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Identification of Alkenyl- and Arylpalladium Hydrides with the Aid of Hydrosilanes

Tieqiao Chen,[1] Yongbo Zhou,[1] Shuang-Feng Yin,[1] Yalei Zhao,[2] Midori Goto,[2] and Li-Biao Han*[2]
[1]*College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China*
[2]*National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565*

(Received June 25, 2013; CL-130588; E-mail: libiao-han@aist.go.jp)

For the first time, the long-proposed thermodynamically unstable catalytic intermediates alkenyl and aryl complexes sp^2C–Pd–H have been isolated through the reduction of the palladium acetates with hydrosilanes and subsequent stabilization of the hydridopalladiums with hydrosilanes. The structures of these hydridopalladiums were established by X-ray analysis.

Regarding efficiency and generality, perhaps no other metal can compete with palladium, which is widely used as a catalyst in various chemical transformations.[1] The isolation of a palladium intermediate involved in the catalytic reactions is not only pivotal for understanding the reaction mechanism, but also crucial for designing a better catalyst. This kind of research has been performed extensively in the past decades.[1,2]

Hydridopalladium complexes have an exceptional relevance to palladium-mediated reactions.[2,3] Whereas heteroatom Z–Pd–H complexes (Z: a heteroatom or group) have been isolated successfully in the past, the hydridopalladium intermediate bearing a C–Pd–H skeleton remains rather unexplored owing to its chemically labile character (Figure 1).[2,4–6] Needless to say, these C–Pd–H hydridopalladiums are the key intermediates for two very important reactions in organic synthesis, i.e., C–H activation and C–H bond-forming reactions such as reductions of organohalides, alkenes, and alkynes, isomerization, the Heck arylation, and others (Figure 2).[2,3] Despite extensive studies in the past, no general example of such a hydridopalladium has been fully characterized.[2] Although some C–Pd–H hydridopalladiums stabilized by a rigid tridentate PCP ligand etc. could be isolated, they were too stable to undergo reactions such as reductive eliminations involved in the catalytic sequences and, therefore, are hardly recognized as representatives of C–Pd–H intermediates involved in Pd-mediated catalytic reactions.[5] Therefore, despite its pivotal relevance to C–H activation and C–H bond-forming reactions, an unambiguous identification of such a general C–Pd–H intermediate has not yet been achieved, not to mention the clarification of its reactivity. Herein, we report the first successful identification of general sp^2C–Pd–H complexes achieved with the aid of hydrosilanes (Figure 1).

Complex **2a** was allowed to react with a variety of reducing agents such as H_2, $NaBH_4$, and Ph_3SnH, in the hope that the corresponding hydridoalkenylpalladium **1a** could be observed (eq 1). However, disappointingly, all these reactions gave the final reduced products stilbenes, and the expected hydridopalladium intermediate **1a** could not be observed at all, indicating the rapid decomposition of **1a** as noticed previously.[4a,4g] Surprisingly, however, when hydrosilanes R_2SiH_2 (R = Ph, Et) were used as the reducing reagents, signals corresponding to the hydridoalkenylpalladium **1a** could be observed clearly. Thus, Ph_2SiH_2 (0.1 mmol) was added to (*E*)-**2a** (0.05 mmol) dissolved in 0.5 mL of C_6D_6 at room temperature. The color of the solution turned gradually from light green to blue. As shown by ^{1}H NMR spectroscopy, a signal assignable to H–Pd was observed at −7.9 ppm (td, 1H, $J_{P\text{–}H} = 14.5$ Hz, $J_{H\text{–}H} = 4.5$ Hz (with C=CH)), indicative of the formation of a hydridoalkenylpalladium complex assignable to (*E*)-**1a**. Changes in ^{31}P NMR spectroscopy were also observed clearly. Thus, as Ph_2SiH_2 was added, in addition to the starting material at 10.8 ppm, a new signal emerged at 20.9 ppm. The full reduction product (*Z*)-stilbene (C=CH: 6.5 ppm) was also observed in the reaction mixture. As estimated from ^{1}H NMR spectroscopy, as (*E*)-**2a** gradually disappeared, the products (*E*)-**1a** and (*Z*)-stilbene increased, i.e., the ratios of (*E*)-**2a**/(*E*)-**1a**/(*Z*)-stilbene as a function of time were as follows: 1 h, 3.5/1.0/0.41; 2 h, 0.71/1.0/0.65; 10 h, 0.5/1.0/7.5; 20 h, 0/0/1.0. Thus, although it could be observed in the reaction, the hydridoalkenylpalladium (*E*)-**1a** gradually decomposed to (*Z*)-stilbene. This hampers the isolation of pure (*E*)-**1a** from the mixture. Fortunately, we found that under similar reaction conditions, (*Z*)-**2a** also reacts with Ph_2SiH_2 to produce the corresponding (*Z*)-**1a** (90% NMR yield) with a characteristic palladium hydride signal at −7.3 ppm (td, 1H, $J_{P\text{–}H} = 12.0$ Hz, $J_{H\text{–}H} = 6.4$ Hz (with C=CH)). Perhaps owing to the steric hindrance around the palladium atom, this hydridoalkenylpalladium complex (*Z*)-**1a** was more stable than (*E*)-**1a**, and only a little decomposition to stilbene was observed at room temperature during the reaction. Unexpectedly, however, although stable in solution, the attempted isolation of (*Z*)-

