Photoelectron spectroscopic and theoretical study of the [HPd(η2-H2)]− cluster anion

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Photoelectron spectroscopic and theoretical study of the [HPd(η²-H₂)]⁻
cluster anion

Xinxing Zhang, Paul J. Robinson, Gerd Ganteför, Anastassia Alexandrova, and Kit H. Bowen

Departments of Chemistry and Materials Science, Johns Hopkins University, Baltimore, Maryland 21218, USA
Departments of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, USA
California NanoSystems Institute, 570 Westwood Plaza, Building 114, Los Angeles, California 90095, USA

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Anion photoelectron spectroscopic and theoretical studies were conducted for the PdH⁻ and PdH₃⁻ cluster anions. Experimentally observed electron affinities and vertical detachment energies agree well with theoretical predictions. The PdH⁻ anionic complex is made up of a PdH⁻ sub-anion ligated by a H₂ molecule, in which the H–H bond is lengthened compared to free H₂. Detailed molecular orbital analysis of PdH⁻, H₂, and PdH₃⁻ reveals that back donation from a d-type orbital of PdH⁻ to the σ⁺ orbital of H₂ causes the H–H elongation, and hence, its activation. The H₂ binding energy to PdH⁻ is calculated to be 89.2 kJ/mol, which is even higher than that between CO and Pd. The unusually high binding energy as well as the H–H bond activation may have practical applications, e.g., hydrogen storage and catalysis. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4929998]

INTRODUCTION

The interaction between transition metals (TM) and hydrogen has always been an intriguing research topic, with applications in hydrogen storage and catalysis. Recently, our joint experimental/theoretical team discovered the PdZnH₅⁻ cluster anion; it possessed an unprecedented planar pentagonal coordination between the H₅⁻ ring and Pt moieties and also exhibited special σ-aromatic character. In this species, the H₅⁻ ring moiety as a whole can be viewed as a η²-H₂ ligand interacting with Pt, and it is in turn stabilized by the Pt atom. More recently, Novick performed a study of [Cu(η²-H₂)F] and [Ag(η²-H₂)Cl] neutral clusters via microwave spectroscopy. He found back-donation from a d-type orbital on these transition metals to the unoccupied σ⁺ orbitals of H₂, this causing the elongation of the H–H bond. The occupied σ orbital of H₂ acts as a “lone pair” and inserts into the lowest unoccupied molecular orbital (LUMO) of the metal halide. In all of these cases, while the geometry of the H₂ moiety does not deviate much from that of the free H₂, the binding energies of H₂ to their transition metals (80–110 kJ/mol) are much greater than typical van der Waals interaction energies. Other η²-H₂ ligation examples were discovered in more complicated transition metal complexes, such as those protected by N, P, or O-based ligands or the π-acceptor ligand, CO.

In the present paper, we report an anion photoelectron spectroscopic (PES) study of the PdH₅⁻ cluster anion in which a H₂ molecule acts as a ligand to PdH⁻. Ab initio calculations closely reproduce the experimental data, confirming the structure of the anion seen in the experiment. In order to understand the bonding between H₂ and PdH⁻, the photoelectron spectrum of PdH⁻ as well as a molecular orbital (MO) analysis of PdH⁻, PdH₃⁻, and H₂ is also presented. The H–H bond in PdH₅⁻ is lengthened compared to that in the free H₂ molecule due to back donation from a d-type orbital of PdH⁻ to the LUMO (the σ⁺ orbital) of H₂. The additional interactions of H₂ and PdH⁻ come from the bonding and anti-bonding combinations of the highest occupied molecular orbital (HOMO, the σ orbital) of H₂ and the σ bonding orbital of PdH⁻.

