Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
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C-H AND C-Cl ACTIVATION BY MONONUCLEAR AND DINUCLEAR PLATINUM COMPLEXES WITH 7-AZAINDOLYL-CONTAINING CHELATES

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Online publication date: 11 August 2010

To cite this Article SONG, DATONG and WANG, SUNING(2004) 'C-H AND C-Cl ACTIVATION BY MONONUCLEAR AND DINUCLEAR PLATINUM COMPLEXES WITH 7-AZAINDOLYL-CONTAINING CHELATES', Comments on Inorganic Chemistry, 25: 1, 1 — 18
To link to this Article: DOI: 10.1080/02603590490486653
URL: http://dx.doi.org/10.1080/02603590490486653

Comments on Inorganic Chemistry, 25: 1–18, 2004

ISSN: 0260-3594 print
DOI: 10.1080/02603590490486653

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C-H AND C-Cl ACTIVATION BY MONONUCLEAR AND DINUCLEAR PLATINUM COMPLEXES WITH 7-AZAINDOLYL–CONTAINING CHELATES

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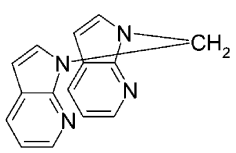
Since Shilov and coworkers[1] demonstrated the catalytic oxidation of CH_4 into CH_3OH and CH_3Cl, using a Pt(II) salt as a catalyst and stoichiometric amount of Pt(IV) species as an oxidant in an aqueous system, the direct and selective functionalization of hydrocarbons by late transition metal complexes has attracted much research effort due to their potential applications on the utilization of hydrocarbon resources from natural gas or petroleum. Much recent work on C-H activations involving Pt metal atoms has been concentrated on cationic mononuclear Pt(II) diimine compounds. This review describes the results from our group on C-H activations using Pt(II) complexes that contain a 7-azaindolyl chelate ligand capable of blocking one binding site of the Pt(II) center. We will focus on a dinuclear Pt(II) compound and its unique reactivity toward C-H bonds. For comparison purposes, related mononuclear Pt(II) compounds and their reactivity toward C-H bonds will also be described. To aid the understanding of the reactivity of the dinuclear Pt(II) compound with C-H bonds, we will also present the results of our investigation on the reaction of the same Pt_2 compound with C-Cl bonds. The potential use of the new Pt(II) compounds, especially the Pt_2 compound in selective C-H activation processes, will be discussed.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support for research activities described in this review.

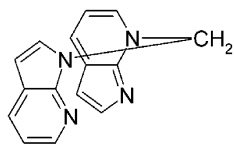
INTRODUCTION

C-H activation and C-X activation by transition metal complexes have been an important and very active research area in inorganic and organometallic chemistry because they allow the direct functionalization of petroleum products. Although many metal complexes are known to be able to activate C-X bonds, most notably Pd complexes,[2] metal complexes that can effectively and catalytically cleave C-H bonds remain rare. Earlier examples on C-H activations involve either late transition metal complexes such as[3–7] $[IrH_2(olefin)_2(PPh_3)_2]^+$, $[IrH_2(O_2CCF_3)(PR_3)_2]$, $Cp^*Ir(CO)_2$ and $Cp^*Rh(PMe_3)(H)_2$ or early transition metal or lanthanide complexes such as[8–9] Cp^*_2YMe or Cp^*_2LnMe. Recently the activation of C-H bonds by cationic Pt(II) complexes has attracted much attention.[10] Extensive mechanistic study of reactions of mononuclear cationic Pt(II) species with C-H bonds has appeared in recent literature. Most previously reported cationic Pt(II) complexes for C-H activation are based on diimine chelate ligands. Our group has recently extended the investigation on C-H activation by cationic Pt(II) complexes to 7-azaindolyl–containing ligand systems. The choice of 7-azaindolyl–containing chelate ligands was mostly based on recent findings[11] by our group that 7-azaindolyl–containing ligands are efficient photoluminescent molecules and are very effective in harvesting photons, hence it may be possible to use this type of ligand to achieve C-H activation photochemically. The results of our investigation indicated that Pt(II) complexes that contain 7-azaindolyl chelate ligands are capable of activating C-H bonds under mild conditions and most of the reactions appear to proceed thermally. Most importantly, we initiated the investigation on using dinuclear Pt(II) complexes for C-H activation. The reactivities displayed by our dinuclear Pt(II) compounds are unique and can only be attributed to the cooperative action of two Pt centers. The cooperative behavior of multiple metal centers can give rise to reaction pathways or products that are impossible or extremely difficult to realize in the mononuclear analogues. In this article, we provide a comprehensive account of the results of our investigation using mononuclear and dinuclear Pt(II) complexes chelated by 7-azaindolyl–containing ligands for C-H activation. The discussion is divided into three sections based on the three types of ligands—BAM, BAB and TTAB—shown below. The choice of these ligands is based on mostly geometric considerations that due to the geometric constraint, these ligands should be able to block one side of the Pt(II) complex, thus

