

C–H Activation at Cationic Platinum(II) Centers

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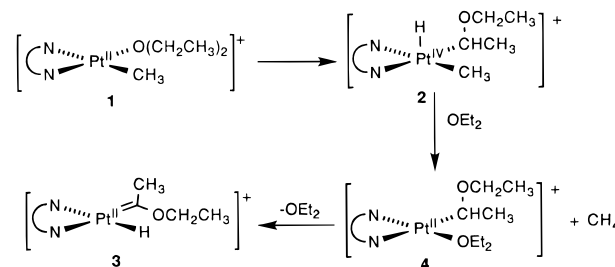
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The oxidation of alkanes to alcohols by aqueous solutions containing $[\text{PtCl}_4]^{2-}$ and $[\text{PtCl}_6]^{2-}$ has been the subject of recent mechanistic studies.² These support a multistep mechanism, in which the key first step, the actual C–H bond activation, involves reaction of alkane with a Pt^{II} complex. Most of our evidence concerning the nature of this step comes indirectly, from studies on the microscopic reverse reaction—protonolysis of Pt^{II} alkyls such as $(\text{tmeda})\text{Pt}(\text{CH}_3)_2$ ($\text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine)—which implicate both a σ complex, $\text{Pt}^{\text{II}}(\text{R}\text{H})$, and an oxidative adduct, $\text{Pt}^{\text{IV}}(\text{R})(\text{H})$, as intermediates.³ To date, however, neither the intermolecular reaction of an alkane and a Pt^{II} complex to give a stable organoplatinum species nor the oxidation of alkanes by Pt^{II} complexes containing amine or phosphine ligands has been reported.⁴ Our findings suggested that a sufficiently electrophilic $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{solvent})]^+$ complex should be able to activate alkane C–H bonds. We report here our preliminary results that demonstrate such reactivity and strengthen the relevance of our model studies to the alkane oxidation mechanism.

Addition of 1 equiv of $[\text{H}(\text{OEt}_2)_n][\text{BAR}_f]$ ($\{\text{BAR}_f = \text{B}(3,5\text{-C}_6\text{H}_3\text{-CF}_3)_2\}_4\}$ ⁵) to an ether solution of $(\text{tmeda})\text{Pt}(\text{CH}_3)_2$ at -70°C gives $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{OEt}_2)][\text{BAR}_f]$ (**1**).⁶ This complex is stable in solution at low temperature and may be isolated as a solid;⁷ but at room temperature in solution it slowly reacts, ultimately giving methane (92% collected by Toepler pump) and the carbene hydride complex **3**.⁸ This transformation presumably proceeds via C–H activation to give **2** (Scheme 1).⁹ Only coordinated ether undergoes C–H activation, as **1** dissolved in $\text{Et}_2\text{O}-d_{10}$ gives only CH_4 , whereas **1**- d_{10} in $(\text{C}_2\text{H}_5)_2\text{O}$ gives CH_3D

Scheme 1



(as well as some CH_4 , CH_2D_2 , and CHD_3 ; see below).¹⁰ Similar chemistry is observed in THF.¹¹

Demonstration of *intermolecular* C–H activation requires a solvent that is not subject to activation itself, does not coordinate so strongly that alkane activation is blocked, and dissolves ionic complexes.¹² Pentafluoropyridine proves to be suitable: reaction of $(\text{tmeda})\text{Pt}(\text{CH}_3)_2$ with $[\text{H}(\text{NC}_5\text{F}_5)_n][\text{BAR}_f]$ ¹³ in NC_5F_5 at 0°C gives $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{NC}_5\text{F}_5)][\text{BAR}_f]$ (**5**).¹⁴ At 85°C in the presence of benzene **5** is converted to the phenyl analog (81% of methane collected by Toepler pump);¹⁵ while under 30 atm $^{13}\text{CH}_4$ the methyl exchange shown in eq 1 is demonstrated by the slow growth of the $\text{Pt}-^{13}\text{CH}_3$ resonance in the ^{13}C NMR spectrum at -21 ppm ($J_{\text{Pt-C}} = 725$ Hz). The latter reaction is accompanied by slow deposition of metallic platinum, which is connected to the C–H activation process: no Pt^0 is observed upon heating **5** to 85°C in the absence of hydrocarbon. Reaction with neopentane gives rapid decomposition of **5** to Pt^0 , while reaction with benzene gives only traces of metallic Pt .¹⁶

