope, A. C.; Ciganek, E. *Org. Synth.* **1963**, *Collect. Vol. 4*, 612.

(63) Wolfsberg, M.; Stern, M. *Pure Appl. Chem.* **1964**, *8*, 225.

(64) Stern, M.; Wolfsberg, M. *J. Chem. Phys.* **1966**, *45*, 4105.

(65) Keller, J. H.; Yankwich, P. E. *J. Am. Chem. Soc.* **1974**, *96*, 2303.

(66) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. *Molecular Vibrations*; McGraw-Hill: New York, 1955.

(67) Schachtschneider, J. H.; Snyder, R. G. *Spectrochim. Acta* **1963**, *19*, 117.

(68) Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1965**, *21*, 169.

(69) Bäckvall, J. E.; Björkman, E. E.; Pettersson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1984**, *106*, 4369.

(70) BEBOVIB-IV by: Sims, L. B.; Burton, G.; Lewis, D. E. *Quantum Chemistry Program Exchange* **1977**, *11*, 337 (available from Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN 47401).

which adjusts bond lengths and force constants according to the bond orders of the breaking and forming bonds. As the bond order of the breaking C–H bond decreases in the transitions state, the remaining carbon and hydrogen atoms approach a planar sp^2 configuration. Although the palladium atom is not formally bonded to carbon in these models, angles are chosen that keep it within a reasonable distance (2.0–2.5 Å) of the carbons of the developing double bond. Off-diagonal **F** matrix elements are calculated by the usual procedure,[72] where

$$F_{mn} = a_{mn}(F_{mm}F_{nn})^{1/2}$$

and the a_{mn} values are given by

$$1 - a_{12}{}^2 - a_{13}{}^2 = D$$

for models A and C and by

$$1 - a_{12}{}^2 - a_{13}{}^2 - a_{24}{}^2 + a_{13}{}^2 a_{24}{}^2 = D$$

for model B. In both sets of models the curvature parameter, D, is given a value of −0.2, and a_{12}, which couples the C- - -H and Pd- - -H or Cl- - -H stretches, is given the rather large value of 1.05 so as to make the hydrogen transfer the major component of the motion along the reaction coordinate. To incorporate the accompanying heavy-atom motion, C- - -H and C$\overset{\text{—}}{\text{- - -}}$C are coupled by a_{13} = 0.31 in models A and C. In model B, a_{13} = 0.22 and, in addition, a_{24} = 0.22 to couple Cl- - -H and Pd- - -Cl.

The isotope effects in Table III include tunnel corrections calculated from the $|\nu_L|^\ddagger$ values and the first term of the Bell equation.[73] The temperature dependences shown in Table IV were obtained from the least-squares fits to the Arrhenius equation for all isotope effects that are within a reasonable distance of the experimental values in Table II.

Model B clearly gives the best fits to the experimental isotope effects. The version with n_{CH} = 0.5 and a hydrogen transfer angle of 140° is not only closest to the observed k_H/k_D with $PdCl_2$ in DMF at 60 °C, it also shows almost the same temperature dependence (Table IV). Other versions of model B with n_{CH} = 0.3–0.5 and hydrogen transfer angles of 120–140° give k_H/k_D values in the same range as the various experimental values at 60 °C in Table II.

The calculated k_H/k_D run consistently below the experimental values for model A, though this model with a transfer angle of 110° and n_{CH} = 0.3 gives k_H/k_D = 3.87, which is close to the last two entries in Table II and not impossibly below the 4.55 obtained in DMF with $PdCl_2$. The fit to the temperature dependence is poor but is within experimental error. While one might offhand expect a four-member transition state to prefer a hydrogen transfer angle near 90°, as we assumed earlier, the fact that the bonds to Pd must be longer than the C- - -H or the C$\overset{\text{—}}{\text{- - -}}$C bonds means that the Pd–C distances would be too close in a square or a rectangular transition state. The distances are about right for transfer angles of 100 or 110°.

