# Regioselective C−H Activation of Toluene with a 1,2-Bis(*N*-7-azaindolyl)benzene Platinum(II) Complex

Shu-Bin Zhao, Datong Song, Wen-Li Jia, and Suning Wang*

*Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada*

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A new organoplatinum(II) complex, Pt(1,2-BAB)$(CH_3)_2$ (**1**) (1,2-BAB = 1,2-bis(*N*-7-azaindolyl)benzene), has been synthesized and fully characterized. Compound **1**, after reacting with 1 equiv of acid $[H(Et_2O)_2][BAr'_4]$, Ar′ = 3,5-bis(trifluoromethyl)phenyl, has been found to be able to activate benzene and toluene C−H bonds under mild conditions. The complexes resulting from C−H activation, {Pt(1,2-BAB)(Ph)$(SMe_2)$}$[BAr'_4]$ (**2**), {Pt(1,2-BAB)$(CH_2Ph)(SMe_2)$}$[BAr'_4]$ (**3**), and {Pt(1,2-BAB)$(CH_2Ph)(CH_3CN)$}$[BAr'_4]$ (**4**), have been isolated and structurally characterized by NMR and single-crystal X-ray diffraction analyses. The investigation by $^1$H NMR on the reaction mixture of **1** with toluene in the presence of $[H(Et_2O)_2][BAr'_4]$ revealed that the *m*-tolyl and *p*-tolyl C−H activation products dominate initially. However, as the reaction time increases, the benzylic C−H activation product becomes the major product (after 3 h, the yield ratio of benzyl:*m*-tolyl:*p*-tolyl is 60%:12%:11%). The cause for the high regioselectivity in toluene C−H activation by complex **1** is not fully understood.

## Introduction

Cationic Pt(II) complexes have been demonstrated to be capable of activating C−H bonds under mild conditions.[1] The mechanism of C−H activation by cationic Pt(II) species has been extensively studied[1] in order to understand and utilize this crucial step in selective and catalytic functionalization of hydrocarbons. Most previously reported cationic Pt(II) complexes that are capable of activating C−H bonds involve a diimine ligand with the general formula 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. Recently we reported the facile benzene C−H bond activations by two isomeric Pt(II) complexes that contain a bis(*N*-7-azaindolyl)-methane ligand (BAM).[2] We have shown that the BAM ligand is capable of blocking the fifth binding site of the Pt(II), as evidenced by the strong agostic interaction between the $CH_2$ group and the Pt(II) center in solution and in the solid state, which makes the BAM Pt(II) complexes potentially useful for regioselective C−H activation. To further enhance the rigidity of the chelate ligand and its blockage of the Pt(II) fifth binding site, a new ligand, 1,2-bis(*N*-7-azaindolyl)benzene (1,2-BAB), has been synthesized by our group. The new 1,2-BAB ligand resembles one-half of the 1,2,4,5-tetrakis(*N*-7-azaindolyl)benzene (TTAB) ligand, whose dinuclear Pt-(II) complex reported recently by our group displays unusual reactivity toward benzene C−H activation[3a] and C−Cl activation.[3b] The complexity of the dinuclear Pt(II) TTAB system (which tends to produce multiple C−H activation products that display complex NMR spectral patterns), however, makes detailed analysis of the C−H activation reaction difficult. The successful synthesis of the 1,2-BAB ligand makes it possible for us to obtain a mononuclear Pt(II) complex that has a coordination environment resembling that in the TTAB $Pt_2$ complex, but without the complication of cooperative effect by the second Pt(II) center so that the steric effect of the bis-7-azaindolyl chelate ligand on the Pt center and its consequence on C−H activation can be examined in detail. We have examined the utility of the 1,2-BAB Pt(II) complex in C−H activation of benzene and toluene. We have found that the cationic Pt(II) complex {Pt(1,2-BAB)$(CH_3)$(solvent)}$^+$ displays a high selectivity toward the activation of the benzylic C−H bond of the toluene molecule, as supported by both crystal structure and spectroscopic evidence. The details are reported herein.

## Experimental Section

All reactions were performed under an inert atmosphere of dry $N_2$ with Schlenk techniques or in drybox. All solvents were distilled by known procedures prior to use. NMR spectra were recorded on Bruker Advance 300 or 500 MHz spectrometers.

(1) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (b) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (c) Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467. (d) Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974. (e) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc*. **2000**, *122*, 10846. (f) Johansson, L.; Tilset, M. *J. Am. Chem. Soc*. **2001**, *123*, 739. (g) Johansson, L.; Ryan, O. B.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc*. **2001**, *123*, 6579. (h) Procelewska, J.; Zahl, A.; van Eldik, R.; Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem*. **2002**, *41*, 2808. (i) Konze, W. V.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 12550. (j) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378. (k) Heyduk, A. F.; Driver, T. G.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 15034.

(2) (a) Song, D. Wang, S. *Organometallics* **2003**, *22*, 2187. (b) Song, D. Wang, S. *Comments Inorg. Chem.* **2004**, *25*, 1.

(3) (a) Song, D.; Jia, W. L.; Wang, S. *Organometallics* **2004**, *23*, 1194. (b) Song, D.; Sliwowski, K.; Pang, J.; Wang, S. *Organometallics* **2002**, *21*, 4978.

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Elemental analyses were performed by Canadian Microanalytical Service, Ltd, Delta, British Columbia. 1,2-Diiodobenzene and 7-azaindole were purchased from Aldrich Chemical Co. The starting materials[4] $Pt_2Me_4(Me_2S)_2$ and[5] $[H(Et_2O)_2][BAr'_4]$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) were prepared by methods described in the literature.