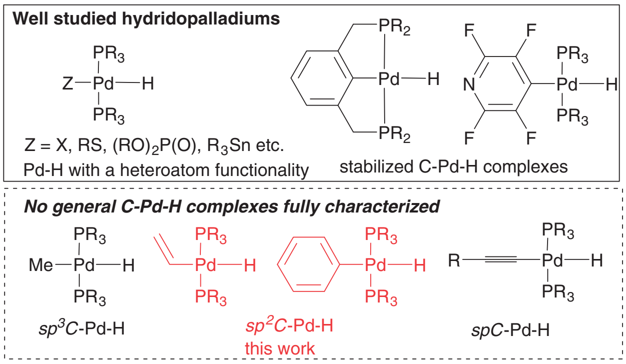


Figure 1. Representative hydridopalladiums.

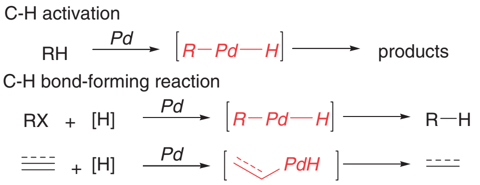


Figure 2. C–Pd–H intermediates involved in catalytic reactions.

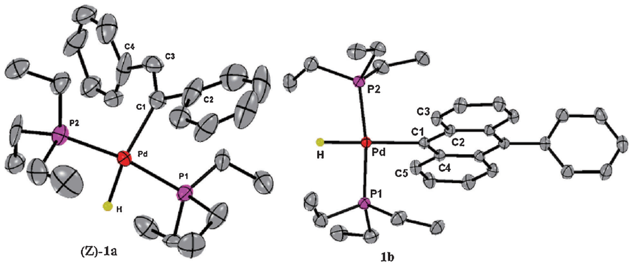
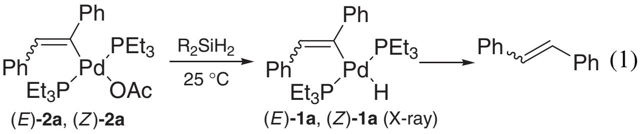


Figure 3. ORTEP representations of (*Z*)-**1a** and **1b**. H atoms except the hydride are omitted for clarity.

1a by removing the volatiles of the reaction mixture under high vacuum resulted in complete decomposition to (*E*)-stilbene, i.e., no (*Z*)-**1a** could survive under high vacuum for a few hours. After experiencing similar failures several times, we came to consider that perhaps a hydrosilane can stabilize the resulting palladium complex (*Z*)-**1a**, since it decomposes quickly in the absence of this hydrosilane.[7] Therefore, the isolation of this palladium complex in the presence of a hydrosilane should work. Indeed, this proved to be true! Thus, by carrying out the reaction of (*Z*)-**2a** (0.1 mmol) with Et_2SiH_2 as solvent (0.2 mL)[7] at room temperature, (*Z*)-**1a** was generated selectively. Without removal of Et_2SiH_2, the mixture was then kept at −30 °C, and light-yellow single crystals of (*Z*)-**1a** were obtained in 50% isolated yield.



Not observed with H_2, $NaBH_4$, and Ph_3SnH

X-ray analysis showed that (*Z*)-**1a** was a neutral mononuclear hydridoalkenylpalladium complex having a distorted square-planar coordination geometry with two PEt_3 molecules ligated to the palladium atom in *trans* manner, as shown in Figure 3. The five atoms Pd, C1, C2, C3, and C4 are not coplanar. C1, C2, C3, and C4 adopt a dihedral angle of 171.0(4)°, while the dihedral angle of Pd, C1, C3, and C4 is −9.0(4)°. Notably, the Pd–H bond length of (*Z*)-**1a** (1.6114 Å) is longer, while the H–Pd–C1 angle (155.17°) is smaller than those of the stabilized mononuclear C–Pd–H hydrido complexes.[4d,5a]

While in the presence of two equivalents of Ph_2SiH_2, the isolated (*Z*)-**1a** in benzene could stand for one day without decomposition, in the absence of Ph_2SiH_2, it decomposed completely in 0.5 h to produce (*E*)-stilbene quantitatively. Remarkably, an added phosphine could not retard the decomposition of **1a**, i.e., complete decomposition of (*Z*)-**1a** to (*E*)-stilbene in benzene also occurred in the presence of four equivalents of PEt_3. The addition of two equivalents of bidentate $Me_2PCH_2CH_2PMe_2$ could not slow down this decomposition either. These observations may indicate that C–H bond-forming reactions (reductive elimination of C–Pd–H) proceed rapidly with a 16e Pd species like **1a**,[8] and do not necessarily require conversion to a more coordinatively unsaturated 14e species.

