# C−H Activation at Pt(II) To Form Stable Pt(IV) Alkyl Hydrides

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The search for selective practical methods of alkane functionalization has led to intensive investigation of the mechanistic details of Shilov's oxidation of alkanes by Pt salts in aqueous solution.[1−3] Strong support has been presented for a pathway in which activation of the alkane C−H bond occurs by oxidative addition to a Pt(II) species and generation of a Pt(IV) alkyl hydride as an undetected intermediate.[2] Consistent with this proposal, the first well-defined example of intermolecular C−H bond activation of alkanes by model Pt(II) centers was recently reported.[1] Although C−H bond activation was clearly established by observation of Pt(II) alkyl/aryl exchange products, Pt(IV) alkyl hydrides were not directly observed. This complicates the distinction between this exchange occurring by a true oxidative addition/reductive elimination sequence or by a $\sigma$-bond metathesis pathway. Unfortunately, in the reported system (Pt(II) complex = [(tmeda)PtMe(NC₅F₅)]⁺), the Pt(IV) C−H oxidative addition products would not be stable to C−H reductive elimination.[1]

Recent reports of unusually stable Pt(IV) alkyl hydrides, Tp^{R′}PtR₂H (R = Ph, Me; Tp^{R′} = Tp′ (hydridotris(3,5-dimethylpyrazolyl)borate) and Tp (hydridotris(pyrazolyl)borate)),[4] led us to examine potential C−H bond activation reactions with Pt(II) complexes that would generate analogous stable Pt(IV) alkyl hydrides. We report here the reaction of K[Tp′PtMe₂][4a] with B(C₆F₅)₃ in arene and alkane solvents, RH (RH = benzene, pentane, and cyclohexane), to yield the Pt(IV) products, Tp′PtMeRH (Scheme 1). This constitutes the first example of the intermolecular oxidative addition of arene and alkane C−H bonds by a Pt(II) species resulting in stable Pt(IV) compounds.

The precursor complex K[Tp′PtMe₂] (**1a**)[5] was prepared by reaction of [PtMe₂(μ-SMe₂)]₂[6] with KTp′ in THF at ambient temperature.[4a] A metathesis reaction of **1a** with [PPN]Cl[7] generated [PPN]Tp′PtMe₂ (**1b**)[5] and single crystals of **1b**, suitable for X-ray diffraction, were grown from a THF solution layered with Et₂O at −33 °C. An ORTEP of **1b** is shown in Figure 1.[8] The geometry of the platinate is a distorted square plane, and the Tp′ ligand is coordinated to the Pt(II) center in a *bidentate* fashion with the nitrogen of the noncoordinated pyrazolyl ring directed away from the Pt center.[9,10]

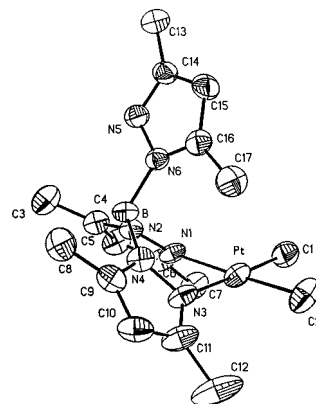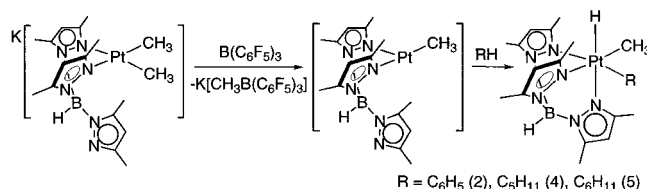The highly electrophilic reagent B(C₆F₅)₃ has been used to abstract a methyl anion from early transition-metal methyl



**Figure 1.** ORTEP drawing of **1b** (PPN[Tp′PtMe₂]·2THF·Et₂O). Ellipsoids are shown at the 50% probability level. Hydrogens, the PPN cation, THF, and Et₂O molecules are not shown.