**Synthesis of 1,2-Bis(*N*-7-azaindolyl)benzene (1,2-BAB).** 1,2-Diiodobenzene (1.65 g, 5.0 mmol), 7-azaindole (1.42 g, 12.0 mmol), CuI (0.19 g, 1.0 mmol), 1,10-phenanthroline (0.36 g, 2.0 mmol), $Cs_2CO_3$ (6.85 g, 21.0 mmol), 3 mL of DMF, and 0.45 mL of dodecane were mixed together and heated at 150 °C under an $N_2$ atmosphere for 72 h. After cooling to ambient temperature, the mixture was diluted with 30 mL of $CH_2Cl_2$ and filtered through a plug of silica gel. The filtrate was then concentrated under reduced pressure, and the residue was flushed through a silica gel column using hexanes/ethyl acetate (3:1) as the eluent. Upon removal of the solvent, a yellow oil of 1,2-BAB formed, which solidified after the addition of hexanes and storage in a refrigerator for several weeks (75% yield). NMR spectra in $CDCl_3$ at 25 °C, $^1$H NMR (ppm): $\delta$ 8.29 (dd, $^3J$ = 4.5 Hz, $^4J$ = 1.5 Hz, 2H; aza), 7.86 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 2H; aza), 7.80 (m, 2H; phenyl), 7.63 (m, 2H; phenyl), 7.09 (dd, $^3J_1$ = 7.5 Hz, $^3J_2$ = 4.5 Hz, 2H; aza), 6.77 (d, $^3J$ = 3.5 Hz, 2H; aza), 6.28 (d, $^3J$ = 3.5 Hz, 2H; aza). $^{13}$C NMR (ppm): $\delta$ aza, 148.3, 143.7, 129.1, 128.8, 120.9 116.7, 101.6; phenyl, 134.3, 129.5, 128.9 (aza = 7-azaindolyl). Anal. Calcd for $C_{20}H_{14}N_4$: C 77.40, H 4.55, N 18.05. Found: C 77.42, H 4.53, N 17.92.

**Synthesis of Pt(1,2-BAB)$(CH_3)_2$ (1).** 1,2-BAB (0.093 g, 0.30 mmol) and 0.0861 g of $Pt_2Me_4(Me_2S)_2$ (0.15 mmol) were mixed in 20 mL of $Et_2O$ and stirred for 5 h at room temperature. The resulting white precipitate was allowed to settle, and the clear solution was decanted. The solid was washed with $Et_2O$ and dried under vacuum to afford Pt(1,2-BAB)$(CH_3)_2$ in 57% yield. NMR spectra in $CD_2Cl_2$ at 25 °C, $^1$H NMR (ppm): $\delta$ 8.56 (dd, satellite, $^3J$ = 5.1 Hz, $^4J$ = 1.3 Hz, $^3J_{Pt-H}$ = 24.1 Hz; 2H, aza), 7.85 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.3 Hz; 2H, aza), 7.72 (m, 2H, phenyl), 7.31 (m, 2H, phenyl), 7.25 (d, $^3J$ = 3.4 Hz; 2H, aza), 6.95 (dd, $^3J_1$ = 7.8 Hz, $^3J_2$ = 5.1 Hz; 2H, aza), 6.65 (d, $^3J$ = 3.4 Hz; 2H, aza), 0.04 (s, satellite, $^2J_{Pt-H}$ = 88.8 Hz; 6H, methyl). $^{13}$C NMR (ppm): $\delta$ aza, 148.9, 145.2, 134.7, 130.7, 130.2, 129.7, 128.7, 122.8, 117.3, 102.2; $CH_3$, −23.2. Anal. Calcd for $C_{22}H_{20}N_4Pt$: C 49.34, H 3.76, N 10.46. Found: C 48.72, H 3.88, N 10.20.

**Benzene C−H Activation by 1. Isolation of [Pt(1,2-BAB)Ph$(SMe_2)$][BAr′$_4$] (2). 1** ( 0.107 g, 0.20 mmol) and 0.202 g of $[H(Et_2O)_2][BAr'_4]$ (0.20 mmol) were mixed in 40 mL of benzene at room temperature. After the mixture was stirred for 1 h, 0.20 mL of $Me_2S$ was added into the system. The reaction mixture was filtered through Celite. Colorless crystals of [Pt(1,2-BAB)Ph$(SMe_2)$][BAr′$_4$], **2**, were obtained by slow diffusion of hexanes into the concentrated solution (71% yield). NMR spectra in THF-$d_8$ at 25 °C, $^1$H NMR (ppm): $\delta$ 8.65 (dd, $^3J$ = 5.5 Hz, $^4J$ = 1.5 Hz; 1H, aza), 8.63 (dd, $^3J$ = 5.5 Hz, $^4J$ = 1.5 Hz; 1H, aza), 8.08 (m; 4H, phenyl of 1,2-BAB), 7.93 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz; 1H, aza), 7.86 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz; 1H, aza), 7.83 (s; 8H, BAr′$_4$), 7.61 (s; 4H, BAr′$_4$), 7.59 (d, $^3J$ = 4.0 Hz; 1H, aza), 7.44 (d, $^3J$ = 4.0 Hz; 1H, aza), 7.25 (dd, $^3J_1$ = 7.5 Hz, $^3J_2$ = 5.5 Hz; 1H, aza), 7.19 (dd, $^3J_1$ = 7.5 Hz, $^3J_2$ = 6.0 Hz; 1H, aza), 7.14 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.0 Hz; 2H, Pt-*Ph*), 6.91 (t, $^3J$ = 7.5 Hz; 2H, Pt-*Ph*), 6.85 (tt, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz; 1H, Pt-*Ph*), 6.80 (d, $^3J$ = 3.5 Hz; 1H, aza), 6.69 (d, $^3J$ = 4.0 Hz; 1H, aza), 1.96 (s, satellite, $^3J_{Pt-H}$ = 60.0 Hz; 6H, $Me_2$S). $^{13}$C NMR (ppm): $\delta$ BAr′$_4^-$, 162.4 (q, $J_{B-H}$ = 50 Hz), 135.0 (br), 129.4 (q, $J_{C-F}$ = 32 Hz), 124.9 (q, $J_{C-F}$ = 272 Hz), 117.6 (br); 1,2-BAB, 148.1, 147.5, 144.5, 144.4, 135.8, 132.84, 132.77, 132.74, 132.5, 132.4, 132.3, 132.1, 130.0, 127.6, 125.0, 124.8, 118.0, 103.7, 103.6; Ph, 137.3, 131.5, 128.9, 124.4; $Me_2$S, 22.0. Anal. Calcd for $C_{60}H_{37}N_4BF_{24}SPt$: C 47.79, H 2.47, N 3.72. Found: C 47.77, H 2.58, N 3.69.