Upon heating **5** at 85°C with cyclohexane- d_{12} , toluene- d_8 , or benzene- d_6 in pentafluoropyridine, the methane isotopomers

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(4) A ^1H NMR signal attributed to $[\text{Pt}(\text{CH}_3)\text{Cl}_5]^{2-}$ was detected in a cooled reaction mixture following oxidation of methane;¹ however, no corresponding signal was observed under reaction conditions using a high-pressure NMR cell: Horvath, I. T.; Cook, R. A.; Millar, J. M.; Kiss, G. *Organometallics* **1993**, 12, 8. The electrophilic activation of arenes by *trans*-(Me_3P)₂Pt(neopentyl)(triflate) has been observed: Brainard, R. L.; Nutt, W. R.; Lee, T. R.; Whitesides, G. M. *Organometallics* **1988**, 7, 2379.

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(6) Related complexes with a different chelating ligand (a substituted 2,2'-bipyridine) have recently been reported: Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809.

(7) $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{OEt}_2)][\text{BAR}_f]$ (**1**): Elem. Anal. Calcd for $\text{C}_{43}\text{H}_{41}\text{N}_2\text{F}_{24}\text{BOPt}$: C, 40.87; H, 3.27; N, 2.22. Found: C, 40.98; H, 3.41; N, 2.21%. ^1H NMR ($\text{THF}-d_8$). δ 0.648 (s with Pt satellites, $J_{\text{Pt-H}} = 77$ Hz); 1.43 (t, 6H); 2.76 (s, 6H); 2.82 (s, 6H); 2.6–3.0 (m, 4H); 3.98 (q, 4H); 7.58 (s, 4H); 7.78 (s, 8H).

(8) $[(\text{tmeda})\text{Pt}(\text{C}(\text{CH}_3)(\text{OCH}_2\text{CH}_3)(\text{H}))][\text{BAR}_f]$ (**3**): Elem. Anal. Calcd for $\text{C}_{42}\text{H}_{37}\text{N}_2\text{F}_{24}\text{BOPt}$: C, 40.43; H, 2.99; N, 2.24. Found: C, 41.19; H, 3.41; N, 2.19%. ^1H NMR ($\text{Et}_2\text{O}-d_{10}$). δ -17.4 (s, 1H, $J_{\text{Pt-H}} = 1640$ Hz); 1.52 (t, 3H); 2.48 (m); 2.58 (s, 3H); 2.84 (s, 6H); 2.90 (s, 6H); 2.6–3.0 (m); 5.23 (q, 2H); 7.58 (s, 4H); 7.78 (s, 8H). ^{13}C NMR ($\text{Et}_2\text{O}-d_{10}$). δ 276 ($J_{\text{Pt-C}} = 1250$ Hz); 82.5 ($J_{\text{Pt-C}} = 140$ Hz); 62.8; 62.7; 52.9; 52.2; 44.9; 43.4 ($J_{\text{Pt-C}} = 160$ Hz) (plus anion peaks in the aromatic region).

(9) At early stages of the reaction ^1H NMR reveals several species which appear to include **4** and a vinyl ether complex in addition to **3**. Over the course of a week all gradually convert to **3**. Although **2** is shown as five-coordinate, we believe such coordinatively unsaturated species exist only as transient intermediates (see ref 3b); most probably in its stable form **2** is six-coordinate, with solvent ether (or, conceivably, O from the ethoxyethyl group) completing the octahedron. The same applies to other five-coordinate structures shown (or implied) here.

