1504 *Organometallics* **2002,** *21,* 1504−1507

Protonation of (PCP)PtH To Give a Dihydrogen Complex

Barbara F. M. Kimmich and R. Morris Bullock*

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000

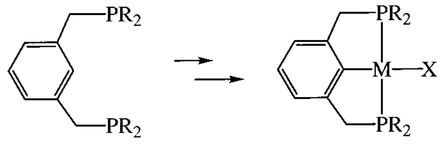
Received October 3, 2001

Summary: Protonation of (PCP)PtH (PCP = η^3-2,6-(^{t}Bu$_2$PCH$_2$)$_2$C$_6$H$_3$) in CD$_2$Cl$_2$ at −78 °C with $[H(OEt_2)_2]^+BAr'_4{}^-$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] gives the Pt^{II} dihydrogen complex $[(PCP)Pt(H_2)]^+$. The H_2 ligand is expelled when the solution is warmed to room temperature, but the dihydrogen complex is re-formed when H_2 is added.

Since dihydrogen complexes were first discovered by Kubas and co-workers in 1984,[1] the large number of studies of such complexes has led to an increased understanding of their reactivity, structures, and bonding.[2] While dihydrogen complexes are now known for many different metals, the majority of them involve a d^6 electron configuration. It was not until 10 years after the first dihydrogen complex that the first example of a d^8 Pt^{II} dihydrogen complex was reported,[3] when Caulton and co-workers published their results on *trans*-$[(P^tBu_3)_2Pt(H)(H_2)]^+OTf^-$. Additional examples of Pt dihydrogen complexes were subsequently reported by Kubas[4] and by Bercaw,[5] but dihydrogen complexes with a d^8 electron configuration (including Rh^I dihydrogen complexes[6] along with Pt^{II} dihydrogen complexes) remain rare in comparison to d^6 dihydrogen complexes.

Moulton and Shaw reported the first examples of a new class of tridentate ligands in 1976.[7] These ligands, shown in generalized form in Scheme 1, have two trans phosphines and an aryl ligand and are commonly called pincer[8] or PCP ligands. Complexes with PCP ligands have been prepared for numerous combinations of metal (M), alkyl group (R), and ligands X trans to the carbon ligand (X = H, halide, alkyl, etc.). Metal complexes with PCP ligands have been successfully used in reactions that are difficult to achieve, including cleavage of carbon−carbon bonds[9] and reduction of CO$_2$.[10] van Koten and others have developed an extensive chemistry using related pincer ligands with nitrogens ("NCN" ligands) in place of the phosphorus.[8,11] A particularly appealing attribute of some metal complexes with PCP ligands is their remarkable thermal stability. Kaska, Jensen, Goldman, and co-workers have developed Ir complexes with PCP ligands as catalysts for the dehydrogenation of alkanes,[12] some of which can be used for hours at 200 °C! Even more thermally stable catalysts were recently reported by Kaska and co-workers, who synthesized Ir complexes with PCP-type ligands containing an anthracene backbone, thus providing an aromatic instead of benzylic bond to the phosphine. Their complexes catalyzed the dehydrogenation of alkanes at 250 °C.[13] Milstein and co-workers found that {[η^3-2,6-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$)]Pd(OCOCF$_3$) was a highly active catalyst for the Heck reaction and that it showed no noticeable degradation even after 300 h at 140 °C.[14]

Scheme 1



PCP-H (PCP)M-X

---

[1] Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451−451.

[2] (a) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory, and Reactivity*; Kluwer Academic/Plenum Publishers: New York, 2001. (b) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913−926. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155−284. (d) Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577−588.

[3] Gusev, D. G.; Notheis, J. U.; Rambo, J. R.; Hauger, B. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 7409−7410.

[4] Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831−11843.

[5] Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1998**, *37*, 2422−2431.

[6] (a) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442−1447. (b) Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839−1844.

[7] Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020−1026.

[8] (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681−1694. (b) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750−3781.

