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Communications

Formation of a Stable Dihydrido(alkyl)platinum(IV) Complex by Water Activation

Ariel Haskel[†] and Ehud Keinan*

Department of Chemistry and Institute of Catalysis Science and Technology, Technion—Israel Institute of Technology, Technion City, Haifa 32000, Israel, and Department of Molecular Biology and The Skaggs Institute for Chemical Biology, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, California 92037

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*Summary: The novel air- and moisture-stable dihydrido(methyl)platinum(IV) complex $TpPtH_2Me$ (**1**; Tp = hydridotris(pyrazolyl)borate) is formed as the sole product by the reaction of TpPtMeCO (**2**) with water. Complex **1** was characterized by elemental analysis, ^1H NMR, ^{13}C NMR, and FTIR. The proposed mechanism of the reaction involves an initial nucleophilic attack by a water molecule on the coordinated carbonyl in **2** with subsequent release of CO_2 followed by protonation at the platinum center to produce **1**.*

The direct, selective oxidation of alkanes has long been a major challenge in transition-metal chemistry.[1] The Shilov system, which employs chloroplatinum salts in aqueous media to catalytically functionalize methane, has been the subject of a number of mechanistic studies over the past few years.[2] Unfortunately, unlike the classical Shilov system, most of the organometallic models used for these studies are extremely air- and moisture-sensitive. A key intermediate in this process was proposed to be a hydrido(alkyl)metal complex. Attempts to prepare such complexes under aqueous conditions resulted in platinum(IV) hydroxo complexes with concomitant release of hydrogen gas, probably via rapid hydrolysis of short-lived platinum(IV) hydrido intermediates.[3,4] Consequently, most of the known hydrido(alkyl)platinum(IV) complexes were prepared and studied in the absence of oxygen and under anhydrous conditions. The dihydrido(alkyl)platinum(IV) complexes seemed to be more elusive than either the hydrido(alkyl)platinum(IV) or the dihydridodihaloplatinum(IV) complexes.[5] Bercaw and co-workers, who studied extensively the individual steps of the catalytic oxidation

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* To whom correspondence should be addressed at The Scripps Research Institute. Incumbent of the Benno Gitter & Ilana Ben-Ami chair of Biotechnology, Technion. E-mail: keinan@scripps.edu.

[†] E-mail: haskel@scripps.edu.

(1) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(2) (a) Shilov, A. E.; Shulpin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2180. (c) Bengali, A. A.; Arndtsen, B. A.; Burger, P. M.; Schultz, R. H.; Weiller, B. H.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *Pure Appl. Chem.* **1995**, *67*, 281. (d) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987. (e) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. (f) Johansson, L.; Ryan, O. B., Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974. (g) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848.

(3) (a) Appleton, T. G.; Hall, J. R.; Neale, D. W.; Williams, M. A. *J. Organomet. Chem.* **1984**, *276*, C73. (b) Canty, A. J.; Honeyman, R. T.; Roberts, A. S.; Traill, P. R. *J. Organomet. Chem.* **1994**, *471*, C8. (c) Canty, A. J.; Fritsche, S. D.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *490*, C18. (d) Canty, A. J.; Fritsche, S. D.; Jin, H.; Honeyman, R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *510*, 281.

(4) (a) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444. (b) A more recent report (Rostovtsev, V. V.; Labinger, J. A.; Bercaw, J. E.; Lasseter, T. L.; Goldberg, K. I. *Organometallics* **1998**, *17*, 4350) argues against the validity of the results presented in ref 4a and suggests that the formation of Pt(IV) hydroxo complexes arises from air oxidation.

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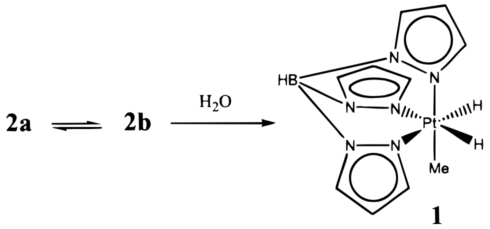
Scheme 1



of alkanes,[6] have recently proposed a dihydrido(alkyl)platinum(IV) complex as a hypothetical intermediate in the low-temperature protonolysis of $(PCy_3)_2Pt(H)R$ (R = CH_3, Ph) which produced methane or benzene.[7]

Here we report on the formation of a stable dihydrido(methyl)platinum(IV) complex, $TpPtH_2Me$ (**1**; Tp = hydridotris(pyrazolyl)borate) via the reaction of TpPtMeCO (**2**) with water (Scheme 1). Remarkably, the air- and moisture-stable complex **1** contains not only two *cis* hydride ligands but also a *cis* methyl ligand.