EXPERIMENTAL AND THEORETICAL METHODS

This work utilized anion PES as its primary probe. Anion PES is conducted by crossing a mass-selected beam of negative ions with a fixed-energy photon beam and energy analyzing the resulting photodetached electrons. This technique is governed by the energy conservation relationship, hv = EBE + EKE, where hv, EBE, and EKE are the photon energy, electron binding (transition) energy, and the electron kinetic energy, respectively. Our photoelectron spectrometer, which has been described previously, consists of one of the several ion sources, a linear time-of-flight mass spectrometer, a mass gate, a momentum decelerator, a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser for photodetachment, and a magnetic bottle electron energy analyzer having a resolution of 35 meV at EKE = 1 eV.
Photoelectron spectra were calibrated against the well-known photoelectron spectrum of Cu$^-$, PdH$^{-1,3}$ anions were generated using a pulsed arc cluster ionization source (PACIS), which has been described elsewhere.$^{17}$ A $\approx 30$ $\mu$s duration, 180 V electrical pulse applied across the anode and sample cathode of the discharging chamber vaporized the Pd atoms. The sample cathode was prepared by firmly pressing Pd powder onto a copper rod. Almost simultaneously, 200 psi of ultra-high purity hydrogen gas was injected into the discharge region, where it was dissociated into hydrogen atoms. The resulting mixture of atoms, ions, and electrons then reacted and cooled as it flowed along a 15 cm tube before exiting into high vacuum. The resulting anions were then extracted and mass-selected prior to photodetachment.

Density functional theory calculations were conducted by applying PBEPBE functional$^{18}$ using the Gaussian09 software package$^{19}$ to determine the geometries of the anionic and neutral clusters. The 6-311++G (3df, 3pd) basis set$^{20}$ on H and the Stuttgart Dresden (SDD) basis set$^{21}$ on Pd were used. The PdH, PdH$^-$, PdH$_2$, and PdH$_3$ clusters were all initially treated with ROHF SCF with the aug-CC-pVTZ-PP$^{22}$ basis set on the Pd atom, and the ATZP$^{23}$ basis set on H atoms. The wavefunctions were then read in the CCSD(T)$^{24}$ and equation of motion coupled-cluster singles doubles and perturbative triples (EOM-CCSD(T))$^{25}$ calculations. The adiabatic detachment energy (ADE) is the energy difference between the anion and the neutral relaxed to the anion’s nearest local minimum. If the local minimum is also the global minimum, the ADE is also the adiabatic electron affinity (EA). The vertical detachment energy (VDE) was obtained by subtracting the energy of the neutral cluster calculated at the geometry of the anion from the energy of the anion. Deeper transitions were calculated by adding the electronic excitation energies of the neutral to the VDE. We note that the agreement with the experimental spectrum improved dramatically with the increase of the basis sets, and also the inclusion of the perturbative-triple excitations in CCSD(T) (EOM-CCSD was insufficient). All calculations were carried out using NW Chem software$^{26}$ and all visualizations of orbitals were generated with VMD.$^{27}$ Atomic charges were calculated using Natural Population Analysis (NPA)$^{28}$ in Gaussian 09 with the SDD basis set on Pd and TZVP$^{29}$ basis set on H. The NPA method has been found to be satisfactory in calculating the charge distribution within a cluster.$^{30,31}$ Density functional theory was implemented using the B3LYP$^{32}$ hybrid functional.

**RESULTS AND DISCUSSION**

Figure 1 presents a portion of the mass spectrum, showing the PdH$_{1,3}^-$ anions. Due to isotopic congestion from Pd and from two different Pd/H stoichiometries, the mass spectrum

![Experimental and Simulated PdH$^-$ and PdH$_2^-$](image1)

**FIG. 1.** The mass spectrum showing PdH$_{1,3}^-$ and the simulated isotopic distributions for both PdH$^-$ and PdH$_2^-$.

![Experimental and Simulated PdH$^-$ and PdH$_2^-$](image2)

