Homogeneous Catalysis

DOI: 10.1002/ange.200900463

Activation of Hydrogen by Palladium(0): Formation of the Mononuclear Dihydride Complex *trans*-[Pd(H)$_2$(IPr)(PCy$_3$)]**

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Metal-catalyzed hydrogenation reactions have been the subject of intensive investigation in organometallic chemistry and catalysis.[1] Late transition metals employed to catalyze this transformation have exhibited impressive performances. In its homogeneous incarnation, transition-metal catalyzed hydrogenation is best mediated by rhodium (notably Wilkinson's catalyst)[2] or iridium[3] complexes. Other metals have fared better in heterogeneous systems, as is the case for palladium whose use in its supported form, Pd/C, is ubiquitous.[1b]

Palladium-catalyzed homogeneous hydrogenation mainly makes use of Pd^{II} complexes, wherein a heterolytic activation of the dihydrogen molecule is believed to occur.[4] Less attention has focused on Pd^0 systems,[5] in view of the reported and rationalized low reactivity of Pd^0 complexes towards H_2.[6] However, in the past decade, efficient hydrogenation systems based on Pd^0 have been reported.[7] Mechanistic investigations suggest that the catalytic manifold involves coordination of the substrate, followed by activation of H_2 to give Pd^{II} species.[8] In this context, the possible involvement of monomeric Pd^{II} dihydride intermediates, formed by homolytic activation of H_2, is generally ruled out since such species have not, to date, been detected.[9] Remarkably, oxidative addition of H_2 to afford dihydride complexes is a well-documented reaction for late transition metals.[10] One of the few exceptions to this generally acknowledged fact is palladium. Indeed, to our knowledge, only polynuclear complexes are known for Pd compounds bearing more than one hydride ligand.[11]

As part of our investigations on the use of *N*-heterocyclic carbenes (NHCs) as stabilizing ligands,[12] a synthetic strategy leading to 14-electron Pd^0 complexes was developed.[13] One of these complexes, [Pd(SIPr)(PCy$_3$)] (SIPr = *N*,*N*′-bis(2,6-(diisopropyl)phenyl)imidazolin-2-ylidine), was successfully used to promote hydrogenation reactions under very mild reaction conditions.[14] During these catalytic studies, the stability of [Pd(SIPr)(PCy$_3$)] under hydrogenation conditions was investigated, and NMR spectroscopic studies indicated the presence of a hydride complex which may have resulted from an oxidative addition of H_2 on [Pd(SIPr)(PCy$_3$)]. However, only partial conversion was detected and the isolation and full characterization of this species was not achieved. Herein, we report, through judicious ancillary ligand selection, the isolation and full characterization of the first monomeric palladium dihydride complex.

As mentioned above, [Pd(SIPr)(PCy$_3$)] only reacts sparingly with H_2. A better candidate for such experiment might be one with a smaller steric bulk. Preliminary experiments were performed with [Pd(IPr)(PPh$_3$)] (IPr = *N*,*N*′-bis-(2,6-(diisopropyl)phenyl)imidazol-2-ylidene) which showed that, after 24 h, under 1 atm of H_2, a hydride species was formed (^{1}H NMR: weak doublet at $\delta = -4.21$ ppm with $J = 17$ Hz) but product formation was incomplete and subsequent decomposition to palladium black took place. We thus opted for [Pd(IPr)(PCy$_3$)], as it contains a more electron-rich phosphane, which might favor product formation, and because IPr is slightly less hindered than its SIPr congener. To our delight, exposure of [Pd(IPr)(PCy$_3$)] (**1**) to H_2 (1 atm) led to almost quantitative conversion of **1** into a novel hydride species **2**.

The ^{31}P{^{1}H} NMR spectrum of **2** exhibited a single resonance at $\delta_P = 68.2$ ppm (δ_P(**1**) = 49.3 ppm). In the ^{1}H NMR spectrum, the imidazole and the isopropyl resonances were shifted downfield by approximately 0.24 ppm with respect to **1**.[15] A doublet appeared at $\delta_H = -4.81$ ppm ($^2J_{H,P} = 16$ Hz), integrating for two protons, which suggested the

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[**] S.F. and S.P.N. gratefully thank the MEC (Spain) and the ICIQ Foundation for financial support. S.P.N. acknowledges the ERC for support in the form of an Advanced Researcher Grant (FUNCAT). J.D.E. and D.M.H. acknowledge the US NSF. We thank Dr. W. Kaminsky, Dr. J. Benet-Buchholz, and E. Escudero Adán for X-ray structures. L.C. thanks the ENEA (www.enea.it) and the HPC team for support and for using ENEA-GRID and the HPC facilities CRESCO (www.cresco.enea.it) Portici (Naples), Italy.