**Toluene C−H Activation by 1. Isolation of [Pt(1,2-BAB)$(CH_2Ph)(SMe_2)$][BAr′$_4$] (3). 1** (0.107 g, 0.20 mmol) and 0.202 g of $[H(Et_2O)_2][BAr'_4]$ (0.20 mmol) were mixed in 20 mL of toluene at room temperature. After the mixture was stirred for 1 h, 0.20 mL of $Me_2S$ was added into the system. The reaction mixture was filtered through Celite. Crude solids of [Pt(1,2-BAB)$(CH_2Ph)(SMe_2)$][BAr′$_4$], **3**, were obtained by slow diffusion of hexanes into the concentrated solution and storage in a refrigerator for several weeks and were further purified by recrystallization from hexanes/$CH_2Cl_2$ (2:1) to afford colorless crystals (41% yield). NMR spectra in $CD_2Cl_2$ at 25 °C, $^1$H NMR (ppm): $\delta$ 8.32 (dd, $^3J$ = 5.5 Hz, $^4J$ = 1.1 Hz; 1H, aza), 8.06 (dd, satellite, $^3J$ = 5.5 Hz, $^4J$ = 1.0 Hz, $^3J_{Pt-H}$ = 45.6 Hz; 1H, aza), 7.99 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.3 Hz; 1H, aza), 7.94 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz; 1H, aza), 7.85 (m; 2H, phenyl of 1,2-BAB), 7.60 (s; 4H, BAr′$_4$), 7.59 (d, $^3J$ = 4.0 Hz; 1H, aza), 7.55 (dd, $^3J$ = 7.6 Hz, $^4J$ = 1.8 Hz; 1H, phenyl of 1,2-BAB), 7.28 (dd, $^3J$ = 7.6 Hz, $^4J$ = 1.8 Hz; 1H, phenyl of 1,2-BAB), 7.26 (d, $^3J$ = 3.6 Hz; 1H, aza), 7.20 (d, $^3J$ = 3.6 Hz; 1H, aza), 7.12 (dd, $^3J_1$ = 5.5 Hz, $^3J_2$ = 7.9 Hz; 1H, aza), 7.03 (t, $^3J$ = 7.1 Hz; 1H, $PtCH_2Ph$), 6.98 (m; 3H, 1H from aza, 2H from $PtCH_2Ph$), 6.71 (m; 4H, 2H from aza, 2H from $PtCH_2Ph$), 2.70 (d, $^2J$ = 10.2 Hz, $^2J_{Pt-H}$ = 103.0 Hz; 1H, Pt$CH_2$Ph), 2.67 (d, $^2J$ = 10.2 Hz, $^2J_{Pt-H}$ = 103.0 Hz; 1H, Pt$CH_2$Ph), 2.13 (s (br), satellite, $^3J_{Pt-H}$ = 53.2 Hz; 3H, $Me_2$S), 1.97 (s (br), satellite, $^3J_{Pt-H}$ = 53.2 Hz; 3H, $Me_2$S). $^{13}$C NMR (ppm): $\delta$ BAr′$_4^-$ 162.1 (q, $J_{B-H}$ = 50 Hz), 135.1 (br), 129.4 (q, $J_{C-F}$ = 32 Hz), 125.3 (q, $J_{C-F}$ = 271 Hz), 117.9 (br); 1,2-BAB, 147.5, 146.9, 144.6, 143.6, 136.8, 136.7, 132.80, 132.55, 131.93, 131.74, 131.61, 131.58, 129.46, 124.82, 124.58, 118.41, 118.17, 104.4, 104.2; $PhCH_2$, 146.0, 129.0, 128.3, 124.6, 6.8; $Me_2$S, 23.0, 22.5. Anal. Calcd for $C_{61}H_{39}N_4BF_{24}SPt$: C 48.14, H 2.58, N 3.68. Found: C 47.48, H 2.65, N 3.70.

**Isolation of [Pt(1,2-BAB)$(CH_2Ph)(NCMe)$][BAr′$_4$] (4). 1** (0.107 g, 0.20 mmol) and 0.202 g of $[H(Et_2O)_2][BAr'_4]$ (0.20 mmol) were mixed in 20 mL of toluene at room temperature. After the mixture was stirred for 1 h, 0.20 mL of $CH_3CN$ was added into the system. The reaction mixture was filtered through Celite. Colorless crystals **4** were obtained by slow diffusion of hexanes into the concentrated solution and storage at room temperature for several days (38% yield). NMR spectra in $CD_2Cl_2$ at 25 °C, $^1$H NMR (ppm): $\delta$ 8.33 (dd, $^3J$ = 5.4 Hz, $^4J$ = 1.2 Hz; 1H, aza), 8.16 (dd, satellite, $^3J$ = 5.7 Hz, $^4J$ = 1.0 Hz, $^3J_{Pt-H}$ = 57.6 Hz; 1H, aza), 7.95 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz; 1H, aza), 7.92 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.4 Hz; 1H, aza), 7.87 (m; 2H, phenyl of 1,2-BAB), 7.75 (s; 4H, BAr′$_4$), 7.58 (d, $^3J$ = 4.0 Hz; 1H, aza), 7.48 (m; 1H, phenyl of 1,2-BAB), 7.41 (m; 1H, phenyl of 1,2-BAB), 7.30 (d, $^3J$ = 3.6 Hz; 1H, aza), 7.29 (d, $^3J$ = 3.6 Hz; 1H, aza), 7.08 (dd, $^3J_1$ = 5.4 Hz, $^3J_2$ = 7.9 Hz; 1H, aza), 7.05 (m; 3H, $PtCH_2Ph$), 7.00 (dd, $^3J_1$ = 5.7 Hz, $^3J_2$ = 7.9 Hz; 1H, aza), 6.82 (m; 2H, $PtCH_2Ph$), 2.87 (d, satellite, $^2J$ = 10.0 Hz, $^2J_{Pt-H}$ = 106.5 Hz; 1H, Pt$CH_2$Ph), 2.70 (d, $^2J$ = 10.0 Hz, $^2J_{Pt-H}$ = 106.5 Hz; 1H, Pt$CH_2$Ph), 2.11 (s; 3H, PtNC$CH_3$). $^{13}$C NMR (ppm): $\delta$ BAr′$_4^-$, 162.2 (q, $J_{B-H}$ = 50 Hz), 135.2 (br), 129.2 (q, $J_{C-F}$ = 32 Hz), 125.0 (q, $J_{C-F}$ = 270 Hz), 117.8 (br); 1,2-BAB, 148.3, 148.0, 147.9, 145.9, 144.4, 137.2, 136.6, 132.43, 132.22, 131.96, 131.84, 131.65, 131.50, 130.20, 118.26, 118.99, 103.9, 103.8; $PhCH_2$, 147.6, 128.7, 128.2, 124.48, 5.90; $CH_3CN$, 124.38, 3.5. Anal. Calcd for $C_{61}H_{36}N_5BF_{24}Pt$: C 48.82, H 2.42, N 4.67. Found: C 49.03, H 2.58, N 4.52.

