Benzene C−H Activation by Two Isomeric Platinum(II) Complexes of Bis(*N*-7-azaindolyl)methane

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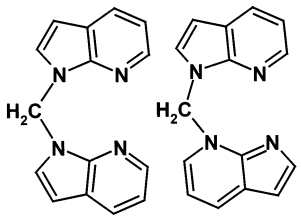
*Summary: Two isomeric Pt(II) complexes, Pt(L1)(CH$_3$)$_2$ (**1a**) and Pt(L2)(CH$_3$)$_2$ (**2a**), based on two isomeric and fluorescent ligands of bis(N-7-azaindolyl)methane, **L1** (symmetric) and **L2** (asymmetric), have been synthesized and fully characterized by NMR and X-ray diffraction analyses. In the presence of [H(Et$_2$O)$_2$][BAr′$_4$] (Ar′ = 3,5-bis(trifluoromethyl)phenyl), both **1a** and **2a** are capable of activating a benzene C−H bond readily at ambient temperature. The products from benzene activation by **1a** and **2a** have been isolated as [Pt(L1)Ph(SMe$_2$)][BAr′$_4$] (**1b**) and [Pt(L2)Ph(SMe$_2$)][BAr′$_4$] (**2b**). The structures of **1b** and **2b** have been determined by X-ray diffraction analyses. The phenyl ligand in **2b** is bound exclusively trans to the pyrrole nitrogen atom of **L2**.*

Since Shilov and co-workers[1] demonstrated the catalytic oxidation of CH_4 into CH_3OH and CH_3Cl, using a Pt(II) salt as a catalyst and stoichiometric amount of Pt(IV) species as an oxidant in an aqueous system, the direct and selective functionalization of hydrocarbons by late transition metal complexes under mild conditions has attracted much research efforts[2] due to their potential applications on the utilization of hydrocarbon resources from natural gas or petroleum. Some recent advances[3] toward this ultimate goal have been demonstrated in processes related to the Shilov system.

Recently, Labinger, Bercaw, Tilset, and other groups[4] have demonstrated that cationic organoplatinum complexes can activate both arene and alkane C−H bonds under relatively mild conditions. Extensive studies have been carried out on the mechanism of C−H activation by cationic Pt(II) complexes[4a−j] to understand the key steps in the catalytic cycle of the Shilov system and to design better and practical catalytic systems. Most previously reported cationic Pt(II) complexes that are capable of activating C−H bonds involve a diimine ligand with the general formula of Ar′N=C(R)C(R)=NAr′ or Ar′N=C(R)CHC(R)=NAr′$^-$. In contrast, the use of cationic Pt(II) complexes containing nitrogen donor atoms that are part of a nitrogen heterocycle in C−H bond activation has hardly been explored.[5] Many nitrogen-containing aromatic heterocyclic ligands are known to be fluorescent. Incorporation of such a ligand to a cationic Pt(II) complex may enable photochemical activation of C−H bonds. Recently we have reported that Pt(II) complexes containing the highly emissive 7-azaindolyl group are capable of facile photochemical activation of C−Cl bonds.[6] Encouraged by this finding, we initiated the investigation on the potential of Pt(II) complexes containing 7-azaindolyl groups in photochemical C−H bond activation. The ligands chosen for our study are two fluorescent isomers of bis(7-azaindolyl)-methane, **L1** and **L2**, reported recently by our group[7]. In addition to being fluorescent, **L1** and **L2** are capable of chelating to a metal center. Furthermore, the isomeric structures of **L1** and **L2** would allow us to study the impact of the subtle electronic difference of the nitrogen donor atoms of these two ligands on C−H bond activation by the corresponding Pt(II) complexes Pt(L1)(CH$_3$)$_2$, **1a**, and Pt(L2)(CH$_3$)$_2$, **2a**.



