

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 ($Pt-Cl + R-H \rightarrow Pt-R + HCl$).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

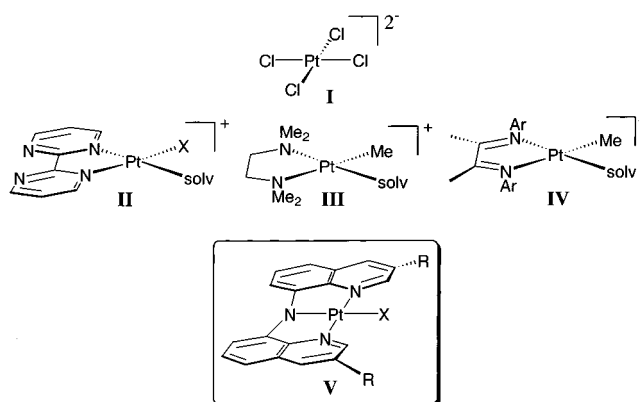


Figure 1. Previously described platinum(II) systems (**I–IV**) that mediate C–H activation processes, and the system featured herein (**V**).

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

Addition of a bis(8-quinolyl)amine ligand, BQAH, to (COD)PtCl₂ 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

(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.

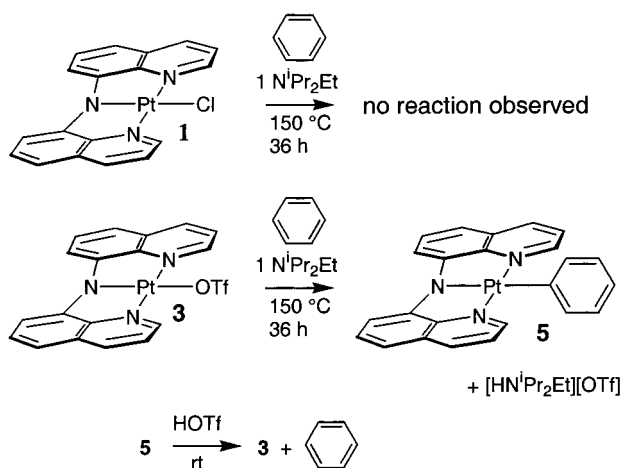
(6) For a recent review of traditional “pincer” complexes of the platinum group metals see: Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750–3781.

(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.

Scheme 1



in dichloromethane quantitatively generates the target triflate complex $(\text{BQA})\text{Pt}(\text{OTf})$ (**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 $[(\text{BQA})\text{Pt}(\text{NCCD}_3)][\text{OTf}]$ (**4**).

Like its chloride counterpart, the triflate complex **3** was stable when dissolved in benzene solution over 36 h at $150\text{ }^\circ\text{C}$. However, heating **3** in benzene with 1 equiv of $\text{N}^i\text{Pr}_2\text{Et}$ changed the reaction course dramatically. Under relatively dilute conditions (0.0054 M in **3**) at $100\text{ }^\circ\text{C}$, a homogeneous red solution was obtained. After several hours, the ammonium salt $[\text{HN}^i\text{Pr}_2\text{Et}][\text{OTf}]$ and a new platinum complex, $(\text{BQA})\text{Pt}(\text{Ph})$ (**5**), could be detected (^1H NMR). Raising the reaction temperature to $150\text{ }^\circ\text{C}$ and stirring for 36 h results in the complete consumption of **3**, the stoichiometric production of $[\text{HN}^i\text{Pr}_2\text{Et}][\text{OTf}]$, and the generation of the phenyl product **5** in high yield ($\sim 90\%$ by ^1H 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 $[\text{Li}][\text{BQA}]$ to $(\text{COD})\text{PtPhCl}$ 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, $3,3'\text{-}^i\text{Pr}_2\text{-BQAH}$ (**6**), proved accessible from a multistep procedure.¹⁰ Lithiation of **6** generated $[\text{Li}][3,3'\text{-}^i\text{Pr}_2\text{-BQA}]$ (**7**), and its subsequent metathesis with $(\text{COD})\text{PtMeCl}$ afforded the benzene-soluble methyl complex $(3,3'\text{-}^i\text{Pr}_2\text{-BQA})\text{PtMe}$ (**8**). Stoichiometric addition of triflic acid to **8** quantitatively produces the triflate complex $(3,3'\text{-}^i\text{Pr}_2\text{-BQA})\text{PtOTf}$ (**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 triflate ligand is positioned trans to the amido N-donor atom of the

