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Net Hydrogenation of Pt−NHPh Bond Is Catalyzed by Elemental Pt

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The addition of H_2 across M−NHR or M−OR moieties is a central reaction for several synthetic transformations. For example, Stryker's reagent, $[(Ph_3P)CuH]_6$, a catalyst for conjugate addition reactions, is generated by hydrogenolysis of a Cu−O^{t}Bu bond.[1,2] Additionally, net H_2 addition across M−O_2CH bonds completes catalytic conversion of CO_2 and H_2 to formic acid,[3] H_2 addition across Pt−OH bonds has been proposed in a cycle for olefin epoxidation,[4] and H_2 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 [(^{t}bpy)Pt(Me)(NH_2Ph)][O_2CCF_3] (**1**) is formed upon reaction of aniline and (^{t}bpy)Pt(Me)(O_2CCF_3)[18] (^{t}bpy = 4,4′-di-*tert*-butyl-2,2′-dipyridyl). The deprotonation of **1** produces (^{t}bpy)Pt(Me)(NHPh) (**2**). For **2**, a broad singlet is observed at 3.99 ppm (^{1}H NMR) due to the amido proton. The methyl ligand resonates at 1.85 ppm (singlet with Pt satellites, $^2J_{\text{Pt−H}} = 84$ Hz) in the ^{1}H NMR spectrum and at −14.2 ppm (singlet with Pt satellites, $^1J_{\text{Pt−C}} = 813$ Hz) in the ^{13}C{^{1}H} NMR spectrum. The solid-state structure of **2** (Figure 1) confirms its monomeric nature.

Reactions of a benzene solution of **2** pressurized with H_2 at room temperature ultimately produce free ^{t}bpy ligand, methane, and aniline. Careful monitoring of the reaction at 45 psi of H_2 revealed the formation of (^{t}bpy)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 ($^1J_{\text{Pt−H}} = 1575$ Hz) in the ^{1}H NMR spectrum as well as a new methyl resonance at 2.21 ppm ($^2J_{\text{Pt−H}} = 83$ Hz). The mechanism for dihydrogen addition across Pd^{II}−OR (R = H or CH_3) bonds proposed by Goldberg, Kemp, Muller, and Fulmer involves 1,2-addition of H_2 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 H_2 with **2** via a similar mechanism would involve Pt mediated 1,2-addition of H_2 to give (^{t}bpy)Pt(Me)(NH_2Ph)(H) with aniline dissociation to form **3** and subsequent decomposition of **3** to methane, Pt(s), and free ^{t}bpy. 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 (^{1}H NMR) the reaction of **2** with H_2 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 C_6D_6 followed by pressurization with H_2 completely suppresses reactivity (see Supporting Information). Next, a solution of **2** pressurized with H_2 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 C_6D_6 was added to the original NMR tube and pressurized with H_2, and the reaction was followed by ^{1}H NMR. A plot of [**2**] versus time reveals no induction period (see Supporting Information). Maitlis' test[22] 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 H_2, 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 H_2. 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 H_2 resulted in no reaction.

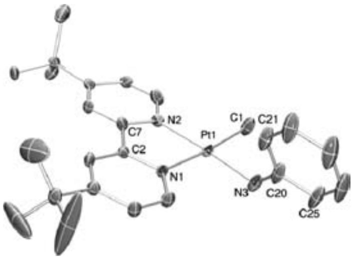
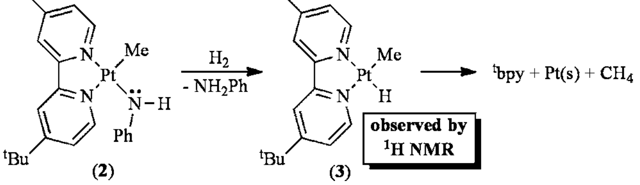


Figure 1. ORTEP of (^{t}bpy)Pt(Me)(NHPh) (**2**) (50% probability; H atoms omitted for clarity). Selected bond lengths (Å): Pt1−N1 2.077(2), Pt1−N2 2.026(2), Pt1−C1 2.040(3), Pt1−N3 2.005(2), N3−C20 1.357(4).

Scheme 1. Reaction of (^{t}bpy)Pt(Me)(NHPh) (**2**) and H_2



The proposed pathway of H_2 addition across the Pt−NHPh 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 H_2 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 H_2 addition across the Pd−OH bond of (PCP)Pd(OH) {PCP = 2,6-bis(CH_2PMe_2)$_2C_6H_3$}, 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 H_2 activation barrier and reaction enthalpy for (PCP)Pd(OMe) (24 and −3 kcal/mol, respectively) are similar to those of the hydroxy analogue.

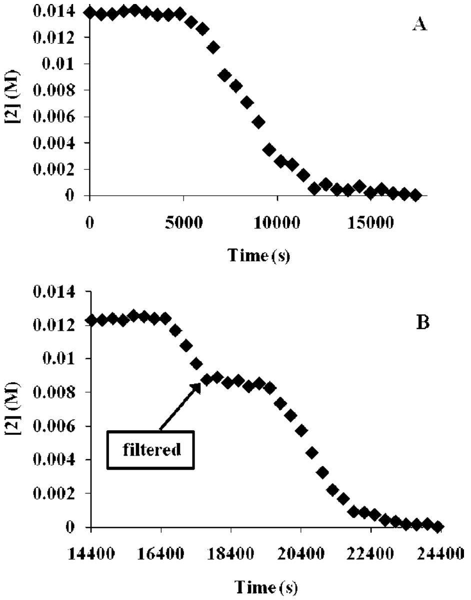

Figure 2. Plots monitoring [**2**] versus time: (A) 200 psi of H_2 at room temperature, (B) reaction solution filtered to remove Pt(s) after initial induction period (plot started after 14 400 s reaction time).

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 H_2, 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 ^{t}bpy ligand, which provides a steric inhibition to H_2 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 H_2-scission barriers for (bpy)M(Me)(NHPh) (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 H_2 activation. The long Pt−H bond distances in the calculated transition state for **2** (Figure 3) are consistent with weak Pt/H_2 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 H_2 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 H_2 by (^{t}bpy)Pt(Me)(NHPh) (**2**) produces (^{t}bpy)Pt(Me)(H) (**3**). However, kinetic studies lead to the conclusion that, rather than direct activation of H_2 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 H_2 addition to M−L bonds by a heterogeneous catalyst.[23,24]

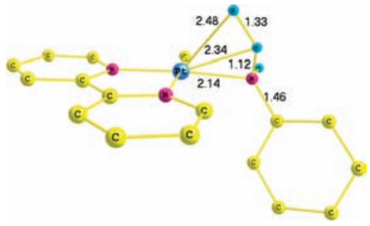

Figure 3. Calculated transition state for activation of H_2 by complex **2**. Most hydrogen atoms omitted for clarity.

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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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