Base-Promoted Benzene C−H Activation Chemistry at an Amido Pincer Complex of Platinum(II)

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Summary: The thermally robust platinum(II) complex (BQA)Pt(OTf) undergoes benzene C−H bond activation at 150 °C but requires the presence of N^iPr_2Et*. The reaction products are the phenyl complex (BQA)Pt(Ph) and a stoichiometric equivalent of* $[HN^iPr_2Et][OTf]$*.*

The potential for inorganic complexes to catalytically mediate the selective functionalization of simple R−H substrates has engendered widespread interest within the organometallic community.[1] Much recent attention has been paid to systems with late transition elements, largely because they offer promise for selectively coupling alkane C−H activation with nonradical oxidation. Motivating much of the interest in platinum chemistry is the early work of Shilov and co-workers, who demonstrated that platinum(II) salts can mediate the catalytic conversion of methane to methanol in aqueous solution.[2] It is presumed that alkane activation in the Shilov system (Figure 1, **I**) initially proceeds through an electrophilic activation step to release aqueous hydrochloric acid and to generate a divalent platinum alkyl (Pt−Cl + R−H → Pt−R + HCl).[3] A related step is presumed to occur in the system reported by Catalytica (Figure 1, **II**).[4] Unfortunately, neither of these systems is well-suited to an intimate study of this initial activation process.

Our group is currently exploring whether pincer-like amido complexes of platinum(II) can mediate intermolecular C−H bond activation processes.[5,6] Herein we communicate a base-promoted, intermolecular benzene C−H activation reaction in which triflic acid is formally lost from a divalent Pt−OTf precursor. While several groups have studied benzene C−H activation processes at cationic platinum(II) (e.g., Figure 1, **III** and **IV**),[7] loss of a stable alkane, such as methane, typically drives these activation reactions.[8] The distinct feature of the C−H activation system described herein is that triflic acid is the formal byproduct of the intermolecular C−H activation process.[9]

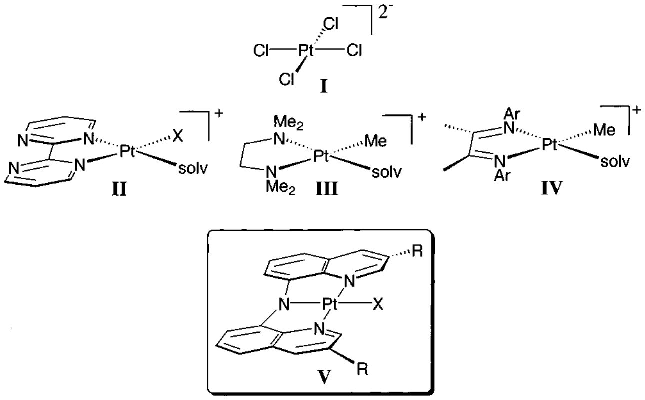

Figure 1. Previously described platinum(II) systems (**I**−**IV**) that mediate C−H activation processes, and the system featured herein (**V**).

Addition of a bis(8-quinolinyl)amine ligand, BQAH, to $(COD)PtCl_2$ in the presence of triethylamine base affords the thermally robust complex (BQA)PtCl (**1**).[5] Suspensions of complex **1** can be superheated in benzene at 150 °C for days without decomposition. To test whether soluble bases might promote reactivity between **1** and benzene, we focused our attention on the relatively noncoordinating tertiary amine N^iPr_2Et. However, stirring a heterogeneous solution of **1** in benzene with N^iPr_2Et at 150 °C resulted in no net reaction: the starting chloride complex **1** was quantitatively recovered from the reaction solution (Scheme 1) and none of the anticipated salt byproduct, $[HN^iPr_2Et][Cl]$, was formed. To derive a more reactive platinum complex, we exchanged the chloride ligand for a labile triflate group. This was most effectively accomplished by a two-step procedure: addition of the lithium salt [Li][BQA][5] to (COD)PtMeCl afforded the methyl complex (BQA)PtMe (**2**) in excellent yield. Protonation of **2** with triflic acid

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[1] For some leading references see: (a) Cho, J.-Y.; Iverson, C. N.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 12868−12869. (b) Chen, H. Y.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995−1997. (c) Jensen, C. M. *Chem. Commun.* **1999**, 2443−2449. (d) Peterson, T. H.; Golden, J. T.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 455−462. (e) Eisenstein, O.; Crabtree, R. H. *New J. Chem.* **2001**, *25*, 665−666. (f) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017−11018.

