Hydrocarbon Activation at a Cationic Platinum(II) Diimine Aqua Complex under Mild Conditions in a Hydroxylic Solvent

Lars Johansson,[†] Olav B. Ryan,[‡] and Mats Tilset*,[†]

*Department of Chemistry, University of Oslo
P.O.Box 1033 Blindern, N-0315 Oslo, Norway
SINTEF Applied Chemistry
Department of Hydrocarbon Process Chemistry
P.O.Box 124 Blindern, N-0314 Oslo, Norway*

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The direct, selective conversion of alkanes into value-added chemical products has long been a "holy grail" for chemists[1] and intensified efforts toward this goal have been made during the past few years.[2] The reaction mechanism of the classical Shilov system, in which methane is catalytically functionalized by Pt[II] salts in aqueous media, has been probed in some detail.[3] The actual C−H activation step in this reaction has recently been extensively investigated by the Bercaw group, utilizing a (tmeda)-Pt[II] model system.[4,5] The observed exchange of labeled $^{13}CH_3$ for CH_3 between $(tmeda)Pt(NC_5F_5)(CH_3)^+$ and $^{13}CH_4$ in penta-fluoropyridine, a solvent of low basicity and coordinating ability, demonstrated the activation of methane C−H bonds. Although intermediates in the exchange reaction were not observed, circumstantial evidence suggested an oxidative addition pathway involving a Pt[II] methane σ-complex and a Pt[IV] methyl hydride complex. Further demonstrating the potential for alkane activation at Pt complexes, Goldberg and co-workers showed through the reaction between $(\eta^2\text{-}Tp')Pt^{II}(CH_3)$ and various hydrocarbons R−H that it is possible to trap the normally elusive 5-coordinated oxidative addition product by intramolecular pyrazole coordination, ultimately producing Pt[IV] complexes $(\eta^3\text{-}Tp')Pt(H)(CH_3)$-(R).[6] Most recently, Pt-catalyzed conversion of methane to methyl bisulfate was achieved with the complex $(bpym)PtCl_2$ in highly acidic media.[7]

An interesting common feature in the above examples is the success of employing bidentate nitrogen ligands to obtain Pt[II] complexes that are reactive toward C−H bond activation. We have recently[8] reported a study of the one-electron oxidation reactions of Pt[II] complexes $(diimine)Pt(CH_3)_2$ (diimine = ArN= CHCH=NAr or ArN=CMeCMe=NAr, with Ar = p-MeC_6H_4 or p-$MeOC_6H_4$) in acetonitrile. For the diimine $(p$-$MeOC_6H_4)N=$ CHCH=N(p-$MeOC_6H_4$), the oxidation resulted in intermolecular methyl transfer reactions giving $(diimine)Pt^{IV}(NCMe)(CH_3)_3^+$ and $(diimine)Pt^{II}(NCMe)(CH_3)^+$. The latter was presumably formed via the intermediacy of $(diimine)Pt(CH_3)^+$, an analogue of the species believed to be responsible for the C−H activation in Bercaw's $(tmeda)Pt^{II}$ system.[5] In this contribution, we report that benzene and methane C−H activation can be achieved at a related $(diimine)Pt$ aqua complex in a hydroxylic solvent, under mild and neutral conditions.

The protonation of the above-mentioned $(diimine)Pt(CH_3)_2$ complexes with HOTf, HBF_4, or $H(Et_2O)_2BAr_f$ in the poorly coordinating solvents dichloromethane and nitromethane invariably led to extensive decomposition as evidenced by the plethora of new signals that appeared in the ^1H NMR spectra of the solutions after the reactions. We have tentatively attributed this behavior to a propensity of the in situ generated $(diimine)Pt(CH_3)^+$ species to undergo intermolecular reactions with the diimine ligands of adjacent Pt complexes. This degradation presumably might be avoided by appropriate protection of the *N*-aryl groups of the diimine. A 3,5-bis(trifluoromethyl)phenyl substituted diimine[9] (henceforth to be denoted N−N) was selected as a new ligand; the corresponding dimethylplatinum complex **1**[10] was

