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Competitive C−H Bond Activation and β-Hydride Elimination at Platinum(II)

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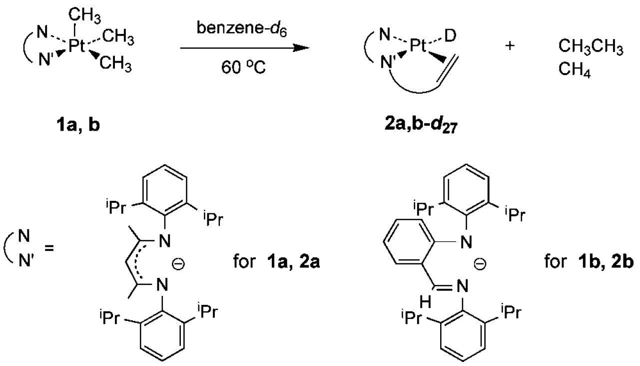
With an available open site at the metal center, β-hydride elimination is typically a very facile reaction.[1] For example, both theoretical and experimental studies have found barriers for β-hydride elimination/olefin insertion in diphosphinePt(II)alkyl complexes to be less than 10 kJ/mol.[2] In this contribution, we report a system wherein intermolecular C−H bond activation of arenes is shown to be not only competitive but actually faster than β-hydride elimination. In contrast, intermolecular alkane C−H bond activation was observed to be slower than intramolecular β-hydride elimination.

Thermolysis of the five-coordinate platinum(IV) complex (nacnac)Pt(CH$_3$)$_3$ (**1a**) (nacnac = $[\{(o\text{-}{}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{NC}(\mathrm{CH}_3)\}_2\mathrm{CH}]^-$)[3] in benzene-$d_6$ was reported to lead to reductive elimination of ethane, methane, and formation of the platinum(II) olefin hydride complex **2a-*d*$_{27}$**.[4] Similar chemistry has now been observed with the related five-coordinate complex (AnIm)Pt(CH$_3$)$_3$ (**1b**) (AnIm = $[o\text{-}\mathrm{C}_6\mathrm{H}_4\text{-}\{\mathrm{N}(\mathrm{C}_6\mathrm{H}_3{}^i\mathrm{Pr}_2)\}(\mathrm{CH{=}NC}_6\mathrm{H}_3{}^i\mathrm{Pr}_2)]^-$). It had been proposed in the study of **1a** that reversible formation of **2a** was likely on the pathway to H/D exchange and formation of **2a-*d*$_{27}$**.[4] Herein, we provide definitive evidence that H/D exchange occurs prior to β-hydride elimination. The comparison of the reactivity of the two ligands nacnac and AnIm in this context is also important. Although β-diketiminate (nacnac) ligands have become popular in recent years,[5] one complication that has been observed is the sensitivity of the central (γ) carbon to electrophilic attack.[6] To protect the ligand backbone from this type of reactivity, modified nacnac ligands, such as the anilido−imine ligand (AnIm)[7] where a phenyl group has been incorporated into the ligand backbone, have been developed. Despite the similar structural features and overall reactivity shared by **1a** and **1b**, remarkable differences in reaction rates were observed. Modification of the bidentate nitrogen ligand has a significant impact on both the rate of reductive elimination from platinum(IV) and of olefin insertion at platinum(II).

The new five-coordinate Pt(IV) complex (AnIm)Pt(CH$_3$)$_3$ (**1b**) was prepared in 70% yield by the reaction of [Pt(CH$_3$)$_3$OTf]$_4$ with 4 equiv of the potassium salt of the anilido−imine ligand in toluene. Complex **1b** was characterized by ^{1}H NMR spectroscopy, X-ray crystallography, and elemental analysis.[8] The ^{1}H NMR spectrum of complex **1b** (benzene-d_6) displays a singlet with platinum satellites at 1.14 ppm ($J_{\mathrm{Pt-H}}$ = 73.8 Hz) integrating to 9H and corresponding to the three Pt−CH_3 groups, indicating that the complex is fluxional in solution.[9] The analogous Pt−CH_3 signal of the nacnac derivative **1a**, appears at 1.10 ppm ($J_{\mathrm{Pt-H}}$ = 74.0 Hz).[3]

The solid-state structures of **1a**[3] and **1b** are also similar. The X-ray structure of **1b** (Supporting Information Figure S1) reveals that like **1a**, complex **1b** is square pyramidal. The platinum−methyl distances for **1b** (Pt−C1 (trans to anilido nitrogen) = 2.056(5) Å, Pt−C2 (trans to imine nitrogen) = 2.047(5) Å, and Pt−C3 (trans to open site) = 2.016(5) Å) are comparable to those for **1a** (Pt−C1 (trans to nitrogen) = 2.056(4) Å, and Pt−C2 (trans to open site) = 2.038(7) Å).