**$^1$H NMR Analysis of the Reaction Mixture of Toluene C−H Activation. 1** (0.050 g, 0.093 mmol) and 0.095 g of $[H(Et_2O)_2][BAr'_4]$ (0.093 mmol) were mixed in 8 mL of toluene at room temperature. A small amount of the reaction mixture, during the course of the reaction, was taken out at regular time intervals and put immediately into vials that contain $CD_3CN$ for terminating the reaction. The samples in the vials were

(4) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.
(5) Brookhart, M.; Grant, B.; Volpe, J. *Organometallics* **1992**, *11*, 3920.

**Table 1. Crystallographic Data for Compounds 1−4**

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| formula | $C_{22}H_{20}N_4Pt_1$ | $C_{60}H_{37}N_4F_{24}S_1B_1Pt_1$ | $C_{61}H_{39}N_4F_{24}B_1S_1Pt_1$ | $C_{61}H_{36}N_5F_{24}S_1B_1Pt_1$ |
| fw | 535.54 | 1507.87 | 1521.92 | 1500.85 |
| space group | $P2_1/n$ | $P2/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 15.528(4) | 21.705(5) | 12.725(4) | 12.712(3) |
| $b$, Å | 12.698(3) | 12.645(3) | 13.160(4) | 13.046(3) |
| $c$, Å | 19.665(5) | 23.116(5) | 18.895(6) | 18.856(4) |
| α, deg | 90.00 | 90 | 99.790(5) | 100.179(4) |
| $\beta$, deg | 102.008(5) | 107.449(3) | 100.730(5) | 98.503(4) |
| $\gamma$, deg | 90.00 | 90 | 94.316(6) | 94.680(4) |
| $V$, Å$^3$ | 3792.5(18) | 6053(2) | 3044.8(5) | 3025.4(12) |
| $Z$ | 8 | 4 | 2 | 2 |
| $D_{calc}$, g cm$^{-3}$ | 1.876 | 1.655 | 1.660 | 1.648 |
| $\mu$, cm$^{-1}$ | 74.13 | 24.69 | 24.55 | 24.37 |
| $2\theta_{max}$, deg | 56.58 | 56.78 | 56.66 | 56.72 |
| no. of reflns measd | 26 089 | 41 674 | 20 884 | 16 666 |
| no. of reflns used | 8928 | 14 245 | 13 596 | 12 063 |
| ($R_{int}$) | (0.0808) | (0.0576) | (0.0492) | (0.0224) |
| no. of params | 487 | 922 | 1045 | 1046 |
| final $R$ [$I > 2\sigma(I)$] | | | | |
| R1[a] | 0.0634 | 0.0954 | 0.0586 | 0.0478 |
| wR2[b] | 0.0932 | 0.2311 | 0.0682 | 0.0763 |
| $R$ (all data) | | | | |
| R1[a] | 0.1725 | 0.2059 | 0.2004 | 0.1029 |
| wR2[b] | 0.1083 | 0.2622 | 0.0832 | 0.0895 |
| GOF on $F^2$ | 0.920 | 0.941 | 0.760 | 1.042 |

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

then dried and the residues were analyzed by $^1$H NMR spectroscopy by using $CD_2Cl_2$ as the solvent. The $^1$H NMR spectrum of the reaction mixture recorded after 48 h showed a mixture of products consisting of [Pt(1,2-BAB)($CH_2$Ph)-($NCCD_3$)][BAr′$_4$] (**4**, 81%), [Pt(1,2-BAB)(*p*-tolyl)($NCCD_3$)][BAr′$_4$] (**4b**, 6%), and [Pt(1,2-BAB)(*m*-tolyl)($NCCD_3$)][BAr′$_4$] (**4c**, 13%). The cationic complex [Pt(1,2-BAB)($CH_3$)($NCCD_3$)]$^+$ was not observed after ∼40 h. Part of the $^1$H NMR spectrum of the mixture at the high-field region that is characteristic of the isomers of the tolyl and the benzyl is provided here. $^1$H NMR ($\delta$, ppm), **4**: 2.87 (d, satellite, $^2J$ = 10.0 Hz, $^2J_{Pt-H}$ = 106.5 Hz; 1H, -$CH_2$Ph), 2.71 (d, $^2J$ = 10.0 Hz, $^2J_{Pt-H}$ = 106.5 Hz; 1H, -$CH_2$Ph); **4b**: 2.23 (s; 3H, *p*-$CH_3$Ph); **4c**: 2.20 (s; 3H, *m*-$CH_3$-Ph). The assignment of the chemical shifts to the tolyl isomers is based on previous work reported by Tilset and co-workers.[1g]

**X-ray Diffraction Analysis.** Single crystals of **1** were obtained from the solution of THF/hexanes. Single crystals of **2** were obtained from the solution of benzene/hexanes. Single crystals of **3** were obtained from the solution $CH_2Cl_2$/hexanes. Single crystals of **4** were obtained from the solution of toluene/hexanes. All data were collected on a Siemens P4 X-ray diffractometer with a CCD-1000 detector, operated at 50 kV and 30 mA at ambient temperature. The data for **1**−**4** were collected over $2\theta$ ranges of ∼58°. No significant decay was observed during the data collection. The structural solution and refinement were performed on a PC using Siemens SHELXTL software (version 5.10).[6] Neutral atom scattering factors were taken from Cromer and Waber.[7] Empirical absorption correction was applied to all crystals. All structures were solved by direct methods. Most of the non-hydrogen atoms were refined anisotropically. Most of the $CF_3$ groups in **2**−**4** display rotational disorders, which were modeled and refined successfully. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. The crystal data quality of **2** is relatively poor due to the poor quality of the crystal and inadequate absorption correction. The crystal data for **1**−**4** are listed in Table 1. Important bond lengths and angles are given in Table 2.

(6) *SHELXTL NT Crystal Structure Analysis Package*, Version 5.10; Bruker AXS, Analytical X-ray System: Madison, WI, 1999.

(7) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, AL, 1974; Vol. 4, Table 2.2A.

