Palladium Complexes

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Characterization of a Palladium Dihydrogen Complex[**]

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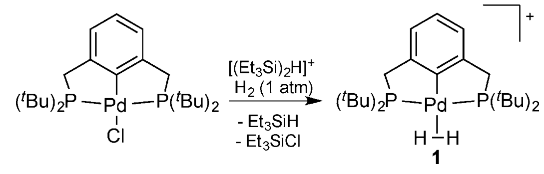
Abstract: *The preparation and isolation of the first palladium dihydrogen complex is described. NMR spectroscopy reveals a very short H—H bond length, but the hydrogen molecule is activated toward heterolytic cleavage. An X-ray crystal structure suggests that proton transfer to the* ^{tBu}PCP *(*κ^3*-2,6-(*$^tBu_2PCH_2)_2C_6H_3$*) pincer ligand is possible. The basicity of the ipso-carbon atom of the pincer ligand was investigated in a related complex.*



Scheme 1. Formation of the dihydrogen complex **1**.

Dihydrogen complexes have been intensively investigated since their discovery by Kubas et al.[1] Since that time, dihydrogen complexes have been reported for most of the transition metals utilized in homogeneous catalysis. Dihydrogen complexes are often cited as intermediates in various catalytic pathways, such as in hydrogenation reactions. As isolated complexes, H_2 ligands have been described as having a structure along a continuum between that of the dihydrogen complex and the dihydride product resulting from oxidative addition of the H_2 ligand.[2]

The majority of known dihydrogen complexes contain d^6 metal centers; only a small subset of the reported complexes have a d^8 configuration. We recently reported a nickel dihydrogen complex[3] which is a proposed intermediate in the electrocatalytic production of hydrogen.[4] Only three other Ni^{II} dihydrogen complexes have been characterized[5] and there is one recent example of a d^{10} dihydrogen complex of nickel.[6] The remaining Group 10 examples are square-planar platinum complexes.[7] Other reported examples of d^8-configured metal dihydrogen complexes are limited to a few Rh^I pincer complexes[8] and two reports of cobalt complexes.[9] No Ir^I dihydrogen complexes have been isolated, but ^{tBu}PCP pincer complexes of Ir are thought to be in equilibrium between a dihydride–solvento octahedral complex and the square-planar dihydrogen complex.[10] Herein, we report the first dihydrogen complex of palladium.

The cationic pincer Pd^{II} complex $[(^{tBu}PCP)Pd(H_2)]^+$ (**1**) ($^{tBu}PCP = \kappa^3$-2,6-($^tBu_2PCH_2)_2C_6H_3$) was synthesized using a procedure analogous to that reported for $[(^{tBu}PCP)Ni(H_2)]^+$ (Scheme 1).[3] Reaction of colorless (^{tBu}PCP)PdCl[11] with the chloride-abstracting reagent, $[(Et_3Si)_2(\mu\text{-}H)][B(C_6F_5)_4]$[12] in fluorobenzene under H_2 (ca. 1 atm) affords an orange solution of complex **1**. The synthesis of cation **1** was attempted using $K[B(C_6F_5)_4]$ and $Na[B(C_6F_5)_4]$ as chloride-abstraction reagents in fluorobenzene under an atmosphere of H_2. No product formation was detected by ^1H NMR spectroscopy over several weeks.

The ^1H NMR spectrum of **1** shows a broad singlet at $\delta = 1.7$ for the dihydrogen ligand. Layering a solution of **1** with alkane solvent resulted in the precipitation of crystals suitable for X-ray crystallography. The major component is shown in Figure 1.

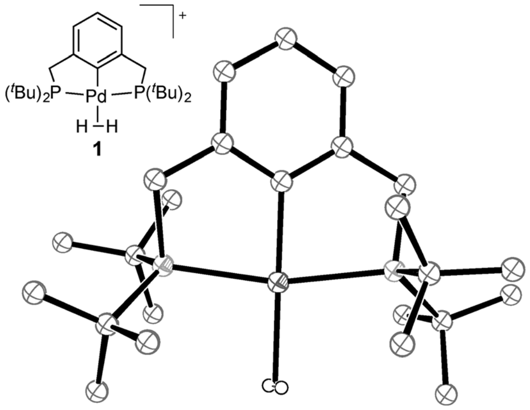


Figure 1. ORTEP[13] diagram of $[(^{tBu}PCP)Pd(H_2)][B(C_6F_5)_4]$ (**1**). Thermal ellipsoids are set at 30% probability. The hydrogen atoms (other than the dihydrogen ligand), anion, disordered fluorobenzene solvent molecule, and the minor component (17%) have been omitted for clarity.

