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Carbon Monoxide Promoted Reductive Elimination of Hydrogen from Tp′ Platinum Complexes

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Abstract: Acid-assisted reductive elimination of hydrogen from Tp′PtH_3 and of methane and hydrogen from Tp′$PtMeH_2$ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) is examined herein. Loss of H_2 is observed from solutions containing platinum(IV) complexes of the type Tp′Pt(R)$(H)_2$ (R = Me, H) upon protonation and addition of a ligand such as CO. Results of kinetic studies on reductive elimination of H_2 and formation of [κ^2-(HTp′)Pt(R)(L)][BAr′$_4$] products from intermediates derived from Tp′Pt(R)$(H)_2$ precursors are described. Elimination appears to occur from cationic 6-coordinate [κ^2-(HTp′)Pt(R)$(H)_2$(L)][BAr′$_4$] species.

Introduction

Activation of H_2 by and reductive elimination of H_2 from transition metal complexes are two fundamental reactions in organometallic chemistry; these are crucial steps in many catalytic reactions.[1−5] Of the two processes, H_2 activation has been more widely investigated than has hydrogen elimination.[6−9]

Hydrogen production currently involves steam reformation of hydrocarbons produced from fossil fuels, and consequences of this are high cost and dependence on a limited resource. Significant research has focused on the synthesis of catalysts capable of producing hydrogen from biomass, water, or other renewable resources.[10−14] To move toward a hydrogen economy an inexpensive route for the production of hydrogen is needed.

One well-known method of either producing or purifying H_2 is the water gas shift reaction (WGSR). This reaction is thermodynamically favorable at standard temperature and pressure, but without a catalyst high temperatures and high pressures are required for rapid reaction.[2,15] Some homogeneous catalysts accomplish this process under mild conditions, but they have not been adapted to industrial processes.[15−19] Lowering both temperature and pressure for WGSR conversion of water and CO to hydrogen and CO_2 is highly desirable.

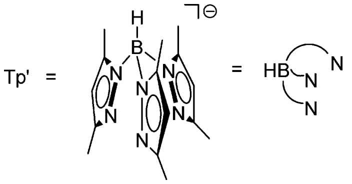

Figure 1. Tp′ ligand (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate).

Here we report initial studies of CO-assisted, acid-induced elimination of hydrogen from Tp′Pt di- and trihydride complexes (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) (Figure 1) which are in turn synthesized by WGS chemistry. The resulting Pt(II) carbonyl complexes can then be reoxidized to Pt(IV) polyhydrides thus completing the WGSR in stepwise fashion. Examination of the individual steps of this reaction may provide insight for future catalyst development in the growing field of aqueous organoplatinum chemistry.[20]

Results and Discussion

Synthesis of Tp′PtH_3 (1). In the original synthesis of Tp′PtH_3 (**1**)[21] (Scheme 1) heating Tp′$PtMe_2H$ (**2**)[22] in $HSiEt_3$ produced the key intermediate Tp′Pt$(SiEt_3)(H)_2$ in ca. 20% yield. Replacement of the triethylsilyl group by a proton was effected by refluxing in MeOH/CH_2Cl_2. While this method required only two steps from reagent **2**, the product was obtained in a 13% overall yield. An alternative synthetic route was therefore sought in order to make **1** a viable starting material for future reactions.

A sequence of clean reactions converts Tp′$PtMe_2H$ (**2**) into Tp′$PtMeH_2$ (**3**),[23] (Scheme 2) and we hypothesized that it might

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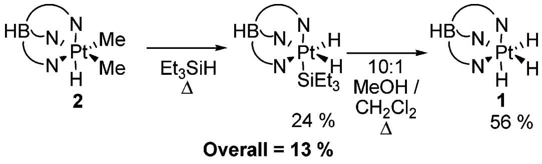
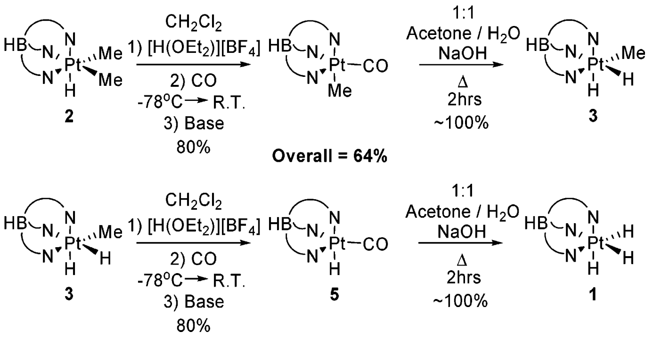
Scheme 1. Previous Synthesis of Tp′PtH$_3$ (**1**)



Scheme 2. Synthesis of Tp′PtH$_3$ (**1**) from Tp′PtMe$_2$H (**3**)



be possible to repeat this sequence to access the trihydride (**1**). This method required the synthesis of Tp′Pt(H)(CO) (**5**) followed by oxidation of **5** in H$_2$O/acetone to form the trihydride **1** in a manner similar to that used by Keinan to synthesize TpPtMeH$_2$ from TpPt(Me)(CO).[24]

Tp′Pt(H)(CO) (**5**) is synthesized by protonation of Tp′PtMeH$_2$ with [H(OEt$_2$)$_2$][BAr′$_4$] [BAr′$_4$ = tetrakis(3,5-trifluoromethylphenyl)borate] at −78 °C in CH$_2$Cl$_2$ followed by purging the reaction mixture with CO while warming to room temperature. Loss of methane and trapping with CO generates [κ^2-(HTp′)-Pt(H)(CO)][BAr′$_4$] (**4**), which is then deprotonated in situ by reaction with NEt$_3$ at −78 °C to form Tp′Pt(H)(CO) (**5**).

Solution phase IR (CH$_2$Cl$_2$) for **5** shows one B−H absorption at 2526 cm^{-1} indicating that the Tp′ ligand is bound in κ^3 fashion,[25] one Pt−H absorption at 2216 cm^{-1}, and one CO absorption at 2070 cm^{-1}, suggesting the presence of only one geometric isomer. Most platinum(II) complexes are square planar and hence 4-coordinate, but the π acidity of the CO ligand makes the metal center sufficiently electron deficient here that it adopts a 5-coordinate structure. The closely related complex Tp′Pt(Me)(CO) was shown to be present in both κ^2 and κ^3 forms in solution.[26] The analogous TpPt(Me)(CO) complex with no methyls on the pyrazole rings also is fluxional in solution with both 4-coordinate and 5-coordinate geometries easily accessible,[24,27,28] but has a solid-state structure that is square planar with the Tp binding in a bidentate fashion.[29] X-ray quality crystals of the neutral Tp′Pt(H)(CO) complex **5** were obtained by layering a CH$_2$Cl$_2$ solution of **5** with hexanes at 4 °C. The X-ray crystal structure shows Tp′ to be tridentate, and thus the complex is 5-coordinate. The three Pt−N bond lengths of 2.088, 2.139, and 2.489 Å (Figure 2) reflect weak binding of the third Tp′ arm and suggest that the geometry of the complex lies between square planar and trigonal bipyramidal. The hydride ligand position was not refined.