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1−4**

| | | | |
|---|---|---|---|
| Compound **1** | | | |
| Pt(1)−C(22) | 2.025(12) | Pt(2)−N(4) | 2.095(10) |
| Pt(1)−C(21) | 2.048(10) | Pt(2)−N(2) | 2.121(11) |
| C(22)−Pt(1)−C(21) | 87.8(5) | C(22)−Pt(1)−N(2) | 93.4(4) |
| C(22)−Pt(1)−N(4) | 178.3(5) | C(21)−Pt(1)−N(2) | 178.8(4) |
| C(21)−Pt(1)−N(4) | 92.9(4) | N(4)−Pt(1)−N(2) | 85.8(3) |
| Compound **2** | | | |
| Pt(1)−C(23) | 2.018(11) | Pt(1)−S(1) | 2.290(4) |
| Pt(1)−N(4) | 2.153(10) | S(1)−C(22) | 1.75(2) |
| Pt(1)−N(2) | 2.144(11) | S(1)−C(21) | 1.821(17) |
| C(23)−Pt(1)−N(4) | 171.2(5) | N(2)−Pt(1)−S(1) | 175.9(3) |
| C(23)−Pt(1)−N(2) | 89.4(4) | C(22)−S(1)−C(21) | 100.8(11) |
| N(4)−Pt(1)−N(2) | 86.5(4) | C(22)−S(1)−Pt(1) | 111.5(7) |
| C(23)−Pt(1)−S(1) | 94.6(4) | C(21)−S(1)−Pt(1) | 106.6(7) |
| N(4)−Pt(1)−S(1) | 89.8(3) | | |
| Compound **3** | | | |
| Pt(1)−S(1) | 2.249(2) | S(1)−C(29) | 1.736(8) |
| Pt(1)−N(1) | 1.877(6) | S(1)−C(28) | 1.745(7) |
| Pt(1)−C(21) | 2.052(7) | C(21)−C(22) | 1.488(9) |
| Pt(1)−N(2) | 2.146(6) | | |
| N(1)−Pt(1)−C(21) | 87.2(3) | N(1)−Pt(1)−N(2) | 87.2(2) |
| C(21)−Pt(1)−N(2) | 171.2(3) | C(22)−C(21)−Pt(1) | 119.0(5) |
| N(1)−Pt(1)−S(1) | 174.4(2) | C(29)−S(1)−C(28) | 100.5(4) |
| C(21)−Pt(1)−S(1) | 94.7(2) | C(29)−S(1)−Pt(1) | 111.8(3) |
| N(2)−Pt(1)−S(1) | 90.26(17) | C(28)−S(1)−Pt(1) | 110.7(3) |
| Compound **4** | | | |
| Pt(1)−N(5) | 1.965(5) | N(5)−C(28) | 1.110(7) |
| Pt(1)−N(4) | 2.014(4) | C(28)−C(29) | 1.460(9) |
| Pt(1)−C(21) | 2.058(5) | C(21)−C(22) | 1.498(7) |
| Pt(1)−N(2) | 2.148(4) | | |
| N(5)−Pt(1)−N(4) | 177.79(19) | C(21)−Pt(1)−N(2) | 170.4(2) |
| N(5)−Pt(1)−C(21) | 90.3(2) | C(22)−C(21)−Pt(1) | 116.9(3) |
| N(4)−Pt(1)−C(21) | 89.4(2) | C(28)−N(5)−Pt(1) | 176.1(6) |
| N(5)−Pt(1)−N(2) | 92.62(18) | N(5)−C(28)−C(29) | 177.8(8) |
| N(4)−Pt(1)−N(2) | 87.32(16) | | |

## Results and Discussion

**Synthesis of 1,2-Bis(*N*-7-azaindolyl)benzene (1,2-BAB).** 1,2-BAB was initially obtained in ∼40% yield using Ullmann condensation reaction between 7-azaindole and 1,2-dibromobenzene in the presence of $CuSO_4$ and $K_2CO_3$ as catalyst and HBr scavenger, respectively. However, due to the large steric hindrance at the 1,2-

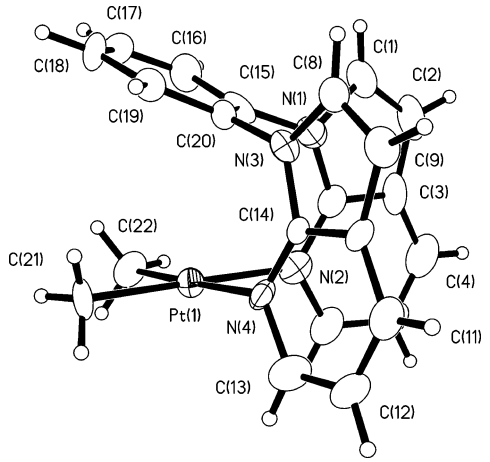



**Figure 1.** Structure of compound **1** with 50% thermal ellipsoids and labeling schemes.

position (the attachment of the second 7-azaindolyl group is sterically hindered by the first 7-azaindolyl group), the reaction requires a fairly high temperature (240 °C), which leads to considerable loss of the starting materials via thermal evaporation and thermal decomposition and a relatively low yield. Using 1,2-diiodobenzene instead of 1,2-dibromobenzene under the same reaction conditions led to extensive decomposition. The best synthetic procedure for 1,2-BAB is using the homogeneous catalysis method developed by the Buchwald group,[8] where 1,2-diiodobenzene and 7-azaindole were reacted in the presence of CuI, 1,10-phenanthroline, and $Cs_2CO_3$ in DMF at 150 °C under $N_2$ atmosphere for 72 h. By this procedure, the yield of 1,2-BAB was increased to ∼75%. The details of this procedure are described in the Experimental Section.

**Synthesis and Structure of Pt(1,2-BAB)$(CH_3)_2$ (1).** The Pt(II) complex **1** was obtained in 57% yield from the reaction of 1,2-BAB with $Pt_2Me_4(\mu\text{-}SMe_2)_2$. The structure of **1** was confirmed by NMR spectroscopy, elemental analyses, and single-crystal X-ray diffraction analysis. There are two independent molecules in the asymmetric unit with similar structural features, one of which is shown in Figure 1. The Pt(II) center has a square planar coordination geometry with two nitrogen donor atoms from the chelate ligand occupying two coordination sites and two methyl groups *trans* to each of the nitrogen donor atoms. The most interesting feature of **1** is the capping of the fifth coordination site by the phenyl ring of the 1,2-BAB ligand, which is clearly imposed by the geometry of the 1,2-BAB ligand. The shortest atomic separation distance between the Pt(II) center and the phenyl ring is 3.10 Å, while the longest separation distance (with C(17) and C(18)) is 4.18 Å. The two 7-azaindolyl groups are almost perpendicular to the phenyl group of the chelate ligand, evidenced by the fact that the dihedral angles between the two 7-azaindolyl planes and the phenyl group of the chelate ligand are 80.1° and 75.6°, respectively. The phenyl group of the chelating ligand and the Pt(II) coordination plane is nearly parallel, as indicated by the dihedral angle (28.2°) between the two planes. The geometry and the environment around the Pt(II) center resemble those observed[3b] in $Pt_2(CH_3)_4$(ttab).

