Evidence for Associative Methane Loss Following Protonation of (Diimine)Pt^{II}(CH$_3$)$_2$: Three-Coordinate 14-Electron Cations L$_2$Pt(CH$_3$)$^+$ Are Not Necessarily Intermediates in C–H Activation at Cationic Pt Complexes

Lars Johansson and Mats Tilset*

Department of Chemistry, University of Oslo
P.O. Box 1033 Blindern, N-0315 Oslo, Norway

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The development of methods for direct, selective oxidation of methane to value-added products remains a major challenge to chemists.[1] During the past decade, important advances toward this goal have been demonstrated in processes[2] related to the classical Shilov system,[3] in which methane is catalytically converted to methanol by Pt^{II}/Pt^{IV} salts in aqueous media. The nature of the C–H activation at Pt^{II} in the Shilov system has been the subject of experimental[4] and theoretical[5] investigations. Considerable mechanistic insight has been obtained from stoichiometric model reactions between cationic Pt^{II} complexes and hydrocarbons,[4b–d] as well as studies on the reverse reaction–elimination of alkanes from Pt^{IV} hydridoalkyl species.[4a,e–g] Relatively stable Pt^{IV} hydridomethyl complexes are available if a suitable ligand occupies the coordination site trans to the hydride,[4a,e–g,6] and have been extensively used to study the mechanism for reductive elimination of methane (Scheme 1). Substantial evidence has demonstrated the need to dissociate the ligand trans to the hydride (a) before reductive elimination occurs.[4a,e–g,5e] The resulting 5-coordinate intermediate undergoes reductive C–H coupling (b) to form a methane σ complex before the final loss of methane and ligand reattachment (c).

Nevertheless, there are still mechanistic details that remain unclear. For example, it has not been clearly established whether the last step (c) of the reaction is dissociative or associative.[7,8]

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(7) The protonolysis of *trans*-(PEt$_3$)$_2$Pt(H)(Cl) by HCl in methanol showed a first-order dependence on [Cl$^-$], interpreted in terms of associative displacement of methane by Cl$^-$. See ref 4a.

(8) Associative mechanisms have been reported for solvent exchange reactions at (L–L)Pt(CH$_3$)(DMSO)$^+$ species (L–L = various chelating diimines and diamines). Romeo, R.; Scolaro, L. M; Nastasi, N.; Arena, G. *Inorg Chem.* **1996**, *35*, 5087.
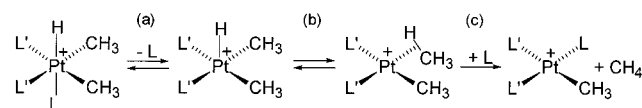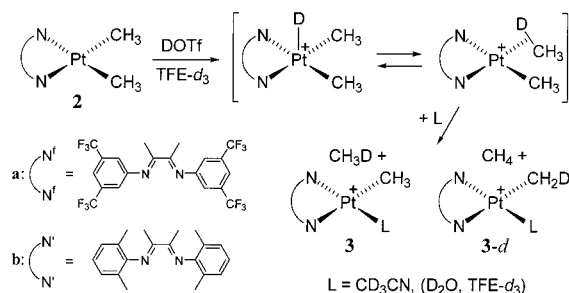
The former necessitates the existence of a highly reactive, 3-coordinate, 14-electron L$_2$Pt(CH$_3$)$^+$ species on the reaction coordinate. The principle of microscopic reversibility then dictates that the first step in methane C–H activation is also dissociative, with methane attacking the unsaturated metal center.

Recently, we reported that methane C–H activation occurs at the aqua complex (N^f-N^f)Pt(CH$_3$)(H$_2$O)$^+$BF$_4^-$ (**1**; N^f-N^f = ArN= CMe–CMe=NAr, Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$)) under unusually mild conditions in the poorly coordinating solvent 2,2,2-trifluoroethanol (TFE).[9] The reaction between **1** and CD$_4$ led to extensive deuterium scrambling and formation of CH$_n$D$_{4-n}$ isotopomers, as previously seen for the related species (tmeda)Pt(CH$_3$)(NC$_5$F$_5$)$^+$-BAr$_f^-$.[4b,c,10] This phenomenon was explained in terms of the dynamic equilibrium (b) in Scheme 1. The reaction between **1** and methane was inhibited by addition of ~0.3 M water, indicating preequilibrium loss of water prior to the rate-limiting step. Two alternative scenarios that account for this behavior might be envisioned: (1) a preequilibrium *dissociative* pathway via the coordinatively unsaturated 14-electron intermediate (N^f-N^f)Pt(CH$_3$)$^+$ followed by methane coordination to give the σ-methane complex (N^f-N^f)Pt(σ-CH$_4$)(CH$_3$)$^+$, or (2) a solvent-assisted associative pathway via the TFE complex (N^f-N^f)Pt(CH$_3$)-(TFE)$^+$.[11] We report here results from studies of the microscopic reverse reaction, the elimination of methane through protonolysis of Pt^{II} dimethyl complexes, that strongly suggest that the latter mechanism operates at least in some cases.