Model C, which has a hydrogen transfer angle of 180°, deviates from the experimental results in the opposite sense from model A. The k_H/k_D values for transition state that are anywhere near central (n_{CH} = 0.7–0.3) are far too large. Only a very product-like transition state (n_{CH} = 0.1) gives a k_H/k_D value and Arrhenius parameters near the experimental values. While such a transition state cannot be totally excluded, it seems distinctly less likely than the more central ones of model B.

Summary. The hydrogen–deuterium isotope effects observed for the formation of **2** from **1**-d_2 and Na_2PdCl_4 in AcOH or from $PdCl_2$ in DMF rule out mechanism A, insertion of Pd into the carbon–hydrogen bond. Both the isotope effects and the kinetic results rule out mechanism C, removal of an allylic hydrogen by external acetate. Only mechanism B, deprotonation by a basic ligand, seems fully consistent with the experimental results. Calculated isotope effects for transition-state models of the three suggested mechanisms are also most consistent with mechanism B in terms of magnitude and temperature dependence.

Experimental Section

General. Melting points were determined on a Büchi melting point apparatus and are uncorrected. ^1H NMR spectra were obtained on Varian EM-390 (90 MHz), Varian XL-200 (200 MHz), and General Electric QE300 (300 MHz) spectrometers. ^{13}C NMR were taken on JEOL FX60Q (15 MHz), Varian XL-200 (50 MHz), and General Electric QE300 (75 MHz) instruments. Spectra were determined in $CDCl_3$ solution and chemical shifts are reported downfield from Me_4Si unless otherwise noted. Infrared spectra were determined on Perkin-Elmer IR-1320 and Nicolet 7199C instruments. Routine EI mass spectra were determined on a Finnigan MAT CH5 spectrometer at 70 eV unless otherwise noted. GC–MS was performed on a VG Analytical 7070 instrument with 70-eV EI after separation on an OV-17 capillary column in a Hewlett-Packard 5890 gas chromatograph. FI mass spectra were determined on a Finnigan MAT 731 by summing repeated scans of the molecular ion region on a multichannel analyzer. Elemental analyses were performed by J. Nemeth and associates at the University of Illinois Microanalytical Laboratory.

Capillary GC was performed on a Hewlett-Packard 5793A instrument with H_2 carrier and FID using a 25 m × 0.2 mm SE52 column. Preparative GC was performed on a Varian Aerograph A-90 with He carrier and TCD on column A, 2.44 m × 0.953 cm copper, containing 20% SE30 on Chromosorb A 45/60; on column B, 2.44 m × 0.953 cm copper with 20% FFAP on Chromosorb WHP 60/80; or on column C, 2.44 m × 0.953 cm copper, containing 20% OV-17 on Chromosorb A 45/60.

Computer programs written in Microsoft BASIC were run on IBM PC, Commodore 64, and Apple Macintosh computers, or in Turbo Pascal on the IBM PC.

Reagents. Diethyl ether and tetrahydrofuran were distilled from Na/benzophenone ketyl. Hexane was distilled from 4-Å molecular sieves. EtOAc was distilled from Na_2CO_3. Reagent grade DMF was stored over 4-Å molecular sieves for 1 week prior to use. Reagent grade AcOH was used after adding 1–2% distilled Ac_2O. Piperidine was fractionally distilled from KOH and stored over KOH. Benzoquinone was doubly sublimed. $(PhCN)_2PdCl_2$ was prepared by the method of Kharasch et al.[5] Other reagents were purchased as reagent grade and were used as received.

Rate Constant Determinations by ^1H NMR for Allylic Palladation. Typical AcOH Solution. To ca. 9 mL of acetic acid-d_4 were added 80.3 mg (0.45 mmol) of $PdCl_2$, 53.4 mg (0.91 mmol) of NaCl, 38.5 mg (0.45 mmol) of NaOAc-d_3, and ca. 25 mg (0.23 mmol) of 1,4-benzoquinone. The mixture was stirred at 60 °C for 8–10 h. The solution was cooled and diluted to 10 mL with more solvent. The concentration of Na_2PdCl_4 was 0.4529 M. Other solutions were from 0.03882 to 0.04353 M in Na_2PdCl_4.

