for reactions 9 and 9a. Since S_H is fixed by this particular set of constraints, only k_{H-HH} and P_H can vary. The optimized values of k_{H-HH} and P_H converged to within 0.1%: $k_{H-HH} = (1.966 \pm 0.7) \times 10^{-5}$ M^{-1} s^{-1} and $P_H = 9.47 \pm 0.3$. The constraint that $S_H = S_D$ was then removed, and the optimization process was continued. The best values for the parameters were $k_{H-HH} = (1.93 \pm 0.7) \times 10^{-5}$ M^{-1} s^{-1}; $P_H = 9.50 \pm 0.3$; $S_H = 1.07 \pm 0.04$; $S_D = 1.11 \pm 0.04$. The two values for S_H and S_D are nearly equal as anticipated. The next step was to examine the effect of the constraint $S_HS_D = 1.19$ on the computed values of S_H and S_D. The value 1.19 was replaced successively by 1.10 and 1.30, yielding values for S_D of 1.10 and 1.11. Since the constraint on S_HS_D forces S_H to be 0.99 and 1.17, it would appear that S_D is determined by the kinetic data while S_H is sensitive only to the constraint. This is not surprising since S_D contains the term k_{D-HH} which is determined by the main reaction of (10), while S_H contains the term k_{H-HD} which is obscured by the strong contribution of reactions 9 and 9a. A careful analysis of this problem suggests that both S_H and S_D might be obtained if additional runs employing AH$^-$ and AHD as starting materials had been employed.

Since data for reactions 9 and 10 should *not* fit a single second-order reversible kinetic expression, these data afford a good opportunity to test whether deviations from a second-order reversible mechanism can be revealed by discrepancies between k_1/k_2 and K_{eq}. The data for reactions 9 and 10 were fitted to eq 8 with no constraint on k_1/k_2 (see Table II). For the reaction AD$^-$ + AHH, the ratio of k_1/k_2 is algebraically identical with $2k_{D-HH}/k_{H-HD}$. The value of the latter is $2S_HS_D$ or 2.38, while the computed ratio of k_1/k_2 is only 1.85. The deviation is nearly 25% and is about 2-4 times larger than the estimated standard deviation of $2S_HS_D$ (±0.12-0.24). By contrast, the deviation between k_1/k_2 and K_{eq} for the other examples in Table II range from 0% to 13% and all are within the experimental error of K_{eq}. For the reaction between AH$^-$ + ADD, the secondary reaction is more important, and this is reflected in the high value for $k_{D-DH}/2k_{H-DD}$ of 3.57 (Table II) compared with the experimental value of 0.59 (i.e., $S_HS_D/2$).

The rate constants from Table II show that neglecting the secondary reaction results in a substantial error of about 30-45% for the primary isotope effect. If this low value of k_H/k_D (i.e., 6.5-7.3) is substituted for $P_H = 9.50$, the computed concentrations of [AH$^-$] at various times deviate significantly from those calculated by using the correct rate expression and the optimized values of P_H, S_H, and k_{H-HH}. This is shown in Figure 2 for run DFM-III-30.

These examples provide an excellent argument for the earlier suggestion that the agreement between k_1/k_2 and K_{eq} is one necessary criterion for a unique relationship between a set of data and a second-order reversible rate expression. While such agreement cannot prove a second-order mechanism, the present examples are especially satisfying since the same data give an excellent fit to different rate expressions, but the parameters calculated for one of them do not give consistent agreement between k_1/k_2 and K_{eq}.

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Communications to the Editor

Molecular Structure of Dichloro(*endo*-dicyclopentadiene)palladium(II). Unsymmetrically Bound Olefins and the Preferred Site of Nucleophilic Attack

Laura L. Wright, Richard M. Wing,* and Michael F. Rettig

Department of Chemistry, University of California
Riverside, California 92521

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The activation of coordinated olefins toward nucleophilic attack has been a topic of interest for a number of years.[1] While nucleophiles react readily with coordinated olefins, this is not the case for unactivated olefins. The source of activation by the metal center has recently been discussed by Eisenstein and Hoffmann in this journal.[2] They have suggested that the activation results from an unsymmetrically oriented olefin, i.e., one that has laterally "slipped" the metal away from the symmetric η^2-π complex:

In order to test this hypothesis it is necessary to examine a conformationally constrained complex which shows selectivity toward nucleophilic attack to see if this slipping or an analogous distortion is observed and whether the activation of the olefin occurs in the direction predicted. We report here the molecular structure of such a system.

