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C−H Activation by a Diplatinum(II) Complex: Isolation and Structures of [$Pt_2(CH_3)(SMe_2)Ph_2$(ttab)][BAr'_4] and [$Pt_2(H_2O)_2Ph_2$(ttab)][BAr'_4]$_2$ (ttab = 1,2,4,5-Tetrakis(1-*N*-7-azaindolyl)benzene)

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*Summary: The dinuclear Pt(II) complex $Pt_2(CH_3)_4$(ttab) (**1**; ttab = 1,2,4,5-tetrakis(1-N-7-azaindolyl)benzene) has been found to activate multiple benzene molecules by cleaving a C−H bond in the presence of [$H(Et_2O)_2$][BAr'_4] (Ar′ = 3,5-bis(trifluoromethyl)phenyl). The unprecedented dinuclear Pt(II) product [$Pt_2(CH_3)(SMe_2)Ph_2$(ttab)][BAr'_4] (**2**), which contains two phenyl groups on one Pt(II) center, has been isolated from the 1:1 reaction of **1** with [$H(Et_2O)_2$][BAr'_4]. The novel dinuclear Pt(II) complex [$Pt_2(H_2O)_2Ph_2$(ttab)][BAr'_4]$_2$ (**3**) has been isolated from the 1:2 reaction of **1** with [$H(Et_2O)_2$][BAr'_4] when reagent-grade solvents were used in the recrystallization process. The structures of **2** and **3** have been established by X-ray diffraction analyses.*

Cationic Pt(II) complexes have been demonstrated to be capable of activating C−H bonds under mild conditions.[1] Most previously reported systems, however, involve mononuclear Pt(II) complexes. In benzene C−H activation using the dimethyldiimine Pt(II) complex $PtL(CH_3)_2$ (L = N,N′-chelate ligand) as the starting material and in the presence of an acid, the net result is the isolation of the cationic product $[Pt^{II}(L)(L')Ph]^+$, where L′ is either a solvent molecule or a neutral donor ligand such as ether or SMe_2. Previous mechanistic studies established that the cationic $[Pt^{II}(L)(L')Ph]^+$ compound can undergo oxidative addition by a second benzene to form $[Pt^{IV}(L)(L')Ph_2(H)]^+$, which usually reproduces $[Pt^{II}(L)(L')Ph]^+$ via reductive elimination of benzene. As a consequence, species such as $[Pt^{II}(L)Ph_2]$ resulting directly from benzene activation by using mononuclear Pt(II) complexes have not been reported previously. In fact, the previously well-established mechanism on cationic mononuclear Pt(II) systems[1] implies that it is not possible to obtain species such as $[Pt^{II}(L)Ph_2]$ unless ligand redistribution occurs. In addition, a mononuclear cationic species such as $[Pt^{II}(L)(L')Ph]^+$ is relatively difficult to oxidize due to the positive charge, a key step proposed for catalytic functionalization of hydrocarbons via C−H activation by cationic Pt(II) compounds.[1] These limitations of using cationic mononuclear Pt(II) complexes in catalytic C−H activation could be overcome, however, if an appropriate multinuclear Pt(II) complex is used in the C−H activation process. As the first step in establishing an appropriate dinuclear Pt(II) system for C−H activation, we investigated the utility of the dinuclear Pt(II) complex $Pt_2(CH_3)_4$(ttab) (**1**; ttab = 1,2,4,5-tetrakis(1-*N*-7-azaindolyl)benzene), reported[2] recently by our group, in C−H activation. The coordination environment of the Pt(II) center in **1** resembles those of previously known mononuclear dialkyldiimine Pt(II) complexes used for C−H activation. In addition, compound **1** is known to readily cleave C−Cl bonds facilitated by the two Pt(II) centers and the central phenyl ring of the ttab ligand to form the unusual dinuclear Pt^{IV} species $Pt_2(CH_3)_4$(ttab)Cl_2 (**1a**), where the central benzene ring of the ttab ligand is transformed into a cyclohexadienyl dianion.[2] Therefore, we anticipated that **1** could be useful for C−H activation in addition to C−Cl bond cleavage. Our preliminary investigation on the reactions of compound **1** with benzene revealed that **1** is indeed capable of activating C−H bonds in benzene and the isolated products display some surprising features. Our preliminary findings are reported herein.