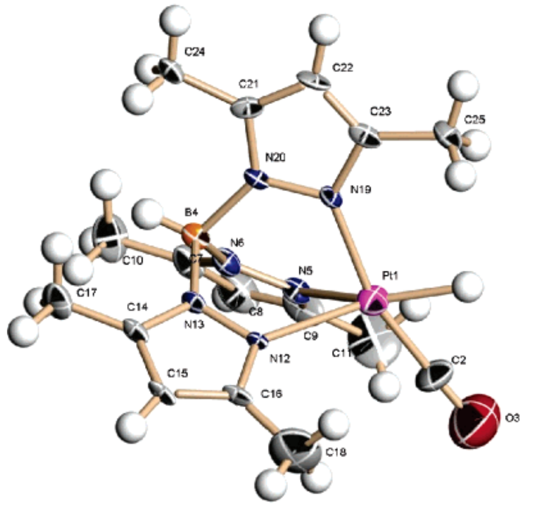


Figure 2. X-ray structure of Tp′Pt(H)(CO) (**5**). Ellipsoids are drawn with 50% probability. Selected bond distances in angstroms (Å): Pt1−C2 = 1.827, Pt1−N5 = 2.139, Pt1−N12 = 2.489, Pt1−N19 = 2.088, C2−O3 = 1.138. Selected bond angles in degrees (deg): C2−Pt1−N5 = 102.0, C2−Pt1−N12 = 115.4, N5−Pt1−N12 = 81.5, C2−Pt1−N19 = 163.6, N5−Pt1−N19 = 85.5, N12−Pt1−N19 = 79.8.

Note that the weakly bound third Tp′ arm is approximately trans to the vacant site. In other words the weak interaction is positioned axially relative to a square-planar point of departure for this d^8 complex. The strong trans influence of the CO ligand produces a Pt−N bond distance of 2.088 Å while the strong trans influence of the hydride ligand produces a Pt−N bond distance of 2.139 Å.

Reflux of Tp′Pt(H)(CO) (**5**) in acetone/water (1:1) under slightly basic conditions yields Tp′PtH$_3$ (**1**) quantitatively. This method is analogous to that used to synthesize Tp′PtMeH$_2$ from Tp′Pt(Me)(CO).[23,24] This reaction likely occurs by a WGS type mechanism in which water or a hydroxide ion attacks the carbonyl carbon forming a CO$_2$ linkage so that the complex can then lose CO$_2$ and form the [Tp′Pt(R)H] anion, such that addition of a proton yields Tp′Pt(R)H$_2$ (R = Me, H). Heating Tp′Pt(H)(^{13}CO) (**5***) in acetone-d_6/D$_2$O with catalytic NaOH in an NMR tube yielded Na^{13}CO$_3$H which was converted to ^{13}CO$_2$ which was observed by ^{13}C NMR after addition of one drop of HBF$_4$·Et$_2$O.

The new synthesis of **1** (Scheme 2), a simple extension of the synthesis of the dihydride (**3**), requires four steps, but the overall yield from **1** (64%) is significantly improved from the two step route (13%). Many dihydride complexes have been reported in the literature; most of them are synthesized from hydride sources or from activation of H$_2$.[6,30−33] The fact that the hydrides in complexes **3** and **1** come from H$_2$O is significant because H$_2$ elimination from these complexes would represent completion of the water gas shift reaction.

Protonation of Tp′PtH$_3$ (1). In the absence of added ligands, reaction of Tp′PtH$_3$ (**1**) with [H(OEt$_2$)$_2$][BAr′$_4$] at −78 °C in CD$_2$Cl$_2$ results in a color change from colorless to light orange, but ^{1}H NMR analysis shows no signals corresponding either to dihydrogen or to the hydride associated with the [κ^2-(HTp′)Pt-

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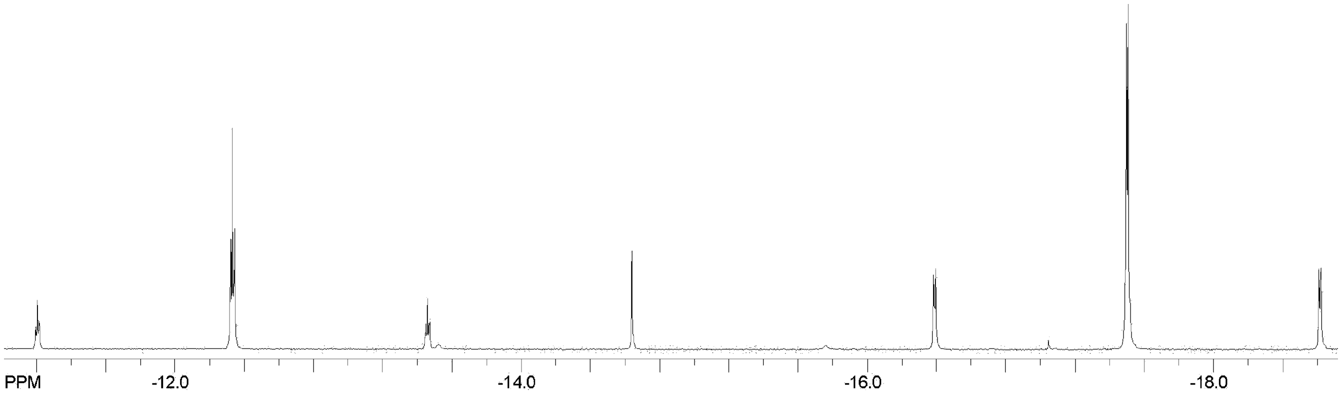


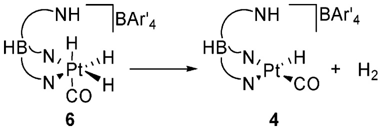
Figure 3. 500 MHz ^{1}H NMR spectra (193 K) showing hydride signals for [κ^2-(HTp′)Pt(H)$_3$(CO)][BAr′$_4$] (**6**) (t, −12.33; d, −17.51) and [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**) (s, −14.64).

(H)(solv)][BAr′$_4$] complex which is visible by NMR after loss of methane from the methyl dihydride (**3**).[23] The only species visible by ^{1}H NMR at low temperature is the neutral trihydride reagent. Upon warming to room-temperature some dihydrogen loss was detected along with formation of Tp′H and platinum black. The observed H_2 must be formed after dissociation of Tp′H from Pt otherwise the Tp′Pt(II) monohydride cation would be observed. NMR suggests that Tp′PtH$_3$ is difficult to protonate and only a small amount of [HTp′PtH$_3$]$^+$ is ever generated. Typically, not more than 50% of the starting material is consumed in this reaction.

Dramatically different results are obtained if protonation of Tp′PtH$_3$ (**1**) is conducted under a CO atmosphere. This reaction ultimately yields [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**), a product compatible with loss of H_2. This result resembles reactivity observed by Keinan and co-workers in their study of TpPtMeH$_2$.[34] They reported H_2 loss from TpPtMeH$_2$ upon addition of PMe$_3$ at room temperature, but no loss of H_2 without added phosphine even when heated to 70 °C. They proposed two possible mechanisms for this process, both involving an initial dissociation of one Tp arm. In one pathway, subsequent PMe$_3$ coordination forms a 6-coordinate species which then eliminates H_2. The second pathway involves formation of a 4-coordinate η^2-H_2 species followed by loss of H_2 and coordination of PMe$_3$.