(8) Klapars, A.; Antilla, J. C.; Huang, X. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 7727.

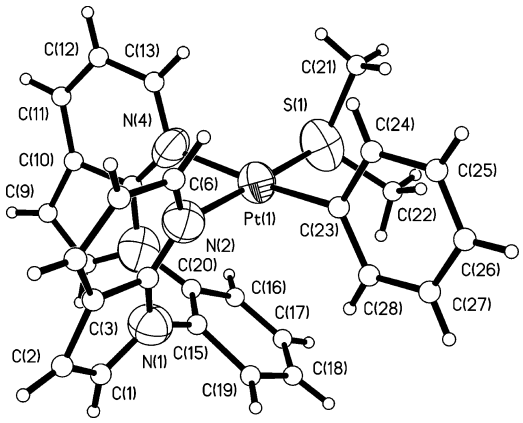



**Figure 2.** Structure of the cation in compound **2** with 50% thermal ellipsoids and labeling schemes. For clarity, all carbon atoms are shown as isotropic spheres.

**Benzene C−H Activation and the Structure of {Pt(1,2-BAB)Ph$(SMe_2)$}[BAr′$_4$] (2).** The utility of complex **1** in C−H bond activation was first examined by the reaction of its cation with benzene. The cationic Pt(II) complex {Pt(1,2-BAB)$(CH_3)$(solvent)}$^+$ (solvent could be either benzene or diethyl ether from the acid) was obtained in situ by the addition of 1 equiv of acid [H$(Et_2O)_2$][BAr′$_4$] (Ar′ = 3,5-bis(trifluoromethyl)phenyl) to the benzene solution of **1** at ambient temperature. After 1 h, the reaction was terminated by the addition of dimethyl sulfide. The benzene C−H activation product [Pt(1,2-BAB)Ph$(SMe_2)$][BAr′$_4$], **2**, was isolated in ∼71% yield as a crystalline product.

Compound **2** was fully characterized by NMR spectroscopy and elemental and single-crystal X-ray diffraction analyses. The structure of the cation portion of **2** is shown in Figure 2. The Pt(II) center adopts a typical square planar coordination geometry, with one phenyl group and one $SMe_2$ ligand being *trans* to the two nitrogen donor atoms of the chelate ligand. As observed in **1**, the phenyl group of the chelate ligand caps one side of the Pt coordination plane. The dihedral angle (33.4°) between the phenyl ring of the 1,2-BAB ligand and the Pt coordination plane is much larger than that in **1**, and the longest atomic separation distance between the phenyl ring of the 1,2-BAB and the Pt center (4.38 Å) is also longer than that in **1**, which are clearly the consequence of increased steric congestion in **2**. The phenyl ligand is nearly perpendicular to the Pt coordination plane, with the dihedral angle between the two planes of ∼95.5°. The shortest separation distance between the phenyl ligand and the phenyl ring of the 1,2-BAB ligand is 3.55(1) Å (C(28)−C(19)), and those between the phenyl ligand and the N(1) 7-azaindolyl ring are 3.63(1) Å (C(28)−N(2)) and 3.66(1) Å (C(24)−C(6)). The phenyl ligand is also almost perpendicular to the phenyl ring of the 1,2-BAB ligand and the N(1) 7-azaindolyl ring (dihedral angle = 73.5°, 86.9°, respectively). The two methyl groups of the $SMe_2$ ligand, albeit indistinguishable in the $^1$H spectrum, display distinct satellite peaks due to coupling to the $^{195}$Pt nucleus. The structure of the BAr′$_4^-$ anion is provided in the Supporting Information. The formation and isolation of compound **2** demonstrated that complex **1** is indeed a useful reagent for facile C−H activation of aromatic molecules.

**Toluene C−H Activation and the Structures of {Pt(1,2-BAB)($CH_2Ph$)($SMe_2$)}[BAr′$_4$] (3) and {Pt(1,2-BAB)($CH_2Ph$)($CH_3CN$)}[BAr′$_4$] (4).** Previous mechanistic study on C−H activation by cationic Pt(II) complexes has established that the aryl C−H bond activation is usually thermodynamically favored over the benzylic C−H bond in methyl-substituted benzene such as toluene or xylene.[1] Preferential activation of the benzylic C−H bond can however be achieved by using sterically bulky chelate ligands on the Pt(II) center, as demonstrated by Bercaw, Tilset, et al.[1a−j] In Bercaw and Tilset's Pt(II) systems, the chelate ligand is a diimine, Ar′N=C(R)C(R)=NAr′ (R = H or Me), whose steric bulk can be controlled by the size and the position of the substituents on Ar′. In contrast to the bulky diimine ligand Ar′N=C(R)C(R)=NAr′ (e.g., Ar′ = mesityl, 3,5-di-*tert*-butylphenyl, etc.) investigated by Bercaw, Tilset, et al., the 1,2-BAB ligand is much less sterically bulky. However, once bound to the Pt(II) center, the 1,2-BAB ligand has a very rigid shape, with the central phenyl ring effectively blocking one side of the Pt coordination plane. To determine if this blocking effect imposed by the 1,2-BAB ligand can lead to any regioselective C−H activation of methyl-substituted benzenes, we examined the reaction of complex **1** with toluene.

The bulk reaction of toluene with complex **1** was carried out in the same manner as the reaction of benzene with **1**. The cationic Pt(II) complex, {Pt(1,2-BAB)($CH_3$)(solvent)}$^+$, was first generated in situ by the addition of 1 equiv of acid [H($Et_2O$)$_2$][BAr′$_4$] (Ar′ = 3,5-bis(trifluoromethyl)phenyl) to the toluene solution of **1** at ambient temperature. After 1 h, the reaction was terminated by the addition of $SMe_2$. The C−H activation product with the formula [Pt(1,2-BAB)($CH_2Ph$)($SMe_2$)]-[BAr′$_4$] (**3**) was isolated as a pure crystalline solid in 41% yield. The methyl group was not observed in the $^1$H NMR spectrum. Instead, a quartet characteristic of a AB coupling pattern with $^{195}$Pt coupling satellites was observed, which is consistent with a $CH_2$ group where the two protons have different chemical environments. $^1$H NMR spectral data established unambiguously that in **3** instead of the aryl C−H bond, the benzylic C−H bond of the toluene molecule was activated. The two methyl groups of $SMe_2$ appear as two distinct sets of chemical shifts with $^{195}$Pt coupling satellite peaks. Compound **3** is stable in solution at ambient temperature, as evidenced by the absence of any notable NMR spectral change over the period of more than 3 days.