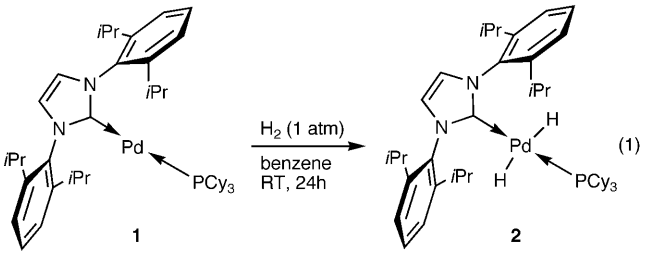
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900463. CCDC 707593 (**2**) and 707594 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

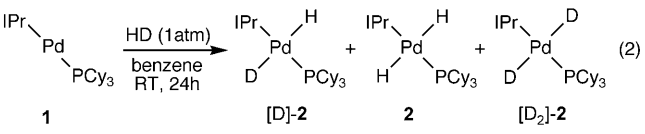
presence of two hydride ligands *cis* to the phosphorus atom.[16] However, to confirm this hypothesis, and to rule out other possibilities, such as a dynamic *cis* dihydride or a dihydrogen complex, further NMR spectroscopic experiments were conducted.

The relaxation time T_1 of the hydride resonance in complex **2** was measured as a function of temperature using a standard inversion recovering sequence. The minimum T_1 of 420 ms occurred at 270 K (500 MHz). Dihydrides and dihydrogen complexes can be distinguished by their minimum T_1 value, by following the method of Halpern and coworkers.[17] This method is not straightforward when multiple nuclei contribute to the overall relaxation rate, defined as R ($R=1/T_1$). For complex **2**, the contributions of the phosphorus atom and the other H atoms present in the molecule have to be considered. To determine these contributions, we prepared the monohydride complex [Pd(H)(Cl)(IPr)(PCy$_3$)] (**3**). Complex **3** was formed quantitatively as a white solid by addition of an equimolar amount of HCl (4 M in dioxane) to a THF solution of **1**.

Halogeno-hydride complexes of Pd^{II} have been extensively studied and well characterized.[18] However, palladium hydride complexes bearing NHC ligands remain rare,[19] possibly as a result of the instability of such complexes towards reductive elimination of the imidazolium salt.[20] Complex **3** is indefinitely stable both in the solid state and in solution (even upon heating at 80 °C) under Ar atmosphere, giving no sign of reductive elimination of the IPr hydrochloride salt. The $^{31}P\{^1H\}$ NMR spectrum of **3** displayed a singlet at $\delta_P = 48.2$ ppm, while in the ^1H NMR spectrum the hydride resonance appears as a doublet at $\delta_H = -14.89$ ppm ($^2J_{H,P} = 2$ Hz). In the $^{13}C\{^1H\}$ NMR spectrum, the carbenic carbon signal appeared as a doublet centered at $\delta_C =$ 190.5 ppm ($^2J_{C,P} = 137$ Hz).

The minimum relaxation time constant for the hydride resonance in **3**, $T_1 = 590$ ms, occurred at 270 K (500 MHz). Comparison of the relaxation rate in **2** and **3** ($R_2 - R_3$) allowed for determination of the HH relaxation-rate contribution, R_{HH}, in **2**, which is 0.69 s^{-1}.[21] This value excluded the possibility of a η^2-H$_2$ complex,[22] and suggested formulation of **2** as the *trans* dihydride complex. Its formation would then proceed according to Equation (1).





Reaction of **1** with HD gas [Eq. (2)], afforded complex [D]-**2**, for which the ^1H NMR hydride signal appeared as a multiplet centered at $\delta = -4.72$ ppm ($^2J_{H,D} = 7$ Hz, $^2J_{H,P} =$ 16 Hz; Figure 1). The value for the H–D coupling constant is consistent with the formation of the *trans* isomer.[23] Interestingly, in addition to the resonance of complex [D]-**2**, the hydride resonance of complex **2** was also present in the ^1H NMR spectrum. Comparison of the integration value of the two hydride signals with the integration of the isopropyl CH resonance of the IPr ligand (3 vs. 12), strongly suggested the presence of the bis-deuterated complex [D$_2$]-**2**. The presence of all three isotopomers was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 1), in which three resonances, integrated for their statistical distribution, appeared: a singlet at $\delta_P = 68.22$ ppm (**2**), a 1:1:1 triplet at $\delta_P = 68.28$ ppm ([D]-**2**) and a five-line pattern at $\delta_P = 68.33$ ppm ([D$_2$]-**2**). The mechanism of this isotope exchange reaction is under investigation.