Compound **1** is insoluble in benzene. Upon the addition of 1 equiv of [$H(Et_2O)_2$][BAr'_4] (Ar′ = 3,5-bis(trifluoromethyl)phenyl)[3] at ambient temperature to the benzene suspension of **1**, the solid of **1** gradually disappeared over a period of ∼1 h. The subsequent addition of excess SMe_2 resulted in the isolation of [$Pt_2(CH_3)(SMe_2)Ph_2$(ttab)][BAr'_4] (**2**) as a crystalline material in ∼34% yield. In addition to **2**, an NMR study of the reaction mixture revealed that multiple products are present. Due to the complexity of the NMR spectra, it is not possible to identify all products using NMR. Attempts to isolate other products were not successful. The structure of **2** was determined by single-crystal X-ray diffraction analysis[4] and is shown in Figure 1. Each Pt center in **2** has a typical square-planar coordination geometry with typical bond lengths and angles.[5] The Pt−Pt separation distance in **2** is 7.049(2) Å, similar to that of **1**. The central benzene ring is in close contact

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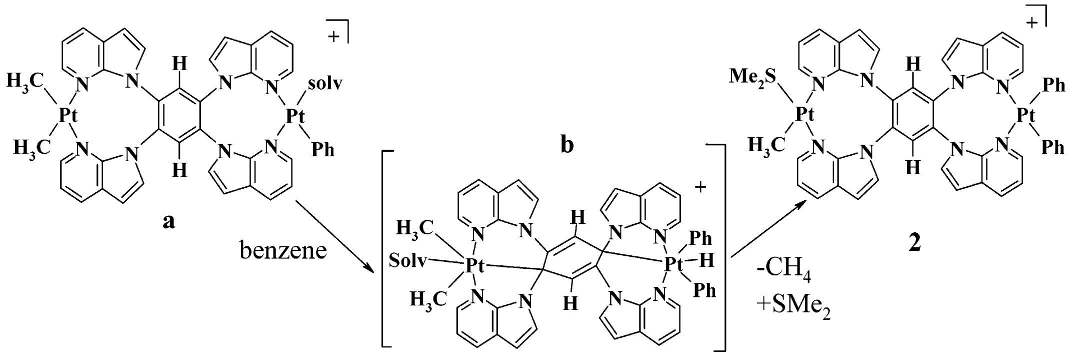
Scheme 1



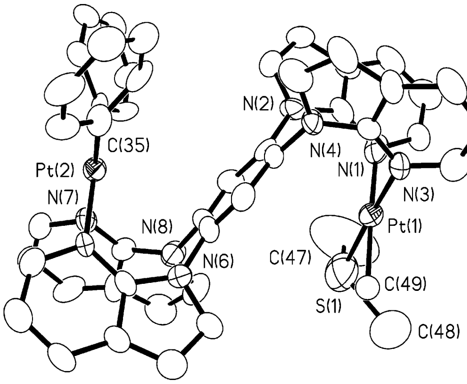


Figure 1. Structure of the cation in **2**. For clarity, hydrogen atoms are omitted and all carbon atoms are shown as ideal spheres. Important bond lengths (Å) and angles (deg): Pt(1)−C(49) = 2.041(10), Pt(1)−N(3) = 2.056(11), Pt(1)−N(1) = 2.080(13), Pt(2)−C(41) = 1.959(14), Pt(2)−C(35) = 1.993(13), Pt(2)−N(7) = 2.120(10), Pt(2)−N(5) = 2.125(11); C(49)−Pt(1)−N(1) = 174.8(4), N(3)−Pt(1)−S(1) = 171.0(4), C(35)−Pt(2)−N(7) = 175.6(6), C(41)−Pt(2)−N(5) = 174.8(4).