Olefin Solutions. To a 1-mL volumetric flask were added 100 μL of methylenecyclohexane and 25 μL of p-xylene before filling with acetic acid-d_4. The olefin concentration was 0.841 M.

Correction of Reagent Concentrations for Temperature. A 50-mL volumetric flask was calibrated in 0.5-mL increments from 48 to 52 mL with H_2O at room temperature. Approximately 48 mL of AcOH or DMF was placed in the flask at 22 °C and the temperature was varied from 27 to 70 °C for DMF and 33–80 °C for AcOH. The temperature control of the circulating-water bath was rated at ±0.02 °C and the temperature was determined to the nearest 0.1 °C. The volume of the solvent in the flask was estimated to the nearest 0.1 mL. A linear least-squares fit of volume vs temperature for each solvent gave correlation coefficients of 0.999 and provided corrected volumes for the temperatures used in the kinetic study. The decreased reagent concentrations relative to 22 °C were used in all kinetics calculations.

Typical Kinetic Run. With a 500-μL syringe, 350 μL of the $PdCl_2$ solution was placed in a 5-mm NMR tube. The sample was allowed to reach thermal equilibrium at the reaction temperature in a water bath with better than 0.02 °C control. The sample was then placed in the equilibrated probe and a spectrum was taken to check for impurities and instrumental resolution. The olefin solution (50 μL) was added and the sample inverted at least three times, keeping the sample in the water bath when possible. A timer was started with the first inverstion and the sample was returned to the probe within ca. 30 s of removal. The instrument was locked and tuned within 2–3 min. The instrument was programmed to accumulate four or eight spectra per time point with a 5-s delay between pulses. Since the flip angle was 45–50°, protons having T_1 values of 2 s or less regain >99% of their Boltzmann spin distributions between pulses. The middle pulse of each set was timed to the nearest second. The FIDs were acquired and stored at intervals ranging from 40 s to 5 min, with 7–10 time points per run. The integration regions

---

(71) Sims, L. B.; Lewis, D. E. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1984; Vol. 6, Chapter 4.

(72) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 64–66.

(73) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: New York, 1980; pp 60–63.

were as follows (in ppm): *p*-xylene, 7.05–6.95; methylenecyclohexane, 4.62–4.49; **2**, 4.26–4.18, 3.62–3.56, 2.65–2.59. The extent of reaction x was determined from the ratio of product area to the sum of product and starting olefin integrals. Statistical corrections were made when the number of protons at each site were unequal. When more than one site per molecule was integrable, all were integrated and the average was used to calculate x. Equations 1 and 2 were used to compute the rate constants by a linear least-squares procedure.[15] Equation 2 provided marginal fits and wildly varying rate constants with changes in acetate concentration.

The NMR probe temperature was calibrated at a different time by measuring $\Delta\nu$ of an ethylene glycol sample. The relationship between the actual temperature and that displayed is constant unless the probe is disassembled. The temperatures used in the Arrhenius plots are considered to be accurate to within 0.5 °C.

Attempts to achieve pseudo-first-order conditions were hampered by insolubility of Na_2PdCl_4 in AcOH at one extreme and insensitivity of the NMR instrument at the other. The AcOH solutions appeared to be saturated near 0.13 M Na_2PdCl_4. The requirements for accurate integration were 4–5-s delays between pulses, no more than 8 pulses per time point, and product concentrations above 0.005 M. The Na_2PdCl_4 and olefin concentrations could be decreased by a factor of only 3 and still meet these requirements. The following data for reactions at 70 °C show that the calculated rate constants are indeed constant over the concentration ranges available and that eq 1 is appropriate. The data are listed as [methylenecyclohexane], [Na_2PdCl_4], and $k_{obsd} \times 10^3$ M^{-1} s^{-1}: 0.09984, 0.01226, 2.96; 0.3494, 0.1225, 2.18; 0.09984, 0.1225, 2.72 and 2.39; 0.3494, 0.1225, 4.09.