Low-Temperature NMR Studies. Efforts to probe the mechanism of hydrogen formation in the Tp′PtH$_3$ system were undertaken. Proton NMR experiments under a CO atmosphere at 193 K show a single initial product upon protonation of the trihydride (**1**): coupled hydride signals appear at δ −12.33 ppm (t, 1H, $^2J_{\mathrm{H-H}}$ = 4.4 Hz, $^1J_{\mathrm{Pt-H}}$ = 1120 Hz) and δ = −17.51 ppm (d, 2H, $^2J_{\mathrm{H-H}}$ = 4.4 Hz, $^1J_{\mathrm{Pt-H}}$ = 1108 Hz) (Figure 3). Given the presence of three hydride ligands reflected in the NMR data, we formulate the product as 6-coordinate Pt(IV) carbonyl complex [κ^2-(HTp′)Pt(H)$_3$(CO)][BAr′$_4$] (**6**) in which the unique hydride is trans to CO and the two equivalent hydrides are cis to CO. Similar types of trapping experiments using nitriles have been used to access other cationic Pt(IV) hydride species.[35,36] Experiments using ^{13}CO gas yield [κ^2-(HTp′)Pt(H)$_3$(^{13}CO)][BAr′$_4$] (**6***). The hydrides of **6*** appear as a doublet of triplets at δ −12.33 ppm (dt, 1H, $^2J_{\mathrm{C-H}}$ = 90 Hz, $^2J_{\mathrm{H-H}}$ = 4.4 Hz, $^1J_{\mathrm{Pt-H}}$ = 1120 Hz) and a doublet of doublets at δ −17.51 ppm (dd, 2H, $^2J_{\mathrm{C-H}}$ = 6 Hz, $^2J_{\mathrm{H-H}}$ = 4.4 Hz, $^1J_{\mathrm{Pt-H}}$ = 1108 Hz). The large $^2J_{\mathrm{C-H}}$ coupling for the hydride at δ −12.33 ppm reinforces the notion that it is located trans to CO, and the small ^{13}CO coupling to the hydrides at δ −17.51 ppm indicates that they are cis to CO. As the reaction mixture warms to room temperature, loss of dihydrogen can be detected by ^{1}H NMR spectroscopy as a singlet appears at δ 4.57 ppm, the chemical shift where H_2 appears in CD_2Cl_2. If the solution is subjected to a freeze pump thaw cycle, this peak disappears. Formation of the H_2 elimination product [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**) can be detected by the growth of a hydride peak at −14.64 ppm ($^1J_{\mathrm{Pt-H}}$ = 1122 Hz); the yield is ca. 90%. At low temperatures this process is slow, making it possible to monitor the reaction by NMR.

Scheme 3. Products of Protonation of Tp′PtH$_3$ (**1**) under CO



Trapping Ligands Other Than CO. When similar NMR experiments are performed with α-olefins (ethylene, propylene, 1-butene, or 1-pentene) added to the solution instead of CO gas, H_2 loss is observed at even lower temperatures. No 6-coordinate olefin bound species, analogous to [κ^2-(HTp′)Pt(H)$_3$(CO)][BAr′4], is observed by NMR even at 150 K; the observed products are H_2 and [κ^2-(HTp′)Pt(H)(L)][BAr′$_4$] (L = $H_2C{=}CH_2$,[23] $H_2C{=}CHCH_3$, $H_2C{=}CHCH_2CH_3$, $H_2C{=}CHCH_2CH_2CH_3$). With these olefins no 6-coordinate cationic trihydride adducts are detected as stable intermediates; likely the olefin trihydride cations are higher in energy than the CO trihydride cation and cannot be seen by NMR. This change in reaction coordinate precludes a kinetic study of the rate of disappearance of an intermediate. No reaction with internal olefins is observed, probably because of their increased steric bulk.

When acetonitrile is used as a trapping ligand after protonation, the 6-coordinate nitrile-bound species, [κ^2-(HTp′)Pt(H)$_3$(NCMe)][BAr′$_4$] (**7**), is observed by NMR at low temperature. The cationic acetonitrile adduct has hydride signals in the ^{1}H NMR spectrum at δ −19.94 ppm (s, $^1J_{\mathrm{Pt-H}}$ = 1166 Hz, 2H, Pt-*H*), and at δ −24.08 ppm (s, $^1J_{\mathrm{Pt-H}}$ = 1423 Hz, 1H, Pt-*H*). Upon warming to room temperature no H_2 loss is observed and the only platinum species visible by NMR is the starting material, neutral Tp′PtH$_3$ (ca. 50%) with the rest of the material having undergone decomposition.

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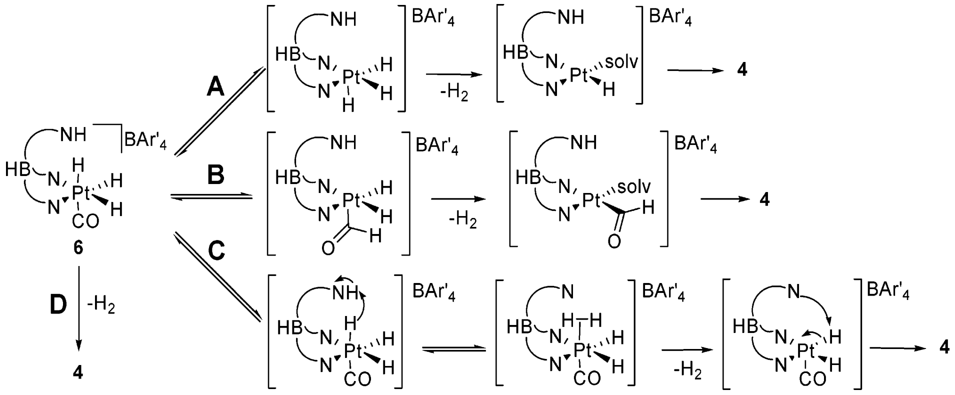
Scheme 4. Possible Pathways for H_2 Elimination from the Trihydride Carbonyl Cation (**6**)



Addition of either PMe_3 or PMe_2Ph as the trapping reagent results in a small but detectable amount of H_2 loss, but undesirable side reactions of the phosphines with acid precluded detailed study. Use of 3,5-dimethylphenyl isocyanide or isopropyl isocyanide as trapping ligands after protonation results in observation of a 6-coordinate species. Upon warming only a small amount of hydrogen loss is observed; the major species observable at room temperature is starting material. The isocyanide ligands may be too bulky to coordinate to the metal strongly, or they may be sufficiently basic to buffer the solution acidity.

Mechanistic Studies. Although we have shown that CO binds to the trihydride before H_2 elimination to form complex **6**, there are still several pathways by which H_2 elimination could occur from this complex (Scheme 4). Most reductive eliminations from octahedral Pt(IV) occur via coordinatively unsaturated 5-coordinate intermediates;[26,37−44] there are multiple ways in which a 5-coordinate intermediate could be implicated here. Pathway **A** is pre-dissociation of CO from **6**, elimination of H_2, then recoordination of CO; pathway **B** is migration of a hydride to CO, elimination of H_2, followed by deinsertion of the CO from the formyl ligand to yield the Pt(II) product **4**. Another possibility which does not involve direct reductive elimination from Pt(IV) is pathway **C** in which one of the hydrides couples with the proton on nitrogen, H_2 is lost, and the Pt(IV) dihydride is deprotonated by nitrogen yielding complex **4**. The simplest possibility is direct elimination of H_2 from the 6-coordinate complex **6**, pathway **D**. Yet another possibility is dechelation of a Tp′ arm from **6** resulting in a 5-coordinate intermediate which could eliminate H_2, followed by coordination of the arm.