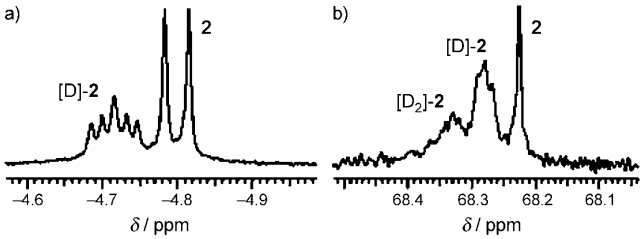


Figure 1. a) ^1H and b) $^{31}P\{^1H\}$ NMR spectra of the three isotopomers **2**, [D]-**2**, and [D$_2$]-**2**, formed from the reaction of **1** with HD gas.

Density functional (DFT) calculations were carried out to assess the relative stabilities of the *cis* and the *trans* isomers. We found the *trans* isomer to be lower in energy by 6.5 kcal mol^{-1} (in THF) compared to the *cis* isomer. We then examined the thermodynamics of the hydrogenation reaction (1), and found it to be exothermic by 3.1 kcal mol^{-1}.[15]

Furthermore, the structure of the *trans*-dihydride complex **2** was unambiguously confirmed by single-crystal X-ray diffraction (Figure 2).

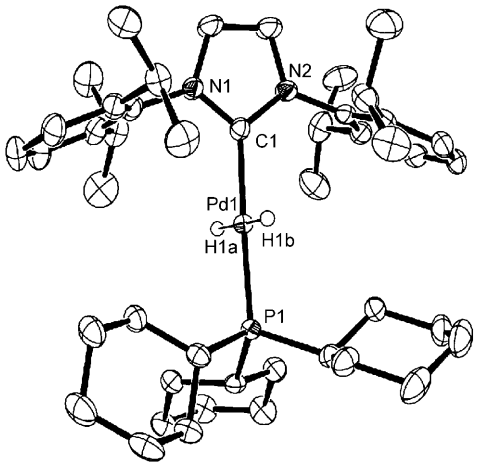


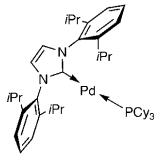
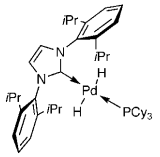
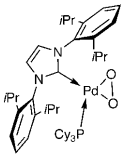
Figure 2. ORTEP representation of **2** [Pd(H)$_2$(IPr)(PCy$_3$)]. Thermal ellipsoids are set at 50% probability. H atoms, with the exception of H1a and H1b, are omitted for clarity.

The metal center in **2** has an approximately square planar coordination geometry, slightly distorted by steric interactions between the IPr and PCy_3 ligands. The two hydrogen atoms on Pd were located and refined with isotropic thermal parameters. The location of the hydrogen atoms coincides with free voids surrounding the Pd center.

The formation of **2** proved to be extremely sensitive to oxygen and water. When extreme precautions were not taken to avoid the presence of air and H_2O, the amount of dihydride complex **2** present in solution was substantially lowered. Indeed, in the presence of O_2, the peroxo complex [Pd(η^2-O_2)(IPr)(PCy_3)] **4** was formed.[15] As expected, the $^{13}C\{^1H\}$ resonance for the Pd carbene carbon atom in complex **4** has a coupling constant, $^2J_{C,P} = 16$ Hz, that was considerably lower than the corresponding coupling constants for complexes **1**, **2**,and **3** ($^2J_{C,P} = 90$, 138, and 137 Hz, respectively). This value reflects the *cis* configuration of the IPr and the PCy_3 ligands in **4**. In this reaction, it remains unclear whether coordination of O_2 takes place on the starting material **1** or on the dihydride product **2**, as preliminary studies suggested that the dihydride species is more reactive towards dioxygen than **1**.

The Pd–$C_{carbene}$ and Pd–P bond lengths in **4** are substantially longer than those in **1** and **2** (Table 1). As expected, the

Table 1: Selected bond lengths [Å] and angles [°] for complexes **1**, **2**, and **4**.