Complex **2**[8] (10 mg, 0.022 mmol) was dissolved in acetone−H_2O (1:1, 0.5 mL), and the mixture was kept at room temperature for 24 h. The white precipitate (6.9 mg, 0.016 mmol, 73%) was collected and dried under reduced pressure and then analyzed by elemental analysis,[9] ^{1}H NMR, ^{13}C NMR, and FTIR. The same result was obtained under either air or argon atmosphere. In addition to the Pt−Me signal at 1.04 ppm ($^2J_{Pt-H}$ = 65.4 Hz, 3H) in the ^{1}H NMR spectrum, a 2:1 ratio of all pyrazolyl signals was observed, indicating a symmetrical structure of **1**, with two identical and one different pyrazolyl ring. The fact that both the H3 and H3′ pyrazolyl hydrogens exhibited platinum satellites confirmed that all three pyrazolyl rings were attached to the platinum metal. A diagnostic Pt^{IV}−H signal at −20.04 ppm ($^1J_{Pt-H}$ = 1276 Hz, 2H) was consistent with two hydride ligands.[10] To rule out a nonclassical conformation of **1** (η^2-H_2), a T_1 temperature-dependence experiment was carried out in acetone-d_6. Complex **1** exhibited a minimal value of T_1 (748 ms) at −70 °C, which characterizes classical hydride ligands.[11]

The ^{13}C NMR spectrum of **1**[12] showed a remarkable high-field Pt−CH_3 signal at −30.4 ppm ($^1J_{Pt-C}$ = 561.5 Hz).[13] The C3 and C3′ carbon signals at 141.0 ppm ($^2J_{Pt-C}$ = 27.3 Hz, 2C) and 144.5 ppm ($^2J_{Pt-C}$ = 35.3 Hz, 1C) reflected once again the above-mentioned symmetry of **1** with all three pyrazolyl groups being attached to the platinum atom. A similar conclusion could be drawn from the C4 and C4′ carbon signals, whose intensities showed approximately a 2:1 ratio. In contrast, C5 and C5′ overlapped to form a broad signal.

Infrared spectroscopy was particularly useful for the structure determination of **1** (see the Supporting Information). Complex **2** was characterized by a very strong CO signal at 2087 cm^{-1}. This signal was missing in **1**, which exhibited a strong Pt^{IV}−H signal at 2253 cm^{-1}.[14] Furthermore, when **2** was reacted with acetone-d_6/D_2O this platinum−hydride absorption was shifted to 1626[15] cm^{-1}, as expected for a platinum−deuteride complex. Crystals of **1** were grown from a 1:1 mixture of acetone and water at −20 °C and analyzed by X-ray crystallography. Unfortunately, the low quality of the crystal did not allow for accurate structure determination (R_1 = 0.1904).[16]

The mechanistic details by which complex **1** was formed are of special importance, because they could provide valuable information about two key transformations in organometallic chemistry: C−H activation with transition metals and the WGS reaction.[17] It is likely that introduction of the two hydride ligands occurs via two different mechanistic steps: (a) a nucleophilic attack by a water molecule on the coordinated carbonyl followed by release of CO_2, as is known for the WGS reaction, and (b) oxidative addition of a water molecule (protonation of the platinum metal).

Variable-temperature NMR experiments have indicated that **2** in $CDCl_3$ solution is fluxional at room temperature[18] but adopts a trigonal-bipyramidal geometry, **2a**, at low temperatures. In the solid state, however, the molecule takes a square-planar geometry, **2b**, with the Tp group becoming a bidentate ligand.[19] The fluxional behavior of **2**, although not yet fully understood, is apparent from its ^{1}H NMR spectral data.[20] The trigonal-bipyramidal geometry of **2** at low temperature (−40 °C) is secured by ^{13}C NMR spectra, which show platinum coupling to all C-3 pyrazole rings.[21] Therefore, we suggest that, in solution, **2a** and **2b** coexist in equilibrium. Another indicator for the

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(5) (a) Anderson, D. W. W.; Ebsworth, E. A. A. V.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1973**, 854. (b) Blacklaws, I. M.; Ebsworth, E. A. A. V.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1978**, 753. (c) Blacklaws, I. M.; Brown, L. C.; Ebsworth, E. A. A. V.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 877. (d) Falk, C. D.; Halpern, J. *J. Am. Chem. Soc.* **1965**, *87*, 3523.

(6) (a) Luinstra, G. A.; Wang, S. S.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (c) Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta*, **1998**, *270*, 467.

(7) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1998**, *37*, 2422.

(8) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1974**, *13*, 1996.