Experiments were conducted to probe whether CO binding is reversible. Protonation of **1** under ^{12}CO followed by removal of gas via three freeze, pump, thaw cycles and refilling with ^{13}CO yields a significant amount of the 6-coordinate trihydride-^{13}CO complex, indicating facile exchange between bound and free CO gas in solution. The reversibility of the hydrogen elimination reaction was also investigated. Protonation of Tp′PtD_3 (**1-*d*$_3$**) at low temperature under CO and H_2 leads to elimination of D_2 with no incorporation of H into the platinum product. No HD or Pt-D formation is detected from stirring [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**) in CD_2Cl_2 under D_2 at room temperature, indicating that H_2 loss is irreversible.

Experiments at various CO pressures and constant temperature provide further support for facile reversible loss of CO. An increase in the rate of hydrogen production with increasing CO pressure is observed. Elimination of hydrogen from the five coordinate product of CO loss from **6** would yield an inverse rate relationship with CO pressure. This qualitative rate data, coupled with the fact that no H_2 loss is seen in the absence of CO, allows us to rule out pathway **A** as a possibility. Protonation of Tp′PtH_3 (**1**) with [D(OEt$_2$)$_2$][BAr′$_4$] or protonation of Tp′PtD_3 (**1-*d*$_3$**) with [H(OEt$_2$)$_2$][BAr′$_4$] under CO resulted in no elimination of HD, ruling out Pathway **C**.

Pathway **B**, the insertion-deinsertion pathway, could explain why H_2 loss is faster using olefins than CO. Insertion of olefins into metal hydride bonds to form alkyl ligands is typically facile,[45,46] while CO insertion to form stable formyl ligands is unlikely.[47,48] Attempted synthesis of Tp′Pt(H)$_2$(CHO) from Tp′Pt(H)(CO) by stepwise H^-, H^+ addition yielded the desired product along with Tp′PtH_3 as determined by ^{1}H NMR spectroscopy.[49] This illustrates that Tp′Pt(H)$_2$(CHO) does not lose H_2 but rather can lose CO to form the neutral trihydride **3**.

In the case of ethylene addition, if a 6-coordinate trihydride olefin cation is formed, then it could undergo insertion leading to a five coordinate ethyl dihydride cation. This intermediate would seem more likely to lose ethane than hydrogen, based on known reactions with [HTp′PtMeH$_2$]$^+$.[23] The NMR for Tp′PtH_3 plus acid and ethylene contains a large signal due to hydrogen, but no signal for ethane is detected, so an ethyl

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(49) Reaction products determined by ^{1}H NMR. The formyl hydride anion [Tp′Pt(H)(CHO)][K] displays coupled formyl proton and hydride signals at 13.93 ($^2J_{\mathrm{Pt-H}} = 268$ Hz, $^3J_{\mathrm{H-H}} = 7$ Hz), and −16.09 ($^2J_{\mathrm{Pt-H}} = 1620$ Hz, $^3J_{\mathrm{H-H}} = 7$ Hz) respectively (ppm, THF-d_8, 283 K). The neutral formyl dihydride Tp′Pt(H)$_2$(CHO) displays coupled formyl proton and hydride signals at 12.85 ($^2J_{\mathrm{Pt-H}} = 182$ Hz, $^3J_{\mathrm{H-H}} = 4$ Hz), and −17.96 ($^2J_{\mathrm{Pt-H}} = 1340$ Hz, $^3J_{\mathrm{H-H}} = 4$ Hz) respectively (ppm, THF-d_8, RT).

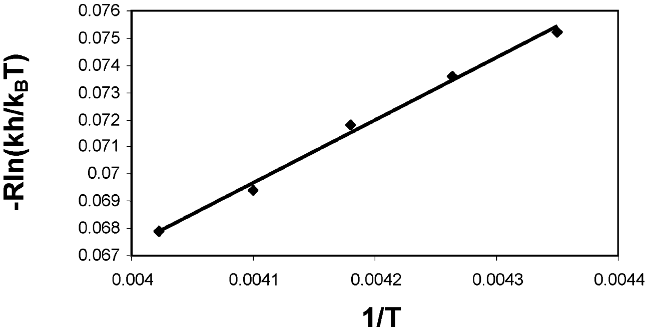

Figure 4. Eyring plot of H_2 loss from **6** under 18.7 psi CO.

dihydride intermediate seems unlikely. If a 3-coordinate platinum ethyl species resulted from H_2 elimination, then it could be trapped by excess ethylene, but we see no evidence for a platinum ethyl ethylene complex. Reaction of $[D(OEt_2)_2][BAr'_4]$ with Tp′PtD$_3$ (**1-*d*$_3$**) under C_2H_4 ethylene resulted in [Tp′DPt(D)(C_2H_4)]$[BAr'_4]$ with no incorporation of D into the ethylene ligand and no formation of a platinum hydride. This evidence rules out pathway **B** as a viable mechanism for H_2 loss. Dechelation of a Tp′ arm to form a reactive 5-coordinate intermediate is kinetically indistinguishable from direct elimination; however dechelation of Tp′ from Pt(IV) is unprecedented at the low temperatures used in these reactions. Since the platinum center is electron deficient ($\nu_{co} = 2130\ \mathrm{cm}^{-1}$) the Tp′ arms are probably tightly bound. Direct elimination of H_2 from the cationic 6-coordinate intermediate **6**, pathway **D**, remains the mechanism of choice.

Kinetic Studies. Kinetic experiments performed with ^1H NMR spectroscopy between 225 and 245 K monitored the disappearance of the hydride signals of the platinum(IV)(CO) adduct (**6**). Disappearance of intermediate **6** and formation of platinum(II) product **4** display first order kinetics over several half-lives, probably because the concentration of CO in solution is effectively constant. The rate at 239 K under 18.7 psi CO was found to be $4 \times 10^{-4}\ \mathrm{s}^{-1}$, giving rise to a $\Delta G^{\ddagger}$ value of 17.2 (± 0.1) kcal/mol. An Eyring plot (Figure 4) was constructed using rate constants from this admittedly narrow temperature range at 18.7 psi CO; $\Delta H^{\ddagger}$and $\Delta S^{\ddagger}$ are 23.0 (± 1) kcal/mol and 24.5 (± 4) eu, respectively.

Measurement of the rate of D_2 loss from [κ^2-(HTp′)Pt(D)$_3$(CO)]$[BAr'_4]$ (**6-*d*$_3$**), formed by protonation of Tp′PtD$_3$ (**1-*d*$_3$**), at 239 K under 18.7 psi CO allows for calculation of an isotope effect of $k_H/k_D = 2.2$ (± 0.1) by comparison with the rate of H_2 loss from **6** under the same conditions. Isotope effects of similar magnitude have been reported for H_2 elimination from other systems.[6,50,51] It has been demonstrated previously that oxidative addition of H_2 to a metal center results in an *inverse* equilibrium isotope effect,[50−56] and this has also been shown to hold for the coordination of H_2 in η^2-H_2 complexes.[57−60] Because of the stronger affinity of the metal to bind D_2 than H_2 a *normal* isotope would be expected for dissociation of D_2 relative to H_2 as is observed in this case.