Variation in concentration of acetate was performed with 0.09984 M methylenecyclohexane and 0.03638 M Na_2PdCl_4 at 70 °C. The results are given as (equiv of NaOAc)/Pd and $k_{obsd} \times 10^3$ M^{-1} s^{-1}: 0.33, 2.24; 1.0, 2.91; 3.0, 8.80. The threefold increase in k_{obsd} at the highest acetate concentration is attributed to an increase in ionic strength. A run with 1 equiv of NaOAc and 2 equiv of $NaClO_4$ gave 5.85×10^{-3} M^{-1} s^{-1} while the control with 1 equiv of acetate gave 1.34×10^{-3}, a fourfold increase.

Di(μ-chloro)bis(methylenecyclohexyl)dipalladium Chloride. To 2 mL of methylenecyclohexane containing 10–20 mg of 1,4-benzoquinone was added 90 mg of $(PhCN)_2PdCl_2$, and the mixture was stirred overnight at 25 °C. The rust-colored powder was collected and washed with pentane. Insolubility and equilibrium with the olefin prevent obtaining the ^{1}H NMR spectrum.

Anal. Calcd for $C_{14}H_{24}Pd_2Cl_2$: C, 30.74; H, 4.42; Cl, 25.93. Found: C, 30.84; H, 4.24; Cl, 25.75.

Deuteriation of Ketones. Cyclohexanone and cycloheptanone were deuteriated by several exchanges, vigorously stirred at reflux in a $THF/D_2O/K_2CO_3$ mixture for 2–5 days each. Typical proportions were 100 mL of THF, 30–40 mL of D_2O, 30–40 mL of ketone, and 5–10 g of K_2CO_3. When the mixtures were considered to be equilibrated, the layers were separated and solid NaCl was added to the organic layer to separate more D_2O. The aqueous layer was extracted twice with ca. 30-mL portions of pentane. The organic extracts were combined and dried with successive portions of Na_2SO_4. Kugelrohr distillation was often omitted in early exchanges but always performed with material >80 atom % D. The extent of deuteriation was monitored by ^{1}H NMR early in the cycle and by EIMS in later exchanges. When the ketone appeared to be >98 atom % D, FI mass spectrometry was used in a more careful isotopic analysis. When this level had been reached one more exchange was performed under the driest conditions. The final FI mass spectrum showed greater than 98% d_4 material in most cases.

2,2,6,6-Tetradeuteriomethylenecyclohexane. Tetradeuteriocyclohexanone was treated by the method of Wittig and Schöllkopf.[55] Instead of distilling off the Et_2O completely and isolating the product by further distillation, the Et_2O was incompletely distilled. The material was then subjected to preparative GC purification on column A with efficient collection at dry ice temperatures. The recovery was quantitative, giving a 68% yield. The chemical purity was judged to be >99.8% by capillary GC and isotope purity of >98.8% d_4 material was determined by FIMS. A lack of allylic hydrogens was shown by ^{1}H NMR.

Improved Wittig reaction procedures in DMSO[56] allow enolization and deuterium loss and are not recommended.[57] Peterson methylenation procedures[58] were also performed, but a side product, hexamethyldisiloxane, has the same boiling point as the product olefin. No chromatographic separation or hydrolysis procedures were effective for removal of this impurity.

2-Chloro-2,7,7-trideuteriocycloheptanone. The procedure was based on that of Rogič and Masilamani.[59] To 21.6 g (0.186 mol) of distilled 2,2,6,6-tetradeuteriocycloheptanone in ca. 200 mL of CH_2Cl_2 was added 27.5 g (0.204 mol) of freshly distilled SO_2Cl_2 with stirring. The solution turned yellow and back to colorless within a few seconds with vigorous gas evolution. As this subsided, a solution of 6.14 g (0.186 mol) of MeOD and 3.72 g (0.186 mol) of D_2O was added dropwise over 1 min. After the mixture was stirred 10 min, 16 g of anhydrous Na_2CO_3 was added and stirred until CO_2 evolution ceased, ca. 15 min. Anhydrous Na_2SO_4 (10 g) was added and the mixture stirred for 10 min. The solution was filtered and the solvent removed under reduced pressure. Kugelrohr distillation gave 24.7 g of colorless liquid containing ca. 86% 2-chlorocycloheptanone, 6% 2,7-dichlorocycloheptanone, and 8% starting ketone as judged by GC retention time comparison to authentic materials. The yield of 2-chlorocycloheptanone was estimated to be 77%. No further purification was performed since the impurities did not affect the subsequent reactions. The absence of α-protons was indicated by ^{1}H NMR.