Protonation of (N^f-N^f)Pt(CH$_3$)$_2$ (**2a**) or (N'-N')Pt(CH$_3$)$_2$ (**2b**; N'-N' = ArN=CMe–CMe=NAr, Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$) with 1 equiv of HOTf[10] in TFE causes elimination of methane, presumably via (N-N)Pt^{IV}(H)(CH$_3$)$_2^+$ and (N-N)Pt^{II}(CH$_3$)(σ-CH$_4$)$^+$ intermediates.[12] Coordination of a suitable ligand (L = TFE, H$_2$O, MeCN) produces the observed cationic (N-N)Pt^{II}(CH$_3$)(L)$^+$ products **3**. If the protonolysis is performed with DOTf, two extremes might be envisioned for the outcome of the reaction (Scheme 2). If the scrambling process is slow relative to the loss

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(10) Abbreviations: tmeda = tetramethylethylenediamine; BAr$_f^-$ = (3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B$^-$; OTf$^-$ = triflate.

(11) A direct preequilibrium displacement of water by methane in the C–H activation experiments performed in TFE can be ruled out: The methane binding step must be rate determining in order to account for the fact that H/D exchange within a proposed (N^f-N^f)Pt(CH$_3$)(σ-CD$_4$)$^+$ intermediate is much faster than methane binding to the substrate (see ref 9).

(12) Two (N^f-N^f)Pt(CH$_3$)$_2$(H)(L)$^+$ species can be observed after protonation in CD$_2$Cl$_2$ (no MeCN) at low temperature (see ref 9b). Low-temperature protonation of poorly soluble **2** in TFE-d_3 (no MeCN) leads to production of **3** and methane with no detectable intermediates.
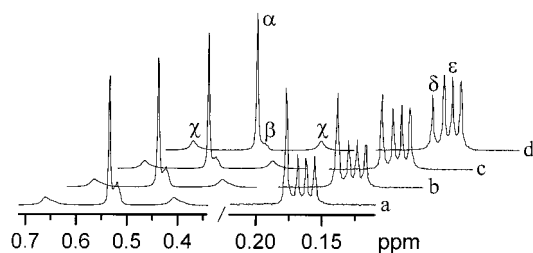
Figure 1. Selected parts of the ¹H NMR spectra (300 MHz) of products obtained after treatment of **2b** with 1 equiv DOTF in: (a) TFE-d_3. CD$_3$-CN was added after complete reaction. (b) 0.5 M CD$_3$CN/TFE-d_3. (c) 2.0 M CD$_3$CN/TFE-d_3. (d) 6.0 M CD$_3$CN/TFE-d_3. Legend: (α) PtC*H₃* of **3b**; (β) PtC*H₂*D of **3b**-*d*; (χ) ¹⁹⁵PtC*Me* of **3b/3b**-*d* (^2J(¹⁹⁵Pt−H) = 75 Hz); (δ) CH$_4$; (ϵ) CH$_3$D (^2J(D−H) = 1.9 Hz).

Table 1. Methane Isotopomer Mixtures (%) Formed in the Reaction between **2a/b** and DOTf

	2a		**2b**	
solvent	CH$_4$	CH$_3$D	CH$_4$	CH$_3$D
TFE-d_3	41	59	37	63
0.5 M CD$_3$CN/TFE-d_3	35	65	33	67
2.0 M CD$_3$CN/TFE-d_3	31	69	28	72
6.0 M CD$_3$CN/TFE-d_3	28	72	15	85
0.5 M D$_2$O/TFE-d_3	40	60		

of methane from the σ complex, **3** and CH$_3$D are expected as the only products.[13] On the other hand, if the scrambling occurs rapidly compared to the methane loss, a mixture of **3**/CH$_3$D (1:1) and **3**-*d*/CH$_4$ (1:1) would be formed; complete scrambling would result in a 43:57 mixture[14] of CH$_4$ and CH$_3$D. If scrambling and methane loss occur at comparable rates, product distributions between these extremes should arise. Moreover, the product distribution should be dependent on [L] for an associative displacement of methane by L, whereas a dissociative process should give a product distribution independent of [L].[15]
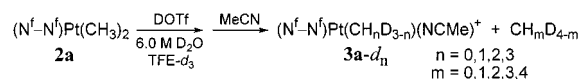
Solutions of **2a** and **2b** in TFE-d_3 with various amounts of acetonitrile-d_3 present were treated with 1 equiv of DOTf. The relative amounts of methane isotopomers CH$_4$ and CH$_3$D produced were determined by integration of the ¹H NMR spectra (see Figure 1 for **2b**). The results are summarized in Table 1. In the absence of CD$_3$CN, essentially complete scrambling occurred for **2a** and somewhat less complete for **2b**. The data show that the CH$_4$:CH$_3$D ratio decreases with increasing [CD$_3$CN] for both complexes.[16] A concomitant increase in the **3**:**3**-*d* ratio is also seen,

