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Steric Impact of Neutral N,N-Chelates on the Structure and Stability of Five-Coordinate Platinum(IV) Complexes: *fac*-$Pt^{IV}Me_3$ Complexes of BAB and BAM

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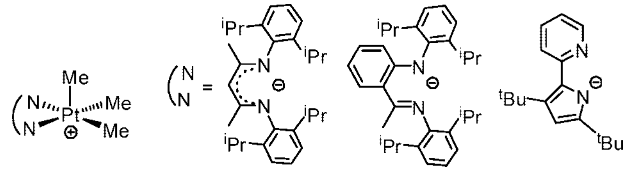
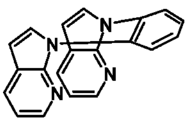
Summary: Two neutral 7-azaindolyl derivative ligands, BAB and BAM, have been found to have a distinct impact on the structure and stability of five-coordinate $Pt^{IV}Me_3$ complexes. A five-coordinate Pt^{IV} complex of BAB and two six-coordinate Pt^{IV} complexes of BAM have been isolated, which display distinct dynamic behavior in solution. The BAM ligand can be converted to an N,C,N-chelate that forms a stable six-coordinate Pt^{IV} complex.

Five-coordinate Pt^{IV} species have been postulated as key intermediates in the Shilov direct methane functionalization processes.[1] Specifically, the involvement of such species has been suggested to be in the C−H activation step via oxidative addition at a Pt^{II} center and in the subsequent reductive coupling step via ligand dissociation at a six-coordinate Pt^{IV} center that leads to the functionalization of the carbon atom. Therefore, the investigation of Pt^{IV} chemistry, particularly that of five-coordinate Pt^{IV} compounds, is important, due to their great mechanistic implications and relevance in Pt^{II}-catalyzed C−H activation/functionalization processes.[2–4] Despite recent advances in Shilov chemistry, five-coordinate organoplatinum(IV) species remain scarce and challenging, due to difficulties in synthesizing and isolating such coordinatively unsaturated species. As a result, only a few examples of five-coordinate organoplatinum(IV) compounds have been reported.[1d,4,5] It is noteworthy, however, that all previously known five-coordinate Pt^{IV} compounds employ anionic N,N-chelating ligands,[4a] as illustrated in Chart 1. Although the steric bulkiness of the N,N-chelate ligand is evidently effective in stabilizing the five-coordinate Pt(IV) center,[4b,c,5] recent work by Goldberg and co-workers seems to indicate that it may not always be necessary in achieving five-coordinate Pt^{IV} compounds.[4a]

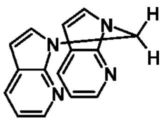
Chart 1



Recently, we developed a series of neutral 7-azaindolyl derivative N,N-chelating ligands (N,N-L) for arene C−H activation using cationic the Pt^{II} complexes $[Pt(CH_3)(N,N-L)(solv)]^+$.[6,7] The precursor complexes $Pt(CH_3)_2(N,N-L)$, where N,N-L = 1,2-bis(*N*-7-azaindolyl)benzene (BAB),[6a,b] bis(*N*-7-azaindolyl)methane (BAM),[6c] 1,2,4,5-tetrakis(*N*-7-azaindolyl)-benzene (TTAB),[7] displays two unique features. First, the fifth coordination site of the Pt^{II} center is partially blocked by the linker in the N,N-L chelate ligand, which allows the stabilization and isolation of a η^3-MeCHPh intermediate in *regio-* and *diastereo*selective ethylbenzene C−H activation by $[Pt(N,N-L)Me(solv)]^+$.[6a] Second, the separation distance between the linker group and the Pt^{II} center in these complexes is short, which can either induce a strong three-center−four-electron $Pt^{II}\cdots H-C$ interaction[8] in $PtMe_2(BAM)$[6a,c] or promote unusual reactivity, as demonstrated by the unique behavior of $Pt_2(TTAB)Me_4$ toward C−H and C−Cl bond activation and the isolation of a rare dinuclear Pt(IV) complex.[7] To further understand the role of our N,N-L chelate ligands in Pt^{II}-mediated C−H activation, we recently started the investigation of relevant Pt^{IV} chemistry. We report herein our preliminary findings of the steric impact of BAM and BAB ligands on the syntheses, structures, and stability of five-coordinate $Pt^{IV}Me_3$ complexes.