The X-ray structure confirms that the pincer complex **1** has square-planar geometry. The fourth coordination site contains a dihydrogen ligand with an internuclear distance (d_{HH}) far shorter than is realistic (0.42 Å). Metal hydrides are difficult to locate by X-ray crystallography and the technique also tends to underestimate the d_{HH} value in the H_2 ligand as a result of facile rotation.[14] To accurately determine d_{HH}, two solution-state NMR methods have been shown to give reliable structural information.

The coupling constant between the H and D atoms in a HD ligand has been empirically related to d_{HH}.[15] The partially deuterated analogue of complex **1** was prepared by

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employing HD gas in the synthetic procedure. Complex [D]-**1** has one of the highest $^1J_{HD}$ values reported to date (37.1 ± 0.5 Hz; ^{1}H and ^{2}H NMR spectra are shown in Figure 2). This $^1J_{HD}$ value corresponds to a d_{HH} of 0.81 ± 0.02 Å.[14]

Figure 2 also shows the presence of a statistical distribution of H_2, HD, and D_2 ligands. This isotopic scrambling is likely caused by the presence of adventitious base (such as H_2O) in the solution.[16]

When two hydrogen atoms are close together, dipole–dipole relaxation is very efficient, leading to short T_1 values. The relaxation time T_1(minimum) can be quantitatively related to d_{HH}, as described by Halpern and co-workers.[17] Measurements of T_1 values were carried out for the signal attributed to the dihydrogen ligand in complex **1**. At 298 K, the T_1 value was determined to be 21 ± 1 ms. The lowest T_1 value recorded was 15 ± 5 ms at 268 K, which corresponds to $d_{HH} = 1.0 \pm 0.2$ Å. At lower temperatures, the signal was too broad to record meaningful T_1 data.

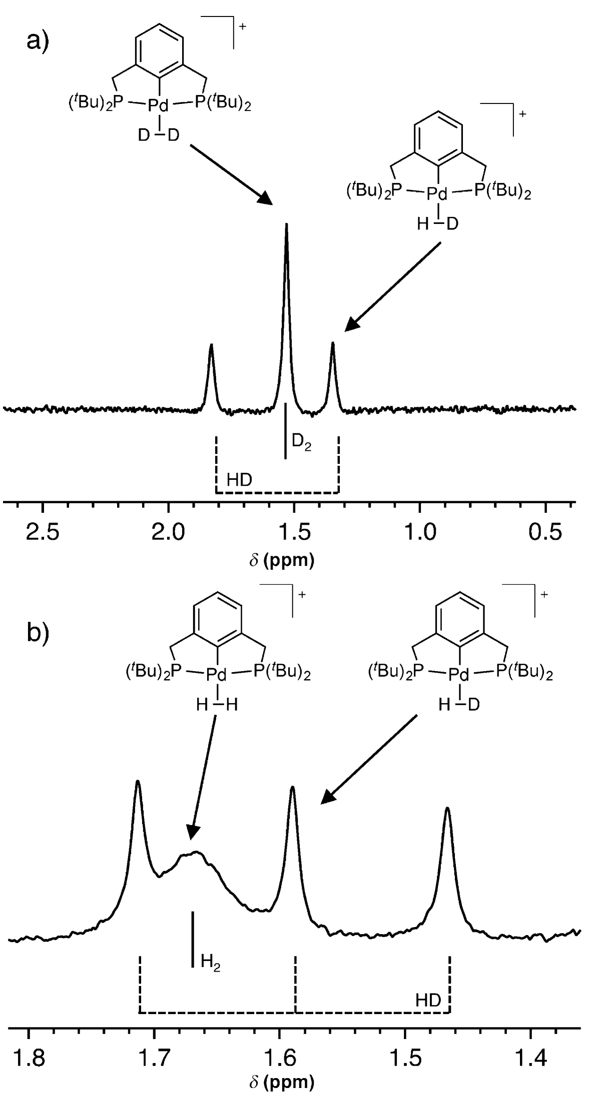
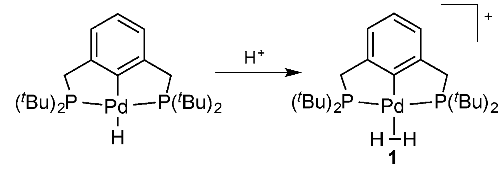