[9] (a) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699−701. (b) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1965−1966. (c) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774−9775. (d) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406−12415. (e) van der Boom, M. E.; Kraatz, H.-B.; Ben-David, Y.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1996**, 2167−2168. (f) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415−13421. (g) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1998**, 917−918. (h) Rybtchinski, B.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 4528−4529. (i) van der Boom, M. E.; Kraatz, H.-B.; Hassner, L.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 3873−3884. (j) Gandelman, M.; Vigalok, A.; Konstantinovski, L.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 9848−9849. (k) Gauvin, R. M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2001**, *20*, 1719−1724.

[10] Kaska, W. C.; Nemeh, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1988**, *7*, 13−15.

[11] (a) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423−431. (b) Gossage, R. A.; Ryabov, A. D.; Spek, A. L.; Stufkens, D. J.; van Beek, J. A. M.; Rudi, v. E.; van Koten, G. *J. Am. Chem. Soc.* **1999**, *121*, 2488−2497.

[12] (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2083−2084. (b) Gupta, M.; Kaska, W. C.; Jensen, C. M. *J. Chem. Soc., Chem. Commun.* **1997**, 461−462. (c) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840−841. (d) Xu, W.-W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. *J. Chem. Soc., Chem. Commun.* **1997**, 2273−2274. (e) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087. (f) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017−11018. (g) Jensen, C. M. *J. Chem. Soc., Chem. Commun.* **1999**, 2443−2449.

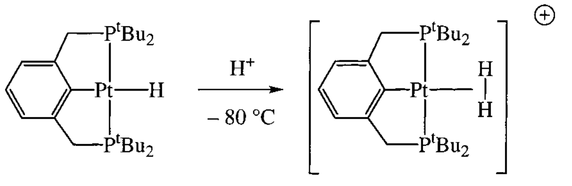
[13] Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H.-J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596−3600.

10.1021/om0108651 CCC: $22.00

We report here the protonation of (PCP)PtH to give a (PCP)Pt^{II} dihydrogen complex. In the remainder of this paper we use the abbreviation PCP to indicate [η^3-2,6-($^tBu_2PCH_2)_2C_6H_3$)], with R = ^{t}Bu.)

Results and Discussion

Protonation of (PCP)PtH To Give [(PCP)Pt(H_2)]$^+$. Protonation of (PCP)PtH in CD_2Cl_2 at −78 °C with $[H(OEt_2)_2]^+BAr'_4{}^-$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] leads to clean formation of the dihydrogen complex $[(PCP)Pt(\eta^2\text{-}H_2)]^+BAr'_4{}^-$ (eq 1). The dihydrogen resonance of this complex appears as a broad singlet at δ 0.18 (J_{Pt-H} = 306 Hz). The T_1 of the dihydrogen resonance of $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ was 14 ms at −86 °C and increased to 23 ms at −38 °C. When the solution of $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ was warmed to 22 °C, gas evolution (H_2) was observed. The solution was cooled back to −80 °C, and the NMR spectrum showed a mixture of 30% $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ and 70% of a new complex assigned as $[(PCP)Pt(ClCD_2Cl)]^+$. When this solution was placed under 4 atm H_2, the dihydrogen complex was replenished, indicating that the H_2 ligand can displace the very weakly bound methylene chloride ligand. Precedent for the displacement of a CH_2Cl_2 ligand on Pt by H_2 comes from the work of Kubas and co-workers,[4] who prepared *trans*-$[(P^iPr_3)_2Pt(H)(H_2)]^+BAr'_4{}^-$ from the reaction of H_2 with *trans*-$[(P^iPr_3)_2Pt(H)(ClCH_2Cl)]^+BAr'_4{}^-$.