[2] Kushch, K. A.; Lavrushko, V. V.; Misharin, Yu. S.; Moravsky, A. P.; Shilov, A. E. *New J. Chem.* **1983**, *7*, 729−733.

[3] (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2181−2192. (b) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550−557.

[4] Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560−564.

[5] Peters, J. C.; Harkins, S. B.; Brown, S. D.; Day, M. W. *Inorg. Chem.* **2001**, *40*, 5083−5091.

[6] For a recent review of traditional "pincer" complexes of the platinum group metals see: Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750−3781.

[7] (a) Holtcamp, M. W.; Labinger, J. A., Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848−849. (b) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739−740. (c) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100−5101.

[8] Goldberg and co-workers showed that an octahedral platinum(IV) species, resulting from C−H activation, can be stable to alkane loss by use of a potentially tripodal ligand. See: Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235−10236.

[9] Cycloplatination reactions that result from orthometalation and generate acid have been described. See, for example: Ryabov, A. D.; van Eldik, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 783−784.

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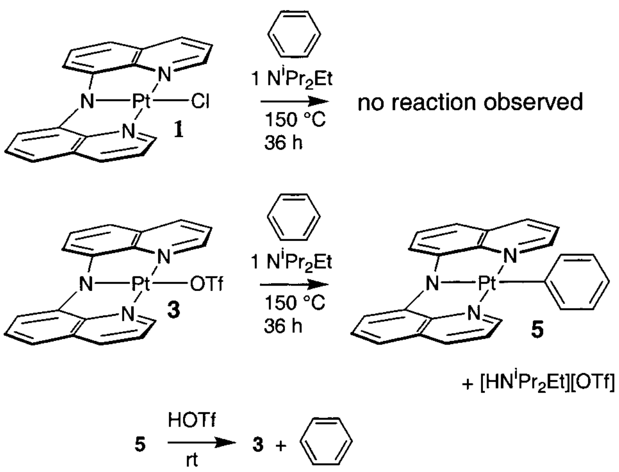
Scheme 1



in dichloromethane quantitatively generates the target triflato complex (BQA)Pt(OTf) (**3**), which readily precipitates from solution and is isolable in 99% yield as an analytically pure red solid. Spectroscopic NMR data for **3** were best obtained in CD_3CN, which quantitatively produces the adduct complex [(BQA)Pt($NCCD_3$)][OTf] (**4**).

Like its chloride counterpart, the triflato complex **3** was stable when dissolved in benzene solution over 36 h at 150 °C. However, heating **3** in benzene with 1 equiv of N^{i}Pr$_2$Et changed the reaction course dramatically. Under relatively dilute conditions (0.0054 M in **3**) at 100 °C, a homogeneous red solution was obtained. After several hours, the ammonium salt [HN^{i}Pr$_2$Et][OTf] and a new platinum complex, (BQA)Pt(Ph) (**5**), could be detected (^{1}H NMR). Raising the reaction temperature to 150 °C and stirring for 36 h results in the complete consumption of **3**, the stoichiometric production of [HN^{i}Pr$_2$Et][OTf], and the generation of the phenyl product **5** in high yield ($\sim$90% by ^{1}H NMR spectroscopy; Scheme 1). Air-stable **5** can be isolated in pure form by chromatographing the solution through a silica plug followed by removal of the volatiles (70% yield). The identity of product **5** has been confirmed from (i) FAB MS data obtained from the crude reaction mixture and (ii) its independent synthesis by the addition of [Li][BQA] to (COD)PtPhCl and comparison of their spectral data.