1,2,2-Trideuteriocyclohexanecarboxylic acid was prepared by the method of Gutsche[60] using D_2O and impure 2-chloro-2,7,7-trideuteriocycloheptanone. The isolated yield was 56%. ^{13}C NMR: cyclohexanecarboxylic acid, δ 182.7, 43.0, 28.8, 25.7, 25.4; 1,2,2-trideuteriocyclohexanecarboxylic acid, δ 182.4 (C=O), 42.4 (t, J_{CD} = 19.5 Hz, α to C=O), 28.7, 25.5, 25.4, 21.3–28.1 (m); FIMS 97.1% d_3, 2.4% d_2.

1,2,2-Trideuterio-*N*,*N*-dimethylcyclohexanecarboxamide was prepared from 1,2,2-trideuteriocyclohexanecarboxylic acid by the method of Cope and Ciganek[61] in 77% isolated yield.

***N*,*N*-Dimethyl-1,2,2-trideuteriocyclohexylmethylamine** was prepared from the amide by the method of Cope and Ciganek[61] in 88% isolated yield.

2,2-Dideuteriomethylenecyclohexane was prepared from the amine by the method of Cope and Ciganek[62] in 74% isolated yield. ^{1}H NMR (360 MHz) δ 4.60 (s, 2 H, vinyl), 2.13 (s, 2 H, allyl), 1.55 (s, 6 H). FIMS indicated 99.2% d_2 olefin. Capillary GC showed less than 0.2% of product had a retention time different from that of **1**-d_2.

Di(μ-chloro)bis(η³-2-methylenecyclohexyl)dipalladium (2) Prepared by the Procedure of Trost. The procedure and proportions of Trost[8] were used in smaller scale reactions. The purification of the product by chromatography on silica with $CHCl_3$ eluent was required in every case. The typical yields of 70–80% were less than the 92% yield reported by Trost; mp 132–139 °C (lit.[8] mp 131–138 °C). The melting point range of the product varied somewhat as decomposition accompanies melting. No impurities were detected by ^{1}H NMR.

Di(μ-chloro)bis(η³-2-methylenecyclohexyl)dipalladium (2) Prepared by Reaction in DMF Solution. Solid $PdCl_2$ (0.15 g, 0.85 mmol) was stirred with 15 mL of DMF for 1 h at 60 °C. Methylenecyclohexane (150–200 μL, 1.25–1.7 mmol) was added and the flask was sealed. After the solution was stirred at 60 °C for 3–20 h, it was cooled and poured into a benzene–H_2O mixture and extracted with three 15 -mL portions of benzene. Washing with brine and drying over $MgSO_4$ was followed by removal of solvent on the rotary evaporator. The resulting yellow oil spontaneously crystallized within 1 h. The crystalline mass was washed with pentane, collected by vacuum filtration, and washed with pentane. The yields averaged 35–45%, based on $PdCl_2$. Yields greater than 50% were rare but did occur on three occasions, giving 52%, 64%, and 70%.

Di(μ-chloro)bis(η³-2-methylenecyclohexyl)dipalladium (2) Prepared by Reaction in Benzene with Added DMF. To 150 mg (0.85 mmol) of $PdCl_2$ in 12–15 mL of benzene was added 0.13, 0.33, or 3.27 mL (1.68, 4.26, or 42.6 mmol) of DMF, and the mixture stirred at 60 °C for 15–30 min. Methylenecyclohexane (200 μL, 161 mg, 1.68 mmol) was added, the flask was sealed, and the solution was stirred for 12 h at 60 °C. The workup procedure was the same as for reactions in DMF. Yields were 45%, 33%, and 46% in these cases.

