phosphate which cyclizes via the illustrated anti-boat conformation. Further experiments to demonstrate this point explicitly are in progress.[16]

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[16] **Note Added in Proof:** We have now experimentally confirmed that trichodiene synthetase cyclizes (3*R*)-nerolidyl pyrophosphate.

$Pd(\eta^1-H_2)$ and $Pd(\eta^2-H_2)$: Ligand-Free End-on and Side-on Bonded Molecular Dihydrogen Complexes

Geoffrey A. Ozin* and Jaime García-Prieto

Lash Miller Chemical Laboratories
University of Toronto
Toronto, Ontario, Canada M5S 1A1

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As part of our program on H_2 and CH_4 activation on single metal atoms,[1] we have discovered a system that yields molecular dihydrogen complexes rather than hydrides. Following Kubas' seminal discovery of $W(CO)_3(PR_3)_2(\eta^2-H_2)^2$ containing side-on bound molecular dihydrogen a flurry of reports appeared on other dihydrogen complexes including $Cr(CO)_5(H_2)$,[3-5] $Cr(CO)_4(H_2)_2$,[3] $[Ir(H)(H_2)(PPh_3)_2(C_{13}H_8N)]^+$,[6] *trans*-$[M(H)(H_2)(PPh_2CH_2CH_2PPh_2)_2]BF_4$,[7] and $[IrH_2(H_2)_2L_2]^+$, where L = $P(C_6H_{11})_3$.[8] Interestingly, some reports of intrazeolite dihydrogen complexes of Ni^+ and Pd^+ exist in the earlier literature.[9,10] In conjunction with ab initio quantum chemical calculations on model M + H_2 potential energy surfaces,[11] a clearer insight into the H_2 activation process and the role and properties of precoordinated molecular dihydrogen is developing.

Despite this impressive progress there still did not exist any experimental information on the most basic of all systems, namely, $M(H_2)$, a "ligand-free molecular dihydrogen complex".

As a direct outcome of our work with the Pd/H_2 system at low temperatures we have discovered that ground-state $4d^{10}$ Pd atoms "spontaneously" react with H_2 in rare gas matrices to produce molecular dihydrogen complexes.

The work can be briefly described as follows. Pd atoms react on deposition with H_2-doped Kr and and Xe matrices at 12 K (Figures 1 and 2). Optical and IR spectroscopy, in conjunction with Pd concentration studies, H_2, HD, and D_2 isotope substitution experiments, thermal annealing, and wavelength-selective photochemistry, define the products to be $Pd(\eta^1-H_2)$ coexisting with $Pd(\eta^2-H_2)$ in Kr, while $Pd(\eta^2-H_2)$ exclusively exists in Xe,[12] (Figures 1 and 2). The fact that small matrix changes (Kr to Xe) can induce such alterations in the mode of coordination of dihydrogen, from η^1-H_2 to η^2-H_2, implies that the energy differences between $Pd(\eta^1-H_2)$ and $Pd(\eta^2-H_2)$ are of the same order of magnitude as matrix interactions. The lack of observable isotope scrambling in H_2/D_2 and HD experiments and the nonobservation

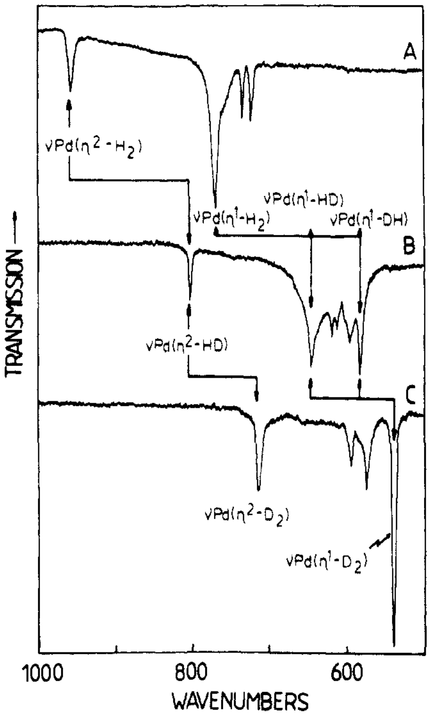

Figure 1. Infrared spectrum of (A) $Pd/H_2/Kr \cong 1/10^3/10^4$, (B) $Pd/HD/Kr \cong 1/10^3/10^4$, and (C) $Pd/D_2/Kr \cong 1/10^3/10^4$ deposited at 10–12 K. The vibrational assignments are indicated. Resolution, 2 cm^{-1}. A preliminary N.C.A. of $Pd(\eta^1-H_2)/Pd(\eta^1-HD)/Pd(\eta^1-DH)/Pd(\eta^1-D_2)$ for a linear configuration favors the assignments denoted in the figure for this species.