**FIG. 2.** The anion photoelectron spectra of PdH$^-$ and PdH$_3^-$, each taken with 3.49 eV laser.

<table>
<thead>
<tr>
<th>Species</th>
<th>Expt.</th>
<th>Theoretical</th>
<th>Final configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdH$^-$</td>
<td>EA $\sim$ 1.2</td>
<td>ADE 1.288</td>
<td>N/A</td>
</tr>
<tr>
<td>X 1.29</td>
<td>1.29</td>
<td>$\ldots 1\Sigma^{-,2}$, $1\Pi$, $\Delta^4$, $2\Sigma^1$</td>
<td></td>
</tr>
<tr>
<td>A 2.04</td>
<td>2.07$^b$</td>
<td>$\ldots 1\Sigma^{-,2}$, $1\Pi$, $\Delta^4$, $2\Sigma^2$</td>
<td></td>
</tr>
<tr>
<td>B 2.22</td>
<td>2.39$^b$</td>
<td>$\ldots 1\Sigma^{-,2}$, $1\Pi$, $\Delta^4$, $2\Sigma^2$</td>
<td></td>
</tr>
<tr>
<td>PdH$_3^-$</td>
<td>EA $\sim$ 1.7</td>
<td>ADE 1.784</td>
<td>N/A</td>
</tr>
<tr>
<td>X 1.94</td>
<td>1.97</td>
<td>$\ldots 2a^1_12b^2_21a^2_23a^2_24a^1_1$</td>
<td></td>
</tr>
<tr>
<td>A $\sim$ 2.9</td>
<td>2.81</td>
<td>$\ldots 2a^1_12b^2_21a^2_23a^2_24a^1_1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.81</td>
<td>$\ldots 2a^1_12b^2_21a^2_23a^2_24a^1_1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.82</td>
<td>$\ldots 2a^1_12b^2_21a^2_23a^2_24a^1_1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.19</td>
<td>$\ldots 2a^1_12b^2_21a^2_23a^2_24a^1_1$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$aug-CC-pVTZ-PP$^{22}$ basis set was used for Pd and ATZP basis set was used for H. $^b$Indicates doubly degenerate features.
is complicated. To help dissect it, we have also presented simulated isotopic distributions for PdH− and PdH3− below the actual mass spectrum. The very little ion intensity at mass = 110 indicates that there is only negligible Pd− or PdH2− in the ion beam, which will not affect the PES. PdH3− species are the major anions seen. The photoelectron spectrum of PdH− was taken at mass = 106, and the photoelectron spectrum of PdH3− was taken at mass = 108 and 113. The lack of other PdH4− species in the mass spectrum suggests the special stabilities of PdH−1,3. Figure 2 presents the photoelectron spectra of PdH−1 and PdH−3. For PdH−, several peaks were observed. The positions of the first three peaks are marked by X, A, and B and are tabulated in Table I for comparison with the calculated spectra. The X peak located at 1.29 eV corresponds to the VDE. The A peak appears to show splitting, which may be due to the double degeneracy of this feature, as shown theoretically (see Figure 3). The peaks of PdH− are relatively sharp, consistent with the fact that the structural difference between the anion and its neutral is small (see Figure 3). This leads to a large Franck-Condon overlap for this (origin) transition. The adiabatic EA, defined as the energy difference of the ground state of the anion and the ground state of the neutral, is estimated from the threshold of the first EBE band. The EA of PdH is thus estimated to be ∼1.2 eV. The calculated ADE value is 1.288 eV (see Table I), in good agreement with the experimental value. Therefore, ADE and EA are actually one and same value in this case.

For PdH3−, the threshold EBE of a prominent broad band, X, occurs at ∼1.7 eV (EA) and peaks at 1.94 eV (VDE). Other features can be observed on the higher EBE end, but

FIG. 3. The structures and MOs of PdH−/0. Bond lengths (Å, in black) and NPA charge distributions (e, in red) are also included.

FIG. 4. The structures and MOs of PdH3−/0. Bond lengths (Å, in black) and NPA charge distributions (e, in red) are also included.
they are not well-resolved. We tentatively indicate a peak at $E_{BE} = 2.9$ eV, marked as A, but there could be more than one transition under these features, as indeed is supported by calculations. The relatively broad peak in the PdH$^-$ spectrum suggests significantly more structural difference between the anion and its neutral than was seen in the case of PdH$^+$ and its corresponding neutral. The calculated ADE value is 1.784 eV; this value agrees well with experiment. Again, ADE and EA are the same. Excellent agreements between experimental and theoretical values can be observed in Table I. The final electron configurations corresponding to each photodetachment transition are also displayed in Table I, and the MOs from which the corresponding electron detachments take place are depicted in Figures 3 and 4.

The calculated results for PdH$^{−0}$ and PdH$^{−0}_3$, including bond lengths (Å, in black), NPA charge distributions ($e$, in red), and molecular orbitals (MO) are displayed in Figures 3 and 4. For PdH$^-$, the Pd–H bond distance is 1.538 Å, very close to that of the neutral (1.530 Å). The Pd atom takes most of the negative charge. The HOMO-5 and HOMO are the bonding and anti-bonding orbitals of the Pd–H single bond from the combination of $d^z_\pi$ orbital of Pd and $s$ orbital of H. The HOMO-1 to HOMO-4 are the non-bonding $d$ orbitals of Pd, and the HOMO-6, HOMO-7 are the non-bonding $p$ orbitals of Pd.