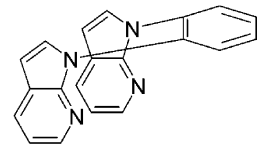
making the C-H activation more selective, compared to the previously reported ligand systems (e.g. Ar'N=C(R)C(R)=NAr' or Ar'N=C(R)CHC(R)=NAr'$^-$).[10] In addition, the blockage of the fifth coordination site of the Pt center may also facilitate the isolation of Pt(IV) hydride intermediates proposed for C-H activation by cationic Pt(II) compounds. For the mononuclear Pt(II) compounds, the discussion will focus on C-H bond activation. For the dinuclear Pt(II) compound, both C-H and C-Cl bond activation reactions will be discussed since there appears to be a common link between these two types of reactions in terms of the dinuclear reaction intermediate involved.



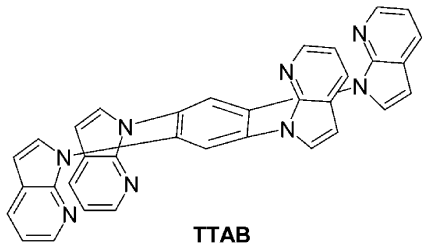
BAM1



BAM2



1,2-BAB



TTAB

C-H ACTIVATION BY Pt(II) BAM COMPLEXES[12]

BAM1 and BAM2 ligands are structural isomers. Their reactions with $Pt_2Me_4(\mu\text{-}SMe_2)_2$ yielded the corresponding $Pt(BAM1)(CH_3)_2$, (**1**) and $Pt(BMA2)(CH_3)_2$, (**2**), respectively. The structures of **1** and **2** are shown in Figure 1. The key feature of these two structures is that due to the geometric constraint, the methylene group of the BAM1 and BAM2 ligands in both complexes is situated above the PtN_2C_2 plane with the Pt-C (CH_2) separation distance being 3.172(3) Å and 3.190(7) Å for **1** and **2**, 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[12] with the Pt(II) center, as supported by the Pt-H

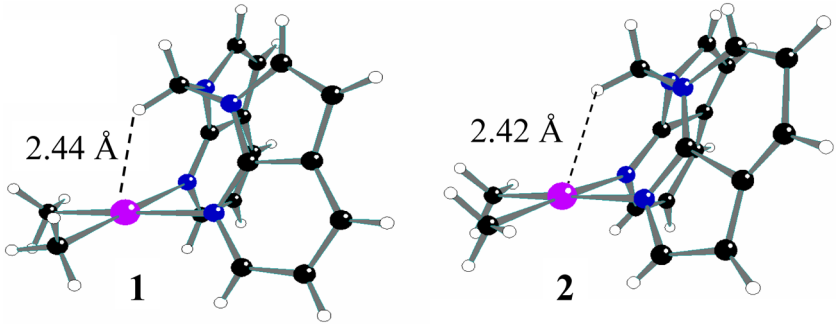


Figure 1.

contact distances. The agostic interactions are apparently retained in solution, as evidenced by the fairly large coupling constants between CH_2 protons and the Pt center in the ^1H NMR spectra of **1** and **2** (Figure 2 shows the two CH_2 protons' coupling pattern in **1**).

Compounds **1** and **2** are capable of cleaving C-H bonds in benzene under mild conditions. The reaction of 1 equiv of $[H(Et_2O)_2][BAr'_4]$ (Ar'=3,5-bis(trifluoromethyl) phenyl) with the benzene solution of **1** or **2** at ambient temperature, followed by the addition of Me_2S resulted in the isolation of air- and moisture-stable complexes [Pt(BAM1)Ph $(SMe_2)][BAr'_4]$, **1a** or [Pt(BAM2)Ph$(SMe_2)][BAr'_4]$ **2a** in nearly quantitative yield (Scheme 1). Based on the previously established mechanism,[10] we believe that the reactive species of the C-H activation is a cationic Pt(II) complex generated by the protonolysis of **1** or **2** and the removal

