Structural Characterization of an Intermediate in Arene C−H Bond Activation and Measurement of the Barrier to C−H Oxidative Addition: A Platinum(II) η^2-Benzene Adduct

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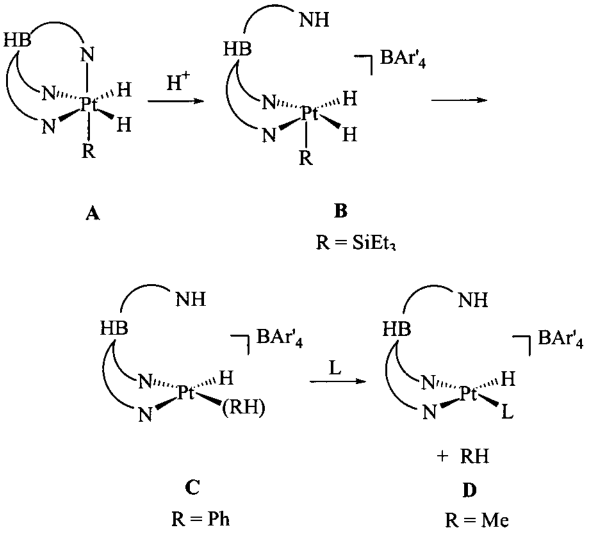
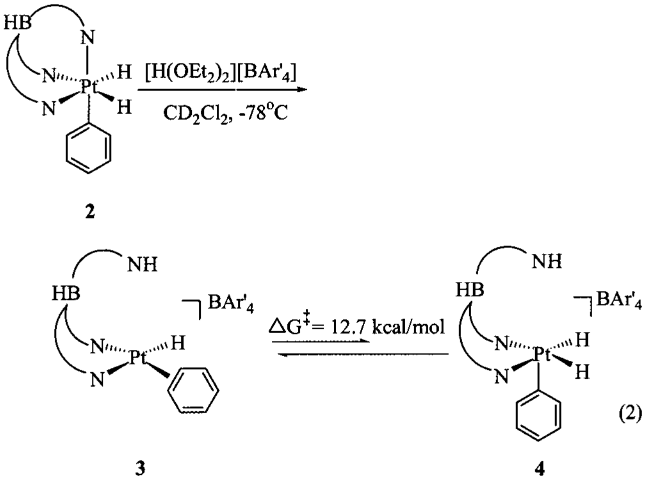
Transition metal arene complexes display multifaceted coordination chemistry,[1] and they are key intermediates in aromatic C−H bond activation.[2,3] Most recently, Johansson, Tilset, Labinger, and Bercaw have detected by NMR spectroscopy a platinum(II) benzene complex, [(diimine)Pt(η^2-C_6H_6)(CH_3)]$^+$ (**1**), a precursor to arene C−H oxidative addition.[4] Given the importance of η^2-arene intermediates in aromatic C−H bond activation at late transition metals in general, and at platinum in particular,[4,5] we now report acid-assisted reductive elimination of benzene from a Pt(IV) phenyl dihydride complex to form a Pt(II) η^2-benzene hydride complex which has been characterized by NMR spectroscopy and by single-crystal X-ray diffraction.[6] Isolation of a ground-state η^2-benzene adduct with an adjacent hydride ligand has allowed us to quantitatively assess the barrier to oxidative addition of a benzene C−H bond to Pt(II) by monitoring exchange of the hydride and arene signals in variable temperature NMR experiments.

Protonation of Pt(IV) complexes of the type TpPt(R)($H)_2$ (**A**) [Tp = hydridotris(pyrazolyl)borate; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate;[7] R = alkyl, aryl, or silyl[8]] initiates a cascade of reactions **A**→**B**→**C**→**D** as shown in eq 1. Protonation of Tp′Pt($SiEt_3$)($H)_2$ leads to an isolable five-coordinate cationic silyl dihydride Pt(IV) complex, [κ^2-(HTp′)Pt($H)_2$($SiEt_3$)][BAr'_4] (intermediate **B** in eq 1) [BAr'_4 = tetrakis(3,5-trifluromethylphenyl)borate], which has been structurally characterized.[9] Protonation at a pyrazole nitrogen atom promotes reductive elimination of methane from Tp′PtMe($H)_2$, and ultimately leads to isolable cationic Pt(II) hydride complexes of the type [κ^2-(HTp′)Pt(H)(L)][BAr'_4] (**D**) after addition of a trapping ligand, L (intermediates **B** and **C** are not observed).[8g] For R = aryl, we show here that it is possible to isolate the putative Pt(II) (RH) adduct (**C**) prior to ligand exchange.