Dichloro(*endo*-dicyclopentadiene)palladium(II) was prepared following the procedure of Chatt.[1b] Recyrstallization by slow evaporation of a CH_2Cl_2 solution of the diene complex yielded golden-yellow platelets suitable for single-crystal X-ray diffraction. Cone axis and zero-layer precession photographs clearly gave the monoclinic space group $P2_1/c$ and least-squares refinement of 12 carefully centered reflections with $2\theta > 35°$ [$\lambda_{\text{Mo}K\alpha} = 0.70926$ Å] resulted in cell dimensions of $a_0 = 11.346$ (7) Å, $b_0 = 7.687$ (4) Å, $c_0 = 17.429$ (6) Å, and $\beta = 138.50$ (2)°. Using the θ-2θ scan method (scan = $1.5 + 0.692\tan\theta$) for the range $3 \le 2\theta \le 45°$, 1185 unique reflections with $I > 2\sigma(I)$ were collected on an automated Picker FACS I diffractometer. The dimensions of the crystal used during data collection were ca. 0.3- × 0.4- × 0.1 mm. No correction for absorption was made; μ(Mo Kα) = 23 cm^{-1}.

The structure was solved by the heavy-atom method.[3] From a three-dimensional Patterson map, the position of the palladium was determined, and subsequent electron density maps yielded the positions of all the chlorine, carbon, and hydrogen atoms. The palladium and chlorine atoms were refined with anisotropic temperature factors, and the real and imaginary parts of their anomalous dispersion were considered.[4] Full-matrix least-squares

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(1) (a) Chatt, J.; Valerino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2496-2507. (b) *Ibid.* **1957**, 3413-3416. (c) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135-5141. (d) Hines, L. F.; Stille, J. K. *Ibid.* **1972**, *94*, 485-490. (e) Wipke, W. T.; Goeke, G. L. *Ibid.* **1974**, *96*, 4244-4249. (f) Goeke, G. L. Ph.D. Thesis, Princeton University, 1973. (g) De Renzi, A.; Palumbo, R.; Paiaro, G. *J. Am. Chem. Soc.* **1971**, *93*, 880-883. (h) Betts, S. J.; Harris, A.; Haszeldine, R. N.; Parish, R. V. *J. Chem. Soc. Sec. A* **1971**, 3699-3705.

(2) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 6148-6149. (b) Eisenstein, O.; Hoffmann, R. *Ibid.* **1981**, *103*, 4308-4320.

(3) The crystal structure of the platinum analogue has been published twice. In the first publication the residual was only down to 13% and only three carbon-platinum bond lengths were reported. Baenziger, N. C.; Doyle, J. R.; Richards, G. F.; Carpenter, C. L. "Advances in the Chemistry of Coordination Compounds"; Kirshner, S., Ed.; The MacMillan Co.: New York, 1961; pp 136-137. In the second structure no geometrical parameters were reported due to high standard deviations in bond lengths (±0.15 Å) and angles (±5-6°). Avitabile, G.; Ganis, P.; Lepore, U.; Panunzi, A. *Inorg. Chim. Acta* **1973**, *7*, 329-330.

(4) (a) "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. IV. (b) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w_i(|F_{oi}| - |F_{ci}|)^2/\sum w|F_{oi}|^2]^{1/2}$; $w_i = 1/\sigma^2$, with σ given as per Corfield et al. (Corfield, P.; Doedens, R.; Ibers, J. *Inorg. Chem.* **1967**, *6*, 197-210) using a value of 0.045 as the fudge factor *p*.

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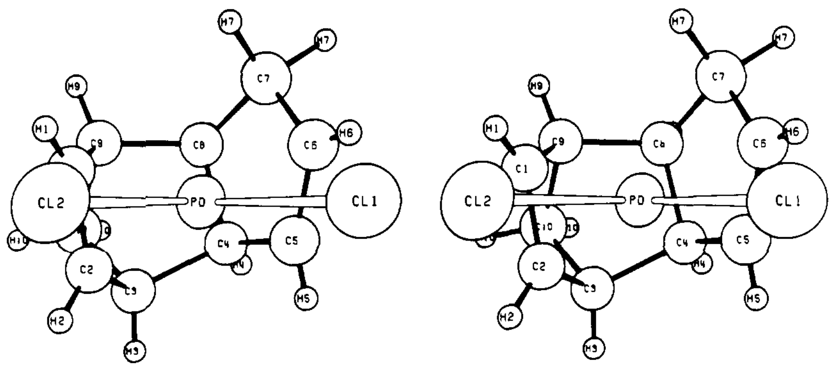


Figure 1. Stereopair drawing of dichloro(*endo*-dicyclopentadiene)palladium(II) looking edge on to the square plane.