Scheme 3

$$(N^f\text{−}N^f)Pt(CH_3)_2 \xrightarrow[\substack{6.0\ M\ D_2O \\ TFE\text{-}d_3}]{DOTf} \xrightarrow{MeCN} (N^f\text{−}N^f)Pt(CH_nD_{3-n})(NCMe)^+ + CH_mD_{4-m}$$

$$\mathbf{2a} \qquad\qquad\qquad\qquad \mathbf{3a}\text{-}d_n \quad \substack{n = 0,1,2,3 \\ m = 0,1,2,3,4}$$

suggesting that H/D scrambling is effected only by the equilibrium process depicted in Scheme 1. The decrease in the CH$_4$:CH$_3$D ratio at increasing [MeCN] is most readily explained by an associative mechanism for the exchange of acetonitrile for methane at (N-N)Pt^{II}(CH$_3$)(σ-CH$_4$)$^+$.[17] By the principle of microscopic reversibility, this implies that *substitution of methane for MeCN at (N-N)Pt(CH₃)(NCMe)⁺ should occur associatively and that MeCN predissociation to provide a 3-coordinate intermediate is not required.*

The strength of Pt−L bonding at (N-N)Pt(CH$_3$)(L)$^+$ decreases in the order L = MeCN > H$_2$O > TFE > CH$_4$.[9b,13b] It is of particular interest to determine whether an associative mechanism also applies for methane coordination at (N-N)Pt(CH$_3$)(L)$^+$ for L = the better leaving groups H$_2$O and TFE (i.e. in the system where we have demonstrated true methane C−H activation).[9,12b] The reaction of **2a** with DOTf was therefore carried out in the presence of D$_2$O in TFE-d_3. The CH$_4$:CH$_3$D ratio obtained at [D$_2$O] = 0.5 M is essentially identical to that in neat TFE-d_3, that is, complete scrambling has occurred. This is consistent with both mechanisms that may show inhibition by water for the C−H activation (i.e. preequilibrium dissociative or solvent-assisted associative mechanisms). Water is expected to be a considerably poorer entering ligand than acetonitrile, less apt at competing with the intramolecular scrambling process in an intermolecular displacement of methane.

At higher [D$_2$O] a completely different outcome ensued. At [D$_2$O] = 6.0 M, the full range of methane isotopomers was observed by ¹H NMR (Scheme 3). The multiple D incorporation must result from reversible protonations at **2a**.[18] Presumably, this process is facilitated by the higher basicity of water relative to TFE and acetonitrile.[19]

In conclusion, we have shown that methane loss from protonated (N-N)Pt(CH$_3$)$_2$ complexes may proceed associatively, with the very important implication that methane associatively enters the coordination sphere of (N-N)Pt(CH$_3$)(L)$^+$ complexes in C−H activation reactions.

(13) (a) No H/D exchange occurs between the intermediates (N-N)Pt^{II}(CH$_3$)-(σ-CH$_4$)$^+$/(N-N)Pt^{IV}(H)(CH$_3$)$_2^+$ and TFE-d_3 under these conditions, i.e. deprotonation of the intermediates is slow compared to methane loss. See refs 9b,13b. (b) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846.
(14) D will be located in a σ-CH$_3$D ligand 57% (4/7) of the time, producing CH$_3$D, and in a CH$_2$D ligand that remains bonded to the metal 43% of the time. H/D kinetic isotope effects are ignored in this analysis.
(15) Competitive capture of a 3-coordinate intermediate by L and CH$_4$ could also give an [L]-dependent product ratio. However, this can be ruled out under the actual reaction conditions, since methane loss is irreversible on the experimental time scale (minutes at ambient temperature). Methane coordination is the rate-limiting step in the C−H activation process and takes place on a time scale of days at 45 °C even at elevated methane pressure (ref 9b).

(16) Bulk solvent effects should be insignificant since the dielectric constants for TFE and acetonitrile are of similar order (ϵ_{TFE} = 26.7, Evans, D. F.; McElroy, M. I. *J. Solution Chem.* **1975**, *5*, 405; ϵ_{MeCN} = 37.5, Harwood, L. M.; Moody, C. J. *Experimental Organic Chemistry*; Blackwell Science: Great Britain, 1995; pp 740).
(17) The rate of the scrambling process, i.e. step (b) and methane "rotation" at Pt (Scheme 1) is assumed not to be affected by [MeCN].
(18) Interestingly, this behavior is consistent with Shilov's original observation of multiple methane H/D exchange by Pt^{II} in aqueous solution, and clearly strengthens the relevance of our model system in this respect. Goldshlegger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zhur. Fiz. Khim.* **1969**, *43*, 2174. See also ref 1e.
(19) Analogous multiple solvent D incorporation into methane was also observed in the protonation of (tmeda)Pt(CH$_3$)$_2$ in methanol-d_4, a solvent more basic than TFE-d_3. See ref 4a.