(1)

$H^+ = [H(OEt_2)_2]^+ BAr_4'{}^-$, HOTf, $HBF_4 \bullet OEt_2$

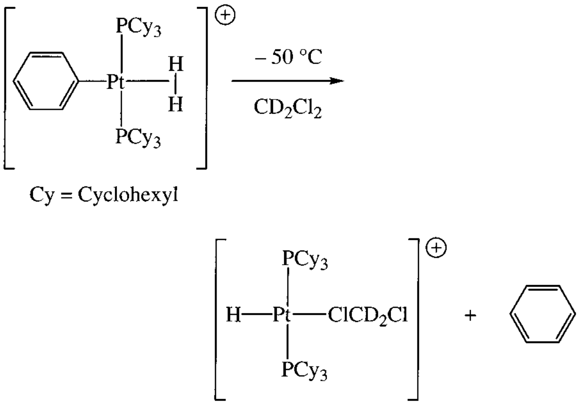
When a solution of $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ was kept under H_2 at 22 °C for about 2 weeks, some irreversible decomposition was observed. Although $[(PCP)Pt(H_2)]^+$ and $[(PCP)Pt(ClCD_2Cl)]^+$ were the two major complexes (~40% each) observed in the NMR spectrum, some decomposition to (PCP)PtCl occurs through reaction with the CD_2Cl_2 solvent. Along with (PCP)PtCl, a small amount (<5%) of free PCP−H ligand is observed, as well as some precipitate presumed to be Pt(0). In a separate experiment, about 63% conversion to (PCP)PtCl was observed when a solution of (PCP)PtH was heated in CD_2Cl_2 at 70 °C for 12 h.

The dihydrogen complex with a triflate counterion is readily observed by low-temperature NMR upon protonation of (PCP)PtH with triflic acid (CF_3SO_3H, abbreviated as HOTf). The T_1 of the dihydrogen ligand of $[(PCP)Pt(H_2)]^+OTf^-$ was 14 ms at −80 °C. Further evidence for the assignment as a dihydrogen ligand comes from the protonation of (PCP)PtH by DOTf to give $[(PCP)Pt(HD)]^+OTf^-$. The 1:1:1 triplet ($^1J_{H-D}$ = 33.4 Hz) observed for the HD ligand is characteristic of bound HD ligands, and the magnitude of the coupling constant is similar to those observed in other Pt(H_2) complexes.[3−5] The large $^1J_{H-D}$ indicates that the H−D bond is comparatively little activated (compared to free HD) and is suggestive of a short H−D distance.

Warming of the solution of $[(PCP)Pt(H_2)]^+OTf^-$ to 22 °C, followed by recording an NMR spectrum at low temperature, gave evidence for the formation of (PCP)PtOTf. As was observed with the $BAr'_4{}^-$ counterion, addition of H_2 to (PCP)PtOTf resulted in conversion back to the dihydrogen complex $[(PCP)Pt(H_2)]^+OTf^-$. The dihydrogen complex $[(PCP)Pt(H_2)]^+OTf^-$ is stable for at least 3 days at −80 °C, but decomposes over a period of days at room temperature.

Protonation of (PCP)PtH with $HBF_4{\cdot}Et_2O$ produces $[(PCP)Pt(H_2)]^+BF_4{}^-$, which has spectroscopic characteristics similar to those found with the $BAr'_4{}^-$ and OTf^- counterions. When this complex is warmed, several products were observed by ^{1}H and ^{31}P NMR. Plausible products include $[(PCP)Pt(ClCD_2Cl)]^+BF_4{}^-$, $[(PCP)Pt(OEt_2)]^+BF_4{}^-$, and $(PCP)PtFBF_3$.