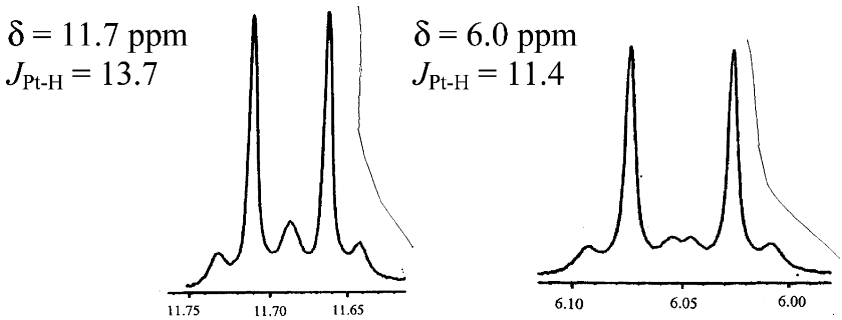
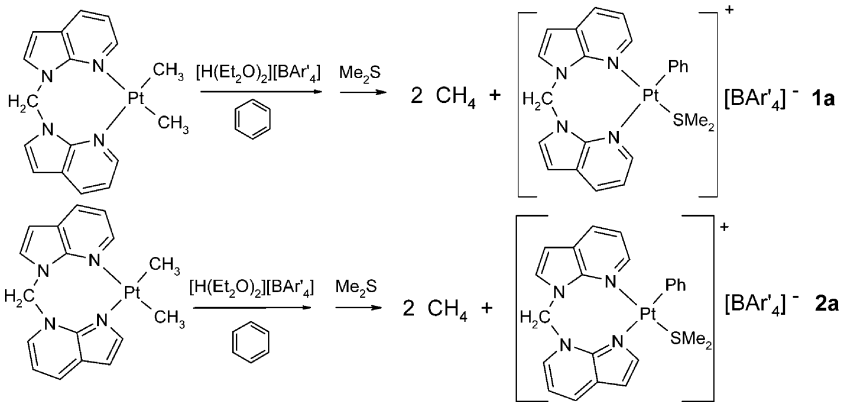


Figure 2.



Scheme 1.

of one of the methyl ligands 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 $[Pt(BAM1)(CH_3)(S)]^+$ or $[Pt(BAM2)(CH_3)(S)]^+$, S=Et_2O or benzene, which activates benzene to produce the phenyl group. The structures[11] of **1a** and **2a** resemble those of the parent molecules **1** and **2**, as shown in Figure 3. The methylene group of the chelate ligand in **1a** and **2a** shows strong agostic

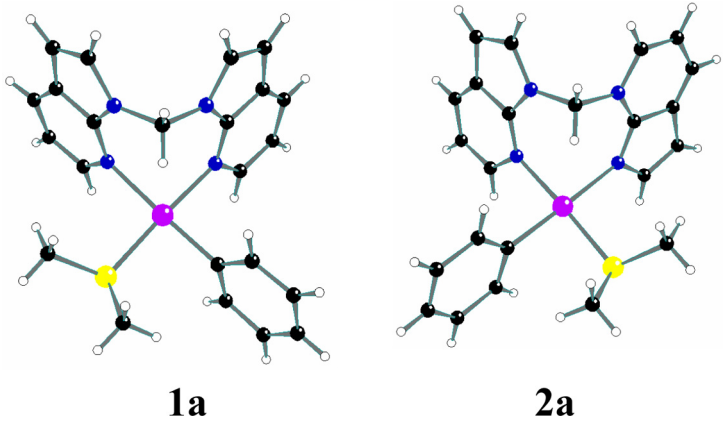


Figure 3.

interactions with the Pt(II) center, similar to those observed in **1** and **2**. Because compound **2** has a chiral structure due to the asymmetry of the BAM2 ligand, 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, based on ^{1}H NMR and crystal structural data, **2a** 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 to the pyrrole nitrogen atom has not been fully understood, but it has some implications on the potential use of **2** in selective C-H activations of chiral substrates.

Although both BAM1 and BAM2 are luminescent, we found no evidence that light played a role in the C-H activation process involving **1** and **2**. The observed C-H activation by **1** and **2** was found to be a thermal process.

C-H ACTIVATION BY[13] Pt(1,2-BAB)$(CH_3)_2$

Our second approach to the design of new Pt(II) complexes for C-H activation was to introduce an aromatic linker for the 7-azaindolyl groups to enhance the steric blockage of the Pt(II) center. For this purpose, ligand 1,2-BAB was synthesized and the Pt(II) complex **3** was obtained readily from the reaction of 1,2-BAB with $Pt_2Me_4(\mu\text{-}SMe_2)_2$. **3** was found to be very effective for C-H cleavage in benzene. The structure of **3** as shown in Figure 4 resembles those of **1** and **2** where the PtC_2N_2 plane is blocked on one side by the phenyl group of the 1,2-BAB ligand. The contact

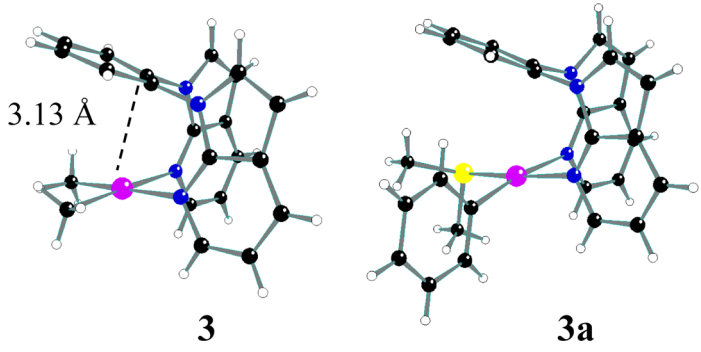
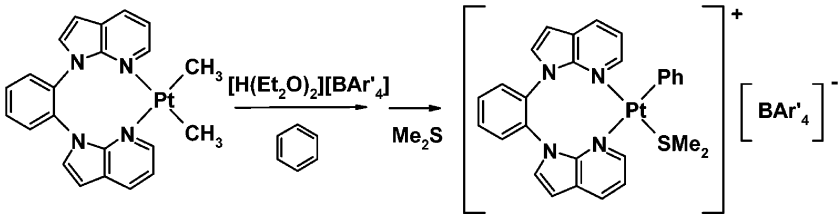


Figure 4.