	 **1**[13]	 **2**	 **4**
Pd–C	2.0292(9)	2.009(2)	2.056(3)
Pd–P	2.2212(3)	2.2385(6)	2.3303(7)
C-Pd-P	170.88(2)	173.08(7)	105.24(7)

C-Pd-P angle found for **4** was much smaller than the those for **1** and **2**, confirming in the first case a *cis* arrangement of the NHC and PCy_3, and a *trans* arrangement for the dihydride complex.

To examine whether there was truly something unique with the system bearing mixed ligands, it seemed of interest to investigate the reactivity of homoleptic Pd^0 complexes towards H_2. Reactions of [Pd(PCy_3)$_2$] and [Pd(IPr)$_2$] with H_2 in [D_6]benzene were monitored by ^1H NMR spectroscopy. In the case of [Pd(PCy_3)$_2$], no hydride signal was detected even after several weeks or when experiments were carried out at low temperature. For [Pd(IPr)$_2$], a very weak signal at $\delta_H = -4.80$ ppm was detected, but the reaction did not proceed to any significant extent. These observations, as well as those for [Pd(SIPr)(PCy_3)] and [Pd(IPr)(PPh_3)], emphasize that ligand tuning is crucial in the success of the H–H bond activation reaction. In the case of **1**, the stereoelectronic properties of both the NHC[24] and phosphane[25] ligands lead to an optimal situation for the detection and isolation of palladium species resulting from H_2 activation.

In summary, we have reported the activation of H_2 by a mixed NHC-phosphane Pd^0 complex, leading to the formation of an unprecedented monomeric dihydride palladium species. The isolation of a dihydride complex demonstrated the feasibility of direct activation of H_2 by a Pd^0 complex. These results may pave the way for mechanistic studies on catalytic hydrogenation and for the development of new catalytic systems. Further studies aimed at understanding the stability and reactivity of this species are ongoing in our laboratories.

Experimental Section

All manipulations were carried out under an Argon atmosphere, using standard dry box, Schlenk and vacuum line techniques. [Pd(IPr)(L)] (L = PPh_3, PCy_3, IPr),[13] [Pd(SIPr)(PCy_3)][13] and [Pd(PCy_3)$_2$][26] were synthesized according to literature procedures. Anhydrous solvents were purchased from Aldrich and used as received unless otherwise specified. NMR spectra were recorded on Bruker instruments (400 MHz and 500 MHz) in [D_6]benzene. Variable-temperature NMR spectroscopy was carried out in [D_8]toluene. Mass spectra were recorded on a Waters LCT Premier instrument. Elemental analyses were performed by Universidad Complutense de Madrid and Columbia Analytical Services, Inc., Tucson, AZ.

2 (*trans*-[Pd(H)$_2$(IPr)(PCy_3)]): A J. Young NMR tube was charged with [Pd(IPr)(PCy_3)] (**1**, 5.0 mg, 6.4 μmol) and then filled with C_6D_6 (dried over Na/K alloy) by vacuum transfer. After freezing the solution, the atmosphere over the solution was replaced with H_2 gas (1 atm). After 24 h, the solution was analyzed by NMR spectroscopy. ^1H NMR (500 MHz): $\delta = 7.23$ (t, $J = 10$ Hz, 2H, CH-*p*), 7.18 (d, $J = 10$ Hz, 4H, CH-*m*), 6.73 (s, 2H, CH imid), 3.25 (sept, $J = 5$ Hz, 4H, C*H*(CH_3)$_2$), 2.0–1.0 (m, CH_2 + CH Cy), 1.59 (d, $J = 5$ Hz, CH(C*H*$_3$)$_2$), 1.19 (d, $J = 5$ Hz, CH(C*H*$_3$)$_2$), −4.81 ppm (d, $J_{P,H} = 16$ Hz, 2H, Pd–H); $^{13}C\{^1H\}$ NMR (125.8 MHz): $\delta = 200.5$ (d, $J_{C,P} = 138$ Hz,C carbene), 146.8 (C arom), 136.9 (C arom), 128.6 (CH arom), 122.8 (CH arom), 127.7 ppm (d, $J_{C,P} = 4$ Hz, CH imid); $^{31}P\{^1H\}$ NMR (202.5 MHz): $\delta = 68.1$ ppm; elemental analysis calcd for $C_{45}H_{71}N_2PPd$: C 69.52, H 9.20, N 3.60; found: C 70.42, H 9.06, N 3.47.