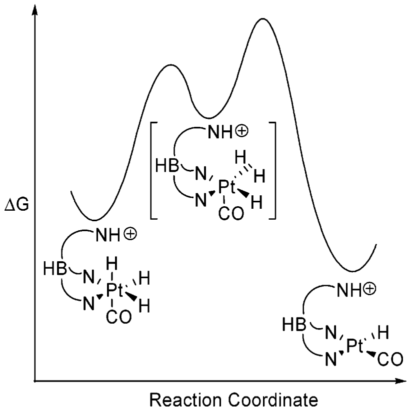

Figure 5. Possible reaction coordinate diagram for elimination of H_2 from **6**.

The normal isotope effect and positive entropy of transition state formation suggest that the barrier to reductive coupling of H_2 is lower than the barrier to dissociation of H_2 (Figure 5). In such a case the transition state is becoming less ordered resulting in positive entropy of activation. It has been shown that dissociation of H_2 can account for a normal isotope effect of this magnitude (vida supra). A lower barrier for reductive coupling to form H_2 in the coordination sphere than for dissociation of H_2 is consistent with the mechanism proposed for elimination of CH_4 from Tp′Pt systems. The barrier for reductive coupling of methane was previously found to be lower than the energy barrier for dissociation of methane.[23,26,34,41,61] A reaction profile of this type would indicate that the observed isotope effect of 2.2 is a combination of a kinetic isotope effect due to the irreversible dissociation of H_2, a secondary kinetic effect due to the additional M−D bond, and an equilibrium effect from the reversible reductive coupling.

***π*-Acid Induced H_2 Elimination?** A possible explanation for generation of hydrogen in the presence of CO is that with an electron-withdrawing CO ligand bound to platinum there may be too little electron density at the metal to maintain a Pt(IV) dihydride formulation, and formation of an η^2-H_2 Pt(II) species is favored. If the metal is electron rich a dihydride will be favored, but with decreasing electron density an η^2-H_2 ligand will be more likely to form. The protonated CO trihydride complex [κ^2-(HTp′)Pt(H)$_3$(CO)]$[BAr'_4]$ (**6**) is highly electron-deficient as judged by the C−O stretching frequency determined by in situ FTIR spectroscopy ($\nu_{CO} = 2130\ \mathrm{cm}^{-1}$).

The surprising low-temperature hydrogen generation with ethylene present could be due to the larger size of ethylene relative to CO, perhaps increasing unfavorable steric interactions with the Tp′ ligand and increasing the energy of the 6-coordinate adduct. It could also be that the ethylene π^* orbitals have more effective overlap with a single filled metal dπ orbital, thus making ethylene a single faced π-acid uniquely suited to increase the rate of H_2 elimination. There is relevant experimental evidence regarding ethylene as a strong single-faced π-acid. The complexes Tp′Pt(Me)(CO)[26] and Tp′Pt(Ph)(CO)[62] both exhibit

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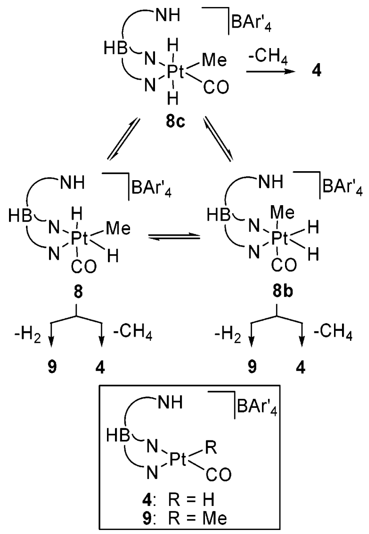
solution IR and NMR data consistent with rapid interconversion between κ^2 and κ^3 binding modes of Tp′. However, the analogous ethylene complexes, Tp′Pt(Me)($H_2C{=}CH_2$)[26] and Tp′Pt(Ph)($H_2C{=}CH_2$),[62] have spectroscopic data consistent with only κ^3 bound Tp′. These complexes are aptly described as octahedral Pt(IV) metallocyclopropane complexes,[26] and this is reflected in the crystal structure of Tp′Pt(Ph)($H_2C{=}CH_2$) that has Pt−N bond lengths of 2.140, 2.168, and 2.220 Å.[62] In comparison, the bond lengths for Tp′Pt(H)(CO) are 2.088, 2.139, and 2.489 Å clearly showing that the third pyrazolyl is bound much more weakly, and thus indicating that this complex is more similar to square planar d^8 Pt(II), than to octahedral Pt(IV).

Protonation of Tp′PtMeH_2 (3). When reactions analogous to the protonation of trihydride (**1**) are performed with the methyl dihydride (**3**) under CO, it is possible to observe similar 6-coordinate species, namely [κ^2-(HTp′)Pt(Me)$(H)_2$(CO)][BAr′$_4$] (**8**) and [κ^2-(HTp′)Pt(Me)$(H)_2$(^{13}CO)][BAr′$_4$] (**8***). In the absence of added ligand, protonation of Tp′PtMeH_2 induces rapid methane loss even at 193 K.[26] However, by having CO in solution before acidification it was possible to trap the 5-coordinate intermediate that leads to methane loss. Complex **8** has hydride signals at δ −12.33 (d, $^2J_{H-H} = 5.5$ Hz, $^1J_{Pt-H} = 1166$ Hz) and δ −17.84 (d, $^2J_{H-H} = 5.5$ Hz, $^1J_{Pt-H} = 1193$ Hz). The ^{13}C labeled carbonyl complex **8*** resembles complex **6*** in that the downfield hydride has a 94 Hz $^2J_{C-H}$ coupling while the upfield signal has only a 3.2 Hz ^{13}C−H coupling. No ^3J coupling to the CO carbon is detected for the methyl protons. These data indicate that **8** has one hydride trans to CO, leaving the other hydride and the methyl ligand cis to CO. This octahedral species, **8**, appears to lose either H_2 or CH_4 to form either **4** or [κ^2-(HTp′)Pt(Me)(CO)][BAr′$_4$] (**9**).[26] This result is surprising because in previous experiments we observed only loss of CH_4 from Tp′PtMeH_2 (**3**) upon protonation and trapping with an added ligand. However, the solution of protonated **3** in those experiments was allowed to warm slightly before trapping ligand was added. It has previously been shown that complex **3** will easily lose methane from the 5-coordinate species when protonated in the absence of a trapping ligand.[23] When CO is present, the protonated species is trapped. Either CH_4 or H_2 can be eliminated from the resulting cationic 6-coordinate species, with a ratio of CH_4 to H_2 loss about ∼5:1. Complex **8** has a carbonyl trans to hydride configuration that is similar to the (dppe)Ir(Et)$(H)_2$(CO) complex reported by Eisenberg and coworkers, from which C−H and H−H coupling and elimination are competitive,[6] as in this case.