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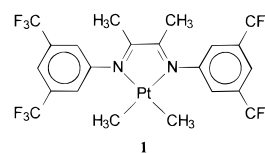
straightforwardly prepared in its reaction with $Pt_2Me_4(\mu\text{-}SMe_2)_2$. The two CF_3 groups serve to sterically as well as electronically protect each ring against electrophilic attack by reactive cationic Pt species. In addition, the CF_3 groups also decrease the electron density[11] and thence increase the electrophilicity of the metal center. This effect should further activate the complex with respect to reactions with hydrocarbon C−H bonds.

For the investigation of the reactivity of derivatives of **1** toward hydrocarbons, it was desirable to prepare 16-electron complexes of the type $[(N-N)Pt(CH_3)^+](L)$, were L is a weakly coordinated neutral or anionic ligand. High reactivity might be achieved in a solvent that is both inert and has a poor affinity for the electrophilic metal center, while at the same time being sufficiently polar to dissolve the cationic complex. For this purpose, we selected 2,2,2-trifluoroethanol (TFE), a low-nucleophilicity but quite strongly ionizing solvent[12] that has been frequently used in the investigations of organic nucleophilic substitution reactions. Importantly, deuterated TFE-d_3 is available, although relatively expensive, for NMR studies.

When 1 equiv of HBF_4·Et_2O is added to a dichloromethane solution of **1** at −40 °C in the presence of ca. 3 equiv of water, an orange suspension is formed. Removal of the solvent and drying in vacuo gives an air-stable product that appears to be the

* Corresponding author. E-mail: mats.tilset@kjemi.uio.no.
† University of Oslo.
‡ SINTEF.

(1) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995,** *28,* 154.
(2) (a) Shilov, A. E.; Shulpin, G. B. *Chem. Rev.* **1997,** *97,* 2879. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed. Engl.* **1998,** *37,* 2180. (c) Bengali, A. A.; Arndtsen, B. A.; Burger, P. M.; Schultz, R. H.; Weiller, B. H.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *Pure Appl. Chem.* **1995,** *67,* 281. (d) Crabtree, R. H. *Chem. Rev.* **1995,** *95,* 987.
(3) For leading references, see ref 2a and: (a) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995,** *504,* 75. (b) Hutson, A. C.; Lin, M.; Basickes, N.; Sen, A. *J. Organomet. Chem.* **1995,** *504,* 69.
(4) Abbreviations: tmeda = tetramethylethylenediamine; Tp′ = hydridotris-(3,5-dimethylpyrazolyl)borate; bpym = 2,2′-bipyrimidine; OTf⁻ = triflate; BAr_f⁻ = [3,5-(CF_3)_2C_6H_3]_4B⁻.
(5) (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.
(6) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997,** *119,* 10235.
(7) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998,** *280,* 560.
(8) Johansson, L.; Ryan, O. B.; Rømming, C.; Tilset, M. *Organometallics* **1998,** *17,* 3957.

(9) The diimine ligand was synthesized by modification of methods for the preparation of similar diimines: tom Dieck, H.; Svoboda, M.; Grieser, T. *Z. Naturforsch.* **1981,** *36B,* 823. For details, see Supporting Information.
(10) (N−N)Pt(CH_3)_2 (**1**). Prepared from the diimine and $Pt_2(CH_3)_4(\mu\text{-}SMe_2)_2$ (Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983,** *2,* 1643). ^1H NMR (200 MHz, dichloromethane-d_2) δ 1.14 (s, $^2J(^{195}Pt-H) = 87.2$ Hz, 6 H, PtCH_3), 1.35 (s, 6 H, NC*Me*C*Me*N), 7.57 (s, 4 H, ArH_o), 7.89 (s, 2 H, ArH_p). ^{19}F NMR (188 MHz, dichloromethane-d_2) δ −63.14 (s, ArCF_3).
(11) This is corroborated by the following reversible electrode potentials for the first ligand-centered reductions of (ArN=CMeCMe=NAr)Pt(CH_3)_2 (cyclic voltammetry, acetonitrile/0.1 M Bu_4NPF_6): Ar = p-MeC_6H_4, $E°$ = −1.75 V;[8] p-$MeOC_6H_4$, −1.76 V;[8] 3,5-$(CF_3)_2C_6H_3$, −1.42 V vs Cp_2Fe/Cp_2-Fe^+.
(12) (a) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976,** *98,* 7667. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry,* 3rd ed.; Harper and Row: New York, 1987; pp 335−340.