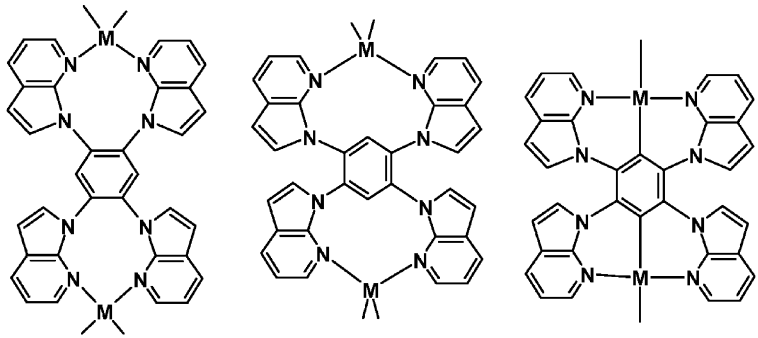
Scheme 2.

distance between the Pt(II) center and the phenyl group of the chelate ligand is ~3.13 Å.

Compound **3** reacts with benzene in the same manner as compounds **1** and **2** do (Scheme 2). At ambient temperature, protonolysis of complex **3** in benzene solution followed by the addition of Me_2S results in the benzene C-H activation product [Pt(1,2-BAB)Ph(SMe_2)][BAr'$_4$], **3a** in a high yield. The structure of **3a** is shown in Figure 4. No cationic Pt(IV) hydride species were isolated from the reaction. Again, the reaction of **3** with benzene was found to be a thermal process. Due to the unique structural features and shapes of molecules **1–3**, we believe that these mononuclear Pt(II) compounds should be able to do selective C-H bond activation for certain substrates. This is yet to be investigated fully by our group.

C-H AND C-CI ACTIVATION BY A DINUCLEAR COMPOUND $Pt_2(TTAB)(CH_3)_4$

To achieve dinuclear Pt(II) compounds that are capable of activating C-H bonds, we designed and synthesized the new ligand[13] 1,2,4,5-tetrakis(7-azaindolyl)benzene (TTAB). The TTAB ligand is an extension of the 1,2-BAB ligand. Based on the ligand geometry, there are three possible chelate modes for TTAB to bind to two metal ions shown as 1,2-chelation, 1,3-chelation and cyclometallation. $ZnCl_2$, $PdCl_2$ and PtR_2 compounds that adopt the 1,2-chelation mode have been observed by our group.[14] The 1,3-chelate mode was only observed for Ag(I) complexes.[14] The third bonding mode where cyclometallation occurs has been observed in 1,3-BAB Pd(II) and Pt(II) complexes,[11b,11d] but not yet for the TTAB ligand.



The reaction of $Pt_2(CH_3)_4(Me_2S)_2$ with the TTAB ligand yielded the 1,2-chelate complex[15] $Pt_2(TTAB)(CH_3)_4$, (**4**) in good yield. As shown in Figure 5, compound **4** possesses an inversion center symmetry. The coordination environment around each Pt(II) center resembles that of **3**. The central benzene ring of the TTAB ligand is situated midway between the two Pt(II) coordination planes with the short contact distance between the carbon atoms of the central phenyl ring and the Pt(II) atom being ~3.11 Å. Compound **4** displays remarkable reactivity towards C-H bonds. To understand the reactivity of **4** with C-H bonds, it is necessary to review the reactivity of **4** with C-Cl bonds.[15]

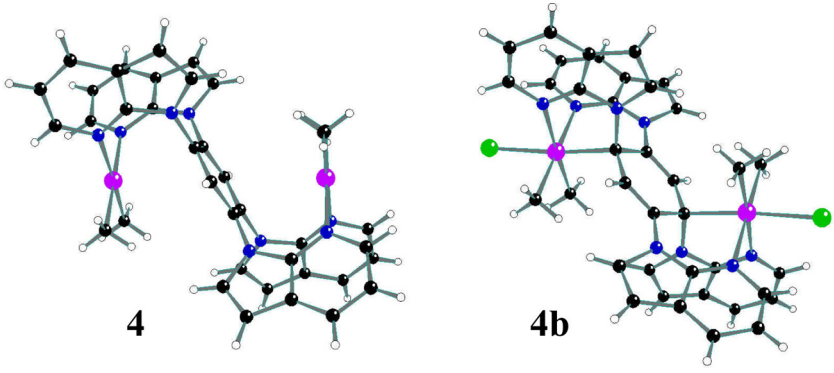
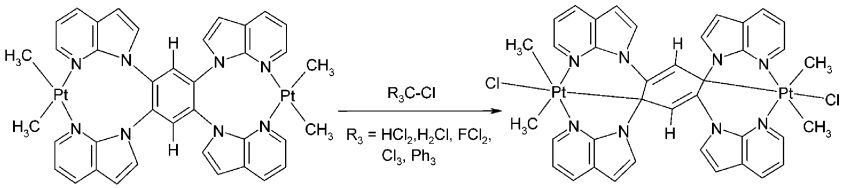


Figure 5.