3 (*trans*-[Pd(H)(Cl)(IPr)(PCy_3)]): Compound **1** (42.0 mg, 54 μmol) was dissolved in THF (1 mL) and treated with HCl (20 μL of a 4 M solution in dioxane). After stirring at room temperature for 4 h, evaporation of the solvent afforded the product (44 mg, quantitative yield). ^1H NMR (400 MHz): $\delta = 7.28$ (t, $J = 8$ Hz, 2H, CH-*p*), 7.21 (d, $J = 8$ Hz, 4H, CH-*m*), 6.70 (s, 2H, CH imid), 3.33 (sept, $J = 8$ Hz, 4H, C*H*(CH_3)$_2$), 1.87 (br q, $J = 12$ Hz, 3H, CH Cy), 1.73 (br d, $J = 12$ Hz, 6H, CH_2), 1.65 (br m, 9H, CH_2), 1.57 (d, $J = 8$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.29 (br q, $J = 12$ Hz, 6H, CH_2), 1.16 (br m, 9H, CH_2), 1.12 (d, $J = 8$ Hz, 12H, CH_2), −14.99 ppm (d, $J = 2$ Hz, 1H, Pd–H); $^{13}C\{^1H\}$ NMR (125.8 MHz): $\delta = 190.5$ (d, $J_{C,P} = 137$ Hz,C carbene), 146.8 (C arom), 136.7 (C arom), 129.5 (CH arom), 123.5 (CH arom), 123.2 (d, $J_{C,P} = 4$ Hz, CH imid), 34.1 (d, $J_{C,P} = 20$ Hz, CH Cy), 30.2 (d, $J_{C,P} = 2$ Hz, CH_2), 28.6 (*C*H(CH_3)$_2$), 27.5 (d, $J_{C,P} = 11$ Hz, CH_2), 26.5 (CH_2), 25.9 (CH(*C*H$_3$)$_2$), 22.5 ppm (CH(*C*H$_3$)$_2$); $^{31}P\{^1H\}$ NMR (162 MHz): $\delta = 48.2$ ppm; ESI MS: *m*/*z* calcd for $C_{45}H_{70}ClN_2PPd$: 810.4; found: 810.4; elemental analysis calcd for $C_{49}H_{78}ClN_2O_2PPd$ [*M*+dioxane]: C 65.39, H 8.74, N 3.11; found: C 65.32, H 8.43, N 3.41.

4 [Pd(η^2-O_2)(IPr)(PCy_3)]: Compound **1** (100.0 mg, 127 μmol) was dissolved in benzene (10 mL). Air was bubbled through the solution for 15 min after which time evaporation of the solvent afforded **4** (102.0 mg; quantitative yield). ^1H NMR (400 MHz): $\delta = 7.24$ (t, $J = 3$ Hz, 2H, CH-*p*), 7.17 (under C_6D_6 signal, 4H, CH-*m*), 6.65 (s, 2H, CH imid), 3.22 (br m, 4H, C*H*(CH_3)$_2$), 1.72–1.59 (m, 27H), 1.25 (br m, 12H, Cy), 1.10 (br m, 6H, Cy), 1.05 ppm (d, $J = 8$ Hz, 12H, CH(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz): $\delta = 192.0$ (d, $J_{C,P} = 16$ Hz,

C carbene), 146.3 (C arom), 136.9 (C arom), 129.9 (CH arom), 125.0 (CH arom), 124.1 (s, CH imid), 33.5 (d, $J_{C,P}=15$ Hz, CH Cy), 30.0 (d, $J_{C,P}=2$ Hz, CH_2), 28.8 ($CH(CH_3)_2$), 27.4 (d, $J_{C,P}=11$ Hz, CH_2), 26.6 (CH_2), 26.2 ($CH(CH_3)_2$), 23.3 ppm ($CH(CH_3)_2$); $^{31}P\{^1H\}$ NMR (162 MHz): $\delta=53.7$ ppm; MS (MALDI-TOF): *m/z* calcd for $C_{45}H_{69}N_2PPd$ [$M-(O_2)$]: 774.4; found 774.4; elemental analysis calcd for $C_{45}H_{73}N_2O_4PPd$ [$M+2H_2O$]: C 64.08, H 8.72, N 3.32; found: C 64.26, H 8.40, N 3.20.

Received: January 24, 2009
Revised: March 18, 2009
Published online: June 12, 2009

Keywords: carbenes · homogeneous catalysis · hydrides · hydrogen · palladium

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