L1 **L2**

The organoplatinum(II) complexes **1a** and **2a** were obtained in ∼80% yield by the reactions of **L1** and **L2** with Pt$_2$Me$_4$(μ-SMe$_2$)$_2$,[8] respectively. The structures of these two complexes were determined by single-crystal

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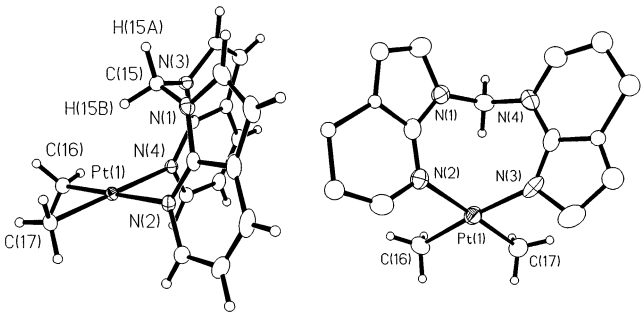
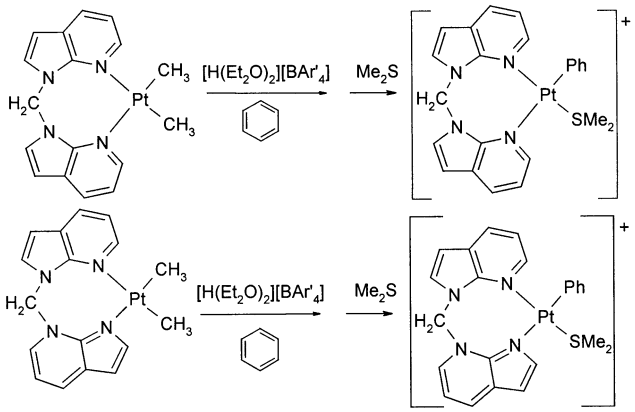


Figure 1. Molecular structures of **1a** (side view, left) and **2a** (top view, right). Due to the disordering of **2a**, only CH_2 protons are shown. For a complete drawing of **2a**, please see the Supporting Information. Selected bond lengths (Å) and angles (deg) for **1a**: Pt(1)−C(17) 2.040(4), Pt(1)−C(16) 2.054(4), Pt(1)−N(4) 2.153(3), Pt(1)−N(2) 2.164(3), C(17)−Pt(1)−N(4) 178.66(14), C(16)−Pt(1)−N(2) 179.12(14); **2a**: Pt(1)−C(17) 2.014(7), Pt(1)−C(16) 2.057(7), Pt(1)−N(3) 2.083(9), Pt(1)−N(2) 2.141(6), C(16)−Pt(1)−N(3), 176.4(3), C(17)−Pt(1)−N(2) 178.9(3).

X-ray diffraction analyses.[9] As shown in Figure 1, the Pt(II) center in both complexes adopts a typical square planar coordination geometry. The ligands **L1** and **L2** are chelated to the Pt(II) center in both complexes. One important feature is that due to the geometric constraint, the methylene group of the diimine ligand in both complexes is situated above the PtN_2C_2 plane with the Pt−C (CH_2) separation distance being 3.172(3) and 3.190(7) Å for **1a** and **2a**, respectively. As a result, the fifth coordination site of the Pt(II) center is partially blocked. The C−H bonds of the methylene group show strong agostic interactions[10] with the Pt(II) center, as supported by the Pt−H contact distances, Pt···H(15B) ≈ 2.44 Å (**1a**), 2.43 Å (**2a**), Pt···H(15A) ≈ 3.99 Å (**1a**), 3.98 Å (**2a**). Agostic interactions involving Pt centers have been observed previously.[10e] These interactions are retained in solution, as shown by the fairly large coupling constants between H(15A), H(15B) and the Pt center in the ^{1}H NMR spectra of **1a** and **2a**.[11]

Our preliminary investigation indicates that compounds **1a** and **2a** are useful starting materials for C−H activations involving aromatic C−H bonds. For example,