There is a small amount of another isomer of **8** present (**8b**) (Scheme 5) which has a hydride signal at δ −16.72 (s, $^1J_{Pt-H} = 1201$ Hz) and a methyl signal at δ 0.53 (s, $^2J_{Pt-H} = 55$ Hz). Presumably, this is the isomer with CO trans to methyl. This isomer formulation is further confirmed when ^{13}CO is used: the $^2J_{C-H}$ coupling from the ^{13}CO to the two equivalent hydrides is only 4 Hz, indicating that they are both located cis to CO. Complexes **8** and **8b** slowly convert to a third species which has a single hydride signal at δ −17.05 (s, $^1J_{Pt-H} = 1212$ Hz). This third species (**8c**), the most thermodynamically stable of the three isomers, eventually becomes the major species in solution. Methane loss, but not dihydrogen loss, is observed from complex **8c**. The hydride signal for **8c** shows 4 Hz $^2J_{C-H}$ coupling when ^{13}CO is used so cis CO, hydride ligands are indicated. An attractive geometry with CO trans to N for **8c** is presented in Scheme 5. There is precedence for a trans dihydride carbonyl structure being thermodynamically favored over a cis dihydride carbonyl structure,[63] but this formulation requires coincidental equivalence of the trans hydride NMR signals in order to fit the limited data available for **8c** at this point. Only methane loss seems feasible from a trans-dihydride isomer in accord with our observations.

Scheme 5. Isomerization Following Protonation of Tp′PtMeH_2 (**3**) under CO



Protonation of Tp′PtMeD_2 under CO at 193K results in immediate isotope scrambling in the 6-coordinate cationic carbonyl species. Observation of CH_3, CH_2D, and CHD_2 isotopomers of the H_2 loss product [κ^2-(HTp′)Pt(Me)(CO)]-[BAr′$_4$] (**9**) upon warming indicates that this scrambling is a result of reversible reductive coupling to form methane in the coordination sphere. The isotope scrambling is complete in the initial ^{1}H NMR, thus it was not possible to monitor this process by NMR.

If the methyl dihydride is protonated at 193K and CH_3CN is quickly added, then it is again possible to trap the 5-coordinate methyl dihydride cation and form the 6-coordinate cation [κ^2-(HTp′)Pt(Me)$(H)_2$(NCMe)][BAr′$_4$] (**10**) which has inequivalent hydride signals at −20.67 (s, $^1J_{Pt-H} = 1265$ Hz, 2H, Pt-*H*) and −24.08 (s, $^1J_{Pt-H} = 1496$ Hz, 1H, Pt-*H*). Warming of this complex results in elimination of methane only and formation of [κ^2-(HTp′)Pt(H)(NCMe)][BAr′$_4$],[23] once again showing the necessity of a π-acid for the elimination of H_2.

Conclusions

Low-temperature NMR spectra reported here show that after protonation opens a coordination site, carbon monoxide adds to Pt, and reductive elimination of H_2 occurs from the resulting 6-coordinate complex. The isotope effect (2.2 ± 0.1) and reaction entropy (24.5 ± 4 eu) are consistent with a mechanism involving reversible reductive coupling to form coordinated dihydrogen followed by rate-limiting irreversible dissociation

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of dihydrogen. Significant hydrogen elimination occurs when either CO or ethylene is used as a trapping ligand. We postulate that the π-acid character of these ligands withdraws sufficient electron density from the metal so that it is reluctant to support the platinum(IV) dihydride structure. Surprisingly, elimination of H_2 occurs at lower temperatures with ethylene than with CO even though CO would typically be considered the stronger π-acid. However, examination of the structures of Tp′Pt(R)CO (R = Me, H) complexes compared to the structures of Tp′Pt(R)($H_2C{=}CH_2$) (R = Me, Ph) provides relevant data. The Pt(II) carbonyl complexes have only weak coordination of the third Tp′ arm and are thus more similar to Pt(II) square planar complexes. The Tp′Pt(II) ethylene complexes have strong coordination of all three Tp′ arms and resemble octahedral Pt(IV) complexes. For these Tp′Pt complexes the single faced π-acid ethylene ligand seems to be a uniquely effective π-acid. This feature may explain why it facilitates H_2 loss at such low temperatures compared to the cylindrically symmetrical CO π-acid. Also, it is important to note that the neutral hydride complexes were generated by WGS chemistry and thus elimination of H_2 from Tp′PtH_3 represents net production of H_2 from H_2O and CO, a stoichiometric water gas shift reaction.

Experimental Section

Materials and Methods. All reactions were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was flame dried under vacuum and cooled under N_2 before use. Diethyl ether, methylene chloride, acetonitrile, toluene, and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina.[64] Tetrahydrofuran was distilled from sodium/benzophenone ketyl. Methylene chloride-d_2 was vacuum transferred from calcium hydride and degassed by several freeze−pump−thaw cycles.

Tp′$PtMe_2H$ (**1**),[22] Tp′$PtMeH_2$ (**2**),[23] Tp′$PtMeD_2$ (**2**-d_2),[23] Tp′$PtPhH_2$,[65] [HTp′Pt($SiEt_3$)H_2][BAr′4],[66] and [H(OEt_2)$_2$][BAr′$_4$][67] were synthesized using published procedures. Carbon monoxide was obtained from Matheson Gas Products, Inc. and ^{13}C labeled carbon monoxide from Cambridge Isotope Laboratories, Inc. All other reagents were used as received.

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 300 MHz, Bruker Avance 400 MHz, or Bruker DRX 500 MHz spectrometers. ^1H NMR and ^{13}C NMR chemical shifts were referenced to residual ^1H and ^{13}C signals of the deuterated solvents. Infrared spectra were recorded on an ASI ReactIR 1000.

Representative [BAr′$_4$]$^-$ NMR Data. ^1H and ^{13}C NMR data for the [BAr′$_4$]$^-$ counterion are reported separately for simplicity. ^1H NMR (CD_2Cl_2, 193 K, δ): 7.77 (br, 8H, *o*-Ar′), 7.60 (br, 4H, *p*-Ar′). ^{13}C NMR (CD_2Cl_2, 193 K, δ): 162.2 (1:1:1:1 pattern, $^1J_{B-C} = 50$ Hz, C_{ipso}), 135.3 (C_{ortho}), 129.4 (qq, $^2J_{C-F} = 30$ Hz, $^4J_{C-F} = 5$ Hz, C_{meta}), 125.1 (q, $^1J_{C-F} = 270$ Hz, CF_3), 117.9 (C_{para}).

Tp′PtH$_3$ (1). Tp′Pt(H)(CO) (**5**) (78 mg, 0.149 mmol) was placed in a Schlenk flask and purged with N_2. A 1:1 mixture of acetone/H_2O (50 mL) was then added along with NaOH (5 drops). The solution was refluxed for 2 h and then cooled to 0 °C. A white powder of Tp′PtH_3 was filtered from the mixture and dried under vacuum. Yield: 73 mg (98%). Tp′PtD_3 (**1-*d*$_3$**) was synthesized in an analogous fashion using D_2O/acetone-d_6. ^1H NMR (CD_2Cl_2, 298 K, δ): 5.85 (s, 3H, Tp′C*H*), 2.38, 2.12 (s, 9H, Tp′C*H*$_3$), −20.03 (s, $^1J_{Pt-H} = 1168$ Hz, 1H, Pt-*H*).

[κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (4). In the drybox, Tp′$PtMeH_2$ (**3**) (100 mg, 0.196 mmol) and [H(OEt_2)$_2$][BAr′$_4$] (223 mg, 0.213 mmol) were added to a 100 mL Schlenk flask. The flask was capped with a septum, removed from the box, and cooled to −78 °C. CH_2Cl_2 (15 mL) was syringed into the flask and was allowed to stir for 5 min. The cold bath was removed and CO was bubbled into solution for 30 min. The solvent was removed in vacuo. The product was recrystallized from CH_2Cl_2/pentane at −30 °C, yielding colorless crystals. Yield: 217 mg (80%). [κ^2-(HTp′)Pt(H)(^{13}CO)][BAr′$_4$] (**4***) was synthesized in an analogous fashion using ^{13}CO gas. ^1H NMR (CD_2Cl_2, 298 K, δ): 9.59 (s, 1H, pz′N*H*), 6.18 6.14, 6.14 (s, 1H each, Tp′C*H*), 2.42, 2.42, 2.34, 2.32, 2.32, 1.77 (s, 3H each, Tp′C*H*$_3$), −14.69 (s, $^1J_{Pt-H} = 1120$ Hz, 1H, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 298 K, δ): 163.0 ($^1J_{Pt-C} = 1790$ Hz, Pt-*C*O); 155.6, 154.0, 150.8, 150.8, 149.8, 145.3 (HTp′*C*CH$_3$); 110.6, 108.9, 108.8 (HTp′*C*H); 16.7, 15.2, 13.3, 13.0, 11.5, 11.3 (HTp′*C*H$_3$). IR (CH_2Cl_2): $\nu_{BH} = 2524$ cm^{-1}, $\nu_{PtH} = 2225$ cm^{-1}, $\nu_{CO} = 2107$ cm^{-1}. Anal. Calcd for $C_{48}H_{36}N_6F_{24}B_2OPt$: C, 41.61; H, 2.62; N, 6.07. Found: C, 41.62; H, 2.66; N, 6.18.

Tp′Pt(H)(CO) (5). [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**) (217 mg, 0.157 mmol) was dissolved in CH_2Cl_2 mixture and run down an alumina column. The solvent was removed and the resulting white powder was crystallized in 10:1 hexanes/CH_2Cl_2 giving colorless X-ray quality crystals. Yield: 78 mg (95%). ^1H NMR (CD_2Cl_2, 298 K, δ): 5.85 (s, 3H, Tp′C*H*), 2.33, 2.26 (s, 9H, Tp′C*H*$_3$), −15.95 (s, $^1J_{Pt-H} = 1057$ Hz, 1H, Pt-*H*). IR (CH_2Cl_2): $\nu_{BH} = 2526$ cm^{-1}, $\nu_{Pt-H} = 2216$ cm^{-1}, $\nu_{CO} = 2070$ cm^{-1}. ^{13}C NMR (CD_2Cl_2, 193 K, δ): 165.1 (Pt-*C*O), 149.4 ($J_{Pt-C} = 38$ Hz, Tp′*C*CH$_3$), 144.9 (Tp′*C*CH$_3$), 105.9 ($^3J_{Pt-C} = 14$ Hz, Tp′*C*H), 15.3 ($J_{Pt-C} = 28$ Hz, Tp′C*C*H$_3$), 12.8 (Tp′C*C*H$_3$). Anal. Calcd for $C_{16}H_{23}N_6BOPt$: C, 36.86; H, 4.45; N, 16.12. Found: C, 36.74; H, 4.46; N, 15.88.

In Situ Generation of [κ^2-(HTp′)Pt(H)$_3$(CO)][BAr′$_4$] (6). Tp′PtH_3 (**1**) (10 mg, 0.02 mmol) and [H(OEt_2)$_2$][BAr′$_4$] (23 mg, 0.02 mmol) were added to an NMR tube in the drybox. The tube was capped with a septum and removed from the box. The tube was purged and filled with the desired pressure of CO 3 times. It was cooled to −78 °C and CD_2Cl_2 (0.7 mL) was added. It was then placed in the NMR with the probe cooled to 193 K. [κ^2-(HTp′)Pt(D)$_3$(CO)][BAr′$_4$] (**6**-*d*$_3$) was synthesized in an analogous fashion using Tp′PtD_3 (**1**-*d*$_3$). [κ^2-(HTp′)-Pt(H)$_3$(^{13}CO)][BAr′$_4$] (**6***) was synthesized in an analogous fashion using ^{13}CO gas. ^1H NMR (CD_2Cl_2, 193 K, δ): 9.76 (s, 1H, pz′N*H*), 6.15, 6.15, 6.07 (s, 1H, Tp′C*H*), 2.40, 2.40, 2.24, 2.20, 2.20, 1.46 (s, 3H, Tp′C*H*$_3$), −12.33 (t, $^2J_{H-H} = 5$ Hz, $^1J_{Pt-H} = 1126$ Hz, 1H, Pt-*H*), −17.51 (d, $^2J_{H-H} = 5$ Hz, $^1J_{Pt-H} = 1114$ Hz, 1H, Pt-*H*). IR (CH_2Cl_2): $\nu_{BH} = 2522$ cm^{-1}, $\nu_{CO} = 2130$ cm^{-1}. Spectral data for [κ^2-(HTp′)Pt-(D)$_3$(CO)][BAr′$_4$] (**6**-*d*$_3$). ^1H NMR (CD_2Cl_2, 193 K, δ): 9.76 (s, 1H, pz′N*H*), 6.15, 6.15, 6.07 (s, 1H, Tp′C*H*), 2.40, 2.40, 2.24, 2.20, 2.20, 1.46 (s, 3H, Tp′C*H*$_3$), −12.33 (t, $^2J_{H-H} = 5$ Hz, $^1J_{Pt-H} = 1126$ Hz, 1H, Pt-*H*), −17.51 (d, $^2J_{H-H} = 5$ Hz, $^1J_{Pt-H} = 1114$ Hz, 1H, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt(H)$_3$(^{13}CO)][BAr′$_4$] (**6***). ^1H NMR (CD_2Cl_2, 193 K, δ): 9.76 (s, 1H, pz′N*H*), 6.15, 6.15, 6.07 (s, 1H, Tp′C*H*), 2.40, 2.40, 2.24, 2.20, 2.20, 1.46 (s, 3H, Tp′C*H*$_3$), −12.33 (dt, $^2J_{C-H} = 90$ Hz, $^2J_{H-H} = 5$ Hz, 1$J_{Pt-H} = 1126$ Hz, 1H, Pt-*H*), −17.51 (dd, $^2J_{C-H} = 4$ Hz, $^2J_{H-H} = 5$ Hz, $^1J_{Pt-H} = 1114$ Hz, 1H, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 193 K, δ): 171.0 (dt, $^1J_{Pt-C} = 570$ Hz, $^2J_{C-H\ trans} = 90$ Hz, $^2J_{C-H\ cis} = 4$ Hz, *C*O).

In Situ Generation of [κ^2-(HTp′)Pt(H)$_3$(NCCH$_3$)][BAr′$_4$] (7). Tp′PtH_3 (**1**) (10 mg, 0.02 mmol) and [H(OEt_2)$_2$][BAr′$_4$] (23 mg, 0.02 mmol) were added to an NMR tube in the drybox. The tube was capped with a septum and removed from the box. It was then cooled to −78 °C and CD_2Cl_2 (0.7 mL) was added. Acetonitrile (6.5 μL, 0.2 mmol) was syringed in and the tube was shaken, it was then placed in the NMR at 193 K. ^1H NMR (CD_2Cl_2, 193 K, δ): 9.77 (s, 1H, pz′N*H*), 6.10, 6.10, 6.04 (s, 1H, Tp′C*H*), 2.39, 2.39, 2.26, 2.26, 2.22, 2.17, 1.48

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(s, 3H, Tp′CH_3, NCCH_3), −19.94 (s, ${}^1J_{\mathrm{Pt-H}} = 1166$ Hz, 2H, Pt-*H*), −24.08 (s, ${}^1J_{\mathrm{Pt-H}} = 1423$ Hz, 1H, Pt-*H*).