**Scheme 1**



R = C₆H₅ (**2**), C₅H₁₁ (**4**), C₆H₁₁ (**5**)

complexes and create an open coordination site at the metal center.[11] Similar reactivity was recently observed upon reaction with Pt(II) methyl complexes.[12] We took advantage of this methodology and reacted B(C₆F₅)₃ with K[Tp′PtMe₂] with the intent of abstracting the Pt(II) methyl group and generating "Tp′PtMe" ($\eta^2$-Tp), a three-coordinate Pt(II) species, which might activate a solvent molecule RH.

Reaction of B(C₆F₅)₃ with K[Tp′PtMe₂] in C₆H₆ does indeed lead to C−H bond activation of the solvent producing Tp′PtMe(Ph)H (**2**) and K[MeB(C₆F₅)₃].[13] **2** was characterized by ¹H NMR spectroscopy in C₆D₆, which showed a diagnostic Pt^{IV}-H signal at $\delta$ −19.35 ($^1J_{Pt-H}$ = 1368 Hz).[14] A significant amount of Tp′PtMe₂H (**3**)[4a,15] (*ca.* 20%, $\delta$ −20.39 ($^1J_{Pt-H}$ = 1358 Hz)) is also formed during these reactions. We attribute the formation

(9) The six-membered PtN₄B ring is in a boat conformation with the Pt and B being respectively, 0.890 and 0.498 Å above the plane defined by N1−N2−N3−N4. The dihedral angle defined by the planes N1−Pt−C1 and N3−Pt−C2 is 3°, and that defined by the planes Pt−N3−N1 and C2−Pt−C1 is 2.8°. Selected bond distances (Å): Pt−C1, Pt−C2, Pt−B, 2.030(8), 2.032(8), 3.366(5), respectively. Selected bond angles (°): N1−Pt−N3, N1−Pt−C1, N3−Pt−C1, N1−Pt−C2, N3−Pt−C2, C1−Pt−C2, 86.0(2), 94.2(3), 178.0(3), 178.0(3), 94.1(3), 85.7(4), respectively.

(10) (a) Rush, P. E.; Oliver, J. D. *J. Chem. Soc., Chem. Commun.* **1974,** 996. (b) Oliver, J. D.; Rice, N. C. *Inorg. Chem.* **1976,** *15*, 2741.

(11) See for example: (a) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997,** *16*, 842 and references therein. (b) Gillis, D. J.; Quyoum, R.; Tuderet, M. J.; Wang, Q.; Jeremic, D.; Roszak, Q. W.; Baird, M. C. *Organometallics* **1996,** *15*, 3600.

(12) (a) Hill, G. S.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1997,** *16*, 525. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996,** 1809.

(13) Comparison of the ¹¹B-NMR spectrum of the reaction mixture containing **2** in C₆D₆ (br s at $\delta$ −15) with that of a sample of MeB(C₆F₅)₃⁻, made from the reaction of MeLi and B(C₆F₅)₃ in C₆D₆ (br s at $\delta$ −15), confirmed that abstraction of methyl anion from **1a** had occurred.

(14) (a) Tp′PtMe(Ph)H (**2**): ¹H NMR (C₆D₆): $\delta$ −19.35 (s, $^1J_{Pt-H}$ = 1368 Hz, 1 H, PtH), 1.62 (s, 3 H, Tp′CH₃), 1.84 (s, $^2J_{Pt-H}$ = 69.4 Hz, 3 H, PtCH₃), 1.87, 2.10, 2.11, 2.18, 2.23 (all s, each 3 H, Tp′CH₃), 5.48 (s, $^4J_{Pt-H}$ = 6.2 Hz, 1 H, Tp′CH), 5.53 (s, $^4J_{Pt-H}$ = 6.4 Hz, 1 H, Tp′CH), 5.59 (s, 1 H, Tp′CH), 6.80 (bt, $^4J_{Pt-H}$ = 13.8 Hz, 1 H, H_m), 7.01 (d, $J_{H-H}$ = 7.6 Hz, $^3J_{Pt-H}$ = 42.8 Hz, 1 H, H_o), 7.03 (tt, $J_{H-H}$ = 2.3 Hz, 7.3 Hz, 1 H, H_p), 7.19 (bt, $^4J_{Pt-H}$ = 13.3 Hz, 1 H, H_m′), 7.82 (d, $J_{H-H}$ = 7.3 Hz, $^3J_{Pt-H}$ = 64.7 Hz, 1 H, H_o′).