Figure 2. a) ^{2}H NMR spectrum (77 MHz) and b) partial ^{1}H NMR spectrum (300 MHz) of partially deuterated $[(^{tBu}PCP)Pd(HD)]^+$ showing $^1J_{HD} = 37.1 \pm 0.5$ Hz.

Dihydrogen complexes are often synthesized by protonation of a hydride ligand. Bullock and co-workers attempted to synthesize complex **1** through protonation of the corresponding neutral metal–hydride complex in dichloromethane solution.[18] We surmised that the dichloromethane was interacting with the metal center, as a solvento ligand or in a radical reaction known to generate metal chlorides from first- and second-row metal hydrides.[19] We find that protonation of $(^{tBu}PCP)PdH$[20] in protio-fluorobenzene with $[HOEt_2][BF_4]$ or $[H(OEt_2)_2][B(C_6F_5)_4]$ resulted in the clean formation of complex **1** (Scheme 2), as confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. Additionally, exposure of this reaction mixture to HD gas produced the same signals in the ^{2}H NMR spectrum as described above for samples of **1**.



Scheme 2. Formation of the dihydrogen complex **1** by protonation of the metal hydride.

The Ni and Pt analogues of complex **1** are known.[2,16] Data for all three Group 10 homologues are summarized in Table 1. In all cases, the hydrogen ligand remains intact, and the d_{HH} value is short. The H_2 ligand is quite labile, exchanging with free dihydrogen in solution (**1** and $[(^{tBu}PCP)Ni(H_2)]^+$). In the case of $[(^{tBu}PCP)Pt(H_2)]^+$, the H_2 ligand is labile enough to be displaced by dichloromethane solvent.[16]

Table 1: Comparison of NMR-derived parameters for Group 10 $[(^{tBu}PCP)M(H_2)]^+$ cations.

	$[(^{tBu}PCP)Pd(H_2)]^+$	$[(^{tBu}PCP)Ni(H_2)]^{+}$[a]	$[(^{tBu}PCP)Pt(H_2)]^{+}$[b]
$^1J_{HD}$ [Hz]	37.1 ± 0.5	34 ± 1	33
d_{HH} [Å][d]	0.81 ± 0.02	0.85 ± 0.02	0.87
T_1 [ms][e]	21	21	23[c]
δ [ppm][f]	1.69	−3.21	0.18

[a] Reported in Ref. [3]. [b] Reported in Ref. [18]. [c] Evolution of H_2 is detected at 295 K. The T_1 of the H_2 ligand resonance was 23 ms at 250 K. [d] Based on $^1J_{HD}$ values. [e] T_1 values measured at 298 K. [f] Chemical shift of the H_2 ligand is given.

A minor component was found to co-crystallize in the lattice of complex **1**. The optimal structure model included 17% of the minor species, in which the dihydrogen complex has undergone proton transfer to give a palladium hydride complex (Figure 3, Figure 4). In this complex, an agostic interaction is detected with the C–H bond of the $(^{tBu}PCP)H$ ligand.

These two structures are presumably of very similar stability. We postulated that both structures might be present in rapid equilibrium in solution. With this in mind, the NMR spectrum of [D]-**1** was examined at temperatures down to 240 K. There was no observable change in the $^1J_{HD}$ value, and

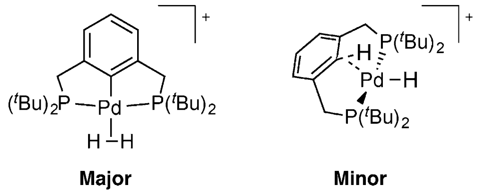


Figure 3. The major and minor components observed in the solid-state structure of complex **1**.