C-Cl Bond Cleavage by 4

The unusual reactivity of **4** towards C-Cl bond activation was discovered accidentally during the characterization of **4** by NMR spectroscopy, where we found that **4** reacted with $CDCl_3$ instantaneously at room temperature to produce $Pt_2(CH_3)_4(TTAB)Cl_2$, **4b** quantitatively (Scheme 3). It was later observed that many other alkyl chlorides and bromides (e.g., CF_3Cl, CCl_4, CH_2Cl_2, $PhCH_2Cl$, $PhCH_2Br$) reacted with **4** in a similar fashion. By monitoring the reactions of **4** with CH_2Cl_2 by NMR in the dark and exposed to light, we have found that light is critical for the reaction to proceed. If the solution was kept in the dark, no reaction was observed. In contrast, if the solution was carried out under ambient light, the reaction reached completion within 24 hr. Compound **4** has a pale yellow color with two broad absorption bands at $\lambda_{max} = 254$ nm and 286 nm, respectively, which are characteristic of the TTAB ligand. The 286 nm band tails off at $\sim$400 nm. Although the precise nature of photon-initiated reaction of **4** with C-Cl bonds is yet to be determined, we believe that the transformation of **4** to **4b** is a radical process initiated by light.

The structure of **4b** was established by X-ray diffraction analyses.[15] As shown in Figure 5, each Pt center is octahedrally coordinated by two nitrogen donor atoms, two methyl groups that are *trans* to the two nitrogen donor atoms, a chloride and a carbon atom of the central C6 ring, which are *trans* to each other with normal bond lengths. The central C_6 ring retains its planarity as observed in **4**. The geometry around the carbon atom that is bound to the Pt center is close to a typical tetrahedron. The octahedral geometry displayed by the Pt center in **4b** is typical for Pt(IV). Based on the bond lengths and angles and the oxidation state of the Pt centers, we considered the central C_6 ring in **4b** as 1,4-cyclohexadiene dianion. Compound **4b** is remarkably stable under air in solution and the solid state. The well-resolved $^3J_{Pt\text{-}H}$ (22.2 Hz) and



Scheme 3.

$^4J_{Pt\text{-}H}$ (7.5 Hz) coupling pattern of the protons on the central C_6 ring with the two Pt(IV) centers in the ^1H NMR spectrum of **4b** (Figure 6) confirms that the Pt-C (central C_6 ring) bond is retained in solution. The overall conversion of **4** to **4b** is a *two-electron oxidation* process where the chlorinated molecule acts as the oxidant. To convert benzene or substituted benzene to the cyclohexadiene dianion (sometimes called benzene dianions), the conventional method in the literature is to use strong reducing agents such as alkaline metals with the help of crown ether to reduce the benzene ring. The most plausible explanation for the unconventional formation of the $TTAB^{2-}$ ion in **4** under oxidizing conditions is that the two Pt(II) centers in **4** are initially oxidized to Pt(III) ions (metalloradicals) by the chlorinated molecule, which in turn, due to its instability, reduces the central benzene ring by giving up one electron from each Pt(III) center, thus becoming Pt(IV) and converting the benzene ring to the dianion (path a in Scheme 4). An alternative mechanism (path b) is that one Pt(II) center is oxidized initially by one C-Cl bond to become a Pt(III) center, the central phenyl ring then oxidizes both Pt centers to produce a Pt(IV) center and a Pt(III) center, and the latter reacts with