(15) Tp′PtMe₂H (**3**): ¹H NMR (C₆D₆): $\delta$ −20.39 (s, $^1J_{Pt-H}$ = 1358 Hz, 1 H, PtH), 1.66 (s, $^2J_{Pt-H}$ = 67.8 Hz, 3 H, PtCH₃), 2.09 (s, 6 H, Tp′CH₃), 2.15 (s, 3 H, Tp′CH₃), 2.19 (s, 6 H, Tp′CH₃), 2.33 (s, 3 H, Tp′CH₃), 5.51 (s, $^4J_{Pt-H}$ = 6.2 Hz, 2 H, Tp′CH), 5.57 (s, 1 H, Tp′CH).

(1) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997,** *119*, 848.

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(3) See: (a) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995,** *504*, 75 and references therein. (b) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E.; Horváth, I. T.; Eller, K. *Organometallics* **1993,** *12*, 895. (c) Hutson, A. C.; Lin, M.; Basickes, N.; Sen, A. *J. Organomet. Chem.* **1995,** *504*, 69 and references therein.

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(5) ¹H NMR data (for **1a** and **1b**) and ¹³C{¹H} NMR data (for **1b**) are provided in the Supporting Information.

(6) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983,** *2*, 1643.

(7) PPN = bis(triphenylphosphoranylidene)ammonium.

(8) **1b**·2(THF)·Et₂O (C₅₃H₅₈BN₇P₂Pt·C₈H₁₆O₂·C₄H₁₀O), MW = 1279.28, pale yellow rhombohedron, triclinic, space group = *P*1, *a* = 13.666(2) Å, *b* = 14.538(3) Å, *c* = 17.631(3) Å, $\alpha$ = 70.85(2)°, $\beta$ = 88.63(2)°, $\gamma$ = 65.92(2)°, *V* = 2996(1) Å³, *Z* = 2, *R*₁ = 0.0436 [*I* > 2σ(*I*)], GOF = 1.053.

of this material to the presence of adventitious water. As recently reported by Puddephatt and co-workers, $H_2O$ complexes to $B(C_6F_5)_3$ to make the very strong acid $H[HOB(C_6F_5)_3]$ that can protonate Pt(II) centers.[12] Protonation of **1a** by acid was previously reported to generate **3**.[4a] To prevent large amounts of **3** from being produced, it was necessary to take scrupulous care to avoid any source of $H_2O$.[16]

When the reaction of $B(C_6F_5)_3$ with **1a** was carried out in $C_6D_6$, the hydride signal for the protonation product, Tp′PtMe$_2$H (**3**), appeared alone in the upfield region. However, the PtC$H_3$ signal assignable to Tp′PtMe(D)(C$_6$D$_5$) (**2**-$d_6$) still appeared at 1.84 ($^2J_{Pt-H} = 69.4$ Hz) along with a set of Tp′ signals identical with those of **2**. This experiment confirmed that the hydride of **2** resulted from solvent activation but that of **3** did not.

Reaction of $B(C_6F_5)_3$ with **1a** in $C_6H_6$ followed by removal of the solvent under vacuum left an oily residue containing Tp′PtMe(Ph)H (**2**), Tp′PtMe$_2$H (**3**), and K[MeB(C$_6$F$_5$)$_3$]. Initial attempts to purify this mixture have been unsuccessful. Dissolution of this product mixture in $C_6D_6$ and heating of the solution for 1 day at 63 °C (or maintaining the solution at ambient temperature for 1 month) results in no changes in the number of products or product ratios. The high thermal stability of complex **2** is similar to that previously reported for **3** and TpPtMe$_2$H and is likely due to the inhibition of formation of a five-coordinate species by the chelate effect.[4]