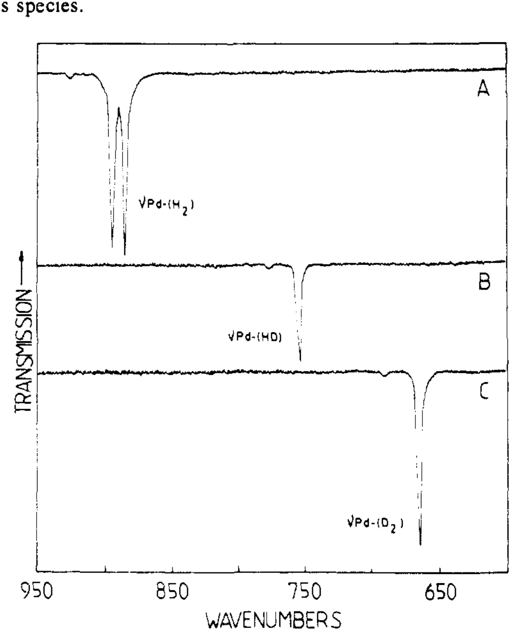

Figure 2. Infrared spectrum of (A) $Pd/H_2/Xe \cong 1/10^3/10^4$, (B) $Pd/HD/Xe \cong 1/10^3/10^4$, and (C) $Pd/D_2/Xe \cong 1/10^3/10^4$ deposited at 10–12 K. The vibrational assignments are indicated. Resolution, 2 cm^{-1}.

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(12) Thermal annealing up to 45 K shows the growth and decay of an additional *unsplit* band in each Pd/H_2, HD, or D_2/Xe sample, blue-shifted by 37.5, 24.0, or 24.5 cm^{-1} with respect to the band observed on deposition. Two distinct trapping sites for $Pd(\eta^2-H_2)$ are therefore defined.

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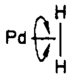
of PdH_x hydrides[13] establish that the dihydrogen moiety maintains its integrity in these matrix reactions.[14]

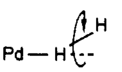
Product distributions as viewed through the IR absorbances of $Pd(H_2)$ and $Pd(D_2)$ in $H_2/D_2/Kr$ and $H_2/D_2/Xe$ mixtures following deposition implies that the reaction of Pd atoms with H_2 is downhill without an appreciable barrier, as predicted by theory.[15] Diagnostic IR signatures for $Pd(\eta^1\text{-}H_2)$ comprise $\nu(Pd–(H_2))$ and $\delta(Pd–H–H)$ modes at 771 and 315 cm^{-1}, respectively, and for $Pd(\eta^2\text{-}H_2)$ a $\nu(Pd–(H_2))$ mode at 894.5/885.5 cm^{-1}. (The vibrational mode involving mainly stretching of the H–H bond is expected to absorb at much higher frequencies, 4200–2500 cm^{-1}, and to exhibit a characteristically very low intensity.[2-10] Under the highest sensitivity conditions in our experiments this IR band passed undetected.) The resemblance of $\nu(M–(X_2))$ stretching modes of $Pd(\eta^1\text{-}X_2)$, 770, 648/585, 546 cm^{-1}, and $Pd(\eta^2\text{-}X_2)$, 960, 804, 714 cm^{-1}, in Kr and $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$, 953, 791, 703 cm^{-1}, for X_2 = H_2, HD, and D_2, respectively, suggest comparable binding energies for end-on- and side-on-bonded dihydrogen in the Pd and W complexes.

Higher resolution IR scans reveal certain fine structure details for $Pd(\eta^1\text{-}H_2)$ and $Pd(\eta^2\text{-}H_2)$ which are indicative of matrix-dependent dynamical effects of the coordinated dihydrogen moiety. For example, the striking 9 cm^{-1} doublet splitting *unique* to the $\nu(Pd–(H_2))$ mode of $Pd(\eta^2\text{-}H_2)$ in Xe but noticeably absent for $Pd(\eta^2\text{-}HD)$ and $Pd(\eta^2\text{-}D_2)$ can be interpreted in terms of a librational mode of dihydrogen in a symmetrical double-well potential created by the matrix cage and illusted by



Using the Pauling model potential,[16] $V_0(1 - \cos 2\theta)$, and the observed 9 cm^{-1}, librational splitting for $Pd(\eta^2\text{-}H_2)$, we calculate the barrier height $2V_0 \cong 1400\ cm^{-1}$. This can then be used to determine the librational splittings for $Pd(\eta^2\text{-}HD)$ and $Pd(\eta^2\text{-}D_2)$ which are calculated to be within the widths of the respective IR lines, namely, less than 3 cm^{-1} (Figure 2). Support for this model stems from the fact that in the more constrained sites of solid Kr, one expects a higher barrier for the librational motion and a concomitant reduction of the splitting,[16] consistent with the nonobservation of this dynamical effect in this matrix.