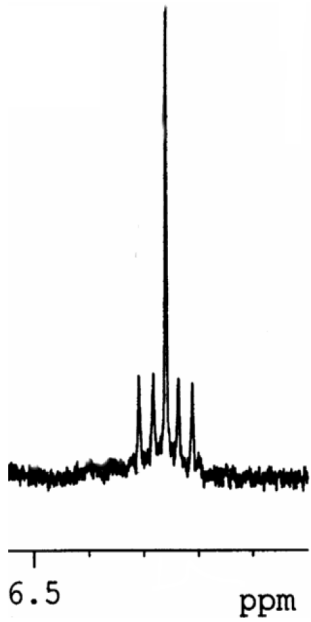
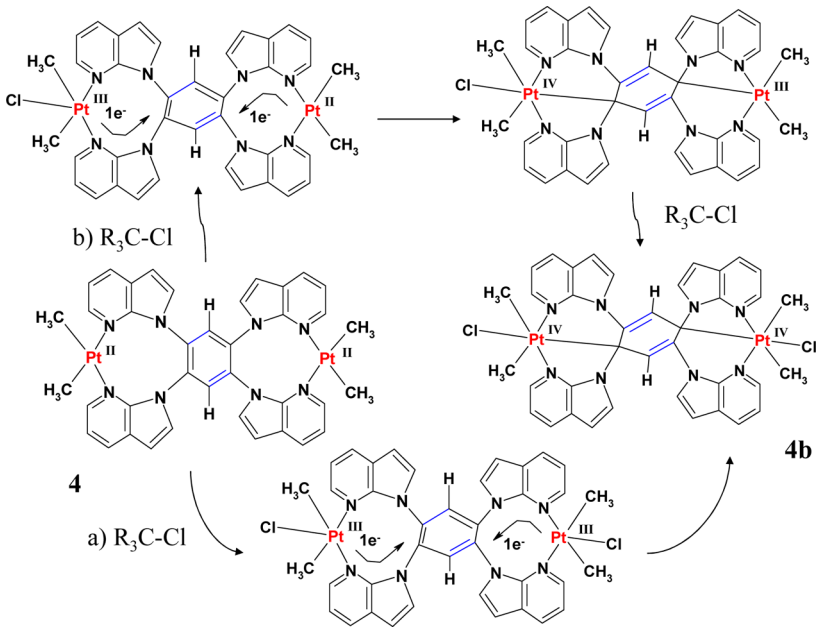


Figure 6.



Scheme 4.

another C-Cl bond to form **4b**. Pt(III) species have been proposed in literature previously as intermediates in oxidative addition reactions of Pt(II) complexes with C-X bonds via radical mechanisms. It has also been well documented previously that when two Pt(II) centers in a dinuclear Pt(II) complex are in close proximity, C-X oxidative additions can lead to the formation of a dinuclear Pt(III) complex or a mixed-valence Pt(III)-Pt(II) complex where the Pt(III) ion is stabilized by the formation of a Pt-Pt bond (or a partial bond). In compound **4b**, instead of the formation of a Pt^{III}-Pt^{III} bond, because of the proximity of the central benzene ring, the electrons are transferred to the benzene ring, resulting in the formation of two Pt-C bonds.

The unusual transformation of **4** to **4b** is clearly facilitated by the geometry of the TTAB ligand that forces the two Pt(II) centers and the central benzene ring to be in close proximity and the joint action of the two Pt centers in **4**.

Puddephatt and coworkers have reported recently their investigation on a diplatinum compound[16] where the Pt centers are linked together by

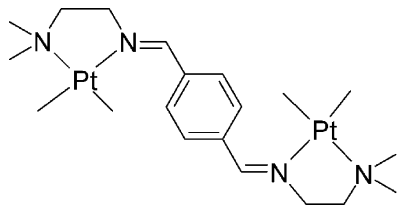


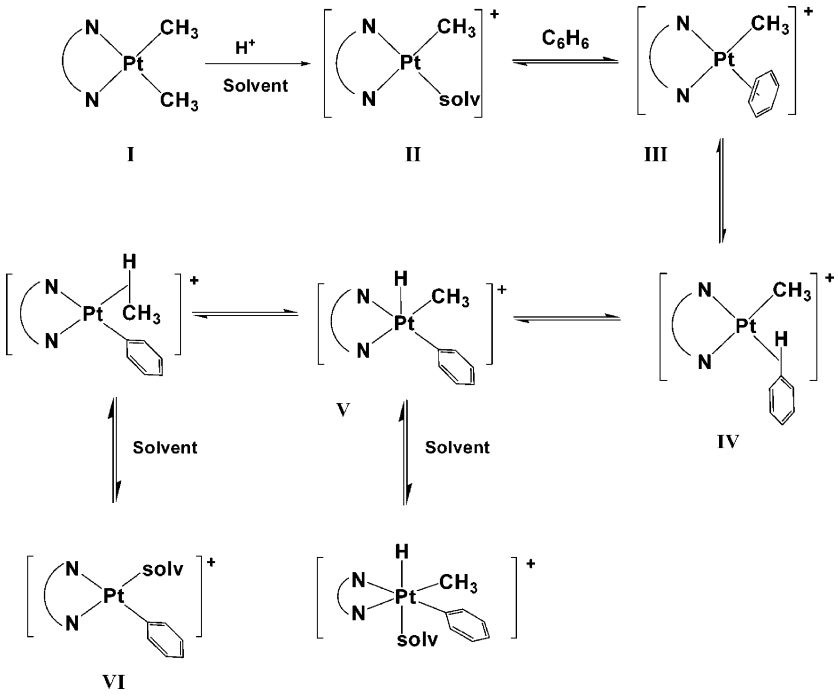
Figure 7.

a relatively flexible ligand and with a much longer Pt-Pt separation distance than that observed in **4** (Figure 7). This diplatinum compound was found not to display any cooperative effects by the two Pt centers in oxidative addition reactions.

C-H Cleavage by 4

The reaction mechanism[10] by mononuclear cationic Pt(II) complexes has been studied extensively and is summarized in Scheme 5, using benzene C-H activation as an example.