with the two Pt(II) centers in the same manner as that observed in **1**, with the shortest Pt−C separation distance being 3.11(1) Å. One surprising feature of **2** is that one of the Pt(II) centers in the complex is bound by two phenyl ligands, while the remaining Pt(II) center is coordinated by one methyl group and a SMe$_2$ ligand. Clearly the previously established mechanism for mononuclear Pt(II) complexes cannot explain the formation of compound **2**. If, however, we allow the involvement of the dinuclear Pt(IV) species **b** as an intermediate in the reaction, the formation of compound **2** could be explained by Scheme 1. The formation of **a** in Scheme 1 (where the coordinated solvent could be either diethyl ether from the starting material [H(Et$_2$O)$_2$][BAr′$_4$] or benzene[1]) could be explained by the established mechanism for mononuclear Pt(II) compounds. Oxidative addition by the second benzene on the same cationic Pt(II) center may lead to the formation of the intermediate **b**. Intermolecular reductive elimination[6] of a CH$_4$ molecule from **b**, the restoration of the central phenyl ring by giving up 2e$^-$ to the two Pt(IV) centers, and the subsequent addition of SMe$_2$ likely lead to the formation of the final product **2**. The proposed structure of **b** is based on the previously reported structure of Pt$_2$(CH$_3$)$_4$(ttab)Cl$_2$ (**1a**), obtained via an overall 2e$^-$ oxidation process of **1** by C−Cl bonds. Although we have not been able to isolate the proposed intermediate **b**, ^{1}H NMR spectra for the reaction mixture consistently showed a chemical shift at ∼6.3 ppm that has a distinct $^4J_{\mathrm{Pt-H}}$ and $^3J_{\mathrm{Pt-H}}$ satellite pattern similar to that[2] of the 1,4-cyclohexadienyl dianion protons in **1a** (see the Supporting Information). The formation of **b** may be facilitated by the short contact distance between the Pt center and the carbon atoms of the central phenyl ring, as observed in **1**. Other processes such as intermolecular ligand redistribution could also account for the formation of **2**. Mass spectroscopic study using ESI-TOF methods (see the Supporting Information)[7] on the reaction mixture of **1** with [H(Et$_2$O)$_2$][BAr′$_4$] in a 1:1 ratio in benzene revealed the presence of other unusual species in the reaction mixture such as [Pt$_2$(ttab)Ph$_3$]$^+$, which further confirmed the complexity and the unusual reactivity of benzene C−H bond activation using the dinuclear Pt$^{\mathrm{II}}$ compound **1**.

When compound **1** was reacted with 2 equiv of [H(Et$_2$O)$_2$][BAr′$_4$] under the same conditions as described for the 1:1 reaction above, multiple products with complex NMR spectra were again observed. In our repeated attempts to isolate crystalline products so that their structures can be conclusively established by X-ray diffraction analyses, various solvent combinations (THF/hexanes, THF/hexanes/SMe$_2$, THF/benzene, THF/benzene/SMe$_2$) and conditions were used in the crystallization process. None of them, however, led to the isolation of a single crystalline compound. The only successful isolation of the crystalline compound [Pt$_2$(H$_2$O)$_2$Ph$_2$(ttab)][BAr′$_4$]$_2$ (**3**) was achieved when the product mixture was dissolved in a reagent-grade THF solvent and this solution was layered with hexane and kept in the air for a few days. The structure of **3** was established by single-crystal X-ray diffraction analysis[4] and is shown in Figure 2. The two cationic Pt(II) centers

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(4) Single crystals of **2** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexanes into its benzene solution, while crystals of **3** were obtained by slow diffusion of hexanes into its THF solution. Data were collected on a Bruker P4 diffractometer with a CCD-1000 detector at ambient temperature. Crystal data for **2**: $C_{17}H_{18}N_4Pt$, triclinic, $P\bar{1}$, $a = 12.252(4)$ Å, $b = 15.023(6)$ Å, $c = 26.440(10)$ Å, $\alpha = 78.814(8)°$, $\beta = 84.714(10)°$, $\gamma = 85.588(9)°$, $V = 4745(3)$ Å^3, $Z = 2$, $R_1 = 0.0211$ ($I > 2\sigma(I)$), GOF = 0.982. Crystal data for **3**: $C_{110}H_{60}B_2F_{48}N_8O_2Pt_2\cdot 4.6THF$, triclinic, $P\bar{1}$, $a = 13.353(5)$ Å, $b = 17.132(6)$ Å, $c = 18.147(7)$ Å, $\alpha = 114.760(8)°$, $\beta = 94.074(10)°$, $\gamma = 100.832(7)°$, $V = 3650(2)$ Å^3, $Z = 1$, $R_1 = 0.0770$ ($I > 2\sigma(I)$), GOF = 0.788.