(9) Anal. Calcd for $C_{10}H_{15}BN_6Pt$: C, 28.24; H, 3.53; N, 19.77. Found: C, 28.39; H, 3.40; N, 19.89.

(10) $TpPtMeH_2$ of **1**: ^{1}H NMR (acetone-d_6/D_2O (9:1), δ): 7.89 (d, 2H, $^3J_{H-H}$ = 2.2 Hz, H-5), 7.86 (d, 1H, $^3J_{H-H}$ = 2.2, H-5′), 7.75 (d, 2H, $^3J_{H-H}$ = 2.2, $^3J_{Pt-H}$ = 8.4 Hz, H-3), 7.64 (d, 1H, $^3J_{H-H}$ = 2.2, $^3J_{Pt-H}$ = 8.8 Hz, H-3′), 6.30 (t, 2H, $^3J_{H-H}$ = 2.2, H-4), 6.24 (t, 1H, $^3J_{H-H}$ = 2.2, H-4′), 1.04 (s, 3H, $^2J_{Pt-H}$ = 65.4 Hz, CH_3), −20.04 (s, 2H, $^1J_{Pt-H}$ = 1276 Hz, Pt−H). IR of **1** (KBr): 2253.2 (ν_{Pt-H}), 2470.9 (br, ν_{B-H}) cm^{-1}.

(11) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

(12) The ^{13}C NMR signal (−30.4 ppm) of the Pt−Me group is remarkably high compared with other reported TpPt(IV)−methyl complexes, where the methyl absorbs at −19.62 and −3.69 ppm.[25b]

(13) $TpPtMeH_2$ (**1**): ^{13}C NMR (acetone-d_6/D_2O (9:1), δ): 144.5 (s, $^2J_{Pt-C}$ = 35.3 Hz, 1C, C-3′), 141.0 (s, $^2J_{Pt-C}$ = 27.3 Hz, 2C, C-3), 136.0 (br, 3C, C-5/C-5′), 106.9 (s, $^3J_{Pt-C}$ = 19.2 Hz, 1C, C-4′), 106.7 (s, $^3J_{Pt-C}$ = 16.05 Hz, 2C, C-4), −30.4 (s, $^1J_{Pt-C}$ = 561.5 Hz, 3C, CH_3).

(14) An intense Pt−H stretching signal has been reported in ref 5a.

(15) Edgell, W. F.; Summit, R. *J. Am. Chem. Soc.* **1961**, *83*, 1772.

(16) A *cis*-dihydrido(bisphosphine)platinum(IV) complex was recently characterized by X-ray crystallography: Edelbach, B. L.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784.

(17) (a) Spencer, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 6, p 292. (b) Cheng, C.-H.; Eisenberg, R. *J. Am. Chem. Soc.* **1978**, *100*, 5968. (c) Clark, H. C.; Jain, V. K. *Coord. Chem. Rev.* **1984**, *55*, 151. (d) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11.

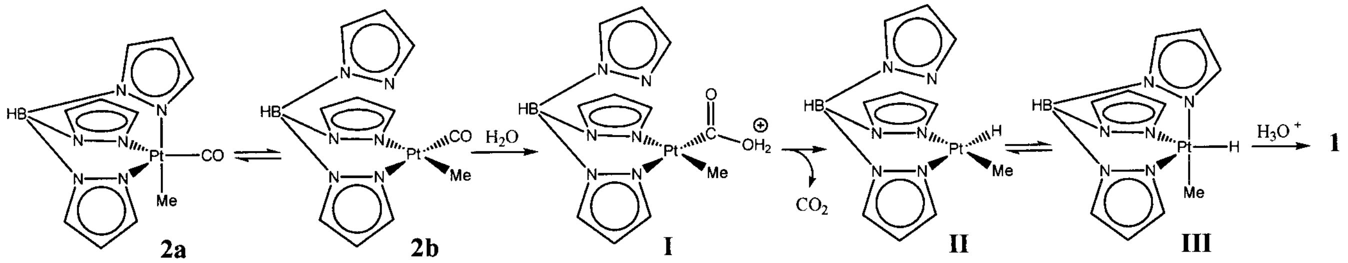
(18) Manzer, L. E.; Meakin, P. Z. *Inorg. Chem.* **1976**, *15*, 3117.

(19) (a) Rush, P. E.; Oliver, J. D. *J. Chem. Soc., Chem. Commun.* **1974**, 996. (b) Rush, P. E.; Oliver, J. D. *J. Organomet. Chem.* **1976**, *104*, 117.

