

Net Hydrogenation of Pt–NHP Bond Is Catalyzed by Elemental Pt

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The addition of H₂ across M–NHR or M–OR moieties is a central reaction for several synthetic transformations. For example, Stryker's reagent, [(Ph₃P)CuH]₆, a catalyst for conjugate addition reactions, is generated by hydrogenolysis of a Cu–O^tBu bond.^{1,2} Additionally, net H₂ addition across M–O₂CH bonds completes catalytic conversion of CO₂ and H₂ to formic acid,³ H₂ addition across Pt–OH bonds has been proposed in a cycle for olefin epoxidation,⁴ and H₂ addition across M–NHR bonds has been implicated in asymmetric hydrogenations.⁵ Despite their importance, reports of well-defined reactions with late(r) transition metal systems are rare and mechanistic studies are limited.^{5–8} Recently, C–H activation of hydrocarbons via net 1,2-addition of C–H bonds across metal–heteroatom bonds using late transition metals (with ≥6 d-electrons) bearing formally anionic ligands (e.g., –NHR or –OR) has been reported.^{9–14} Despite interest in these C–H and H–H bond transformations, questions regarding the mechanism remain.^{10,15–17}

The complex [(^tbpy)Pt(Me)(NH₂Ph)][O₂CCF₃] (**1**) is formed upon reaction of aniline and (^tbpy)Pt(Me)(O₂CCF₃)¹⁸ (^tbpy = 4,4'-di-*tert*-butyl-2,2'-dipyridyl). The deprotonation of **1** produces (^tbpy)Pt(Me)(NHP) (**2**). For **2**, a broad singlet is observed at 3.99 ppm (¹H NMR) due to the amido proton. The methyl ligand resonates at 1.85 ppm (singlet with Pt satellites, ²J_{Pt–H} = 84 Hz) in the ¹H NMR spectrum and at –14.2 ppm (singlet with Pt satellites, ¹J_{Pt–C} = 813 Hz) in the ¹³C{¹H} NMR spectrum. The solid-state structure of **2** (Figure 1) confirms its monomeric nature.

Reactions of a benzene solution of **2** pressurized with H₂ at room temperature ultimately produce free ^tbpy ligand, methane, and aniline. Careful monitoring of the reaction at 45 psi of H₂ revealed the formation of (^tbpy)Pt(Me)(H) (**3**) as an intermediate (Scheme 1 and Figure S4 in the Supporting Information). For complex **3**, a hydride resonance is observed at –14.8 ppm (¹J_{Pt–H} = 1575 Hz) in the ¹H NMR spectrum as well as a new methyl resonance at 2.21 ppm (²J_{Pt–H} = 83 Hz). The mechanism for dihydrogen addition across Pd^{II}–OR (R = H or CH₃) bonds proposed by Goldberg, Kemp, Muller, and Fulmer involves 1,2-addition of H₂ across the Pd–OR moiety, via a σ-bond metathesis type transition state, to produce ROH and a Pd^{II}–H complex.⁸ Thus, reaction of **2** with H₂ via a similar mechanism would involve Pt mediated 1,2-addition of H₂ to give (^tbpy)Pt(Me)(NH₂Ph)(H) with aniline dissociation to form **3** and subsequent decomposition of **3** to methane, Pt(s), and free ^tbpy. We initially presumed this straightforward pathway, which is consistent with the general notion of reactions with related systems.^{5,7,8,13,19,20} Monitoring (¹H NMR) the reaction of **2** with H₂ and a plot of [**2**] versus time reveals an induction period (Figure

2A). The observation of an induction period led us to consider Pt(s) as a heterogeneous catalyst.²¹