(1)

Protonation of Tp′Pt(C_6H_5)($H)_2$ (**2**)[10] with [H($OEt_2)_2$][BAr'_4][11] in CD_2Cl_2 at −78 °C yields a single chiral compound (eq 2).[12]



(2)

No free benzene is observed. A resonance at 11.67 ppm in the

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^{1}H NMR spectrum is assigned to the protonated pyrazole ring.[8f,9,13] The lone platinum-bound hydride resonates unusually far upfield at −30.13 ppm (1H, $^1J_{\mathrm{Pt-H}} = 935$ Hz), and a singlet in the aromatic region at 6.88 ppm, which integrates for six protons, indicates that a cationic benzene adduct, [κ^2-(HTp′)Pt(H)(η^2-C_6H_6)][BAr′$_4$] (**3**), has formed. Only one ^{13}C resonance at 115.3 ppm is observed for the six-ring carbon atoms at −78 °C. Complex **3** slowly undergoes loss of benzene and forms a dicationic hydride-bridged platinum dimer[8g] in CH_2Cl_2 solution at 273 K.

If benzene is added to an NMR sample of complex **3** at 193 K, distinct resonances are observed for free (7.33 ppm) and platinum-coordinated benzene (6.95 ppm), indicating that benzene exchange does not occur on the NMR time scale. As the probe temperature is raised to 252 K, both the platinum-bound benzene and hydride resonances broaden significantly, suggesting that hydrogen exchange is occurring between these positions. The signal for free benzene remains sharp. Using the slow exchange approximation at 252 K, a first-order rate constant of $k = 47$ s^{-1} was determined via line broadening of the hydride resonance, corresponding to a barrier ($\Delta G^{\ddagger}$) for hydrogen exchange of 12.7 kcal/mol. As expected, line broadening of the bound benzene resonance is approximately one-sixth that of the hydride resonance. Hydrogen exchange between the bound benzene and hydride positions is also evident from a spin saturation transfer experiment: irradiating the coordinated benzene resonance at 6.95 ppm at 243 K leads to almost complete disappearance of the hydride resonance. We postulate that the five-coordinate Pt(IV) aryl dihydride intermediate **4** is accessible via oxidative addition from the Pt(II) benzene adduct **3**, but the Pt(II) benzene structure is the ground state (eq 2). This result complements protonation studies involving Pt(IV) silyl complexes, where the five-coordinate Pt(IV) structure is the ground state.[9]

In the Cp*Rh(PMe$_3$) system [Cp* = pentamethylcyclopentadienyl], Jones has established that oxidative addition of benzene occurs via an η^2-benzene adduct Cp*(PMe$_3$)Rh(η^2-C_6H_6) (**5**), but the ground state in this case is the Rh(III) phenyl hydride Cp*(PMe$_3$)Rh(H)(C_6H_5) (**6**).[2c−e,14] The barrier for conversion of **5** to **6** is unknown.

A potentially attractive alternative route to benzene adduct **3**, protonation of Tp′Pt(CH_3)(H)$_2$ and subsequent addition of excess benzene, does not yield the desired product. Note that the Pt(II) benzene adduct **1** was also generated by protonation of a Pt(II) phenyl complex, and *not* by addition of benzene to a Pt(II) solvent species.[4] Addition of 5 equiv of deuteriobenzene (C_6D_6) to a solution of **3** at low temperature does not lead to observable exchange of free and coordinated benzene even after 2 days at 243 K.