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(6) Intermolecular reductive elimination of CH$_4$ has been proposed by the Wayland group: (a) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 1259. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305.

(7) The ESI-TOF experiment was carried out on a Mariner Biospectrometry Workstation using CH$_3$NO$_2$ as the solvent. For details see the Supporting Information.

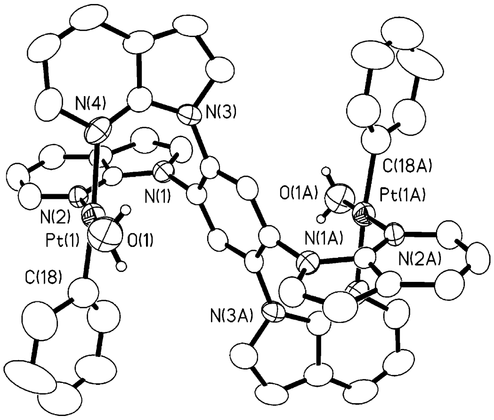

Figure 2. Structure of the cation in **3**. Hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): Pt(1)−C(18) = 1.993(13), Pt(1)−N(2) = 2.036(8), Pt(1)−O(1) = 2.098(8), Pt(1)−N(4) = 2.170(9); N(2)−Pt(1)−O(1) = 175.5(3), C(18)−Pt(1)−N(4) = 175.4(5).

in **3** are related by an inversion center of symmetry, each of which is coordinated by an H_2O and a phenyl group in a cis manner. In the crystal lattice, each of the coordinating H_2O molecules is hydrogen-bonded to two THF solvent molecules. The H_2O molecules are clearly from the nonpurified solvents THF and hexanes. Repeated attempts to isolate the SMe_2 analogue of **3** were unsuccessful. Compound **2** was also isolated as a trace product from the same recrystallization process. Compound **3** could be considered as the "normal" product, consistent with the use of 2 equiv of acid.

Numerous attempts to follow the reaction kinetics by NMR methods did not produce any meaningful results, due to mostly the presence of multiple products, the poor solubility of compound **1** in common and nonreacting organic solvents,[8] and the complexity[8] of the ^{1}H NMR spectra of the products such as **2** and **3**. Despite the lack of a complete understanding of the reaction mechanism, the results of our preliminary investigation have established that the dinuclear Pt(II) compound **1** appears to display unusual reactivity toward benzene[9] and has the potential for use in catalytic C−H activation. Further investigations on this complex and the intriguing diplatinum system in C−H activation are being conducted in our laboratory.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council for financial support.

Supporting Information Available: Tables giving crystal data for compounds **2** and **3**, text giving synthetic procedures and analytical data, and figures giving complete structural drawings for **2** and **3**, mass spectroscopic data, and a ^{1}H NMR spectrum showing the aromatic region for the reaction mixture of **1** with 2 equiv of acid. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) **1** is only sparingly soluble in THF or benzene and reacts with chlorinated solvents rapidly. In compound **2**, none of the four 7-azaindolyl groups have the same environment. The anti structure of **3** shown in Figure 2 has two different 7-azaindolyl groups. In solution, **3** appears to exist in both syn and anti forms with respect to the relative location of the methyl (or H_2O) groups. These facts, along with the presence of phenyl groups, make the aromatic region of the ^{1}H NMR spectra very complex, and it is impossible to assign chemical shifts.

(9) We have recently completed the investigation on benzene C−H activation using a mononuclear analogue of **1**, $Pt(CH_3)_2$(1,2-bis(7-azaindolyl)benzene), and the same reaction conditions as for **2**. Only the single phenyl coordinated compound {Pt(1,2-bis(7-azaindolyl)Ph-(SMe_2))}[BAr′$_4$] was isolated. No evidence of double benzene activation was observed. The details will be reported in due course.