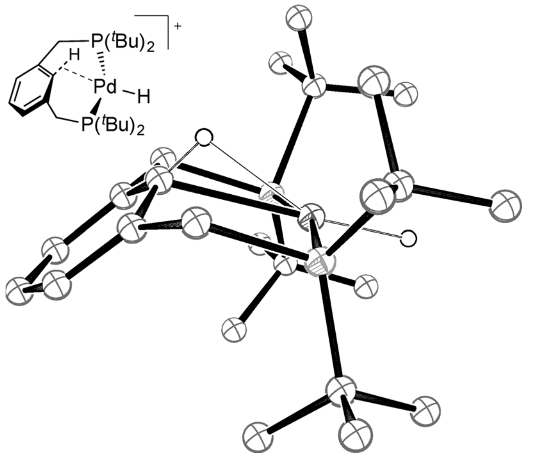
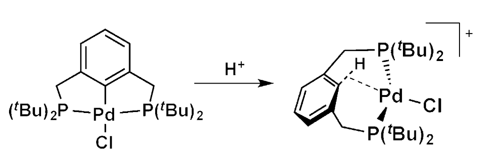


Figure 4. ORTEP[13] diagram of $[(^{tBu}PCP\text{-}H)PdH]^+$ (**1**, minor component; side view). Thermal ellipsoids are set at 30% probability. The hydrogen atoms (other than those interacting with the metal) and the anion, solvent, and the major component have been omitted for clarity.

no signals for the hydride ligand or the aromatic proton were detected.

To further investigate the basicity of the metal–carbon bond in pincer complexes of this type, acids (such as $[HOEt_2][BF_4]$ or $[H(OEt_2)_2][B(C_6H_3(CF_3)_2)_4]$) were added to $(^{tBu}PCP)PdCl$ in dichloromethane (Scheme 3). The ^1H NMR spectrum of the product, $[(^{tBu}PCP\text{-}H)PdCl]^+$ (**2**), indicated the presence of a molecule with decreased symmetry. The $^1J_{CH}$ value for the *ipso*-CH bond of the ligand is 125 Hz, significantly lower than that detected in the free ligand (ca. 160 Hz), suggesting that the C–H bond is interacting with the palladium center.

Layering a solution of **2** in CH_2Cl_2 with pentane resulted in the precipitation of crystals suitable for X-ray diffraction studies. The structure is shown in Figure 5. The plane of the phenyl ring of the ligand is distorted from the plane defined by the Pd, Cl, and P atoms. This closely resembles the distortion detected in the minor component of the crystal structure of **1**.



Scheme 3. Protonation of $(^{tBu}PCP)PdCl$ to generate **2**.

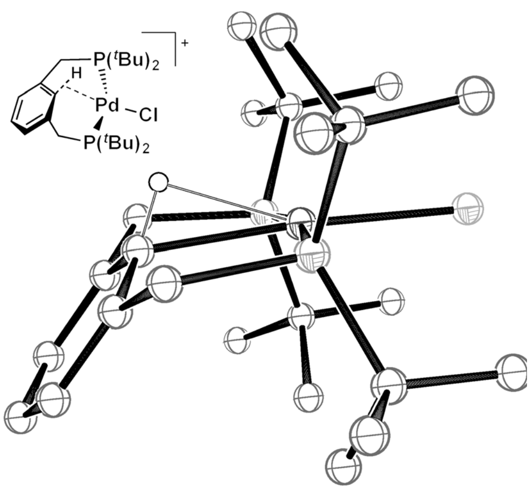


Figure 5. ORTEP[13] diagram of $[(^{tBu}PCP\text{-}H)PdCl]^+$ (**2**; side view). Thermal ellipsoids are set at 30% probability. The hydrogen atoms (other than the H atom participating in the agostic interaction), anion, and solvent have been omitted for clarity.

While PNP pincer ligands have been shown to participate in acid–base chemistry in similar complexes,[21] PCP pincer ligands are often treated as innocent ligands, immune to acidic conditions. These results suggest that reactions occurring in strongly acidic solutions may proceed through agostic complexes with active participation of the ligand. Similar agostic species have been reported by Milstein and co-workers[22] and others.[23]

Complexes **1** and **2** are novel Pd^{II} species with sigma bonds (H-H or C-H) which interact with the metal center. We plan to pursue further investigations into σ-bond complexation by analogous Group 10 pincer complexes.