Di(μ-chloro)bis(η³-2-methylenecyclohexyl)dipalladium (2) Prepared by Reaction in Benzene with Added Amides. The above procedure was used, substituting 5 equiv of the following amides for DMF: tetramethylurea (0.5 mL, 0.49 g, 4.2 mmol), 37% yield; *N*,*N*-diisopropyl-2-methylpropionamide (0.35 g, 4.2 mmol), 19% yield; 1,3-dimethyl-2-imidazolidinone (0.46 mL, 0.48 g, 4.2 mmol), 19% yield.

Di(μ-bromo)bis(η³-2-methylenecyclohexyl)dipalladium Prepared by Reaction in DMF Solution. A procedure identical with that with $PdCl_2$, but with 225 mg (0.85 mmol) of $PdBr_2$, was used. The yield was 29%. Mp 149–51 °C; ^{1}H NMR δ 4.18 (s, 1 H, anti CH), 3.60 (s, 1 H, syn CH_2), 2.60 (s, 1 H, anti CH_2), 2.48 (m, 2 H), 1.4–2.0 (m, 6 H); FT-IR (KBr) 3045, 2980, 2930, 2850, 1475, 1451, 1445, 1420, 1140, 1065, 935, 855, 625 cm^{-1}.

Anal. Calcd for $C_{14}H_{22}Br_2Pd_2$: C, 29.87; H, 3.94; Br, 28.39. Found: C, 30.17; H, 4.04; Br, 29.44. The excess Br in the microanalysis was not within acceptable limits after several recrystallizations. The nearly identical ^{1}H NMR spectra of the analogous chloro- and bromo-bridged complexes indicate the assigned structure is correct and that the sample was difficult to purify. Volger reported discrepancies outside conventional limits for several (π-allyl)palladium chloride complexes.[7]

1-(*N*-Piperidinylmethyl)cyclohexene (4) was prepared by a modification of the procedure of Åkermark.[44] To 100 mg (0.42 mmol) of **2**, dissolved in ca. 10 mL of dry THF, was added 100 mg (0.51 mmol) of

Table V. GC–MS Data for Determination of **4**-d_2:**4**-d_1 for Product Isotope Effects

conditions		relative intensity *m/z* 179	*m/z* 180	*m/z* 181	d_2/d_1
DMF/21 °C	1	21831	110244	126658	5.22
	2	29894	149760	172116	5.14
DMF/60 °C	1	22438	79516	95165	4.56
	2	20463	69381	82852	4.54
DMF/86 °C	1	17652	112802	141044	3.66
	2	13570	86356	107616	3.67
benzene/DMF, 60 °C	1	7379	25784	30482	4.32
	2	11432	39658	46843	4.31
DMF/$PdBr_2$, 60 °C		9415	29141	34826	4.64
Trost method	1	34307	142907	160598	3.43
	2	35146	147545	165975	3.44
AcOH, no acetate	1	9203	32603	36968	3.62
	2	11392	38871	43754	3.54

$AgBF_4$ or the equivalent amount of $AgPF_6$. After standing 5 min, the solution was filtered through a glass wool plug and Celite. Ph_3P (0.232 g, 0.89 mmol) was added and dissolved, followed by ca. 0.5 mL (0.43 g, 5.0 mmol) of piperidine. After stirring 30–60 min, the solution was poured into 20 mL of Et_2O and extracted with 3 × 10 mL of 1 M HCl. The H_2O was removed on the rotary evaporator at 70–80 °C. After cooling and redissolving in 10 mL of H_2O, the solution was filtered through glass wool and made basic with 10 mL of 6 M NaOH. Extraction with 3 × 10 mL of pentane and careful removal of solvent under reduced pressure at room temperature gave an amine–water mixture. Kugelrohr distillation (1 mm, 50 °C) afforded 75 mg (93%) of **4** as a colorless liquid, usually contaminated with 2–3% **5**. Chromatography on silica, eluting with ca. 10% MeOH, 10% EtOAc, and 80% hexane, 0.5% ethyldiisopropylamine provided a pure sample of **4**: ^{1}H NMR δ 5.5 (s, 1 H, vinyl), 2.8 (s, 2 H, allyl α to N), 2.3 (m, 4 H), 2.0 (m, 4 H), 1.5 (m, 10 H); IR (thin film) 3040, 3000, 2930, 2850, 2790, 2740, 1450, 1110 cm^{-1}; MS *m/z* (relative intensity) 179 (38), 178 (24), 98 (100), 84 (74), 55 (21), 42 (18), 41 (32).