As an initial probe of a Pt(s) catalyzed process, we used a standard Hg test.²¹ The addition of Hg to a solution of **2** in C₆D₆ followed by pressurization with H₂ completely suppresses reactivity (see Supporting Information). Next, a solution of **2** pressurized with H₂ was allowed to react until visible formation of Pt(s), at which point conversion of **2** to **3** was observed. The reaction solution was decanted from the tube, a fresh solution of **2** in C₆D₆ was added to the original NMR tube and pressurized with H₂, and the reaction was followed by ¹H NMR. A plot of [**2**] versus time reveals no induction period (see Supporting Information). Maitlis' test²² was performed by monitoring the reaction until past the induction period. The reaction tube was then vented, the solution was filtered through Celite, and the filtrate was placed in a clean NMR tube, pressurized with H₂, and monitored. Figure 2B shows that a second induction period is observed after removal of Pt(s). As additional confirmation, in a separate experiment 10 wt % Pt on activated carbon was added to a solution of **2** before pressurization with H₂. The consumption of **2** reached 50% conversion after 5 min and completion in <1 h. A control experiment with **2** and elemental Pt in the absence of H₂ resulted in no reaction.

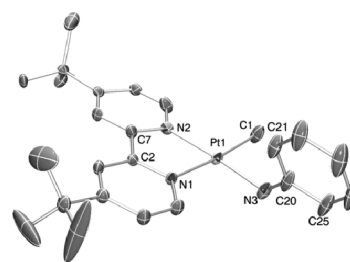
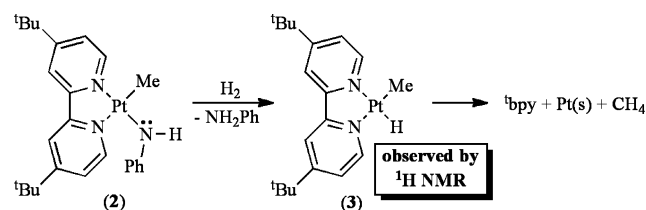


Figure 1. ORTEP of (^tbpy)Pt(Me)(NHP) (**2**) (50% probability; H atoms omitted for clarity). Selected bond lengths (Å): Pt1–N1 2.077(2), Pt1–N2 2.026(2), Pt1–C1 2.040(3), Pt1–N3 2.005(2), N3–C20 1.357(4).

Scheme 1. Reaction of (^tbpy)Pt(Me)(NHP) (**2**) and H₂



The proposed pathway of H₂ addition across the Pt–NHP bond of **2** contrasts the proposed mechanism of hydrogenolysis of related Pd(II) hydroxide and methoxide complexes.⁸ To probe the source of these differences, DFT calculations (B3LYP, pseudopotentials) were

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employed. Reaction of **2** and H₂ to give **3** and aniline is calculated to be exothermic by 6 kcal/mol, but with a barrier of 45 kcal/mol. In contrast, the calculated barrier for H₂ addition across the Pd–OH bond of (PCP)Pd(OH) {PCP = 2,6-bis(CH₂PMe₂)₂C₆H₃}, to give (PCP)Pd–(H) and water, is 21.0 kcal/mol, despite the similar reaction enthalpy (–4 kcal/mol).⁸ At the current level of theory, the calculated H₂ activation barrier and reaction enthalpy for (PCP)Pd(OMe) (**24** and –3 kcal/mol, respectively) are similar to those of the hydroxy analogue.

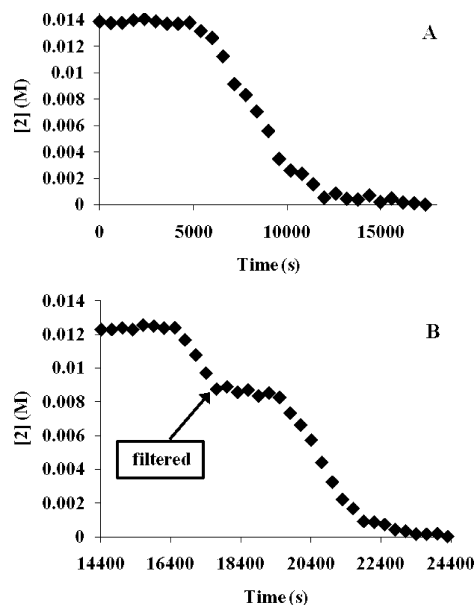


Figure 2. Plots monitoring [2] versus time: (A) 200 psi of H₂ at room temperature, (B) reaction solution filtered to remove Pt(s) after initial induction period (plot started after 14 400 s reaction time).