Experimental Section

All experiments were carried out under argon using Schlenk and glove-box techniques unless otherwise noted. Solvents were dried and vacuum transferred immediately prior to use. Starting materials were synthesized as previously reported. Neutral alumina was used to purify the pincer metal chloride compounds (Alumina Neutral Super I, Catalog # 04589–25, Dynamic Adsorbants, Norcross, GA). The pincer metal chloride starting materials are reasonably stable to H_2O and O_2 and can be handled in air. NMR spectra were recorded at 298 K (unless otherwise noted) on Bruker AV300, AV500, DRX500, or AV700 spectrometers. ^1H NMR chemical shifts are reported relative to residual resonances of the solvent: C_6D_4HF ($\delta = 6.96$, 6.99, 7.17), $CDHCl_2$ ($\delta = 5.32$ ppm). Some ^1H NMR spectra were recorded in protio-fluorobenzene using a solvent suppression pulse program. $^{31}P\{^1H\}$ NMR chemical shifts were externally referenced to H_3PO_4 (85% in H_2O) ($\delta = 0.00$ ppm).

$[(^{tBu}PCP)Pd(H_2)][B(C_6F_5)_4]$ (**1**). $(^{tBu}PCP)PdCl$ (66.0 mg, 535 g mol^{-1}, 123 mmol) was combined with $[(Et_3Si)_2(\mu\text{-}H)][B(C_6F_5)_4]$ (113 mg, 910.58 g mol^{-1}, 123 mmol) in a silylated Schlenk flask with a Teflon valve. Fluorobenzene (ca. 4 mL) was added by vacuum transfer, and a dark orange solution resulted. The solution was frozen (liquid nitrogen), the head space evacuated, and H_2 gas (1 atm) was introduced. Upon thawing, the solution became lighter orange. The solution was again frozen, the head space evacuated, and pentane (ca. 25 mL) was added by vacuum transfer. A solid precipitated from the solution. After the precipitate settled, the supernatant was removed.

The precipitate was washed with pentane twice prior to drying using a hydrogen purge. Yield: 81 mg (55 %). ^{1}H NMR (500 MHz, 298 K, C_6H_5F): $\delta = 1.03$ (vt, 36 H, ^{t}Bu), 3.08 (vt, 4 H, CH_2), 1.7 ppm (s, 2 H, H_2 ligand); signals for aromatic protons coincident with solvent signals. ^{31}P{^{1}H} NMR (202 MHz, 298 K, C_6H_5F): $\delta = 95$ ppm. Elemental analysis calcd (%): C 48.8, H 3.8; found: C 48.2, H 3.5.

[(^{tBu}PCP-H)PdCl][B(C_6F)$_4$] (**2**). (^{tBu}PCP)PdCl (15.0 mg, 535 g mol^{-1}, 28 mmol) and [H(OEt_2)$_2$][B(C_6F_5)$_4$] (23.2 mg, 28 mmol) were combined in a Teflon screw-top NMR tube. CD_2Cl_2 was added by vacuum transfer. Upon thawing, the solution became orange in color. The product was isolated by layering the solution with alkane solvent to precipitate crystals. Yield of isolated product: 8 mg, 53 %. ^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): $\delta = 1.35$, 1.58 (vt, 18 H each, ^{t}Bu), 3.14, 3.70 (d-vt, 2H each, CH_2), 6.3 (s, 1 H, Pd-H-C), 7.31 (m, 2 H, aromatic), 7.96 ppm (t, 1 H, *para*-H). ^{31}P{^{1}H} NMR (202 MHz, 298 K, CD_2Cl_2): $\delta = 4.7$ ppm. Elemental analysis calcd (%): C 47.4, H 3.6; found: C 47.1, H 3.3. The same cationic product is detected by ^{1}H NMR spectroscopy if [$HOEt_2$][BF_4] is used as the acid.

CCDC-989776 (**1**) and 989775 (**2**) 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.

Keywords: agostic interactions · hydride ligands · hydrogen · palladium · tridentate ligands

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