BAB



BAM

It has been recognized that oxidative addition of MeI to various N,N-chelating $Pt^{II}Me_2$ complexes typically occurs in an S_N2 fashion, via initial formation of five-coordinate [(N,N)P-

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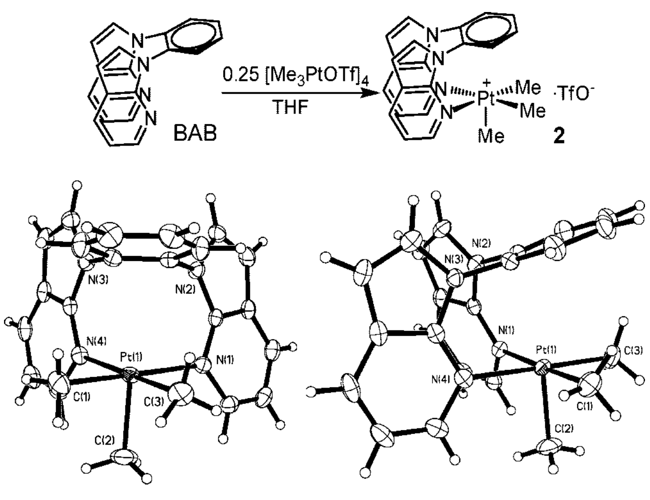

Figure 1. Formation of **2** and front and side views of the structure of the cation.

t^{IV}Me$_3$]$^+$ intermediates, resulting in MeI trans addition adducts.[9] The five-coordinate Pt^{IV}Me$_3$ intermediates may be trapped prior to the binding of I$^-$ with the Pt^{IV} center by appropriate ancillary ligands.[10] Accordingly, because of the steric blockage of one Pt^{II} coordination site by BAB in Pt^{II}(BAB)Me$_2$ (**1**), we anticipated that the oxidative addition of MeI to Pt^{II}(BAB)Me$_2$ (**1**) would likely afford [Pt^{IV}(BAB)Me$_3$]I as a stable five-coordinate complex. As revealed by NMR, **1** reacted readily with MeI at room temperature, but instead of forming the targeted Pt^{IV} complex, the reaction produced the free BAB ligand and the tetrameric complex [PtMe$_3$I]$_4$ quantitatively.[11] This behavior is reminiscent of the reaction of Pt(*L*)Me$_2$ (*L* = 1,5-cyclooctadiene (COD);[12a] norbomadiene (NBD)[12b]) with MeI, an indication that the BAB binding to the Pt^{IV}Me$_3$ moiety is weak and cannot compete with the iodide binding. A similar phenomenon was also observed for the reaction of Pt^{II}(BAM)Me$_2$ with MeI. To avoid iodide competition, [PtMe$_3$(OTf)]$_4$ (OTf = CF$_3$SO$_3$$^-$)[13a] and [PtMe$_3(THF)_{1.5}$]$_2$[PF$_6$]$_2$[13b] were employed for the syntheses of five-coordinate Pt^{IV} complexes.