Scheme 1



1 h after the mixing of 1 equiv of $[H(Et_2O)_2][BAr'_4]$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl)[12] with the benzene solution of **1a** or **2a** at ambient temperature, the addition of Me_2S to the reaction mixture resulted in the isolation of air- and moisture-stable complex $[Pt(L1)Ph(SMe_2)][BAr'_4]$, **1b**, or $[Pt(L2)Ph(SMe_2)][BAr'_4]$, **2b**, in ∼90% yield (Scheme 1). The phenyl ligand bound to the Pt(II) center in **1b** and **2b** originates from the benzene molecules, a direct evidence of C−H bond activation by the Pt(II) complex. On the basis of the previously established mechanism,[4a−j] we believe that the reactive species of the C−H activation is a cationic Pt(II) complex generated by the protonolysis of **1a** or **2a** and the removal of one of the methyl ligand as methane. The Et_2O molecule provided by $[H(Et_2O)_2][BAr'_4]$ or the benzene solvent molecule likely coordinates to the cationic Pt(II) center to saturate the coordination sphere and generates the active cationic species $[Pt(L1)(CH_3)(S)]^+$ or $[Pt(L2)(CH_3)(S)]^+$, S = Et_2O or benzene, which activates benzene to produce the phenyl group. The subsequent addition of Me_2S results in the replacement of the Et_2O ligand or benzene and the isolation of **1b** or **2b**.

The structures[9] of **1b** and **2b** are established by single-crystal X-ray diffraction analyses. As shown in Figure 2, each Pt(II) center adopts a typical square planar geometry with the sulfur atom of Me_2S and the phenyl ligand *trans* to the two nitrogen atoms of the bidentate ligand, respectively. Again, the methylene group of the chelate ligand in **1b** and **2b** shows strong agostic interactions with the Pt(II) center, similar to those observed in **1a** and **2a**. Complex **2a** has a chiral structure due to the asymmetry of the **L2** ligand. Therefore, during benzene C−H activation, the resulting phenyl group has two choices, *trans* to the pyrrole nitrogen or *trans* to the pyridine nitrogen. Interestingly, however, on the basis of ^{1}H NMR and crystal structural

(9) Single crystals of **1a** and **2a** suitable for X-ray diffraction analysis were obtained from their diethyl ether solutions, while crystals of **1b** and **2b** were obtained by slow diffusion of hexanes into their benzene solutions. Data were collected on a Bruker P4 diffractometer with a CCD-1000 detector at ambient temperature. **1a**: $C_{17}H_{18}N_4Pt$, triclinic, $P\bar{1}$, a = 7.6028(15) Å, b = 8.2357(17) Å, c = 13.565(3) Å, α = 77.821(3)°, β = 76.805(3)°, γ = 79.261(4)°, V = 799.8(3) Å^3, Z = 2, R_1 = 0.0211 [$I > 2\sigma(I)$], GOF = 0.982; **2a**: $C_{17}H_{18}N_4Pt$, monoclinic, $P2_1/n$, a = 10.975(4) Å, b = 9.248(4) Å, c = 15.459(6) Å, α = 90°, β = 96.487(9)°, γ = 90°, V = 1558.9(11) Å^3, Z = 4, R_1 = 0.0416 [$I > 2\sigma(I)$], GOF = 0.802; **1b**: $C_{55}H_{35}BF_{24}N_4PtS$, triclinic, $P\bar{1}$, a = 10.772(7) Å, b = 16.044(10) Å, c = 17.578(11) Å, α = 84.698(12)°, β = 75.467(10)°, γ = 88.044(13)°, V = 2928(3) Å^3, Z = 2, R_1 = 0.0704 [$I > 2\sigma(I)$], GOF = 0.983; **2b**: $C_{55}H_{35}BF_{24}N_4PtS$, triclinic, $P\bar{1}$, a = 12.766(5) Å, b = 15.833(6) Å, c = 16.370(6) Å, α = 105.541(8)°, β = 108.804(9)°, γ = 96.231(9)°, V = 2947.9(19) Å^3, Z = 2, R_1 = 0.0408 [$I > 2\sigma(I)$], GOF = 0.865.

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(11) The two protons of the bridging CH_2 group are not identical. H(15B) has a chemical shift at ∼12 ppm and H(15A) at ∼6.3 ppm (see Supporting Information). ^{1}H NMR spectra of **1a** and **2a** taken in $CDCl_3$ or CD_2Cl_2 show Pt−H coupling of both protons with J_{Pt-H} = 13.7 and 11.4 Hz, respectively. The spectra taken in THF-d_8 showed broad and unresolved satellite peaks.