$3,3'\text{-}^i\text{Pr}_2\text{-BQA}$ ligand. For comparison, we obtained X-ray data for the corresponding phenyl complex $(3,3'\text{-}^i\text{Pr}_2\text{-BQA})\text{Pt}(\text{Ph})$ (**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 $\text{N}^i\text{Pr}_2\text{Et}$ produced a stoichiometric equivalent of $[\text{HN}^i\text{Pr}_2\text{Et}][\text{OTf}]$. The anticipated phenyl product **10** is formed (ca. 60–65% as determined by ^1H NMR integration).¹¹ While no platinum metal is deposited, nor free BQAH observed, other ligand-containing platinum products are observed by ^1H NMR; their identity has not yet been established. A control experiment established that the independently prepared phenyl complex **10** is stable in benzene with $\text{N}^i\text{Pr}_2\text{Et}$ 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 $[\text{HN}^i\text{Pr}_2\text{Et}][\text{OTf}]$ into C_6D_6 . We found that neither **3** nor **5** catalyzes detectable proton scrambling into deuteriobenzene at $150\text{ }^\circ\text{C}$ over 36 h, even when a 20-fold excess of $[\text{HN}^i\text{Pr}_2\text{Et}][\text{OTf}]$ was used. Apparently, $[\text{HN}^i\text{Pr}_2\text{Et}][\text{OTf}]$ is too weak an acid, at least in benzene solvent, to drive the reverse reaction at an appreciable rate at $150\text{ }^\circ\text{C}$. Use of a much stronger acid, however, drives the reverse process readily. Thus, addition of HOTf to a benzene slurry of **5** generates the triflate complex **3** rapidly and quantitatively at $25\text{ }^\circ\text{C}$ (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 $\text{N}^i\text{Pr}_2\text{Et}$, 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 $150\text{ }^\circ\text{C}$. We have also found that the rate of formation of **5** is not increased by addition of excess $\text{N}^i\text{Pr}_2\text{Et}$ (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

(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 $(3,3'\text{-}^i\text{Pr}_2\text{-BQA})$ system: addition of triflic acid to a benzene solution of **10** rapidly generates **9**.

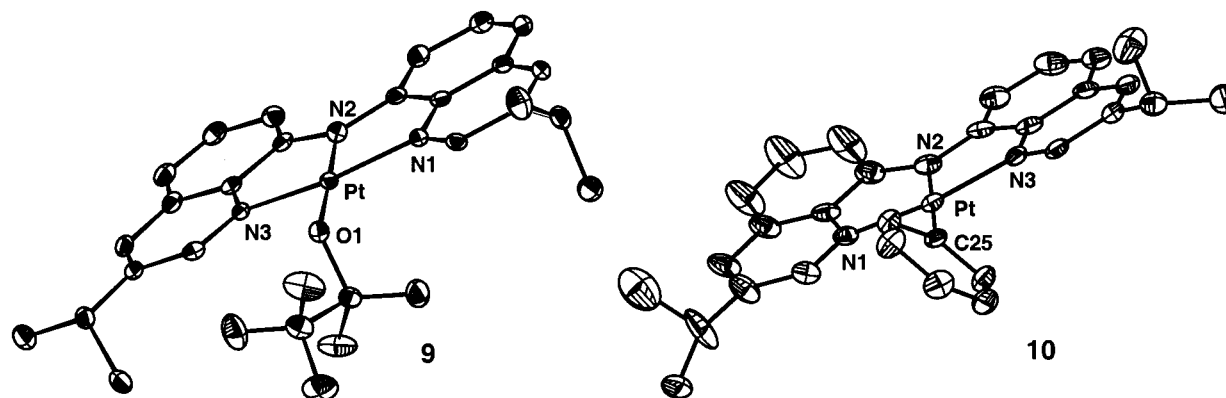
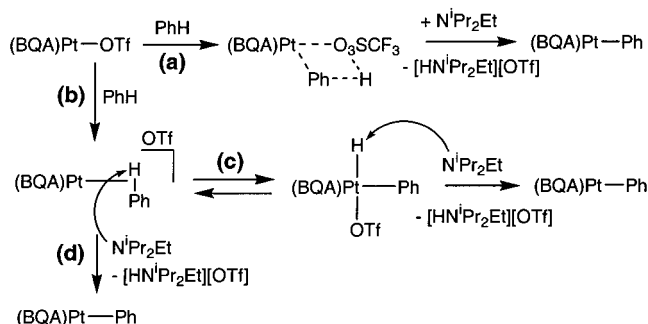


Figure 2. Displacement ellipsoid representations (35%) of complexes **9** and **10**. Selected bond distances (Å) and angles (deg) are as follows. Complex **9**: Pt–N1, 1.994(2); Pt–N2, 1.946(2); Pt–N3, 1.990(2); Pt–O1, 2.097(2); N2–Pt–O1, 179.13(9); N1–Pt–N3, 166.94(10). Complex **10**: Pt–N1, 2.007(3); 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 byprod-

uct. 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(NⁱPr₂Et)](OTf), prior to the reaction with benzene.

(14) We recently suggested a related process in which deprotonation of an sp²-hybridized C–H group of cyclooctadiene occurs on coordination to cationic platinum(II).⁵