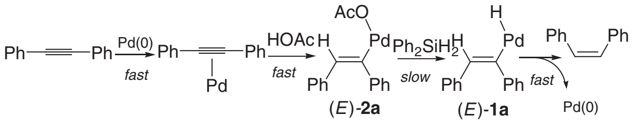
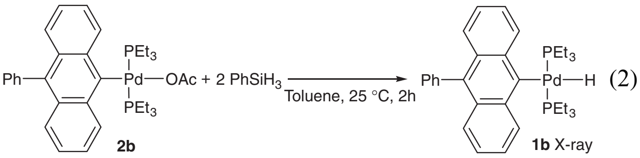


Figure 4. Hydridoalkenylpalladium intermediate involved in the palladium-mediated transfer hydrogenation.

This hydrosilane-based reduction and stabilization seems to be a general route for the generation of other unstable sp^2C–Pd–H complexes. Under similar conditions, arylpalladium acetate **2b** could also react smoothly with $PhSiH_3$ to generate the corresponding hydridoarylpalladium **1b** (eq 2).[9] Thus, as confirmed by ^{1}H and ^{31}P NMR spectroscopies, a mixture of **2b** and $PhSiH_3$ (2 equivs to Pd) in toluene at room temperature produced hydridopalladium **1b** quantitatively in 2 h. Recrystallization from a hexane/toluene mixed solvent in the presence of $PhSiH_3$ at −30 °C, produced pale yellow crystals suitable for X-ray analysis (61% yield). The X-ray analysis of hydridopalladium **1b** (as depicted in Figure 3) unambiguously confirmed the structure with the hydride and aryl group attached to the palladium atom in a *trans* manner with P1, Pd, C1, C4 adopting a dihedral angle of 85.76(8)°. Being similar to complex (*Z*)-**1a**, in the absence of $PhSiH_3$, this arylpalladium hydride **1b** decomposed completely in toluene in 0.5 h to give the corresponding hydrocarbon at room temperature. However, in the presence of two equivalents of $PhSiH_3$, **1b** is even stable at 80 °C, and does not decompose at all for 2 h; indeed, only 39% of the complex decomposed at 120 °C in 10 h. It was noted that a Si–H bond is essential for this kind of stabilization, i.e., silanes such as $PhSiMe_3$ and Me_4Si bearing no Si–H bonds do not stabilize the Pd–H complexes at all. However, it was also confirmed that no H–D exchange occurred between Ph_2SiD_2 with complexes (*Z*)-**1a** or **1b** in toluene at 25 °C within 15 h.[7]



The successful identification of C–Pd–H complexes described above helps to reveal the real mechanism of related Pd-mediated reactions. For example, the isolation of hydridoalkenylpalladiums **1a** leads to an unambiguous confirmation of the long-proposed palladium intermediates involved in the palladium-catalyzed selective transfer hydrogenation of alkynes, which is currently of great interest (Figure 4),[3o–3t,10] in which (*E*)-**2a**, formed via the hydropalladation of the alkyne-coordinated palladium(0) complexes with acetic acid, is reduced to give the hydridoalkenylpalladium (*E*)-**1a**, which subsequently decomposes to produce (*Z*)-stilbene and reproduce the zerovalent palladium complexes. As shown below, both (*E*)-**2a** and (*E*)-**1a** could be identified clearly in the $[Pd(PEt_3)_4]$-catalyzed selective transfer hydrogenation of diphenylacetylene (diphenylacetylene, 0.2 mmol; Ph_2SiH_2, 0.2 mmol; HOAc, 0.2 mmol; $[Pd(PEt_3)_4]$, 0.04 mmol) in C_6D_6. Thus, (*E*)-**2a** and a trace amount of (*E*)-**1a** were the only detectable palladium species at the beginning of the reaction. As estimated from the NMR spectroscopy results, the amount of (*E*)-**2a** (ca. 0.04 mmol) remained constant when the starting diphenylacetylene and Ph_2SiH_2 were present in the mixture, and decreased as these starting materials were consumed. Therefore, the formation of (*E*)-**2a** was fast, and the decomposition of (*E*)-**1a** was also relatively fast. The reduction of (*E*)-**2a** to (*E*)-**1a** was slow, and was the rate-determining step of this palladium-catalyzed transfer hydrogenation.[3q,3r]

In summary, the long-proposed hydridoalkenyl- and hydridoarylpalladium sp^2C–Pd–H intermediates have been isolated and identified successfully for the first time.[11] The isolation of these important palladium intermediates opens up new routes for direct studies on their chemical behaviors, which, until now, have mostly been performed on the basis of theoretic calculations because of the lack of suitable C–Pd–H complexes.[3o,3t,4b] We believe that forthcoming studies on the reactivity of these complexes will not only lead to an in-depth understanding of palladium-catalyzed C–H activation and C–H bond-forming reactions, but may also help in the development of new efficient catalysts.

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7 Due to its high solubility, (*Z*)-**1a** did not precipitate out from the reaction mixture with Ph_2SiH_2. After trial and error, it was found that it could precipitate out with Et_2SiH_2. The mechanism for the stabilization by Si–H is not understood. Possible SiH and Pd interactions were not recognized on NMR spectroscopy at −70 °C.

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9 Hydridophenylpalladium was similarly generated as oil which could not be purified further.

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