Colorless crystals of the benzene adduct [κ^2-(HTp′)Pt(H)(η^2-C_6H_6)][BAr′$_4$] (**3**) were obtained in 90% yield by slow diffusion of pentane into a methylene chloride solution. A single crystal was subjected to X-ray structural analysis; an ORTEP diagram is shown in Figure 1. The hydride ligand on platinum was not located in the difference Fourier map, and thus it is placed in a calculated position. The benzene ligand indeed coordinates in η^2-fashion to the square-planar Pt(II) center. The orientation of the plane of the aromatic ring versus the metal plane is almost perpendicular (tilt angle: 82.5°),[6a,15] and the Pt−C distances (2.24 and 2.21 Å) lie in the expected range for this coordination mode.[6] The orientation of the benzene ring is probably responsible for the unusual upfield shift of the hydride resonance in the ^{1}H NMR spectrum of complex **3**: the hydride ligand is placed in the shielded area directly above the aromatic ring.[16]

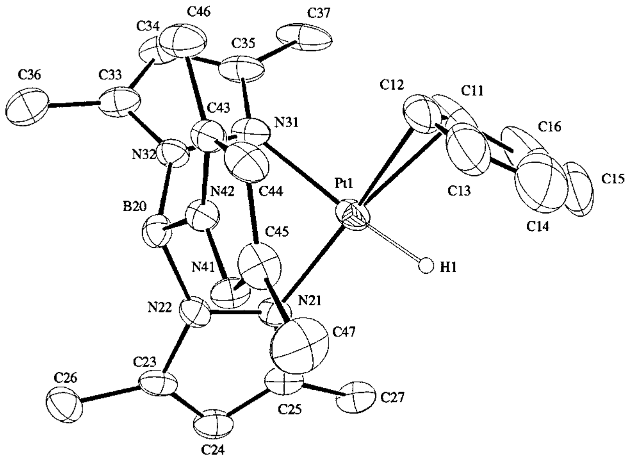

Figure 1. ORTEP diagram of [κ^2-((Hpz*)BHpz*$_2$)Pt(H)(C,C-η^2-C_6H_6)]-[BAr′$_4$] (**3**); ellipsoids are drawn at the 50% probability level, and the BAr′$_4$ counterion is omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex **3**

Pt1−C11	2.241(11)	Pt1−N31	2.171(8)
Pt1−C12	2.214(11)	C11−C12	1.360(24)
Pt1−N21	2.037(6)	C12−C13	1.35(3)
C11−Pt1−C12	35.5(6)	C12−Pt1−N31	94.2(4)
C11−Pt1−N21	167.3(5)	N21−Pt1−N31	87.1(3)
C11−Pt1−N31	99.3(5)	Pt1−C11−C12	71.2(7)
C12−Pt1−N21	155.6(4)	C11−C12−C13	119.7(14)

Isolation and structural characterization of a Pt(II) η^2-benzene complex provide detailed information about an arrested intermediate in aromatic C−H bond activation at platinum. The barrier for the arene C−H oxidative addition reaction which converts a Pt(II) η^2-benzene adduct to a Pt(IV) phenyl hydride complex has been determined and found to be 12.7 kcal/mol.

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Supporting Information Available: Complete synthetic and spectroscopic data (PDF) and crystallographic data, in CIF format, for complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) ^{1}H NMR data for complex **3** (CD_2Cl_2, 193 K, δ): 11.67 (s, 1H, pz*N*H*), 6.88 (s, 6H, PtC$_6$*H*$_6$), 6.26, 5.93, 5.91 (s, 1H each, HTp′C*H*), 2.32, 2.31, 2.27, 1.86, 1.59 (s, 6H, 3H, 3H, 3H, 3H, HTp′C*H*$_3$), −30.13 (s, 1H, $^1J_{\mathrm{Pt-H}} = 935$ Hz, Pt-*H*).

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(14) For certain substituted arenes, the η^2-arene complexes are the more stable isomers. See refs 2d, f.

(15) Pt(II) ethylene complexes also show perpendicular orientation of the ethylene ligand with respect to the platinum square plane, see, e.g.: (a) ref 8f, (b) Baar, C. R.; Jenkins, H. A.; Yap, G. P. A., Puddephatt, R. J. *Organometallics* **1998**, *17*, 4330. (c) Jarvis, J. A. J.; Kilbourn, B. T.; Owston, P. G. *Acta Crystallogr.* **1971**, *B27*, 366.

(16) Bercaw et al. propose a similar benzene orientation to account for the unusual upfield ^{1}H chemical shift of the methyl group in complex **1**.[4]