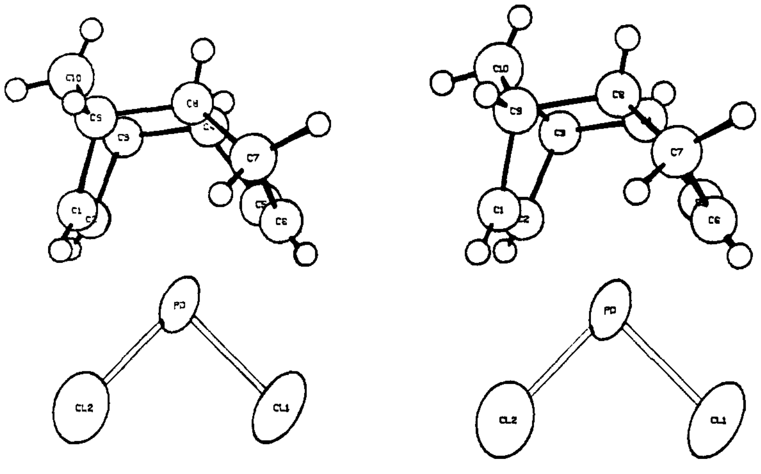
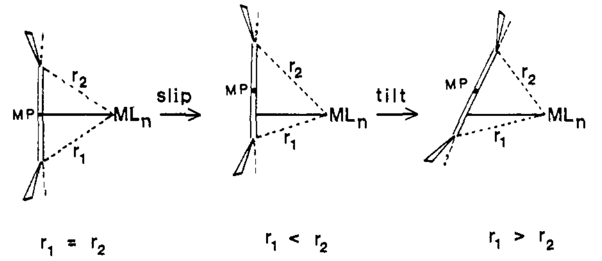


Figure 2. Stereopair drawing of the title compound as viewed from above the square plane.

refinement of all the atom positions and temperature factors yielded an unweighted residual (R) of 4.6% and a weighted residual (R_w) of 4.9%.[4b]

The structure (Figure 1) shows that while both of the double bond midpoints are at normal distances from the central palladium[5] [2.13 (1) vs. 2.10 (2) Å for Pd to the midpoint of C(1)=C(2), MP12, and Pd to the midpoint of C(5)=C(6), MP56, respectively], several geometric deformations are observed upon close examination of the mode of coordination for the C(1)=C(2) double bond. A slipping of the C(1)=C(2) bond axis with respect to the $PdCl_2$ plane has occurred such that its midpoint has moved 0.34 Å away from the plane so that C(1) is closer to the plane. If this were the only deformation, C(2) would now be farther from the metal, but a second more serious deformation away from the normal perpendicular η^2 configuration has also occurred, namely, serious tilting of the C(1)=C(2) bond axis. The C(1)=C(2) bond axis is tilted at an angle to the $PdCl_2$ plane that is 13° away from the normal 90° value. The sum of these distortions brings C(2) in closer to the metal [2.19 (1) Å] and moves C(1) farther away [2.28 (1) Å] (Figure 2). The C(5)=C(6) bond does not show this type of deformation; MP56 is only 0.07 Å out of the $PdCl_2$ plane and is only tilted 2°, thus leaving the Pd–C(5) and Pd–C(6) distances equal at 2.21 (2) and 2.20 (2) Å, respectively.

The dicyclopentadiene ligand itself is locked into a single conformation such that the relative positioning of the two olefinic bonds is already established prior to binding palladium. Upon coordination the diene has one of the double bonds almost perpendicular to the square plane while the other double bond is forced to bind in the more unsymmetrical fashion. While a deformation of the type proposed by Hoffmann[2] has occurred, its effect has been overwhelmed by the tilting of the double bond. The resulting configuration is still clearly the same: one carbon is closer to the metal and the other is farther away. In this



unsymmetrically bound olefin, the more strained (norbornene) double bond, C(1)=C(2), should show increased activation with respect to nucleophilic attack, and C(1) should be the point of attack if the current thesis[2] is to be supported. This is borne out in all published studies of the attack of alkoxides, β-diketones, and amines[1a–c,7] on this diene complex. It has been shown by NMR spectroscopy, degradation, and X-ray crystallography[1c,7,8] that the nucleophile specifically attacks C(1) to form the predicted product.