(20) ^{1}H NMR data of **2** ($CDCl_3$, room temperature, δ): 7.68 (br, 3H, H-3/H-3′ or H-5/H-5′), 7.49 (br, 3H, H-5/H-5′ or H-3/H-3′), 6.30 (br, 3H, H-4/H-4′), 1.02 (s, 3H, $^2J_{Pt-H}$ = 70.2 Hz, CH_3).

(21) ^{13}C NMR of **2** ($CDCl_3$, −40 °C, δ): 164.7 (s, 1C, CO), 142.4 (s, 1C, $^2J_{Pt-C}$ = 37.5 Hz, C-3′), 140.9 (s, $^2J_{Pt-C}$ = 34.4 Hz, 2C, C-3), 136.3 (s, 1C, C-5′), 135.9 (s, 2C, C-5), 106.5 (s, 1C, C-4′), 105.3 (s, 2C, C-4), −17.7 (s, $^1J_{Pt-C}$ = 524.6 Hz, 3C, CH_3).

Scheme 2

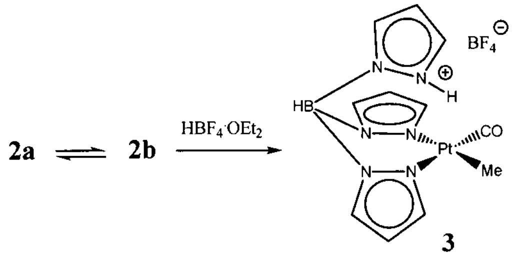


hapticity of the Tp ligand is the nature of the B−H bond, as reflected by ^{11}B NMR[22] and by IR.[23] We measured the IR spectra of **2** in solution (ν_{B-H} 2460 cm^{-1}) and in the solid state (ν_{B-H} 2483.5 cm^{-1}) and observed a significantly broader B−H stretch signal in the former. These results are consistent with equilibrium between **2a** and **2b** in solution.

We propose that the first step in the reaction between **2** and water (Scheme 2) involves a nucleophilic attack by a water molecule on the coordinated carbonyl to produce the acyl intermediate **I**.[17] This intermediate can release a molecule of carbon dioxide to produce intermediate **II**. To verify this WGS-type mechanism, we prepared an isotopically labeled complex, TpPtMe^{13}CO, and followed its reaction with a 1:1 mixture of acetone-d_6 and D_2O using ^{13}C NMR spectroscopy. We found that the carbonyl signal of **2** at 164.70 ppm ($^1J_{Pt-C}$ = 1880 Hz) disappeared slowly with concomitant appearance of a new singlet at 125 ppm (with no coupling to Pt).[24] The assignment of the latter signal to free $^{13}CO_2$ was confirmed by the fact that the intensity of this signal was diminished substantially upon either purging the sample with argon or applying a partial vacuum.

The final step involves direct protonation of either **II** or its pentacoordinated isomer **III** to produce **1**. This step is probably facilitated by the presence of carbonic acid (aqueous CO_2), which was produced in the previous step. An analogous transformation was recently reported by Canty and co-workers, who used acidic reagents, including acetic acid, HBF_4, and phenol, to convert $TpPtMe_2^-$ to $TpPtMe_2(H)$.[25] Similarly, Templeton and co-workers have used HCl to transform $Tp'PtMe_2^-$ to $Tp'PtMe_2(H)$ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate).[26] The oxidative addition of protic acids to platinum(II) complexes represents a common entry to hydridoplatinum(IV) complexes.[27]

Scheme 3



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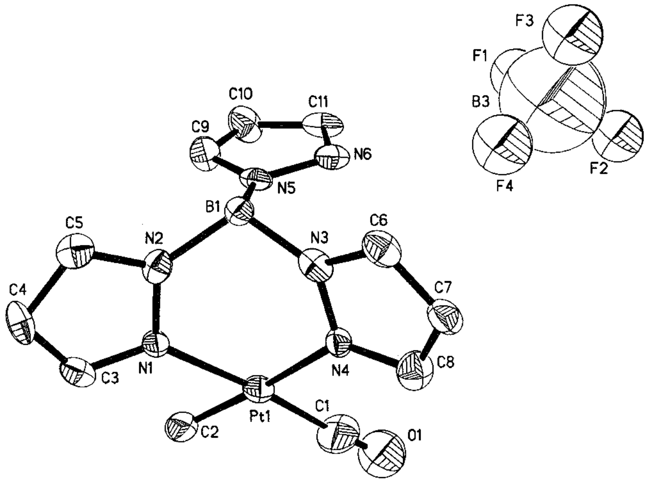

Figure 1. Molecular structure of **3** with the adopted atom numbering (only one of the two molecules of the unit cell is shown). Important distances (Å): Pt1−N1 = 2.050(14), Pt1−N4 = 2.075(13), Pt1−C1 = 1.80(3), Pt1−C2 = 2.08(2). Some relevant angles (deg): N1−Pt1−N4 = 88.7(5), N1−Pt1−C2 = 88.6(7), N4−Pt1−C1 = 94.7(9), C2−Pt1−C1 = 88.1(10).