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aqua complex $[(N-N)Pt(CH_3)(OH_2)]^+(BF_4^-)$ ($2(BF_4^-)$).[13] The ^1H and ^{19}F NMR spectra of **2** in TFE-d_3 are consistent with a species of lower symmetry than **1**, and exhibit separate signals for the two halves of the diimine ligand. The $^2J(^{195}Pt-CH_3)$ coupling constant of 73.3 Hz is close to the observed couplings in related cationic species of the type $(diimine)Pt(CH_3)(L)^+$.[8] However, signals due to coordinated water could not be observed in the NMR spectra of **2** in TFE-d_3, presumably because of facile H/D exchange with the solvent. We have considered the possibility that BF_4^- or the solvent TFE-d_3 might be coordinated at $(N-N)-Pt(CH_3)^+$. Coordination of BF_4^- could be readily discounted because the generation of **2** from **1** with HOTf instead of $HBF_4\cdot Et_2O$ gave a product $2(OTf^-)$ with an identical ^1H NMR spectrum to that of $2(BF_4^-)$ in TFE-d_3. Furthermore, the ^{19}F NMR resonance for $2(BF_4^-)$ appeared at the same chemical shift as the BF_4^- resonances of coordinatively saturated BF_4^- salts. Further support for coordination of water was obtained from the low-temperature (-20 °C) ^1H NMR spectrum of **2** in dichloromethane-d_2 with small amounts of added TFE.[14] A signal attributed to coordinated H_2O appeared at δ 6.51 (br s, 2H). This signal was seen even with as much as 250 equiv of TFE present, establishing that TFE is a much poorer ligand than water. It appears likely that water remains coordinated when TFE is the solvent as well. The elemental analysis of $2(BF_4^-)$ also support that **2** is indeed $(N-N)-Pt(CH_3)(OH_2)^+$. The material $2(BF_4^-)$ as isolated from the reaction is at least 95% pure by ^1H NMR.[15] When dissolved in acetonitrile, $2(BF_4^-)$ cleanly produces $[(N-N)Pt(CH_3)(NCMe)]^+(BF_4^-)$.[16]

In TFE solution, $2(BF_4^-)$ readily reacts with aromatic C–H bonds. For example, it is quantitatively converted to the phenyl-substituted analogue $[(N-N)Pt(C_6H_5)(OH_2)]^+(BF_4^-)$[17] in TFE-$d_3$ (2–3 h, ambient temperature) under elimination of methane in the presence of 30 equiv of benzene (eq 1). Addition of aceto-

(1)

(2)
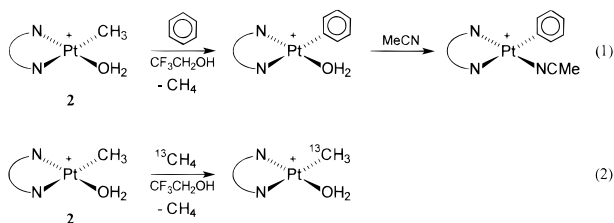
nitrile to the solution after the reaction cleanly gives $[(N-N)Pt-(C_6H_5)(NCMe)]^+(BF_4^-)$.[18] When C_6D_6 is reacted with $2(BF_4^-)$, multiple incorporation of deuterium in the resulting methane (CH_3D, CH_2D_2, CHD_3) is observed by ^1H NMR spectroscopy. Similar behavior was reported in an analogous reaction between $(tmeda)Pt(CH_3)(NC_5F_5)^+$ and C_6D_6,[5b,c] and by analogy, our findings are readily explained by the occurrence of a dynamic