Stahl, Labinger, and Bercaw characterized $[(PCy_3)_2Pt(Ph)(H_2)]^+BAr'_4{}^-$ by low-temperature NMR.[5] This complex eliminates benzene at −50 °C (eq 2). Aside from their use of cyclohexyl groups on the phosphines compared to *tert*-butyls in our PCP complexes, the main difference in their dihydrogen complex and $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ is the chelating ligand of the PCP, which connects both phosphines to the arene ring. The chelation of the PCP ligand affords a substantial stabilizing influence on the dihydrogen complex, since $[(PCy_3)_2Pt(Ph)(H_2)]^+BAr'_4{}^-$ decomposes at −50 °C, whereas $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ slowly decomposes over a period of days at room temperature. The small amounts of free PCP−H ligand observed after several days from decomposition of $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ may form through an elimination of the arene, analogous to that shown in eq 2, followed by dissociation of the phosphine ligand. Intramolecular reductive elimination of an alkane normally requires a cis configuration, but the rigidity of the chelated PCP backbone locks the aryl and dihydrogen ligands into a trans configuration, thereby disfavoring elimination. A dihydride might be more readily able than the dihydrogen complex to obtain a geometry that would be favorable for the elimination of arene, though we have no data indicating that our dihydrogen complex is actually in equilibrium with a dihydride. Proton transfer from the dihydrogen ligand of $[(PCP)Pt(H_2)]^+$ to the arene ring could be a step in the elimination of the arene ligand. Pertinent to this possibility are studies by van Koten and co-workers, who carried out extensive studies on η^1-arenium complexes of platinum with NCN-



Cy = Cyclohexyl

(2)

---

(14) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687−11688.

pincer ligands.[15] Their studies provide information relevant to the formation of C−C bonds between arenes and alkyl groups in Pt complexes, which is of interest in connection with electrophilic aromatic substitutions. Their results may provide some insight into the reactivity of our Pt system.

Attempted Catalytic Reactions. One reason for our interest in these Pt complexes was to explore their possible utility in homogeneous hydrogenation catalysis. Along with the previously mentioned uses of PCP complexes as catalysts for dehydrogenation and the Heck reaction, metal complexes with PCP ligands have also been used in hydrogenation catalysis. Ruthenium complexes with pincer ligands were reported to catalyze the transfer hydrogenation of ketones.[16] We recently developed a series of Mo and W complexes that serve as catalysts for the homogeneous hydrogenation of ketones.[17] These reactions were proposed to proceed by an ionic hydrogenation mechanism, involving proton transfer from a cationic dihydride as the first step. Many cationic dihydrogen complexes are acidic,[18] and hydride transfer capabilities of neutral metal hydrides are well-established.[19] Compared to Pt complexes not containing the tridentate PCP-type ligands, the enhanced stability we observed for $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ appeared to be a promising attribute for our intents to use either $[(PCP)Pt(H_2)]^+$ or $[(PCP)Pt(ClCH_2Cl)]^+$ as possible hydrogenation catalysts. Unfortunately, attempts to use $[(PCP)Pt(H_2)]^+$ as a catalyst for hydrogenation of $Et_2C{=}O$ showed no significant catalytic activity. A variety of solvents (chlorobenzene, THF, and toluene) were employed in these scouting studies, with temperatures as high as 80 °C and pressures of H_2 up to 800 psi. Decomposition of the catalyst precursors was observed, with precipitates thought to be Pt(0) being observed in many cases.

We suspect that the reason for failure of these Pt complexes to function as ionic hydrogenation catalysts is that $[(PCP)Pt(H_2)]^+$ is not sufficiently acidic to effectively protonate the ketone. No hydrogenation of acetone to 2-propanol was observed when HOTf was added to a CD_2Cl_2 solution of (PCP)PtH and acetone. We did find evidence for the expected hydridic reactivity of (PCP)PtH. Hydride transfer from Pt to carbon occurs rapidly when (PCP)PtH is reacted with $Ph_3C^+BF_4^-$ at room temperature, with Ph_3CH being formed in high yield.