In Situ Generation of [κ^2-(HTp′)Pt(Me)(H)$_2$(CO)][BAr′$_4$] (8). Tp′PtMeH_2 (**3**) (10 mg, 0.02 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (23 mg, 0.02 mmol) were added to an NMR tube in the drybox. The tube was capped with a septum and removed from the box. The tube was purged and filled with the desired pressure of CO 3 times. It was cooled to −78 °C and CD_2Cl_2 (0.7 mL) was added. It was then placed in the NMR with the probe cooled to 193 K. [κ^2-(HTp′)Pt(Me)(H)$_2$(^{13}CO)]-[BAr′$_4$] (**8***) was synthesized in an analogous fashion using ^{13}CO gas. ^{1}H NMR (CD_2Cl_2, 193 K, δ): 10.01 (s, 1H, pz′N*H*), 6.10, 6.09, 6.09 (s, 1H, Tp′C*H*), 2.37, 2.36, 2.27, 2.26, 2.15, 1.49 (s, 3H, Tp′CH_3), −12.33 (d, ${}^2J_{\mathrm{H-H}} = 5.5$ Hz, ${}^1J_{\mathrm{Pt-H}} = 1166$ Hz, 1H, Pt-*H*), −17.84 (d, ${}^2J_{\mathrm{H-H}} = 5.5$ Hz, $1J_{\mathrm{Pt-H}} = 1193$ Hz, 1H, Pt-*H*). IR (CH_2Cl_2): $\nu_{\mathrm{BH}} = 2522$ cm^{-1}, $\nu_{\mathrm{CO}} = 2124$ cm^{-1}. Spectral data for [κ^2-(HTp′)Pt(Me)(H)$_2$-(^{13}CO)][BAr′$_4$] (**8***). ^{1}H NMR (CD_2Cl_2, 193 K, δ): 10.01 (s, 1H, pz′N*H*), 6.10, 6.09, 6.09 (s, 1H, Tp′C*H*), 2.37, 2.36, 2.27, 2.26, 2.15, 1.49 (s, 3H, Tp′CH_3), −12.33 (dd, ${}^2J_{\mathrm{C-H}} = 94$ Hz, ${}^2J_{\mathrm{H-H}} = 5.5$ Hz, ${}^1J_{\mathrm{Pt-H}} = 1166$ Hz, 1H, Pt-*H*), −17.84 (dd, ${}^2J_{\mathrm{C-H}} = 3.2$ Hz, ${}^2J_{\mathrm{H-H}} = 5.5$ Hz, ${}^1J_{\mathrm{Pt-H}} = 1193$ Hz, 1H, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt-(Me)(H)$_2$(CO)][BAr′$_4$] (**8b**). ^{1}H NMR (CD_2Cl_2, 193 K, δ): 0.53 (s, ${}^2J_{\mathrm{Pt-H}} = 55$ Hz, 3H, Pt-Me), −16.72 (s, ${}^1J_{\mathrm{Pt-H}} = 1201$ Hz, 2H, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt(Me)(H)$_2$(^{13}CO)][BAr′$_4$] (**8b***). ^{1}H NMR (CD_2Cl_2, 193 K, δ): 0.53 (s, ${}^2J_{\mathrm{Pt-H}} = 55$ Hz, 3H, Pt-Me), −16.72 (d, ${}^2J_{\mathrm{C-H}} = 4$ Hz, ${}^1J_{\mathrm{Pt-H}} = 1201$ Hz, 2H, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt(Me)(H)$_2$(CO)][BAr′$_4$] (**8c**). ^{1}H NMR (CD_2Cl_2, 193 K, δ): −17.05 (s, ${}^1J_{\mathrm{Pt-H}} = 1212$ Hz, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt-(Me)(H)$_2$(^{13}CO)][BAr′$_4$] (**8c***). ^{1}H NMR (CD_2Cl_2, 193 K, δ): −17.05 (d, ${}^2J_{\mathrm{C-H}} = 3.7$ Hz, ${}^1J_{\mathrm{Pt-H}} = 1212$ Hz, Pt-*H*).

In Situ Generation of [κ^2-(HTp′)Pt(Me)(H)$_2$(NCCH$_3$)][BAr′$_4$] (10). Tp′PtMeH_2 (**3**) (10 mg, 0.02 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (23 mg, 0.02 mmol) were added to an NMR tube in the drybox. The tube was capped with a septum and removed from the box. It was then cooled to −78 °C and CD_2Cl_2 (0.7 mL) was added. Acetonitrile (6.5 μL, 0.2 mmol) was syringed in and the tube was shaken, it was then placed in the NMR at 193 K. ^{1}H NMR (CD_2Cl_2, 193 K, δ): 10.56 (s, 1H, pz′N*H*), 6.04, 6.03, 6.03 (s, 1H, Tp′C*H*), 2.34, 2.34, 2.30, 2.30, 2.22, 2.20, 1.45 (s, 3H, Tp′CH_3, NCCH_3), −20.67 (s, ${}^1J_{\mathrm{Pt-H}} = 1265$ Hz, 1H, Pt-*H*), −24.08 (s, ${}^1J_{\mathrm{Pt-H}} = 1496$ Hz, 1H, Pt-*H*).

Structural Data for 5. Crystals from CH_2Cl_2/hexanes at 0 °C; $C_{16}H_{23}B_1N_6OPt$, $M = 521.30$; monoclinic, space group $P2_1/n$; $Z = 4$; $a = 13.5767(5)$, $b = 7.8292(3)$, $c = 18.9222(6)$ Å; $\alpha = 90$, $\beta = 110.744(2)$, $\gamma = 90°$; $U = 1880.94(12)$ Å^3; $D_c = 1.84$ Mg m^{-3}; $T = -100$ °C; max 2θ: 56°; Mo K$_\alpha$ radiation ($\lambda = 0.710\,73$ Å); 4538 unique reflections were obtained and 4525 of these with $I > 2.5\ \sigma(I)$ were used in the refinement; data were collected on a Bruker SMART diffractometer, using the ω scan method. For significant reflections merging *R*-value: 0.0006; Residuals: R_F: 0.065; R_W: 0.170 (significant reflections); GoF: 1.092. The hydride could not be located in the Fourier difference map and was placed in a calculated position. Further structural data is presented in the Supporting Information.

Kinetic Studies. Complex **6** was prepared in situ as described above, then the NMR spectrometer was adjusted to the desired temperature and ^{1}H NMR spectra were taken after specific time intervals. The hydride peaks for **6** were integrated relative to the solvent peak. The data were plotted as a function of ln(integration)/(initial integration) vs time and resulted in a straight line from which the pseudo first-order rate constant was determined. The kinetic isotope effect was determined by comparison of the rate of decay of **6** and **6-*d*$_3$** at 239 K and 18.7 psi CO. The rate of decay of **6-*d*$_3$** was monitored by integration of one of the Tp′ methyl peaks relative to the solvent peak.

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Supporting Information Available: Structure properties for complex **5** are listed in the Supporting Information along with a cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

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