equilibrium between $(N-N)Pt^{II}(CH_3)(\pi\text{-benzene})^+$, $(N-N)Pt^{IV}-(H)(CH_3)(C_6H_5)^+$, and $(N-N)Pt^{II}(\sigma\text{-}CH_4)(C_6H_5)^+$ intermediates. The likely involvement of a methane σ-adduct prompted us to investigate the possible reaction between $2(BF_4^-)$ and methane. It was indeed found that reaction with methane occurs under mild conditions.

When a solution of $2(BF_4^-)$ in TFE-d_3 at 45 °C is exposed to 20–25 bar of $^{13}CH_4$ (ca 20 equiv in solution by ^1H NMR), the exchange of $^{13}CH_3$ for CH_3 in the methyl group in **2** (eq 2) is readily observed by ^1H and $^{13}C\{^1H\}$ NMR. The Pt–CH_3 singlet undergoes a gradual replacement by a doublet, $^1J(^{13}C-H) = 129.0$ Hz, centered at the same chemical shift of δ 0.79. In the ^{13}C NMR spectrum, the Pt-CH_3 resonance at δ -10.2, with ^{195}Pt satellites ($^1J(^{195}Pt-C) = 744$ Hz), grows in intensity. After a reaction time of 45 h, the extent of ^{13}C incorporation was estimated to be ca. 43% of the total Pt–CH_3 present as **2** (^1H NMR integration). When the reaction was performed in the presence of ca. 11 equiv of added water, but under otherwise identical conditions to those above, a substantial decrease in reaction rate was observed; after 48 h the extent of ^{13}C incorporation in the methyl group was merely ca. 24%. This result suggests that the methane C–H activation at **2** requires dissociation of the aqua ligand to generate a vacant coordination site.

Slow decomposition of **2**, accompanied by precipitation of a thus far unidentified red material, was observed under the experimental conditions. By ^1H NMR spectroscopy, the extent of decomposition after 45 h was estimated at ca. 20% with or without methane present when no water was added. Decomposition was diminished to ca. 5% with 11 equiv of water added to the solution. There was no discernible formation of platinum black in these reactions.

Two fundamentally different mechanisms are predominant in the activation of alkane C–H bonds. Oxidative addition is predominant for the late, relatively low-valent metal complexes, whereas the σ-bond metathesis pathway is normally observed for early, usually d^0, metals. Recently, Bergman and co-workers reported alkane activation at the cationic Ir^{III} center $Cp^*Ir(PMe_3)-(CH_3)^+$.[19] Recent theoretical work has suggested that an oxidative addition pathway via Ir^V intermediates is preferred in these reactions.[20] For the current $(diimine)Pt$ system, ongoing DFT calculations suggest that oxidative addition is preferred also in this case.[21]

The C–H activation reactions that we have described at the complex **2** appears to occur under the mildest reaction conditions yet reported for such processes at cationic Pt complexes. The use of a hydroxylic solvent makes these results particularly relevant to the classical Shilov system for alkane activation and functionalization.

(13) $[(N-N)Pt(CH_3)(OH_2)]^+(BF_4^-)$ ($2(BF_4^-)$). ^1H NMR (200 MHz, TFE-d_3) δ 0.79 (s, $^2J(^{195}Pt-H) = 73.3$ Hz, 3 H, PtMe), 1.80 (s, 3 H, NCMeC′MeN), 2.05 (s, 3 H, NCMeC′MeN), 7.58 (s, 2 H, ArH_o), 7.71, (s, 2 H, Ar′H_o), 8.00 (s, 2 H, ArH_p and Ar′H_p). ^{19}F NMR (188 MHz, TFE-d_3) δ -151.83 (s, 4 F, BF_4^-), -63.64 (s, 6 F, ArCF_3), -63.52 (s, 6 F, Ar′CF_3).