Experimental Section

General Methods. All manipulations were carried out under argon using standard Schlenk or vacuum line techniques, or in a drybox. THF was distilled from Na/benzophenone and CH_2Cl_2 was distilled from P_2O_5; deuterated NMR solvents were purified similarly. (PCP)PtCl[7] and $[H(OEt_2)_2]^+BAr'_4{}^-$ [20] [Ar′ = 3,5-bis(trifluoromethyl)phenyl] was prepared as previously described. DOTf and $HBF_4{\cdot}Et_2O$ (85% in Et_2O) were purchased from Aldrich and used without further purification. HOTf was purified by distillation. NMR spectra were recorded on a Bruker AM-300 instrument (300 MHz for ^1H). ^1H NMR spectra were referenced to the residual proton peaks of the deuterated solvents, and ^{31}P NMR spectra were referenced to 85% phosphoric acid. NMR probe temperatures were calibrated using methanol.[21] The T_1 measurements were carried out at 300 MHz using the standard inversion−recovery pulse sequence. For experiments indicated as carried out under 4 atm H_2, a 5 mm NMR tube equipped with a J. Young valve was attached to a vacuum line and cooled in liquid nitrogen (77 K). The tube was then filled with 1 atm H_2. Using this procedure, the pressure of H_2 after the tube was warmed to room temperature will be about 4 atm (298/77 = 3.9).

Preparation of (PCP)PtH. (PCP)PtH was previously prepared from the reaction of (PCP)PtCl with $NaBH_4$.[7] In our hands, higher yields were obtained from a modified preparation using $LiAlH_4$, as used in the synthesis of a related Pd complex.[22] (PCP)PtCl (619 mg, 9.91×10^{-4} mol) and $LiAlH_4$ (50.0 mg, 1.31×10^{-3} mol) were stirred at room temperature in THF (20 mL) for 6 h. The reaction was quenched with H_2O (50 μL), and the solvent was evaporated. The product was extracted with pentane (150 mL), which was evaporated to give (PCP)PtH as a white solid (440 mg, 75%). ^1H NMR (22 °C, CD_2Cl_2): δ −2.32 (t, $J_{P-H} = 16$ Hz, $J_{Pt-H} = 741$ Hz, 1H, PtH); 1.32 (t, $J = 6.8$ Hz, 36H, ^tBu); 3.45 (m, 4H, CH_2); 6.91−7.10 (m 3H, C_6H_3). $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2): δ 87.9 ($J_{P-Pt} = 2895$ Hz).

Preparation of $[(PCP)Pt(H_2)]^+BAr'_4{}^-$. A solution of $[H(OEt_2)_2]^+BAr'_4{}^-$ (9.9 mg, 9.9×10^{-6} mol) in CD_2Cl_2 (500 μL) at −78 °C was added to a solution of (PCP)PtH (5.8 mg, 9.8×10^{-6} mol, 1 equiv) in 500 μL of CD_2Cl_2 in an NMR tube at −78 °C. The tube was inverted to mix the contents and was then placed in an NMR probe precooled to −80 °C. The dihydrogen complex $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ was present in ≥90% purity. ^1H NMR (−90 °C, CD_2Cl_2): δ 0.18 (br s, $J_{Pt-H} = 306$ Hz, 2H, Pt−H_2); 1.23 (t, $J = 7.4$ Hz, 36H, ^tBu); 3.47 (m, 4H, CH_2); 6.82−7.18 (m 3H, C_6H_3); 7.53 (br, 4H, *p*-H of $BAr'_4{}^-$); 7.72 (br, 8H, *o*-H of $BAr'_4{}^-$). $^{31}P\{^1H\}$ NMR (−90 °C, CD_2Cl_2): δ 88.4 ($J_{P-Pt} = 2510$ Hz).

Warming of $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ and Addition of H_2. When the solution of $[(PCP)Pt(H_2)]^+BAr'_4{}^-$ prepared above was warmed to 22 °C for 2 min, gas evolution was observed. The solution was recooled to −80 °C, and the $^{31}P\{^1H\}$ NMR spectrum indicated a 7:3 ratio of $[(PCP)Pt(ClCD_2Cl)]^+$:$[(PCP)Pt(H_2)]^+$. Hydrogen (4 atm) was then added to the tube, and the NMR spectrum indicated that the dihydrogen complex was re-formed, with a 10:1 ratio of $[(PCP)Pt(H_2)]^+$ to $[(PCP)Pt(ClCD_2Cl)]^+$ being determined by NMR. After the tube was left under H_2 (4 atm) at 22 °C for 12 days, ^1H and $^{31}P\{^1H\}$ NMR spectra recorded at 22 °C indicated the following complexes: $[(PCP)Pt(H_2)]^+$ (42%), $[(PCP)Pt(ClCD_2Cl)]^+$ (39%), (PCP)PtCl (16%), and PCP−H (3%). Some dark precipitate had also formed, presumably Pt(0). ^1H NMR of $[(PCP)Pt(ClCD_2Cl)]^+BAr'_4{}^-$ (−80 °C, CD_2Cl_2): δ 1.26 (m, 36H, ^tBu); 3.12 (m, 4H, CH_2); 6.90−7.17 (m, 3H, C_6H_3); 7.53 (br, 4H, *p*-H of $BAr'_4{}^-$); 7.72 (br, 8H, *o*-H of $BAr'_4{}^-$). $^{31}P\{^1H\}$ NMR (−80 °C, CD_2Cl_2): δ 73.4 ($J_{P-Pt} = 2845$ Hz).