For PdH$^{−0}_3$, the Pd–H bond length is 1.660 Å, slightly longer than that of PdH$^-$, and the H–H moiety clearly shows a $\eta^2$ type of ligation. At this stage, we can formally write PdH$^{−0}_3$ as [HPd(\eta^2-H$_2$)]$^-$ as it appears in the title. The H–H bond length is 0.897 Å, 20% longer than free H$_2$ molecule (0.747 Å), indicating that the H–H bond is activated. The NPA charge distribution shows that the H–H moiety is partially negatively charged, which is consistent with the bond elongation and back-donation from the Pd atom. In neutral PdH$_3$, the H$_2$ molecule is further away from the PdH moiety and the H–H bond length is closer to free H$_2$, indicating a weaker interaction between H$_2$ and PdH. The charge on Pd is positive, and thus, the back donation from Pd to H$_2$ is smaller, causing the positive charge on H$_2$ moiety. Figure 5 is the correlation diagram depicting how the MOs of [HPd(\eta^2-H$_2$)]$^-$ are formed from the combinations of the MOs of PdH$^-$ and H$_2$. The HOMO-4, which is a $d$-type orbital of PdH$^-$, back donates into the LUMO of H$_2$ and forms the HOMO-3 of [HPd(\eta^2-H$_2$)]$^-$. This is the combination that causes the H–H bond elongation, charge transfer to H$_2$, and its activation. HOMO-5 of PdH$^-$ combines with the HOMO of H$_2$ and splits into HOMO-4 and HOMO-6 of PdH$_3^-$. HOMO-4 represents the anti-bonding orbital between H$_2$ and PdH$^-$, and HOMO-6 is the bonding orbital. HOMO, HOMO-1, HOMO-2, and HOMO-5 of PdH$_3^-$ are non-bonding orbitals belonging only to PdH$^-$, which are displayed in Figure 4. Note that the degenerate HOMO-1 and HOMO-2 of PdH$^-$ lose degeneracy in PdH$_3^-$ due to symmetry breaking.

The binding energy, $D_0$, of the $\eta^2$-H$_2$ moiety to the PdH$^-$ sub-ion is calculated from the following formula with the CCSD(T) level of theory: $D_0 = E(\text{PdH}^-) + E(H_2) - E(\text{PdH}_3^-) = 89.2$ kJ/mol. This number is comparable to the binding energies between H$_2$ and transition metal halides$^{7–9}$ and higher than the binding energy between Pd and the much more commonly used ligand, CO.$^{33,34}$

CONCLUDING REMARKS

Since Pd$^-$ is isovalent to Cu and isoelectronic to Ag, it is not surprising that H$_2$ also binds to them.$^{7–9}$ Nevertheless, there are also significant differences. For example, since the electron-withdrawing halide atoms in CuCl, CuF, and AgCl reduce the electron density on their transition metal atoms, the extent of H$_2$ back donation in those cases, e.g., CuCl–H$_2$, is also reduced compared to that in PdH$_3^-$. More generally, while the H$_2$ moieties in PdH$_3^-$ are negatively charged, there are many other examples where H$_2$ ligands are positively charged.$^3$ Still, negatively charged hydrogen is key to some processes, e.g., the hydrogenation of CO.$^{35}$

![FIG. 5. The correlation diagram for the valence MOs of PdH$_3^-$.](image-url)
The H₂ bond length in the present study is calculated to be 20.0% longer than in the free H₂ molecule and around 12.5% longer than those reported for H₂ adducts with CuCl, CuF, and AgCl. 7–9 This shows that the H—H bond is more activated in PdH₃. The H—H bond length and charge distribution differences between PdH⁻ and PdH₂ are also examples of the extent of back-donation. In neutral PdH₃, for example, the H₂ moiety is less activated than in anionic PdH⁻, although it is similarly activated compared to H₂ adducts with CuCl, CuF, and AgCl. 7–9 Thus, PdH⁻ might have a role in catalysis. Also, when palladium is used as hydrogen storage material, the best stoichiometry that has been achieved is PdH₇–. When palladium is used as hydrogen storage material, a hydrogen mass density of 0.56%.

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