The reaction of BAB with 0.25 equiv of [PtMe$_3$(OTf)]$_4$ at ambient temperature yielded compound **2**, [Pt(BAB)Me$_3$][OTf], as a colorless crystalline solid in 74% yield (Figure 1). **2** can also be obtained quantitatively by the reaction of compound **1** with MeOSO$_2$CF$_3$ (see Figures S1 and S2 in the Supporting Information). **2** is stable in the solid state or in weakly coordinating solvents such as THF, DMF, and RNO$_2$ (R = Me, Ph). It was fully characterized by NMR and elemental and X-ray analyses. At ambient temperature in CD$_2$Cl$_2$, the Pt^{IV}*Me*$_3$ moiety in **2** displays two broad peaks at 2.17 and 0.61 ppm, respectively, with a 1:2 ratio in the ^{1}H NMR spectrum, indicating the presence of two types of methyl environments and their slow exchange. When the temperature is lowered to 270 K (Figure S5 in the Supporting Information), these two peaks become sharp and well-resolved with distinctive ^{195}Pt$-$^{1}H coupling satellites ($^2J_{\mathrm{Pt-H}}$ = 67.2 Hz for the two equatorial methyls and 84.4 Hz for the axial methyl).[11] Heating to ~45 °C resulted in the coalescence of the equatorial and the axial methyl signals. **2** has a good thermal stability, as evidenced by the fact that over 95% of **2** remained intact in CD$_3$NO$_2$ solution at 60$-$70 °C for 5 days. The addition of 1 equiv of donors such as [^{n}Bu$_4$N]X (X = I$^-$, Br$^-$, Cl$^-$), however, caused rapid degradation of **2** with quantitative formation of free BAB and species such as [Me$_3$PtX]$_4$, which is consistent with the reactivity of **1** toward MeI.

To further confirm **2** as a five-coordinate Pt^{IV} complex, its crystal structure was determined by single-crystal X-ray diffraction analysis.[14] As shown in Figure 1, the Pt^{IV} center in **2** is indeed five-coordinate with a typical square-pyramidal geometry. The sixth coordination site of the Pt^{IV} center is completely capped by the phenyl linker of BAB, with a separation distance of 3.19(1) Å between Pt and the center of the phenyl ring. The lack of a trans ligand makes the Pt$-$C$_{\mathrm{axial}}$ bond length (2.028(3) Å) somewhat shorter than the mean of teh two Pt$-$C$_{\mathrm{equatorial}}$ bond lengths (2.036(4) Å), a trend that is consistent with previously known five-coordinate Pt^{IV}Me$_3$ complexes.[4] The fact that **2** retains its five-coordinate geometry in the presence of OTf and coordinating solvents such as THF led us to suggest that neutral N,N-chelate ligands with appropriate steric protection such as BAB can indeed effectively stabilize five-coordinate Pt^{IV} species.

Despite the similarity between the BAB and BAM ligands, we have shown previously that the BAM CH$_2$ linker is a much less effective steric blocker than the BAB phenyl linker in Pt^{II} complexes.[6a] In accordance with this difference, attempts to obtain the five-coordinate Pt^{IV}Me$_3$ analogue of BAM using a protocol similar to that for **2** were unsuccessful. Instead, the six-coordinate compound **3**, [Pt(BAM)Me$_3$(OTf)], was isolated as a colorless crystalline solid in ~86% yield and characterized by NMR, elemental, and single-crystal X-ray diffraction analyses.[14] As shown in Figure 2, **3** has a six-coordinate Pt^{IV} center with one methyl group being on the same side of the BAM CH$_2$ linker and the OTf group being trans to this methyl group to minimize steric interaction. The Pt$-$C$_{\mathrm{axial}}$ (2.036(3) Å), mean Pt$-$C$_{\mathrm{equatorial}}$ (2.044(3) Å), and mean Pt$-$N (2.282(2) Å) bond lengths in **3** are all consistently longer than those in **2**. The Pt$-$OTf bond distance is 2.259(2) Å, close to that (2.27(2) Å) reported for [PtMe$_3$(OTf)]$_4$.[13a] In addition, the Pt$\cdots$H$'_{\mathrm{CHH'}}$ separation distance is 2.77 Å, considerably lengthened compared to that (2.44 Å) in Pt^{II}(BAM)Me$_2$.[6c] We also attempted the synthesis of [Pt(BAM)Me$_3$][PF$_6$] by replacing the OTf anion with the noncoordinating PF$_6$$^-$ anion, which led to the isolation of another six-coordinate complex, [Pt(BAM)Me$_3$(THF)][PF$_6$] (**3a**).[14] As shown in Figure 2, the structure of **3a** is similar to that of **3**, except that the Pt$-$C bond lengths (Pt$-$C$_{\mathrm{axial}}$ = 2.029(3) Å, Pt$-$C$_{\mathrm{equatorial}}$ = 2.036(3) Å, average) are shorter than those of **3** but similar to those of **2**. The Pt$-$O bond length is 2.293(2) Å, and the Pt$\cdots$H$'$ distance is 2.83 Å. The persistent adoption of the six-coordinate geometry by the BAM complex

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(11) See the Supporting Information.