---

(15) (a) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609−6616. (b) Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 2891−2898. (c) Albrecht, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2001**, *123*, 7233−7246.

(16) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743−745.

(17) (a) Bullock, R. M.; Voges, M. H. *J. Am. Chem. Soc.* **2000**, *122*, 12594−12595. (b) Voges, M. H.; Bullock, R. M. *J. Chem. Soc., Dalton Trans.* **2002**, in press.

(18) (a) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824−1826. (b) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883. (c) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155−9171.

(19) (a) For a review of nucleophilic reactivity of metal hydrides, see: Labinger, J. A. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 10, pp 361−379. (b) Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121−13137. (c) Cheng, T.-Y.; Bullock, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 3150−3155.

(20) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922.

(21) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679−680.

(22) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 738−743.

T_1 Measurements of [(PCP)Pt(H_2)]$^+$BAr′$_4$$^-$. The following T_1 values were determined for the dihydrogen peak of [(PCP)Pt(H_2)]$^+$BAr′$_4$$^-$ in CD_2Cl_2 at 300 MHz: 14 ms (−86 °C), 14 ms (−74 °C), 16 ms (−62 °C), 19 ms (−50 °C), and 23 ms (−38 °C).

Preparation of [(PCP)Pt(H_2)]$^+$OTf$^-$. (PCP)PtH (9.6 mg, 1.6×10^{-5} mol) was dissolved in 0.70 mL of CD_2Cl_2, and the solution was cooled to −80 °C. Triflic acid (HOTf, 1.4 μL, 1.6×10^{-5} mol) was added by syringe, and the tube was inverted to mix the contents. [(PCP)Pt(H_2)]$^+$OTf$^-$ was formed in about 93% yield by NMR. About 7% (PCP)PtOTf was observed, apparently due to unintentional warming of part of the solution, since the ratio of these two complexes did not change significantly after 3 days at −80 °C. ^{1}H NMR of [(PCP)Pt(H_2)]$^+$-OTf$^-$ (−80 °C, CD_2Cl_2): δ 0.23 (br s, $J_{\mathrm{Pt-H}} = 304$ Hz, 2H, Pt−H_2); 1.26 (m, 36H, ^{t}Bu); 3.49 (m, 4H, CH_2) 7.19 (m, 3H, C_6H_3). ^{31}P{^{1}H} NMR of [(PCP)Pt(H_2)]$^+$OTf$^-$ (−80 °C, CD_2Cl_2): δ 88.3 ($J_{\mathrm{P-Pt}} = 2509$ Hz). ^{1}H NMR of (PCP)PtOTf (−80 °C, CD_2Cl_2): δ 1.27 (m, 36H, ^{t}Bu); 3.08 (m, 4H, CH_2) 6.87−7.18 (m, 3H, C_6H_3). ^{31}P{^{1}H} NMR of (PCP)PtOTf (−80 °C, CD_2Cl_2): δ 75.6 ($J_{\mathrm{P-Pt}} = 2901$ Hz).