Scheme 1



Very similar chemical reactivity was observed upon thermolysis of complexes **1a** and **1b** at 60 °C in benzene-d_6 (Scheme 1). The five-coordinate platinum(IV) alkyl complexes both undergo reductive elimination to form ethane, methane, and the platinum(II) olefin hydride complexes **2a-*d*$_{27}$**[4] and **2b-*d*$_{27}$**.

Complex **2b** (prepared by thermolysis of **1b** in benzene) was characterized by ^{1}H NMR spectroscopy and X-ray crystallography;[8] the X-ray structure of **2b** is shown in Figure 1. In complex **2b**, the hydride ligand is located trans to the imine nitrogen, while the cyclometallated olefin group is located trans to the anilido nitrogen. The solid-state structure of **2b** resembles **2a**[4] in that both complexes feature a cyclometallated olefin group that is tilted about 45 °C relative to the square plane of the complex. The platinum−nitrogen bond lengths in **2b** of 2.009(4) Å (trans to olefin) and 2.081(4) Å (trans to hydride) closely match those in **2a** (2.011(4) Å (trans to olefin), 2.089(4) Å (trans to hydride). However, the distances between platinum and the olefinic carbons in **2b** (2.126(5) and 2.116(5)Å) are slightly shorter than those of **2a** (2.152(6) and 2.128(6) Å). In the ^{1}H NMR spectrum of **2b**, the hydride appears at −16.93 as a doublet with platinum satellites ($J_{\mathrm{Pt-H}}$ = 1254 Hz, $^4J_{\mathrm{H-H}}$ = 6 Hz), because of coupling with the imine C-*H*. The Pt−H coupling value of 1254 Hz is slightly higher than in **2a**, where the hydride signal appears at −17.69 ppm with $J_{\mathrm{Pt-H}}$ = 1140 Hz.

A common mechanism for the formation of **2a** and **2b** from **1a** and **1b**, respectively, is proposed (Scheme 2). Upon heating, the five-coordinate platinum(IV) complex undergoes reductive elimination of ethane and subsequently activates one of the ligand isopropyl groups at either the methyl or methine position.[4] Reductive

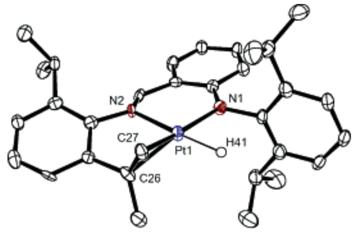


Figure 1. ORTEP drawing of **2b**. (Thermal ellipsoids at 50% probability. Non-hydridic H atoms and a molecule of cocrystallized toluene omitted for clarity). Select bond distances (Å): Pt1−N1 = 2.009(4), Pt1−N2 = 2.081(4), Pt1−C26 = 2.126(5), Pt1−C27 = 2.116(5).

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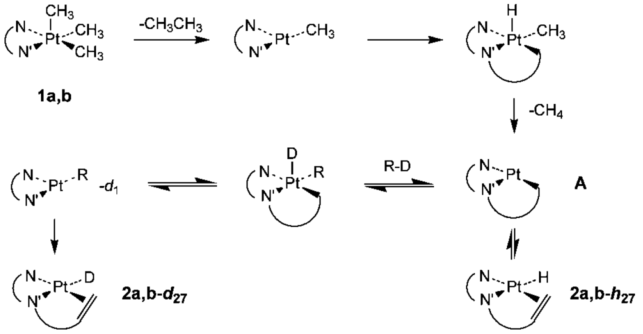
Scheme 2



elimination of methane (CH_4 is the only isotopomer observed) follows, producing the three-coordinate cyclometallated intermediate **A**. Intermediate **A** can undergo a β-hydride elimination to form the product **2a** or **2b**. Intermediate **A** is also capable of C−H bond activation. Oxidative addition of a solvent R−D bond followed by reductive elimination of the ligand isopropyl group leads to deuterium exchange between the solvent and the isopropyl ligand groups. Species **A** may also be generated by olefin insertion at the platinum(II) olefin hydride product (vide infra).

The disappearances of both five-coordinate complexes at 60 °C were monitored by ^{1}H NMR. First-order kinetics were observed but dramatically different rates were documented. Ethane reductive elimination from nacnac five-coordinate complex **1a** was found to be nearly an order of magnitude slower ($k_{\mathrm{obs}} = 3.0(2) \times 10^{-6}\ \mathrm{s}^{-1}$) than ethane reductive elimination from AnIm five-coordinate complex **1b** ($k_{\mathrm{obs}} = 2.1(2) \times 10^{-5}\ \mathrm{s}^{-1}$).