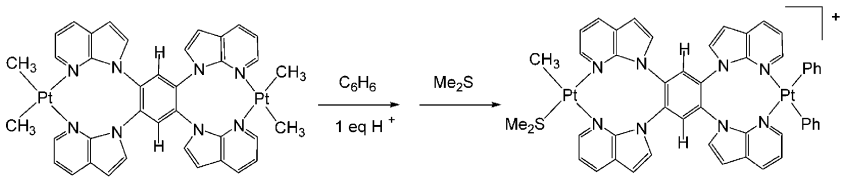
Protonolysis of the Pt(II) dimethyldiimine compund, **I**, generates the active cationic Pt(II) species, **II**, with a weakly coordinating neutral molecule temporarily bonded to the Pt(II) center to saturate the coordination sphere. The neutral solvent molecule in **II** undergoes exchange with a benzene molecule via an associative pathway to form intermediate **III**, in which the benzene molecule functions as a π-donor. The C-H bond of benzene can function as a σ-donor to form a σ-complex, **IV**, which then undergoes oxidative addition to cleave the C-H bond leading to the formation of a cationic Pt(IV) hydride species, **V**. Reductive elimination of a CH_4 molecule from **V** leads to the formation of the product, **VI**, in which a benzene molecule has been activated and converted into a phenyl group bonded to the Pt(II) center. This mechanism indicated that in benzene C-H activation using a mononuclear 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



Scheme 5.

$[Pt^{IV}(L)(L')Ph_2(H)]^+$, 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 implies that it is not possible to obtain species such as $[Pt^{II}(L)Ph_2]$ unless ligand redistribution occurs.

Our investigation on C-H activation by compound **4** revealed some surprising and unique reactivity[17] by the diplatinum system that has no parallel in mononuclear cationic Pt(II) systems. Compound **4** activates benzene readily when treated with $[H(Et_2O)_2][BAr'_4]$ and the products formed are dependent on the stoichiometry of the reactants. The most unusual product $[Pt_2(CH_3)(SMe_2)Ph_2(TTAB)][BAr'_4]$, **4a**, was obtained from the 1:1 reaction of **4** with $[H(Et_2O)_2][BAr'_4]$ in benzene, followed by the addition of Me_2S (Scheme 6). The structure of **4a** is shown in Figure 8. One of the Pt(II) centers in **4a** is bound by two phenyl ligands,



4 **4a**

Scheme 6.

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 **4a**. If, however, we allow the involvement of the dinuclear Pt(IV) species **B** as an intermediate in the reaction, the formation of compound **4a** could be explained by Scheme 7. The formation of **A** in Scheme 7 (where the coordinated solvent could be either diethyl ether from the starting material $[H(Et_2O)_2][BAr'_4]$ or benzene) 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 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 **4a**. The proposed structure of **B** is based on the structure of $Pt_2(CH_3)_4(TTAB)Cl_2$ (**4b**). Although we have not been able to isolate the proposed intermediate **B**, ^1H NMR spectra for the reaction mixture consistently showed a chemical shift at $\sim$6.3 ppm that has a distinct $^4J_{Pt\text{-}H}$ and $^3J_{Pt\text{-}H}$ satellite pattern similar to that of the 1,4-cyclohexadienyl dianion protons in **4b** (Figure 6). 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. Other processes, such as intermolecular ligand redistribution that could also account for the formation of **4a**, cannot be ruled out at this time. Mass spectroscopic study on the reaction mixture of **4** with $[H(Et_2O)_2][BAr'_4]$ in a 1:1 ratio in benzene revealed the presence of other unusual species in the reaction mixture such as $[Pt_2(TTAB)Ph_3]^+$ (**E** in Scheme 7), which further confirmed