Wipke and Goeke[1e,f] have reported that the norbornene double bond in the related 5-vinylnorbornene is even more reactive with respect to nucleophilic attack when interacting with palladium than the analogous bond in dicyclopentadiene. The diene complex of 5-vinylnorbornene cannot be isolated but proceeds on immediately to the chloropalladation product with the chlorine bound to the diene at the analogous carbon (reaction 1). Both 5-vinylnorbornene and dicyclopentadiene are so activated toward attack by methanol that the addition of base is not required in order to obtain the methoxy derivative. In the cases of nor-

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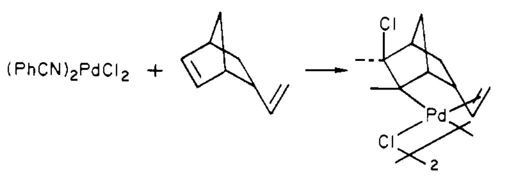
(5) Rettig, M. F.; Wing, R. M.; Wiger, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 2980–2986.

(6) Other angles of interest are C(1)–MP12–Pd = 94 (1)°, C(2)–MP12–Pd = 86 (1)°, C(5)–MP56–Pd = 90 (1)°, C(6)–MP56–Pd = 90 (1)°, Cl(1)–Pd–Cl(2) = 89.3 (2) and MP12–Pd–MP56 = 92.5 (6)°.

(7) Stille, J. K.; Fox, D. B. *J. Am. Chem. Soc.* **1970**, *92*, 1274–1278.

(8) Whitla, W. A.; Powell, H. M.; Venanzi, L. M. *Chem. Commun.* **1966**, 310–311.



(1)

bornadiene and 1,5-cyclooctadiene, base is essential in order to obtain the analogous methoxy complexes.[1f] Since the norbornadiene·$PdCl_2$ complex is relatively unreactive, there must be some source of activation other than just the relief of strain in the norbornene systems. Models show that a metal complex of 5-vinylnorbornene would require the norbornene double bond to be even more seriously tilted than in the case of the dicyclopentadiene·$PdCl_2$ complex. The two double bonds in 5-vinylnorbornene are even less parallel, and when the less substituted vinyl group binds to the metal in a normal perpendicular manner, the norbornene double bond is forced to bind in an extremely unsymmetrical manner.

Thus, we conclude that deformation from the symmetrical η^2–π complex plays a dominant role in directing the attack of nucleophiles on activated double bonds.

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Registry No. Dichloro(*endo*-dicyclopentadiene)palladium(II), 12294-98-3.

Supplementary Material Available: Fractional coordinates and thermal parameters (Table I), bond lengths (Table II), and structure factors (Table III) (10 pages). Ordering information is given on any current masthead page.

Nickel(II)-Promoted Ethanolysis and Hydrolysis of *N*-(2-Pyridylmethyl)urea. A Model for Urease

Robert L. Blakeley,* Anthony Treston, Robert K. Andrews, and Burt Zerner*

Department of Biochemistry, University of Queensland
St. Lucia, Queensland, Australia 4067

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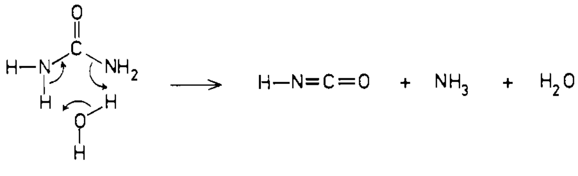
Experiments are reported which establish that O-coordination of the title urea to nickel(II) promotes nucleophilic attack of solvent on the otherwise unreactive carbonyl group of the urea.

The rate of the nonenzymatic degradation of urea in aqueous media is independent of pH between pH 2 and pH 12, falling below pH 2 and rising above pH 12.[1,2] It has been demonstrated at pH values of 7, 13, and 14 that the reaction is an *elimination*, yielding as the sole products ammonia and cyanic acid (eq 1). The



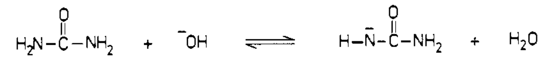
(1)

data support an invariant mechanism of degradation over the entire pH range (eq 1),[3] the falloff below pH 2 being reasonably ascribed to the protonation of urea and the dependence on [$^-$OH] above pH 12 being ascribed to specific base catalysis of the elimination reaction (eq 2a,b).[4] The latter chemistry is adequately supported by a variety of models.[5–7]