As the thermolyses of **1a** and **1b** were monitored, it was observed that even at early reaction times the products **2a**-d_{27} and **2b**-d_{27} contained deuterium in all of the isopropyl and olefinic resonances.[10] To determine whether this deuterium incorporation was occurring through fast, reversible insertion at the platinum(II) olefin hydride complex and subsequent solvent activation (as previously proposed),[4] samples of olefin hydride complexes **2a**-h_{27} and **2b**-h_{27} were independently prepared, heated in benzene-d_6 at 60 °C, and monitored for deuterium incorporation. When heated at 60 °C in benzene-d_6 for 24 h, **2b**-h_{27} showed no detectible deuterium incorporation. Even after continued heating in benzene-d_6 at 60 °C for 60 h, less than 5% deuterium was incorporated. In contrast, when **2a**-h_{27} was heated at 60 °C in benzene-d_6 for 24 h, approximately 25% deuterium incorporation was observed. The greater degree of deuterium incorporation in olefin hydride complex **2a** (25%, as compared to less than 5% for **2b**) is indicative of a lower barrier to olefin insertion for the nacnac complex **2a** than for the AnIm complex **2b.** However, for both complexes, since only the fully deuterated olefin hydride complex is produced by the thermolysis of the five-coordinate platinum(IV) complex under these conditions, it is evident that at 60 °C benzene activation by intermediate **A** is fast relative to β-hydride elimination to form the products. This unusual observation likely results, at least in part, from geometric constraints on the intramolecular β-hydride elimination reaction. Notably, as the temperature is increased, the rate of the intramolecular β-hydride elimination would be expected to increase relative to the intermolecular benzene activation.

At higher temperatures, the AnIm platinum(II) olefin hydride complex **2b** does undergo insertion and solvent activation. When complex **2b**-h_{27} was heated at 130 °C in benzene-d_6, deuterium incorporation was gradually observed over the course of about 8 h. Under the same conditions, deuterium incorporation into **2a**-h_{27} was complete in 30 min, consistent with a higher barrier for olefin insertion with the AnIm ligand than the nacnac ligand.

The reactivity of (nacnac)Pt(CH_3)$_3$ and (AnIm)Pt(CH_3)$_3$ was also compared in alkane solvents. When the thermolysis of **1b** was conducted in cyclohexane-d_{12} at 60 °C for 90 h, the observed product was the protio olefin hydride complex **2b**-h_{27}. When **1a** was heated in cyclohexane-d_{12} at 60 °C for 430 h, the protio olefin hydride product **2a**-h_{27} had incorporated less than 5% deuterium. Since the olefin hydride products **2a**-h_{27} and **2b**-h_{27} exhibited little or no deuterium incorporation from the alkane solvent, for both nacnac and AnIm ligands, the rate of product forming β-hydride elimination must be fast relative to alkane activation at 60 °C.

Although no isotopic exchange was observed in the 60 °C thermolysis of **1b** in cyclohexane-d_{12}, the AnIm olefin hydride complex **2b** was capable of alkane activation at higher temperatures. When an *n*-pentane solution of **2b**-d_{27} was heated at 130 °C for 48 h, deuterium incorporated into the terminal position of *n*-pentane with approximately 87% selectivity (as measured by ^{2}H NMR).[8] A similar selectivity was previously reported for **2a**.[4]

In conclusion, new AnIm complexes **1b** and **2b** display structural characteristics and ^{1}H NMR features similar to their nacnac analogues **1a** and **2a**. Yet, modification of the bidentate nitrogen ligand backbone from nacnac to AnIm dramatically increases the rate of ethane reductive elimination from the five-coordinate platinum(IV) complex and decreases the rate of olefin insertion at the platinum(II) olefin hydride complex. Remarkably, although previous studies indicate β-hydride elimination and olefin insertion reactions at Pt(II) should be facile, for these complexes at 60 °C, intermolecular benzene C−H bond activation is clearly fast relative to intramolecular β-hydride elimination. Intermolecular alkane C−H bond activation, however, is slow relative to β-hydride elimination. As unsaturated Pt(II) complexes have been shown in recent years to be key intermediates in selective hydrocarbon oxidation reactions,[11] recognition of such reactivity preferences will be important for catalyst design.

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Supporting Information Available: Experimental procedures and details, X-ray crystallographic data and CIF files for **1b** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) See Supporting Information.
(9) Cooling a solution of **1b** in CD_2Cl_2 to 220 K did not result in any broadening or decoalescence of the Pt−CH_3 signal.
(10) In the thermolysis of **1b**, the Pt(II) olefin hydride complex having cis imine and hydride groups (***cis*-2b**) was observed as a kinetic product (maximum of 40% of the observed products at 60% conversion). Deuterium was present in all of the isopropyl and olefinic resonances, and ***cis*-2b** reacted further to fully convert to the thermodynamic product **2b** by the end of the thermolysis. See supporting information.
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