Owing to the ease with which **3** and **5** precipitate from a homogeneous solution during attempts to obtain X-ray-quality crystals, we turned our attention to a more soluble system in which the BQA ligand is substituted by isopropyl groups at the 3-position of the quinoline rings. The target ligand, 3,3′-^{i}Pr$_2$-BQAH (**6**), proved accessible from a multistep procedure.[10] Lithiation of **6** generated [Li][3,3′-^{i}Pr$_2$-BQA] (**7**), and its subsequent metathesis with (COD)PtMeCl afforded the benzene-soluble methyl complex (3,3′-^{i}Pr$_2$-BQA)PtMe (**8**). Stoichiometric addition of triflic acid to **8** quantitatively produces the triflato complex (3,3′-^{i}Pr$_2$-BQA)PtOTf (**9**), which is modestly soluble in hot benzene and very soluble in dichloromethane. The increased solubility of **9** did enable us to obtain X-ray-quality crystals suitable for a diffraction study, and its solid-state structure is shown in Figure 2. As expected, the complex adopts a square-planar structure and the triflato ligand is positioned trans to the amido N-donor atom of the 3,3′-^{i}Pr$_2$-BQA ligand. For comparison, we obtained X-ray data for the corresponding phenyl complex (3,3′-^{i}Pr$_2$-BQA)Pt(Ph) (**10**), whose solid-state structure is also shown (Figure 2). The Pt$-$N(amido) bond distance in **10** is appreciably elongated relative to its distance in **9**, due to the relative trans influence of the phenyl versus triflate ligands, respectively.

Similar to the parent system, heating a benzene solution of **9** at elevated temperatures in the presence of N^{i}Pr$_2$Et produced a stoichiometric equivalent of [HN^{i}Pr$_2$Et][OTf]. The anticipated phenyl product **10** is formed (ca. 60$-$65% as determined by ^{1}H NMR integration).[11] While no platinum metal is deposited, nor free BQAH observed, other ligand-containing platinum products are observed by ^{1}H NMR; their identity has not yet been established. A control experiment established that the independently prepared phenyl complex **10** is stable in benzene with N^{i}Pr$_2$Et at elevated temperatures. Thus, its decomposition under the reaction conditions is not likely responsible for the decreased yield of the phenyl product.

Because the parent system affords a cleaner reaction with benzene, we have begun to probe its chemistry more closely. To determine whether the benzene C$-$H activation reaction is reversible under the conditions of the experiment, we independently examined the ability of complexes **3** and **5** to catalyze proton scrambling from [HN^{i}Pr$_2$Et][OTf] into C_6D_6. We found that neither **3** nor **5** catalyzes detectable proton scrambling into deuteriobenzene at 150 °C over 36 h, even when a 20-fold excess of [HN^{i}Pr$_2$Et][OTf] was used. Apparently, [HN^{i}Pr$_2$Et][OTf] is too weak an acid, at least in benzene solvent, to drive the reverse reaction at an appreciable rate at 150 °C. Use of a much stronger acid, however, drives the reverse process readily. Thus, addition of HOTf to a benzene slurry of **5** generates the triflato complex **3** rapidly and quantitatively at 25 °C (Scheme 1).[12] Likewise, addition of HCl to **5** rapidly and quantitatively generates **1**.

The reaction of **3** to generate **5** offers the first well-defined example of a Pt$-$X species that accesses an intermolecular C$-$H bond activation process with concomitant release of acid. That the conversion of **3** to **5** might proceed by the elimination of HOTf, which would then be trapped by N^{i}Pr$_2$Et, seems unlikely. Were this to be the case, sterically more encumbered proton traps should also promote the reaction. We tested 2,6-di-*tert*-butylpyridine and found that it does not promote the benzene activation reaction at 150 °C. We have also found that the rate of formation of **5** is not increased by addition of excess N^{i}Pr$_2$Et (10 equiv), consistent with a reaction whose rate is dependent on triflate dissociation, the C$-$H bond activation step, or both steps.

Several of the possible scenarios which might explain the base-promoted activation reaction described are shown in Scheme 2. We suspect that the operative pathway is one in which benzene associatively displaces triflate from **3** (Scheme 2, path b) and undergoes a subsequent oxidative C$-$H bond cleavage to generate a

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[10] See the Supporting Information.

[11] The yield of **10** formed in this reaction critically depends on the purity of **9**. Samples of **9** that do not give satisfactory combustion analysis invariably give much lower yields of **10**.

[12] This also occurs for the (3,3′-^{i}Pr$_2$-BQA) system: addition of triflic acid to a benzene solution of **10** rapidly generates **9**.