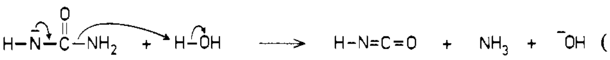
Table I. Ethanolysis and Hydrolysis of *N*-(2-Pyridylmethyl)urea in the Presence of 0.39 M $NiCl_2$[a]

temp, °C	$[1]_0$, M	$[H_2O]$, M	10^5k_{obsd},[b] s^{-1}	$\frac{[3]_\infty}{[1]_0}$[c]	$10^5k'_{EtOH}$, s^{-1}	$10^5k'_{H_2O}$, s^{-1}
80.25	0.025	0.78	17.7	0.064	16.6	1.1
80.25	0.050	0.78	17.1	0.067	15.9	1.1
80.25	0.100	0.78	17.8	0.078	16.4	1.4
80.25	0.050	1.67	20.3	0.100	18.3	2.0
80.25	0.050	3.00	23.1	0.185	18.8	4.3
80.25	0.050	5.22	27.7	0.269	20.2	7.5
70.04	0.050	0.78	5.10	0.086	4.66	0.44
60.02	0.050	0.78	1.50	0.089	1.36	0.134
50.00	0.085	0.78	0.409	0.091	0.372	0.037

[a] $NiCl_2\cdot 6H_2O$ was partially dehydrated at 82 °C in vacuo. The concentration of $NiCl_2$ was determined spectrophotometrically at 395 nm in 1 M HCl. Distilled ethanol was dried over 4A molecular sieves. [b] ±4% (2 standard errors); from loss of 1. [c] 1 = *N*-(2-Pyridylmethyl)urea; 3 = (2-Pyridylmethyl)amine.

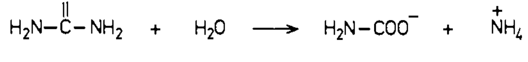


$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 + {}^-OH \rightleftharpoons H-\overset{-}{N}-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O \qquad (2a)$$



$$H-\overset{-}{N}-\overset{O}{\overset{\|}{C}}-NH_2 + H-OH \longrightarrow H-N=C=O + NH_3 + {}^-OH \qquad (2b)$$

Urease catalyzes the *hydrolysis* of urea to form carbamate ion (eq 3).[8] At pH 7.0 and 38 °C, the *urease-catalyzed hydrolysis*



$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O \longrightarrow H_2N-COO^- + \overset{+}{NH_4} \qquad (3)$$

of urea must be at least 10^{14} times as fast as the *spontaneous hydrolysis* of urea which has never been observed.[9] On the balance of available evidence from model studies,[10] and especially from consideration of the structures of molecules which are and are not substrates for urease,[7] we recently postulated that *all* substrates for urease (thus far, urea, *N*-hydroxyurea,[8,11] *N*-methylurea,[7] semicarbazide,[7,12] formamide,[7,13] and acetamide[7]) are activated toward nucleophilic attack on carbon by virtue of O-coordination to an active-site Ni(II) ion as in I. The detailed mechanism[7] arising from this postulate was without precedent in the chemistry of ureas or amides.

Hydroxamic acids reversibly inhibit urease from all sources that have been tested.[14] Wherever the dependence of urease on metal

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[4] Reported values of the pK'_a of urea range from 13.7 to 14.3 while those of its conjugate acid (urea·H^+) range from 0.1 to 0.2: Woolley, E. M.; Hepler, L. G. *Anal. Chem.* **1974**, *44*, 1520–1523.

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[9] The value of k_{cat} for the urease-catalyzed hydrolysis of urea (eq 3) is 5.87×10^3 s^{-1} at pH 7.00 and 38 °C.[7] The rate constant k for the pH-independent degradation of urea (eq 1) at 38 °C is 6.1×10^{-9} s^{-1} where $k = Ae^{-E_a/RT}$, $A = 5.77 \times 10^{14}$ s^{-1} and $E_a = 32.7$ kcal/mol.[2,3a]

[10] N-Coordination of carboxylic acid amides with Cu(II) (Nakon, R.; Angelici, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 3170–3174) and Co(III) (Buckhingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 3451–3456) does *not* produce activation toward alkaline hydrolysis. In contrast, O-coordination of *N*,*N*-dimethylformamide to pentaminecobalt(III) activates the amide by a factor of ~10^4 toward alkaline hydrolysis: Buckingham, D. A.; Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 1726–1729.

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