The reaction of **1a** with $B(C_6F_5)_3$ was also carried out in alkane solvents, and C−H bond activation of pentane and cyclohexane was observed. Due to the limited solubility of **1a** in alkanes, **1a** was stirred as a suspension with the boron reagent in pentane or cyclohexane at 50 °C for 2 days. Removal of the solvent and dissolution of the residue in $C_6D_6$ allowed observation of the Pt(IV) alkyl hydrides, Tp′PtMeRH (R = n-C$_5$H$_{11}$ (**4**) and Cy (**5**)), by $^1$H NMR.[17] The Pt$^{IV}$−H signals appear at $\delta$ −20.73 ($^1J_{Pt-H} = 1393$ Hz) and $\delta$ −21.37 ($^1J_{Pt-H} = 1442$ Hz) for **4** and **5**, respectively. The production of Tp′PtMe$_2$H (**3**) is a significant competing reaction (*ca.* 43%) in these alkane activation reactions, and once again, its formation is attributed to adventitious water.

The reaction of the Pt(II) complex with pentane is highly selective. Only two hydride signals, assignable to **4** and **3**, were observed in the $^1$H NMR ($C_6D_6$) after reaction of **1a** with $B(C_6F_5)_3$ in pentane at 50 °C. The assignment of **4** as the *n*-pentyl derivative (the product resulting from C−H activation at the primary carbon) is based on the observation of the four methylene carbon resonances of the *n*-pentyl ligand in a $^{13}$C{$^1$H}-DEPT NMR spectrum of **4**.[18] The signal for C$_\alpha$ appears at $\delta$ 1.3 ($^1J_{Pt-C} = 637$ Hz).

A plausible pathway for these C−H bond activation reactions is abstraction of an anionic methyl group from [Tp′PtMe$_2$]$^-$ by $B(C_6F_5)_3$ generating the very reactive three-coordinate "Tp′Pt-Me" species ($\eta^2$-Tp′), which then undergoes oxidative addition of a C−H bond of the solvent. The five-coordinate Pt(IV) species, $\eta^2$-Tp′PtMeRH, is then rapidly trapped by the third pyrazolyl ring to form the thermally stable Tp′PtMeR(H).[19]

Support for this analysis of the reaction pathway is obtained by considering the microscopic reverse of this process, reductive elimination of C−H bonds from Pt(IV). We and others have documented the consistent involvement of five-coordinate intermediates (**B**) in C−C and C−H reductive elimination from octahedral Pt(IV) and Pd(IV) centers (**A**; eq 1).[2,20,21] The



R = H, CH$_3$
L = ligand - leaving group
(1)
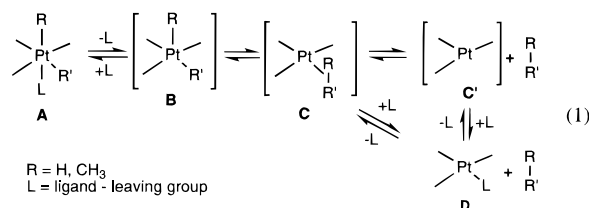
principle of microscopic reversibility then requires that a ligand must be lost from the square-planar Pt(II) complex (**D**) prior to oxidative addition (reverse of eq 1). Complexes such as **C** (four-coordinate C−H/C−C $\sigma$−complexes) and/or a three-coordinate Pt(II) species (**C′**) are likely species along the reaction pathway.

This analysis is consistent with our results and also with the recent report by Labinger and Bercaw of intermolecular alkane C−H activation by [(tmeda)PtMe(NC$_5$H$_5$)]B(Ar$_f$)$_4$ and Whiteside's report of intermolecular arene C−H activation by *trans*-(PMe$_3$)$_2$Pt(CH$_2$CMe$_3$)(SO$_3$CF$_3$).[1,22] Both of these Pt(II) complexes are square-planar species with one particularly weakly bound ligand. Bercaw and Labinger have also reported strong evidence for a Pt(II) C−H $\sigma$-complex, (tmeda)PtMe(CH$_4$)$^+$ (an intermediate analogous to **C**), on the reaction path of C−H reductive elimination of methane from the five-coordinate Pt(IV) species, (tmeda)PtMe$_2$H$^+$.[2]

In summary, oxidative addition to Pt(II) of the C−H bonds of alkanes to form Pt(IV) alkyl hydride complexes, a reaction which has been proposed as the C−H activation step in Shilov alkane oxidation systems, has now been documented in a model system. The success of demonstrating this reactivity has relied on two factors: (1) the generation of a reactive three-coordinate Pt(II) species and (2) rapid trapping of the five-coordinate Pt(IV) species. We will use these principles as we continue our studies of the mechanism and selectivity of oxidative addition/reductive elimination reactions at Pt(II)/Pt(IV).