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(14) Crystal data for **2**: C$_{24}$H$_{23}$F$_3$N$_4$O$_3$PtS, M_r = 699.61, monoclinic, space group $P2_1/c$, a = 10.7240(3) Å, b = 24.2086(8) Å, c = 9.2365(3) Å, β = 99.8930(10)°, V = 2362.26(13) Å^3, Z = 4. Crystal data for **3**: C$_{19}$H$_{21}$F$_3$N$_4$O$_3$PtS, M_r = 637.55, triclinic, space group $P\bar{1}$, a = 6.88210(10) Å, b = 10.91230(10) Å, c = 14.1919(2) Å, α = 92.6570(10)°, β = 91.9620(10)°, γ = 104.9420(10)°, V = 1027.48(2) Å^3, Z = 2. Crystal data for **3a**: C$_{22}$H$_{29}$F$_6$N$_4$OPPt, M_r = 705.55, triclinic, space group $P\bar{1}$, a = 9.2523(11) Å, b = 11.2105(13) Å, c = 13.4198(16) Å, α = 66.8140(10)°, β = 73.8590(10)°, γ = 83.8020(10)°, V = 1229.1(3) Å^3, Z = 2. Crystal data for **4**: C$_{18}$H$_{20}$N$_4$Pt, M_r = 487.47, monoclinic, space group $P2_1$, a = 8.092(5) Å, b = 20.908(13) Å, c = 10.379(7) Å, β = 98.975(7)°, V = 1734.6(19) Å^3, Z = 4.

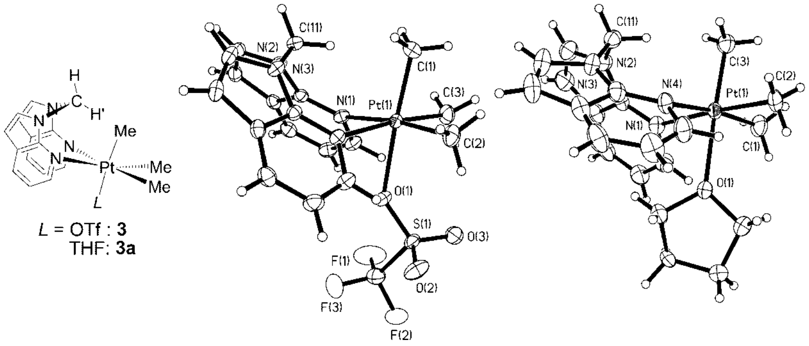


Figure 2. Side views of the structures of **3** (left) and **3a** (right).