The crystal structure of **3** was determined by single-crystal X-ray diffraction analysis. As shown in Figure 3, the coordination environment around the Pt(II) center resembles that of **2**. The dihedral angle (35.7°) between the phenyl ring of the 1,2-BAB ligand and the Pt coordination plane is larger than that observed in **2**, and the longest atomic separation distance between the phenyl ring of the 1,2-BAB and the Pt center (4.44 Å) is somewhat longer than that in **2**, an indication that steric interactions among the ligands in **3** are somewhat greater than those in **2**. The benzylic carbon C(21) is bound to the Pt center with a typical Pt−C bond length. The C(21)−C(22) bond length of 1.488(9) Å is typical for a C−C single bond. The Pt(1)−C(21)−C(22) bond angle is 119.0(5)°. The crystal structure confirmed that the two protons of the methylene group are indeed in different chemical environments. One unexpected feature is the orientation of the benzylic group: instead of orienting away from the 1,2-BAB ligand, it orients toward it; that is, it is on the same side of the Pt(II) coordination plane as the phenyl group of the 1,2-BAB ligand. One possible explanation for this behavior is the $\pi$-interaction between the phenyl ring of the benzyl ligand and the 7-azaindolyl ring of the 1,2-BAB ligand. Indeed, the phenyl ring of the benzyl ligand is in close contact with one of the 7-azaindolyl groups of the 1,2-BAB ligand (the N(1) ring), as evidenced by the short separation distances of N(1)−C(27) (3.23(1) Å) and C(7)−C(27) (3.24(1) Å). The dihedral angle between the N(1) 7-azaindolyl ring and the phenyl ring of the benzyl is 32.6°. Some interactions between the benzyl phenyl group and the 1,2-BAB phenyl group are also evident, as shown by the short contact distances of C(23)−C(16) (3.32(1) Å) and C(25)−C(16) (3.59(1) Å). The dihedral angle between the benzyl phenyl ring and the 1,2-BAB phenyl ring is 64.0°.

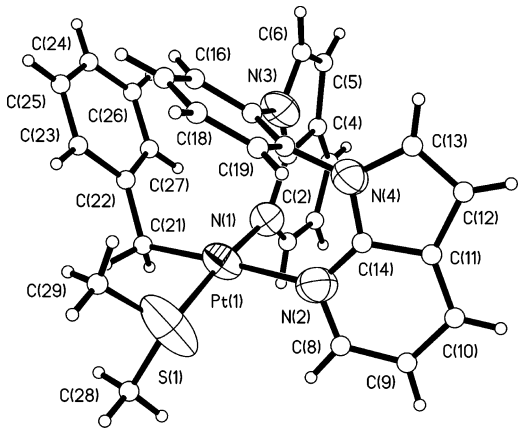



**Figure 3.** Structure of the cation in compound **3** with 50% thermal ellipsoids and labeling schemes. For clarity, all carbon atoms are shown as isotropic spheres.

The isolation and structural characterization of **2** indicated that the cationic complex of **1** is fully capable of activating the aryl C−H bond of the toluene molecule under the same reaction conditions as used for benzene C−H activation. The fact that the benzylic C−H activation product was isolated as the major product from the toluene reaction could be attributed to steric factors, as suggested by Bercaw and Tilset et al.[1a−j] in similar toluene C−H activation by cationic Pt(II) systems. Recently it has been reported by Bercaw and co-workers that the benzylic C−H activation product may also be thermodynamically favored due to the stabilizing effect of a $\eta^3$-bonding mode involving both the methylene group and the phenyl group.[1k]

Since compound **3** is a fairly congested molecule due to the presence of the dimethyl sulfide ligand, it is quite possible that the dimethyl sulfide ligand may have played a role in promoting and stabilizing the benzylic C−H activation product, even though it was only used to terminate the reaction. To rule out this possibility, we repeated the toluene C−H activation process by replacing dimethyl sulfide with acetonitrile as the terminating reagent while the reaction conditions were kept the same. From this reaction, compound **4**, with the formula [Pt(1,2-BAB)($CH_2Ph$)($CH_3CN$)][BAr′$_4$], was

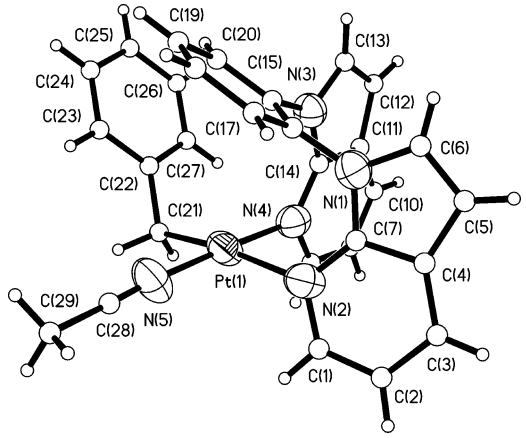



**Figure 4.** Structure of the cation in compound **4** with 50% thermal ellipsoids and labeling schemes. For clarity, all carbon atoms are shown as isotropic spheres.

isolated as a crystalline product in 38% yield. **4** was fully characterized by NMR and single-crystal X-ray diffraction analyses. As observed in **3**, in the $^1$H NMR spectrum, the $CH_2$ protons display an AB pattern with distinct $^{195}$Pt coupling satellites, confirming that the benzylic C−H bond was activated. Compound **4** does not change in solution over extended periods of time at ambient temperature. The structure of **4** shown in Figure 4 resembles that of **3**. The dihedral angle (34.4°) between the phenyl ring of the 1,2-BAB ligand and the Pt coordination plane is similar to that observed in **3**, and the longest atomic separation distance between the phenyl ring of the 1,2-BAB and the Pt center (4.44 Å) is also similar to those observed in **3**. Again, the benzyl group is oriented on the same side as the 1,2-BAB ligand. The phenyl group of the benzyl ligand has a dihedral angle of 38.2° with the phenyl plane of the 1,2-BAB ligand, and 35.4° with the N(3) 7-azaindolyl ring. The shortest atomic separation distance (among nonhydrogen atoms) between the phenyl group of the benzyl and the phenyl group of 1,2-BAB is 3.40(1) Å (C(20)−C(23)) and those between the phenyl group of benzyl and the N(3) 7-azaindolyl ring are 3.29(1) Å (N(4)−C(14)) and 3.33(1) Å (N(4)−C(27)). Again $\pi$-interactions among the aryl rings in **4** may be responsible for the observed orientation of the benzyl group.

The isolation of **3** and **4** demonstrated that the terminating ligand $SMe_2$ or $CH_3CN$ appears to have no significant impact on the preferential formation of the benzylic C−H activation product.