**Supporting Information Available:** Experimental procedures, NMR data for **1(a,b)**, and crystal structure data for **1b** (16 pages). See any current masthead page for ordering and Internet access instructions.

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(16) The boron reagent was recrystallized from pentane prior to use. The glassware was pretreated with bis(trimethylsilyl)acetamide and flame dried under vacuum immediately prior to use. See: Hughes, R. P.; Rose, P. R.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3109.

(17) Tp′PtMeRH (R = C$_5$H$_{11}$ (**4**) and Cy (**5**)): $^1$H NMR ($C_6D_6$): $\delta$ −20.73 (s, $^1J_{Pt-H} = 1393$ Hz, 1 H, PtH), 0.91 (t, $J_{H-H} = 7.3$ Hz, 3 H, Pt(CH$_2$)$_4$C$H_3$), 1.37 (m, 2 H, Pt(CH$_2$)$_3$C$H_2$CH$_3$), 1.48 (m, 2 H, Pt(CH$_2$)$_2$C$H_2$-CH$_2$CH$_3$), 1.63 (s, $^2J_{Pt-H} = 69.0$ Hz, 3 H, PtCH$_3$), 1.66 (m, 2 H, PtCH$_2$(CH$_2$)$_2$CH$_3$), 2.08, 2.09, 2.15, 2.19, 2.25, 2.40 (all s, each 3 H, Tp′C$H_3$), 2.72 (m, $^2J_{Pt-H} \sim 68$ Hz, 2 H, PtC$H_2$(CH$_2$)$_3$CH$_3$), 5.50, 5.57, 5.61 (all s, each 1 H, Tp′CH). **5**: $^1$H NMR ($C_6D_6$) $\delta$ −21.37 (s, $^1J_{Pt-H} = 1442$ Hz, 1 H, PtH), 1.40 (m, 2H, PtCH(C$H_2$)$_5$), 1.54 (m, 4 H, PtCH(C$H_2$)$_5$), 1.67 (s, $^2J_{Pt-H} = 69.5$ Hz, 3 H, PtCH$_3$), 1.80 (m, 4 H, PtCH(C$H_2$)$_5$), 2.06, 2.10, 2.16, 2.17, 2.38, 2.44 (all s, each 3 H, Tp′C$H_3$), 3.14 (tt, $J_{H-H} = 12.0$ Hz, 7.2 Hz, $^2J_{Pt-H} = 88.0$ Hz, 1 H, PtC$H$(CH$_2$)$_5$), 5.47 (s, 1 H, Tp′CH), 5.59 (s, $^4J_{Pt-H} = 6.4$ Hz, 1 H, Tp′CH), 5.63 (s, 1 H, Tp′CH).

(18) Selected $^{13}$C{$^1$H}-DEPT NMR data for **4**, Pt-pentyl CH$_2$ signals: 1.3 (s, $^1J_{Pt-C} = 637$ Hz, C$_\alpha$), 23.0 (s, C$_\delta$), 33.7 (s, C$_\gamma$), 36.1 (s, $^2J_{Pt-C} = 87$ Hz, C$_\beta$).

(19) The alternative that the Pt species which activates the C−H bond of the solvent might be $\eta^3$-Tp′PtMe should also be considered. Such a four-coordinate d$^8$ species would be analogous to the Cp*ML fragments of Ir and Rh well known to undergo oxidative addition of C−H bonds. See: Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Pederson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(20) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889.

(21) Representative examples: (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457. (b) Roy, S.; Puddephatt, R. J.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2121. (c) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83 and references therein. (d) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics*, **1995**, *14*, 4966 (e) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Speck, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

(22) Brainard, R. L.; Nutt, W. R.; Lee, T. R.; Whitesides, G. M. *Organometallics* **1988**, *7*, 2379.