Since we did not have clear experimental evidence for the relative timing of the WGS and protonation steps, we examined the preferred protonation site in complex **2**. Thus, reaction of **2** (10 mg, 0.022 mmol) with HBF_4·(ether) (0.0031 mL, 1 equiv) in either ether (2 mL) or acetone−water (1:1, 1 mL) produced the tetrafluoroborate salt **3** (Scheme 3) in quantitative yield (12.0 mg, 0.022 mmol).[28] Complex **3** was recrystallized from CH_2Cl_2−hexane at 4 °C and analyzed by X-ray crystallography (Figure 1).[29] As can be clearly concluded from the solid-state structure of **3**, the preferred protonation site in **2** is one of the pyrazolyl rings and not the platinum center. This observation supports our assump-

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(22) Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 5148.

(23) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121.

(24) (a) Ziessel, R. *J. Am. Chem. Soc.* **1993**, *115*, 118. (b) Miller, R. G.; Kyle, J. A.; Coates, G. W.; Anderson, D. J.; Fanwick, P. E. *Organometallics* **1993**, *12*, 1161.

(25) (a) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845. (b) Canty, A. J.; Fritsche, S. D.; Jin, H.; Patel, J.; Skelton, B. W.; White, A. H. *Organometallics* **1997**, *16*, 2175.

(26) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684.

(27) (a) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371. (c) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (d) Hill, G. S.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 8745. (e) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946.

(28) ^{1}H NMR data of **3** (D_2O/acetone-d_6 (1:1), δ): 8.08 (d, $^3J_{H-H}$ = 2.2 Hz, 1H, H-3′ or H-5′), 8.02 (d, $^3J_{H-H}$ = 2.2 Hz, 2H, H-3 or H-5), 7.96 (d, $^3J_{H-H}$ = 2.2 Hz, 1H, H-5′ or H-3′), 7.86 (d, $^3J_{H-H}$ = 2.2 Hz, 2H, H-5 or H-3), 6.61 (t, $^3J_{H-H}$ = 2.2 Hz, 2H, H-4), 6.55 (t, $^3J_{H-H}$ = 2.2 Hz, 1H, H-4′), 0.85 (s, 3H, $^2J_{Pt-H}$ = 70.6 Hz, CH_3). ^{19}F NMR (acetone, external standard $Bu_4N^+PF_6^-$, δ) −57.24 ppm (s). Anal. Calcd for $C_{11}H_{14}B_2F_4N_6OPt$: C, 24.50; H, 2.60; N, 15.59; Found: C, 24.60; H, 2.74; N, 15.56.

tion that the initial step in the conversion of **2** to **1** is probably a WGS-type step (Scheme 2) and not protonation at the metal center.

In summary, a novel alkyl dihydride complex, $TpPtMeH_2$ (**1**), is formed as the sole product by the reaction of TpPtMeCO with water in air. We propose that the formation of this product involves an initial nucleophilic attack by a water molecule on the coordinated carbonyl followed by the release of CO_2 to produce a TpPtHMe intermediate, which undergoes protonation at the platinum center to produce **1**. We are currently investigating the chemical reactivity and catalytic properties of **1**.

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Supporting Information Available: A figure giving the IR spectra of **2**, **1**, **1**-d_2, tables of complete crystallographic data, and figures giving additional views of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Data were collected at 298 K with a Siemens P4 diffractometer equipped with a molybdenum sealed tube and a highly oriented graphite monochromator. **3**: empirical formula $C_{11}H_{13}B_2F_4N_6OPt$, formula weight 537.98, colorless plate, monoclinic, space group $P2_1/c$, $a = 11.915(1)$ Å, $b = 12.0221(1)$ Å, $c = 24.628(2)$ Å, $\alpha = 90°$, $\beta = 93.52(1)°$, $\gamma = 90°$, $V = 3491.6(5)$ Å^3, $Z = 8$, R1 = 0.0795 ($I > 2\sigma(I)$), GOF = 1.011. The observation that $Z = 8$ in the space group $P2_1/c$ suggests that the asymmetric unit cell consists of two independent molecules. The solid-state structure of **3** provides mainly atom connectivity in the molecule due to the substantial disorder in the counteranion and in the CO and CH_3 ligands.