(14) At ambient temperature, complex $2(BF_4^-)$ is only poorly soluble in dichloromethane and decomposes slowly under elimination of methane to uncharacterized products. The addition of 250 equiv of TFE improved the solubility: ^1H NMR (200 MHz, dichloromethane-d_2, -20 °C) δ 0.62 (s, $^2J(^{195}Pt-H) = 73.5$ Hz, 3 H, PtMe), 1.81 (s, 3 H, NCMeC′MeN), 2.07 (s, 3 H, NCMeC′MeN), 6.51 (br s, Pt(OH_2)), 7.58 (s, 2 H, ArH_o), 7.70, (s, 2 H, Ar′H_o) 7.96 (s, 2 H, ArH_p and Ar′H_p).

(15) Due to the high reactivity of the complex towards most solvents, we have been unable to establish a satisfactory workup or recrystallization procedure.

(16) $[(N-N)Pt(CH_3)(NCMe)]^+(BF_4^-)$. ^1H NMR (200 MHz, TFE-d_3) δ 0.71 (s, $^2J(^{195}Pt-H) = 74.5$ Hz, 3 H, PtMe), 2.02 (s, 3 H, NCMeC′MeN), 2.10 (s, 3 H, Pt(NCMe)), 2.13 (s, 3 H, NCMeC′MeN), 7.59 (s, 2 H, ArH_o), 7.74, (s, 2 H, Ar′H_o), 8.01 (s, 1 H, ArH_p), 8.04 (s, 1 H, Ar′H_p). ^{19}F NMR (188 MHz, TFE-d_3) δ -152.06 (s, 4 F, BF_4^-), -63.64 (s, 6 F, ArCF_3), -63.41 (s, 6 F, Ar′CF_3).

(17) $[(N-N)Pt(C_6H_5)(OH_2)]^+(BF_4^-)$ (not isolated). ^1H NMR (200 MHz, TFE-d_3) δ 1.91 (s, 3 H, NCMeC′MeN), 2.19 (s, 3 H, NCMeC′MeN), 6.65–6.85 (m, 5 H, Pt–C_6H_5), 7.29 (s, 2 H, ArH_o), 7.65 (s, 1 H, ArH_p), 7.79 (s, 2 H, Ar′H_o), 8.05 (s, 1 H, Ar′H_p). ^{19}F NMR (188 MHz, TFE-d_3) δ -151.95 (s, 4 F, BF_4^-), -63.65 (s, 6 F, ArCF_3), -63.48 (s, 6 F, Ar′CF_3).

(18) $[(N-N)Pt(C_6H_5)(NCMe)]^+(BF_4^-)$. ^1H NMR (200 MHz, TFE-d_3) δ 2.01 (s, 3 H, Pt(NCMe), 2.14 (s, 3 H, NCMeC′MeN), 2.28 (s, 3 H, NCMeC′MeN), 6.65–6.75 (m, 5 H, Pt–C_6H_5), 7.27 (s, 2 H, ArH_o), 7.65 (s, 1 H, ArH_p), 7.81 (s, 2 H, Ar′H_o), 8.07 (s, 1 H, Ar′H_p). ^{19}F NMR (188 MHz, TFE-d_3) δ -152.01 (s, 4 F, BF_4^-), -63.63 (s, 6 F, ArCF_3), -63.37 (s, 6 F, Ar′CF_3). Identical to a sample prepared from $(N-N)Pt(C_6H_5)_2$ and $HBF_4\cdot Et_2O$ in acetonitrile.

(19) (a) Arndtsen, B. A.; Bergman, R. G. *Science* **1996**, *270*, 1970. (b) Luecke, H. F.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11538.

(20) (a) Strout, D. L.; Zaric, S.; Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 6068. (b) Su, M.-D.; Chu, S.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 5373. (c) Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1998**, *120*, 6169.

(21) Heiberg, H.; Swang, O., personal communication.