Anal. Calcd for $C_{12}H_{21}N$: C, 80.38; H, 11.80; N, 7.81. Found: C, 80.60; H, 11.54; N, 7.96.

2-(*N*-Piperidinyl)methylenecyclohexane (5) was isolated from the above product mixture by preparative GC on column B: ^{1}H NMR δ 4.75 (d, J = 2.5 Hz, 1 H, vinyl CH_2), 4.71 (s, 1 H, vinyl CH_2), 2.59 (m, 1 H), 2.35–2.55 (m, 2 H), 2.20–2.35 (m, 2 H), 1.2–2.1 (br, 14 H); GC–MS, *m/z* (relative intensity) 179 (100), 178 (50), 150 (60), 136 (78), 124 (71), 122 (79), 110 (74), 84 (72), 41 (72). Insufficient material was isolated for microanalysis.

(η^3-2-Methylenecyclohexyl)(2,4-pentanedionato-*O*,*O'*)palladium (6). To 75 mg (0.32 mmol) of **2** in ca. 20 mL of benzene was added 75 mg (0.61 mmol) of Na(acac), and the heterogeneous mixture was stirred for 6 h at 25 °C. White solid was present throughout the reaction. The mixture was poured into 30 mL of H_2O and extracted with 2 × 10 mL of pentane, washed with H_2O, and dried over $MgSO_4$. After removal of the solvent on the rotary evaporator, the residue crystallized, giving 91 mg (97%) of **6**: mp 85–88 °C; ^{1}H NMR δ 5.32 (s, 1 H, acac CH), 3.89 (s, 1 H, anti CH), 3.45 (s, 1 H, syn CH_2), 2.54 (t, J = 6.1 Hz, 2 H), 2.47 (s, 1 H, anti CH_2), 1.99 (s, 3 H), 1.97 (s, 3 H), 1.53–1.84 (br, 6 H); FT-IR 2940, 2860, 1580, 1510, 1395, 1255, 1195, 1015, 930, 800 cm^{-1}; MS *m/z* (relative intensity) 304 (3.5), 302 (8.2), 300 (9.3), 299 (7.1), 100 (17), 92 (22), 91 (52), 85 (24), 79 (44), 43 (100), 39 (27).

Anal. Calcd for $C_{12}H_{18}O_2Pd$: C, 47.93; H, 6.03. Found: C, 48.06; H, 6.03.

Determination of Product Isotope Effects. The reactions in AcOH and in DMF solvent were performed as described above. The aqueous AcOH solution was prepared from 25 mL of 70% aqueous AcOH, 500 mg (2.82 mmol) of $PdCl_2$, and 500 mg (3.72 mmol) of $CuCl_2$, which were stirred at 60 °C until the solid dissolved, ca. 4 h. The solution was dissolved into two equal portions and 150 μL of methylenecyclohexane-d_2 was added to each. The solutions were stirred at 60 °C for 18 h. The circulating temperature bath using ethylene glycol achieved temperature control of better than ±0.5 °C at 60 and 86 °C and better than ±0.2 °C at 21 °C. The workup and amination of each sample were the same as above. The amine from each reaction was analyzed by capillary GC–MS with a dynamic peak scanning technique to sample all peaks of interest several times each during elution from the GC column. The 70-eV EIMS of **4** used as a standard for all calculations was the sum of 800 spectra, *m/z* (relative intensity) 181 (0.98), 180 (12.91), 179 (100.0), 178 (63.06), 177 (2.87). Agreement with the molecular ion region calculated from natural isotopic abundances is good: *m/z* 181 (0.919), 180 (14.1), 179 (100). A sample of **4**-d_3 had the identical M − 1 relative intensity of 63 ± 1% of M$^+$ as the unlabeled compound. Table V contains the GC–EIMS intensities on which the product isotope effects are based.