**$^1$H NMR Study of the Toluene C−H Activation.** Since the isolated yield of **3** and **4** is only about 40%, other products are also likely present in the reaction mixture. To determine the product distribution from the toluene C−H activation reaction at ambient temperature, the reaction terminated by acetonitrile was investigated by $^1$H NMR spectroscopy. A small portion (0.5 mL) of the reaction mixture (11.7 mM) was taken out and added to a NMR tube that contains $CD_3CN$ (25 $\mu$L) for terminating the reaction at regular time intervals (initially every 5 min; after 2 h, the samples were collected every 1 h). After the removal of the solvents by vacuum, the $^1$H NMR spectrum of the residue was recorded in $CD_2Cl_2$ (0.4 mL). $^1$H NMR spectra showed that after 5 min of the addition of the acid the starting

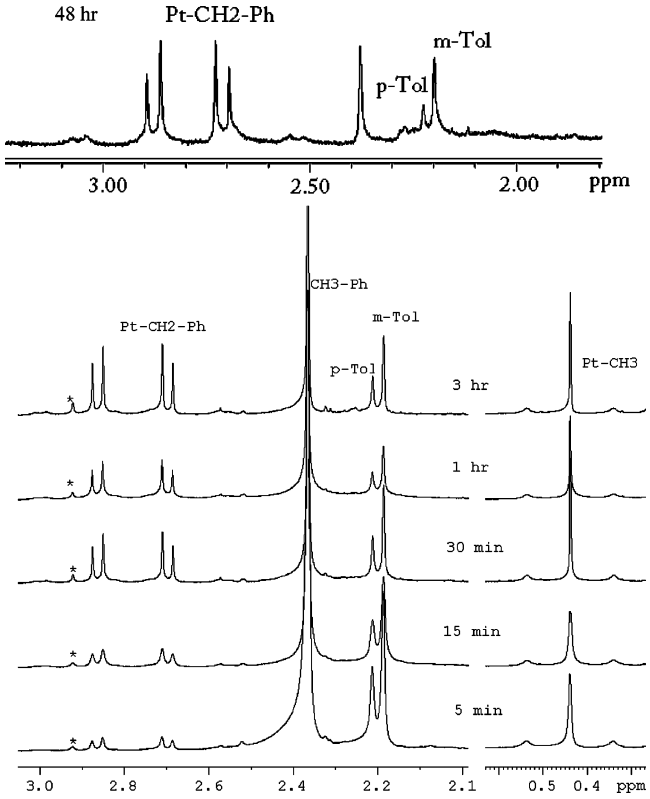
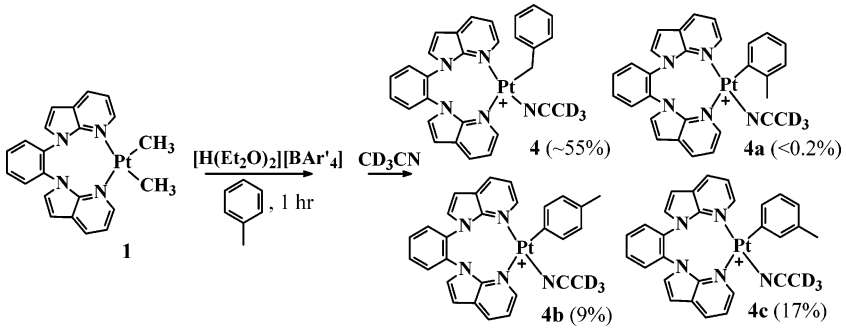



**Figure 5.** $^1$H NMR spectra of the high-field region (in $CD_2Cl_2$ at 298 K) for the reaction mixture of **1** with toluene after the addition of the acid and the termination by $CD_3CN$ at different time intervals ("∗" the *o*-tolyl product).

material Pt(1,2-BAB)$(CH_3)_2$ was completely consumed. The Pt complex distribution after 5 min is {Pt(1,2-BAB)$(CH_3)(CD_3CN)\}^+$ (31%), {Pt(1,2-BAB)$(CH_2Ph)(CD_3CN)\}^+$ (17%), {Pt(1,2-BAB)(*p*-tolyl)$(CD_3CN)\}^+$ (24%), {Pt(1,2-BAB)(*m*-tolyl)$(CD_3CN)\}^+$ (28%), which corresponds to a 69% total yield of C−H activation (the *o*-tolyl product is very little, as shown in Figure 5). As the reaction time increases, the signal of the cationic complex {Pt(1,2-BAB)$(CH_3)(CD_3CN)\}^+$ decreases further and the signals of the toluene C−H activation products increase. One notable change is that after 30 min the benzyl product becomes the major product (43%) and the *p*-tolyl (15%) and *m*-tolyl (20%) compounds become minor products with 22% of unreacted {Pt(1,2-BAB)$(CH_3)(CD_3CN)\}^+$. After 1 h, the product distribution becomes benzyl (55%), *p*-tolyl (9%), *m*-tolyl (17) with 19% unreacted {Pt-(1,2-BAB)$(CH_3)(CD_3CN)\}^+$. After 3 h, the ratio becomes benzyl (60%), *p*-tolyl (11%), *m*-tolyl (12) with 17% unreacted {Pt(1,2-BAB)$(CH_3)(CD_3CN)\}^+$. The signal from the cationic complex {Pt(1,2-BAB)$(CH_3)(CH_3CN)\}^+$ became completely undetectable after ∼40 h. The $^1$H NMR spectrum of the reaction mixture terminated by $CD_3CN$ after 48 h is shown in Figure 5 (top). The product distribution is Pt-$CH_2$Ph (81%), Pt-*m*-tolyl (13%), Pt-*p*-tolyl (6%) (Scheme 1). The NMR results indicate that the benzyl C−H activation appears to be thermodynamically favored since the initial products are dominated by aryl C−H activation. We recorded the $^1$H NMR spectra of the reaction mixture without the addition of the terminating reagent such as $CD_3CN$. The spectra are very complex, and we have not yet observed

**Scheme 1**




any evidence for the formation of the $\eta^3$-bound species as reported by Bercaw in their cationic Pt(II) systems. The cause for the preferential formation of the benzyl C−H activation product displayed by our Pt 1,2-BAB complex therefore remains undermined. We are currently performing a detailed kinetic and 2D NMR investigation on this system, aiming to have a full understanding of the reaction mechanism and the unusually high regioselectivity displayed by our Pt(II) complex in toluene C−H activation. The results will be reported in due course.

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