Figure 3 displays the calculated transition state for H–H activation by **2**. For the amido lone pair (conjugated with the phenyl substituent) to orient to receive a H atom from H₂, it must be aligned perpendicular to the Pt square plane. This orientation would place the phenyl substituent in close proximity to either the Me or the 'bpy ligand, which provides a steric inhibition to H₂ activation. In the calculated transition state, the phenyl substituent may rotate perpendicular to the amide plane, breaking C_{ipso}–N conjugation. Note the longer bond length of 1.46 Å for the C_{ipso}–N bond in the TS (Figure 3) versus 1.39 Å (calcd., 1.36 Å/experimental) in **2**. Comparison of calculated H₂-scission barriers for (bpy)M(Me)(N–HPh) (M = Pd or Pt) and (PCP)Pd(OMe), (bpy)Pt(Me)(NHMe), (bpy)M(Me)(OMe), and (bpy)Pt(Me)(NHPh*) {Ph* denotes a Ph in the MM region of a QM/MM calculation} suggests that the remarkable difference in barriers between (bpy)Pt(Me)(NHPh) and (PCP)Pd(OMe) is due in equal parts to replacement of the metal (Pt → Pd), activating ligand (NHMe → OMe), and supporting ligand (bpy/Me → PCP). The predicted enhancement upon substituting Pd for Pt might be explained by the anticipated increase in electrophilicity of Pd (vs Pt), which would facilitate H₂ activation. The long Pt–H bond distances in the calculated transition state for **2** (Figure 3) are consistent with weak Pt/H₂ activation as one source of a substantial activation barrier. These influences underscore the subtle balance required to access systems that can activate H–H and C–H bonds. In the transition states for H₂ activation by (bpy)M(Me)(NHPh) the calculated Pt–H bond distances are 2.48 and 2.34 Å, while the Pd–H distances for the TS of the complex reported by Goldberg are indeed shorter, 2.12 and 2.14 Å,⁸ despite the near identical covalent radii of Pd and Pt.

The activation of H₂ by (bpy)Pt(Me)(NHPh) (**2**) produces (bpy)Pt(Me)(H) (**3**). However, kinetic studies lead to the conclusion that, rather than direct activation of H₂ across the Pt–NHPh bond, Pt(s) is catalyzing the hydrogenation of the Pt–NHPh moiety, though the specific mechanism of this transformation is not known. To our knowledge, this is the first report of a heterogeneous catalyst for activation of covalent bonds toward addition across an M–X (X = NHR or OR) bond and a rare example of net H₂ addition to M–L bonds by a heterogeneous catalyst.^{23,24}

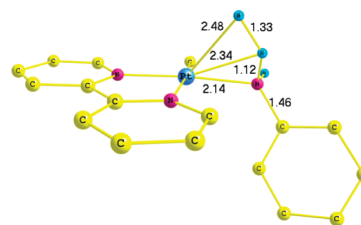


Figure 3. Calculated transition state for activation of H₂ by complex **2**. Most hydrogen atoms omitted for clarity.

Acknowledgment. T.B.G. acknowledges the NSF (CHE-0848693) for funding. T.R.C. thanks the NSF for support (CHE-0701247) and facilities (CHE-0741936). A.W.P. thanks the UNT Toulouse Graduate School for a Dissertation Fellowship.

Supporting Information Available: Characterization data, experimental and computational details including kinetic studies and plots, and X-ray crystallographic data files for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA9102309