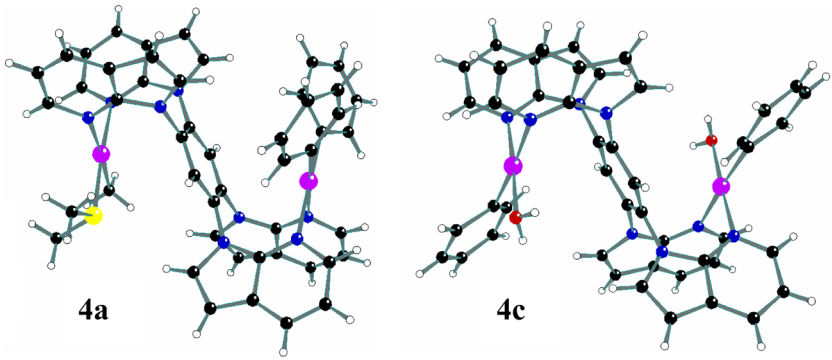
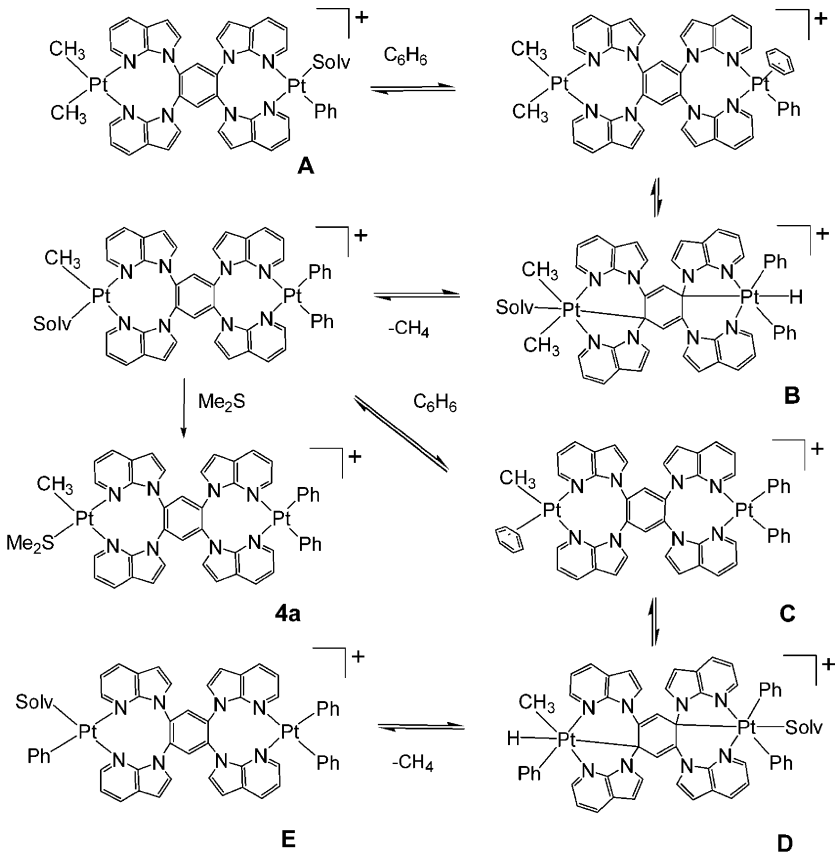


Figure 8.

the complexity and the unusual reactivity of benzene C-H bond activation using the dinuclear Pt^{II} compound **4**.

The coordination environment around the Pt(II) center in **4** resembles that of **3**. The fact[12] that only the "normal" product [Pt(1,2-BAB)-$Ph(SMe_2)$] (**3a**) was observed, but not the diphenyl coordinated product [Pt(1,2-BAB)Ph_2] from the reaction of **3** with $[H(Et_2O)_2][BAr'_4]$ and SMe_2, provides a further support that the cooperative action by the two Pt(II) centers in **4** played an important role in the formation of **4a**.

The 1:2 reaction of **4** with $[H(Et_2O)_2][BAr'_4]$ under the same conditions as described for the 1:1 reaction above yielded multiple products as confirmed by NMR spectra. One of the products, $[Pt_2(H_2O)_2Ph_2$ (TTAB)$][BAr'_4]_2$, **4c**, was isolated as a crystalline product from a reagent-grade THF solvent. The structure of **4c** as established by single-crystal X-ray diffraction analysis[16] is shown in Figure 8. Each Pt(II) center in **4c** is chelated by the TTAB ligand, and coordinated by an H_2O and a phenyl group in a *cis* manner. In the crystal lattice, the coordinated H_2O ligand is hydrogen-bonded to two THF solvent molecules, which perhaps played a key role in promoting the crystallization and isolation of **4c**. It is conceivable that the H_2O ligands in **4c** could be replaced by other ligands such as SMe_2. We have however not been able to isolate these analogues of **4c**. Compound **4c** could be considered as the "normal" product, consistent with the use of 2 equiv of acid and the reaction mechanism proposed for mononuclear Pt(II) compounds (Scheme 5).



Scheme 7.

CONCLUSIONS

7-azaindolyl-containing ligands such as BAM, BAB and TTAB are useful ligands for the formation of mononuclear and dinuclear alkyl Pt(II) complexes that are capable of activating C-H bonds in benzene. These ligands provide steric blockage for the 5th site for the Pt center, thus making them promising for stereo-selective C-H bond activation. In addition, due to their luminescent nature, it may be possible to use these complexes for photochemical C-H bond activation that cannot be achieved under thermal condition. This aspect needs to be examined in future study. In the dinuclear Pt(II) compound, the close proximity between the central

benzene ring and the two Pt(II) centers enables the participation of the central benzene ring in C-H and C-Cl activation process. The role of the central benzene ring of the TTAB ligand could be described as an electron shuffler, enabling reversible electron transfer between the Pt centers and the benzene ring. We believe that the role played by the central benzene ring in **4** is critical and unique in C-H activation. Further detailed mechanistic study on the C-H and C-Cl activation process by **4** will certainly provide valuable information to better understand this complex yet exciting system, which may ultimately lead to the design of better and more efficient systems for catalytic C-H activation. Our group is currently making progress toward this goal.

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