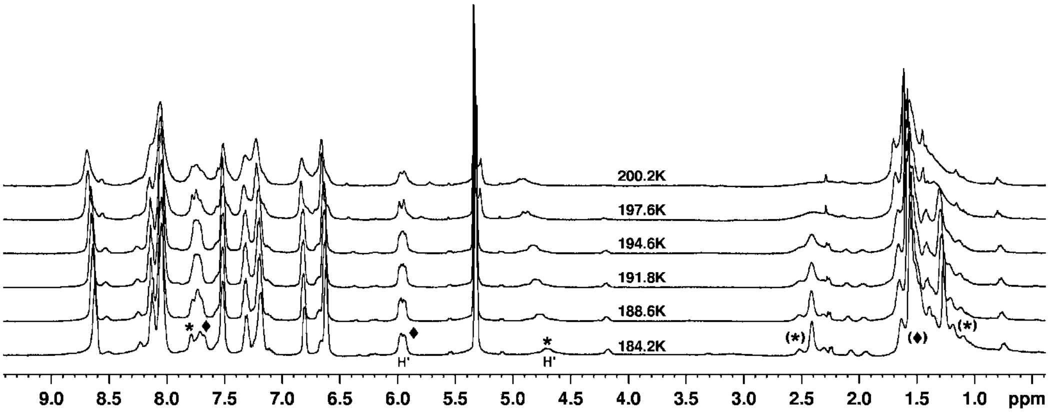
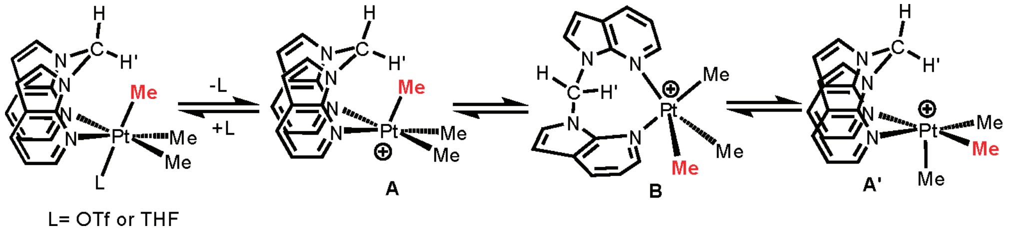


Figure 3. Variable-temperature ^{1}H NMR spectra of compound **3** in CD_2Cl_2. At 184.2 K, two sets of "AB" patterned ^{1}H signals related to the BAM bridging C*HH′* group along with two corresponding sets of ^{1}H signals for the *fac*-PtMe$_3$ moiety were observed, with δ (ppm) for H′, H at 4.71, 7.80 (*) and 5.95, 7.68 (♦), respectively.

Scheme 1



confirms that the BAM ligand is not effective in blocking the sixth coordination site to achieve stable five-coordinate Pt^{IV} complexes.

Consistent with the crystal structures is the distinctively different behavior of **3** and **3a** from that of **2** in solution. Unlike the case for **2**, where the three methyl groups undergo slow exchange at ambient temperature, the methyl groups in **3** and **3a** undergo rapid exchange in solution, as evidenced by the presence of a single sharp methyl signal with characteristic ^{195}Pt$-^1$H satellite peaks ($^2J_{Pt-H} = 73.7$ Hz for **3** and 58.4 Hz for **3a**) in variable-temperature (VT) ^{1}H NMR spectra from 220 to 298 K.[11] As shown by the VT ^{1}H NMR spectra of **3** (Figure 3) and **3a** (Figure S8 in the Supporting Information),[11] below 200 K, the ^{1}H signals of the methyl groups become complex, indicating the presence of more than one species. Furthermore, the aromatic region and the BAM "AB" patterned C*HH′* protons of **3** and **3a** experience a dramatic change, with each peak being resolved into several sets of new peaks.

On the basis of the NMR data, we propose that the L group in compounds **3** and **3a** undergo a dissociation/reassociation process via a five-coordinate species, as shown in Scheme 1.[15] The appearance of a new ^{1}H signal for H′ at 4.71 ppm at 184.2 K for **3** (Figure 3) and its large high-field chemical shift suggest the formation of the five-coordinate Pt^{IV} intermediate **A′**, which is further verified by the observation of a new set of Pt*Me*$_3$ ^{1}H signals: two new peaks at 2.40 and 1.25 ppm, respectively, in a 1:2 ratio. The distinct δ (H′) high-field chemical shift in **A′** can be attributed to the presence of a type of three-center−two-electron Pt$^{IV}\cdots$H−C interaction. The rapid methyl exchange in **3** and **3a** via the $\mathbf{A} \rightleftharpoons \mathbf{B} \rightleftharpoons \mathbf{A'}$ equilibriums indicates that the L group dissociation is fast, even at low temperature. In CD_2Cl_2, the bound THF signals in **3a** can only be observed at temperature below ~220 K (Figure S9 in the Supporting Information),[11] while in d_8-THF solution, the six-coordinate species becomes dominant at ambient temperature (Figure S11 in the Supporting Information). In contrast to the case for **3** and **3a**, the aromatic region of **2** experiences no significant change with temperature (Figure S7 in the Supporting Informa-