Another kind of dynamical effect unique to the $Pd(\eta^1\text{-}H_2)$ species in Kr is apparent from the observation of what seems to be a rotational progression of about 12 cm^{-1} spacing superimposed on the $\nu(Pd–(H_2))$ IR band around 771 cm^{-1}. This structure, which is reproducible from run to run, may be characteristic of hindered rotor dynamics of an end-on-bonded dihydrogen moiety on a heavy Pd atom anchor, represented as



We cannot yet exclude the contribution of ortho/para dihydrogen effects on these dynamical processes.[17,18] Work is continuing on this problem.

Finally, it is noteworthy that one of the low-lying excited states of $Pd(\eta^2\text{-}H_2)$ is calculated by SCF–Xα–SW MO methods[19] to be unbound with an energy around 300–400 nm. The optical spectrum of $Pd(\eta^2\text{-}H_2)$ in Kr and Xe shows very weak absorption in this wavelength range. Broad-band photoexcitation into this region results in photodissociation of $Pd(\eta^2\text{-}H_2)$, with no sign of insertion to PdH_2, fragmentation to PdH + H, or isomerization to $Pd(\eta^1\text{-}H_2)$.

Acknowledgment. The generous financial assistance of the Natural Sciences and Engineering Research Council of Canada's Operating and Strategic Grants programs and an award from the Connaught Foundation of the University of Toronto is gratefully appreciated. G.A.O. is indebted to the 3M Corp., St. Paul, MN, for a 3M research award. We also acknowledge invaluable technical discussions with Dr. Martin Moskovits on $Pd(H_2)$ dynamics, as well as Dr. Douglas McIntosh, Mark Parnis, and John McCaffrey.

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[13] Note that the fundamentals of gaseous PdH and PdD occur at 2083 and 1446 cm^{-1}, respectively. (Basch, H.; Cohen D.; Topiol, S. *Isr. J. Chem.* **1980**, *19*, 233.)

[14] Two additional weak bands were observed at 583 and 351 cm^{-1} in $Pd/H_2/Xe$ samples. These correspond to *pure rotational transitions* $S_0(1)$ and $S_0(0)$ of H_2 isolated in a Xe matrix (Warren, J. A.; Smith, G. R.; Guillory, A. *J. Chem. Phys.* **1980**, *72*, 4901. Prochaska, F. T.; Andrews, L. *J. Chem. Phys.* **1977**, *67*, 1139).

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[18] The existence of a doublet on the low-frequency side of the $\nu(Pd–(H_2))$ mode of $Pd(\eta^1\text{-}H_2)$, Figure 1, could be either an ortho-/para-rotational effect, of a multiple trapping site effect.

[19] Ozin, G. A.; McIntosh, D. F.; Garcia-Prieto, J. work in progress.

Extremely Stereoselective and Stereospecific Reductive Cleavage of β-Lactams: A Highly Efficient Route to Labeled Homochiral Peptides

Iwao Ojima* and Nobuko Shimizu

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794

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Besides its importance as a fundamental structure of β-lactam antibiotics, the β-lactam skeleton has been shown to be useful as a synthetic building block in organic synthesis.[1,2] In fact, we have developed a novel route to peptides through the hydrogenolysis of homochiral 4-aryl-β-lactam intermediates on Pd catalyst, i.e., the "β-lactam synthon method",[3] and successfully applied it to the synthesis of potent enkephalin analogues.[4]

Although it was found that no racemization took place at the original C_3 position of homochiral 4-aryl-β-lactams during the hydrogenolysis on Pd catalyst,[3,4] the stereochemistry of the cleavage of the C_4–N bond had not yet been studied. Conceptually, there are three possibilities (Scheme I): (i) retention of configuration via a palladometallacycle (**1**), (ii) inversion of configuration via an S_N2-type mechanism (**2**), and (iii) racemization via a free radical mechanism (**3**). In order to look at the stereochemistry, D_2 was employed so that the products would have a chiral benzyl group.

First, a pair of homochiral diastereomeric β-lactams, **4a** and **4b**, were used as typical substrates. Compound **4** (36.7 mmg, 0.100

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