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(13) Two independent trials of the activation reaction with **2a** were set up at ambient temperature, one in the dark and the other under ambient light. After 30 min of mixing $[H(Et_2O)_2][BAr'_4]$ with **2a** in benzene at ambient temperature, excess Me_2S was added to the system to stop the reaction. The ^{1}H NMR spectra of the resulting reaction mixtures do not show a significant difference between the two trials. Me_2S inhibits the C−H activation reaction. For example, if **1a** and $[H(Et_2O)_2][BAr'_4]$ were initially mixed in Me_2S, the subsequent addition of benzene does not result in any activation. Instead, a cationic Pt(II) species $[Pt(L1)(CH_3)(SMe_2)][BAr'_4]$ was isolated, which does not activate benzene C−H bonds at ambient temperature. For details, please see the Supporting Information.

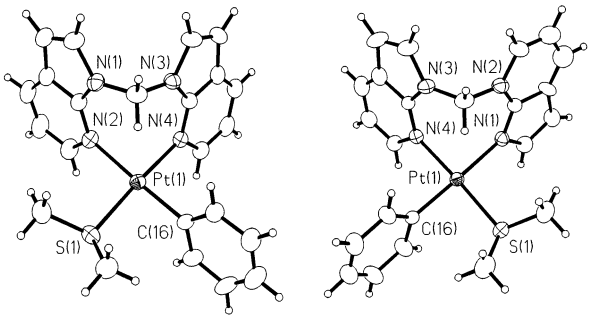

Figure 2. Molecular structures of **1b** (left) and **2b** (right). Selected bond lengths (Å) and angles (deg) for **1b**: Pt(1)−C(16) 2.016(7), Pt(1)−N(4) 2.074(6), Pt(1)−N(2) 2.151(6), Pt(1)−S(1) 2.270(3), C(16)−Pt(1)−N(2) 177.8(2), N(4)−Pt(1)−S(1) 174.33(17); **2b**: Pt(1)−C(16) 2.014(4), Pt(1)−N(4) 2.072(3), Pt(1)−N(1) 2.139(3), Pt(1)−S(1) 2.2752(14), C(16)−Pt(1)−N(1) 178.14(14), N(4)−Pt(1)−S(1) 175.66(10).

data, **2b** is the only product formed from the reaction, where the phenyl group is *trans* to the pyrrole nitrogen. The preferential bonding of the phenyl group opposite the pyrrole nitrogen atom has not been fully understood, but it has some implications on the potential use of **2a** in selective C−H activations of chiral substrates.

Because **L1** and **L2** are very efficient in harvesting photons, we studied the effect of light on benzene C−H activation using **2a**. However, despite our efforts, we did not find any evidence to support that light plays a key role in the C−H activation. Nonetheless, photochemical activation of alkane C−H bonds using **1a** and **2a**, which is being studied in our laboratory, may be viable because alkane C−H activations are in general more difficult to achieve thermally, compared to aromatic C−H activation.

In summary, two new organoplatinum complexes based on novel bis(*N*-7-azaindolyl)methane ligands have been demonstrated to be effective in activating benzene C−H bonds under mild conditions. These new Pt(II) complexes raise several new interesting prospects for C−H activation research. For example, the partial blockage of the Pt(II) fifth coordination site by the CH_2 group and the asymmetric structure of **2a** make these new Pt(II) compounds potentially useful for selective C−H bond activation of arenes. The strong agostic interaction between CH_2 and the Pt(II) center indicates that it may be possible to achieve internal alkane C−H activation by increasing the number of CH_2 units between the 7-azaindolyl units in **L1** and **L2** ligands. The syntheses of such new ligands and the corresponding Pt(II) complexes are being investigated in our laboratory. The use of the new Pt(II) complexes containing 7-azaindolyl donor groups in intermolecular C−H activation of alkanes is being explored, and the results will be reported in due course.

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Supporting Information Available: Detailed experimental procedures and characterization results. Details of crystal structural data, tables of atomic coordinates, complete lists of bond lengths and angles, anisotropic thermal parameters, and hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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