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(15) For examples of intramolecular ligand interconversion processes at Pt centers, see: (a) Nikol, H.; Bürgi, H.-B.; Hardcastle, K. i.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 6319. (b) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706. (c) Tau, K. D.; Uriarte, R.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 6614. (d) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478.

tion) and its methyl interconversion process is rather slow, even at ambient temperature. The activation energy for the methyl exchange process of **2** was determined to be 73 kJ/mol. The relatively slow exchange in **2** can be attributed to the inaccessibility of the sixth coordination site and the poor stability of a trigonal-bipyramidal intermediate similar to **B** due to the strong steric blocking effect imposed by the BAB ligand.

^{1}H NMR experiments also revealed that, in comparison to **2**, complexes **3** and **3a** are more prone to the dissociation of the BAM ligand caused by the addition of donor ligands such as I^- and H_2O, due to the strong steric repulsion of its CH_2 linker with the $PtMe_3$ moiety as well as the poor steric blocking of the BAM group. One way to enhance the stability of BAM Pt^{IV} complexes is to convert the bidentate BAM ligand to a tridentate N,C,N-chelate ligand by removing one H atom from the CH_2 group via deprotonation. Indeed, we have found that the CH_2 group of BAM can be readily deprotonated by either LDA or *n*-BuLi to give the (bis(*N*-7-azaindolyl)methyl)lithium salt, which reacts readily with $[Me_3Pt(THF)_{1.5}]_2[PF_6]_2$ and produces the neutral complex [Pt(*N,C,N*-BAM)Me_3] (**4**) as a colorless solid.[11] Crystallization of **4** was exhausting but eventually successful after many attempts, allowing the unambiguous verification of its structure by X-ray diffraction.[14] The Pt^{IV} center in **4** has an octahedral geometry (Figure 4), with the Pt−C(BAM) bond (2.143(5) Å in average) being considerably longer than the Pt-CH_3 bonds (trans, 2.106(5) Å; cis, 2.042(4) Å; average) due to both geometric constraints and the trans effect. The Pt−N bonds (2.158(4) Å, average) are much shorter than those in **3** and **3a**, clearly due to the much reduced steric congestion in **4**. Compound **4** is stable toward air and moisture as well as I^-. In solution, **4** retains its structure and no dynamic behavior is observed by NMR.

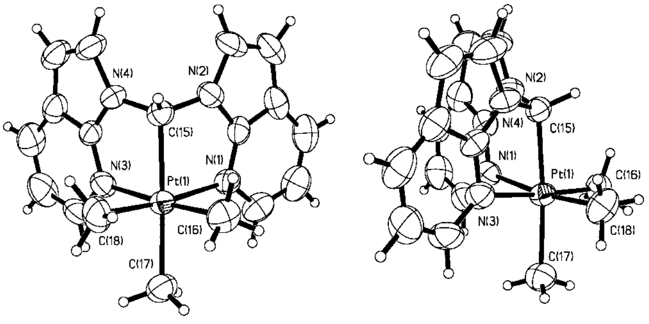

Figure 4. Front and side views of the structure of **4**.

In summary, the first cationic five-coordinate $Pt^{IV}Me_3$ complex with a neutral N,N-chelate ligand, BAB, has been achieved. We have found that the steric blocking by the N,N-chelate ligands has a significant impact on the stability of five-coordinate Pt^{IV} species. The BAB ligand is much more effective in steric blocking, hence stabilizing five-coordinate Pt^{IV} complexes more than the BAM ligand does. A thermolysis study of these compounds is now underway.

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Supporting Information Available: Text, figures, and CIF files giving experimental details, characterization data, ^{1}H NMR spectra, and complete crystal data and diagrams with labeling schemes for **2**, **3**, **3a**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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