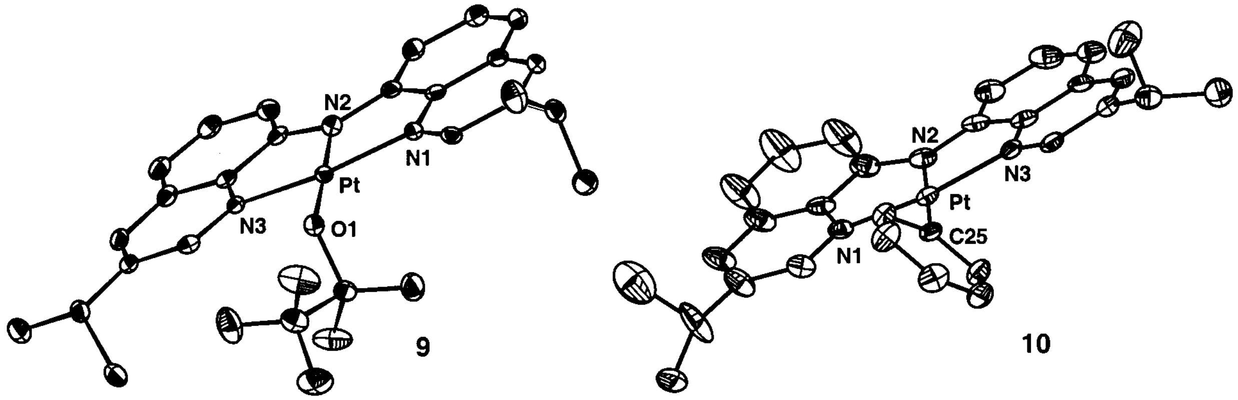
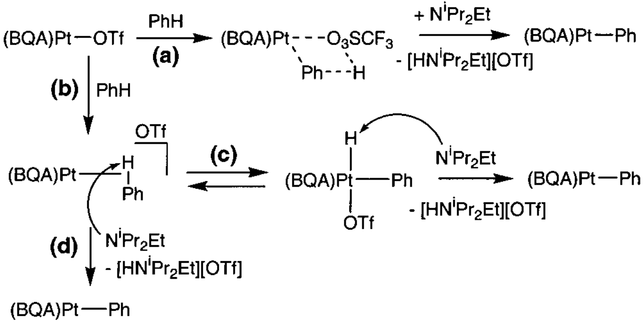


Figure 2. Displacement ellipsoid representations (35%) of complexes **9** and **10**. Selected bond distances (Å) and angles (deg) are as follows. Complex **9**: Pt−N1, 1.994(2); Pt−N2, 1.946(2); Pt−N3, 1.990(2); Pt−O1, 2.097(2); N2−Pt−O1, 179.13(9); N1−Pt−N3, 166.94(10). Complex **10**: Pt−N1, 2.007(3); Pt−N2, 2.020(3); Pt−N3, 2.009(3); Pt−C25, 2.023(4); N2−Pt−C25, 178.07(11); N1−Pt−N3, 163.45(12).

Scheme 2



platinum(IV) hydride (path c).[13] The amine base then displaces the platinum(II) phenyl product by deprotonation of the platinum(IV) hydride. Non-redox processes, such as those that involve heterolytic activation of the Pt−OTf bond (path a) or a simple base deprotonation of benzene activated by precoordination to cationic platinum(II) (path d), also need to be considered.[14] Further studies are necessary to shed light on the mechanism by which the amine base promotes the observed activation chemistry.

To conclude, a bulky amine base promotes an intermolecular benzene C−H activation process at a Pt−X center by formally accepting the reaction's acid byproduct. The strategy employed places a labile triflate group in a position trans to the amido N-donor of the pincer-like amido ligand. This ligand effectively stabilizes the platinum(II) system at the high temperatures (150 °C) necessary to drive the forward reaction and likely labilizes the triflate ligand to allow binding of the benzene substrate. We are now pursuing the possibility that base-promoted C−H activation chemistry may be mediated by other metal systems and applied to other R−H substrates.

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Supporting Information Available: Text giving detailed experimental procedures and tables giving crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Not shown in Scheme 2 is the case where amine base precoordinates platinum, perhaps forming [(BQA)Pt(N^{i}Pr$_2$Et)][OTf], prior to the reaction with benzene.

(14) We recently suggested a related process in which deprotonation of an sp^2-hybridized C−H group of cyclooctadiene occurs on coordination to cationic platinum(II).[5]