Warming of [(PCP)Pt(H_2)]$^+$OTf$^-$ and Addition of H_2. When the solution of [(PCP)Pt(H_2)]$^+$OTf$^-$ prepared above was warmed to 22 °C for 2 min, gas evolution was observed. The solution was recooled to −80 °C, and the ^{31}P{^{1}H} NMR spectrum indicated a 4:1 ratio of (PCP)PtOTf to [(PCP)Pt(H_2)]$^+$-OTf$^-$. Hydrogen (4 atm) was added to the tube, and the NMR spectrum (−80 °C) indicated that the dihydrogen complex was re-formed (87%). After the tube was left under H_2 (4 atm) at 22 °C for 3 days, a ^{31}P{^{1}H} NMR spectrum recorded at 22 °C indicated the following complexes: [(PCP)Pt(H_2)]$^+$ (44%), (PCP)PtOTf (31%), (PCP)PtCl (δ 67.6, 13%), and PCP−H (δ 40.4, 5%).

Preparation of [(PCP)Pt(HD)]$^+$OTf$^-$. Using a procedure analogous to that described above, protonation of (PCP)PtH by DOTf at −80 °C gave [(PCP)Pt(HD)]$^+$OTf$^-$ in 94% yield. ^{1}H NMR of [(PCP)Pt(HD)]$^+$OTf$^-$ (−80 °C in CD_2Cl_2): δ 0.33 (1:1:1 t, $J_{\mathrm{Pt-H}} = 312$ Hz, $J_{\mathrm{H-D}} = 33.4$ Hz, 1H, Pt−HD); 1.27 (t, $J = 7.4$ Hz, 36H, ^{t}Bu); 3.48 (m, 4 H, CH_2) 7.16 (m, 3H, C_6H_3). ^{31}P{^{1}H} NMR of [(PCP)Pt(HD)]$^+$OTf$^-$ (−80 °C in CD_2Cl_2): δ 87.9 (d, $J_{\mathrm{P-Pt}} = 2510$ Hz).

Preparation of [(PCP)Pt(H_2)]$^+$BF$_4$$^-$. Tetrafluoroboric acid (3.1 μL of 85% $HBF_4 \cdot Et_2O$ in Et_2O) was added to a solution of (PCP)PtH (10.7 mg, 1.81×10^{-5} mol) in CD_2Cl_2 (0.70 mL) at −80 °C. The tube was inverted to mix the contents, and the NMR spectrum indicated that [(PCP)Pt(H_2)]$^+$ was formed in >90% yield. ^{1}H NMR (−90 °C, CD_2Cl_2): δ 0.29 (br s, $J_{\mathrm{Pt-H}} = 310$ Hz, 2H, Pt−H_2); 1.26 (m, 36H, ^{t}Bu); 3.48 (m, 4H, CH_2); 7.16−7.21 (m 3H, C_6H_3). ^{31}P{^{1}H} NMR (−90 °C, CD_2Cl_2): δ 88.2 (d, $J_{\mathrm{P-Pt}} = 2509$ Hz).

Warming of [(PCP)Pt(H_2)]$^+$BF$_4$$^-$. When the solution of [(PCP)Pt(H_2)]$^+$BF$_4$$^-$ prepared above was warmed to 22 °C for 1 min, gas evolution was observed. The solution was recooled to −80 °C, and the ^{31}P{^{1}H} NMR spectrum indicated that the relative amount of [(PCP)Pt(H_2)]$^+$BF$_4$$^-$ had decreased to about 29%. Several other decomposition products were also formed, as indicated by ^{31}P{^{1}H} resonances at δ 75.6 (21%), δ 76.7 (19%), and δ 72.9 (17%).

Acknowledgment. We thank the U.S. Department of Energy, Office of Science, Laboratory Technology Research Program, and the Division of Chemical Sciences, Office of Basic Energy Sciences, for support. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-98CH10886 with the U.S. Department of Energy. We thank DuPont Central Research for additional support of this work through a CRADA grant. We gratefully acknowledge Dr. Paul Fagan and Dr. Elisabeth Hauptman (DuPont) for many helpful discussions, and the reviewers for several helpful suggestions.

OM0108651