Control Reaction for Isotopic Fractionation during Amination. A mixture of 51.8 mg (0.216 mmol) of **2**-d_3 and 61.7 mg (0.260 mmol) of **2** in a ratio of 1.20 ± 0.02 was aminated by the usual procedure. Kugelrohr distillation gave 59.8 mg (70%) of isotopic amines **4**. The EIMS analysis by hand measurement of oscillographically recorded flat-topped peak heights determined the d_0:d_3 ratio as 1.07 ± 0.1. This change in the ratio was considered insignificant compared to the large to moderate isotope effects observed.

Determination of Kinetic Isotope Effect in Formation of 2. A mixture of 100 μL each of methylenecyclohexane (80.7 mg, 0.841 mmol) and 95% chemically pure methylenecyclohexane-d_4, 96% d_4 content (79.9 mg, 0.799 mmol), was prepared and 170 μL was added to a solution of 155.2 mg (0.875 mmol) of $PdCl_2$ in ca. 15 mL of DMF at 60 °C. After stirring 8 h and workup as above for reactions in DMF, 78.2 mg (37.5%) of **2** was isolated. The yield of 0.33 mmol represents 20% consumption of olefin. After the typical amination procedure the ratio of the isotopic products **4**-d_0 and **4**-d_3 was determined by GC–MS to be 5.15 ± 0.23. The isotope effect was calculated[46] to be 5.4 ± 1.

Determination of Kinetic Isotope Effect in Isomerization of Methylenecyclohexane. In 10 mL of 90% aqueous AcOH were stirred 20 mg (0.11 mmol) of $PdCl_2$ and 14 mg (0.24 mmol) of NaCl at 60 °C for 20 min. The olefin d_0/d_4 mixture (ratio 1.29 ± 0.03) was added (150 μL, 123 mg, 1.26 mmol) and the flask was sealed. At the appropriate time the solutions were poured into 15 mL of H_2O and 12 mL of pentane, the layers were separated, and the pentane layer was washed twice with 10 mL of H_2O. The pentane solution was filtered through $MgSO_4$ above a glass wool plug in a pipet. A 200-μL portion was reserved for GC analysis, and the remainder was poured into a solution of MCPBA (0.4 g, 2.32 mmol in 15 mL of CH_2Cl_2). The reaction stopped at 4 min showed 18.1 ± 0.4% isomerization by capillary GC determination of the ratio of olefins. The reaction stopped at 6 min showed 26.3 ± 0.8% reaction. The isomeric epoxides were separated by preparative GC on column C, with quantitative collection at dry ice temperatures. The ratios of d_0 and d_4 epoxides of methylenecyclohexane were determined by FIMS to be 1.16 ± 0.04 and 1.07 ± 0.01, respectively. Standard treatments[46] give k_H/k_D as 1.80 and 1.92. The estimated error is ±0.4.

Acknowledgment. We thank J. Carter Cook for the GC–MS isotope ratio analyses and Prof. David Curtin, who provided computer programs for the crystallographic calculations. Support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. 1, 1192-37-6; **1**-d_2, 74975-93-2; **1**-d_4, 3452-02-6; **2**, 53789-97-2; **4**, 104507-68-8; **4**-d_1, 111469-33-1; **4**-d_2, 111469-32-0; **5**, 104507-69-9; **6**, 111469-34-2; Na_2PdCl_4, 13820-53-6; D_2, 7782-39-0; tetradeuteriocyclohexanone, 1006-03-7; 2-chloro-2,7,7-trideuteriocycloheptanone, 111469-28-4; 2,2,7,7-tetradeuteriocycloheptanone, 17616-76-1; 1,2,2-trideuteriocyclohexanecarboxylic acid, 111469-29-5; 1,2,2-trideuterio-*N*,*N*-dimethylcyclohexanecarboxamide, 111469-30-8; *N*,*N*-dimethyl-1,2,2-trideuteriocyclohexylmethylamine, 111469-31-9.

Supplementary Material Available: Results of the geometry calculations on X-ray structures of the 21 Pt–olefin complexes discussed in the text, including structures, atoms involved, and angles and distances (3 pages). Ordering information is given on any current masthead page.