(10) A referee suggested an alternate possibility, that coordinated ether undergoes not oxidative addition to give **2** but rather electrophilic activation to liberate H^+ which subsequently protonolyzes a $\text{Pt}-\text{CH}_3$ bond. This is ruled out by the following crossover experiment: reaction of a mixture of $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{O}(\text{C}_2\text{D}_5)_2)][\text{BAR}_f]$ and $[(\text{tmeda})\text{Pt}(^{13}\text{CH}_3)(\text{OEt}_2)][\text{BAR}_f]$ in $\text{C}_5\text{F}_5\text{N}$ gives no methane containing both ^{13}C and D.

(11) $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{THF})][\text{BAR}_f]$: Elem. Anal. Calcd for $\text{C}_{43}\text{H}_{39}\text{N}_2\text{F}_{24}\text{BOPt}$: C, 40.94; H, 3.12; N, 2.22. Found: C, 41.19; H, 3.41; N, 2.19%. ^1H NMR ($\text{THF}-d_8$). δ 0.586 (s, 3H, $J_{\text{Pt-H}} = 83$ Hz); 1.43 (t, 6H); 2.76 (s, 6H); 2.82 (s, 6H); 2.6–3.0 (m, 4H); 3.98 (q, 4H); 7.58 (s, 4H); 7.78 (s, 8H). This compound also slowly converts to a carbene hydride analogous to **3**.

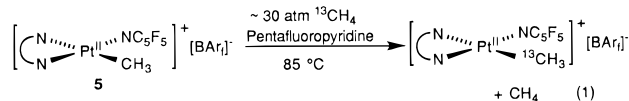
(12) The reaction of $(\text{tmeda})\text{Pt}(\text{CH}_3)_2$ with $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}_f]$ in chlorinated solvents such as dichloromethane and chlorobenzene results in C–Cl activation; the dimer $[(\text{tmeda})\text{PtCl}_2][\text{BAR}_f]$ can be isolated. The initial ^1H NMR spectrum reveals a complex mixture of products, but after several hours a crystalline product is isolated in 60% yield and identified as $[(\text{tmeda})\text{PtCl}_2][\text{BAR}_f]_2$ by X-ray crystallography, elemental analysis, and ^1H NMR. Elem. Anal. Calcd for $\text{C}_{38}\text{H}_{28}\text{N}_2\text{F}_{24}\text{BClPt}$: C, 37.72; H, 2.33; N, 2.32. Found: C, 37.5; H, 2.52; N, 2.37. ^1H NMR (CD_2Cl_2): δ 2.5–3.2 (m, 16H); 7.6 (s, 4H); 7.7 (s, 8H).

(13) Prepared *in situ* by dissolving $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}_f]$ in pentafluoropyridine and removing solvent *in vacuo* (repeated several times).

(14) $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{NC}_5\text{F}_5)][\text{BAR}_f]$ (**5**): Elem. Anal. Calcd for $\text{C}_{44}\text{H}_{31}\text{N}_3\text{F}_{29}\text{BPT}$: C, 38.9; H, 2.3; N, 3.09. Found: C, 38.5; H, 2.7; N, 3.35. ^1H NMR ($\text{THF}-d_8$). δ 0.30 (s, 3H, $J_{\text{Pt-H}} = 75$ Hz); 2.65 (s, 6H); 2.96 (s, 6H); 2.6–3.2 (m, 4H); 7.58 (s, 4H); 7.78 (s, 8H).

(15) $[(\text{tmeda})\text{Pt}(\text{C}_6\text{H}_5)(\text{NC}_5\text{F}_5)][\text{BAR}_f]$: Elem. Anal. Calcd for $\text{C}_{49}\text{H}_{33}\text{N}_3\text{F}_{29}\text{BPT-NC}_5\text{F}_5$: C, 40.8; H, 2.09; N, 3.52. Found: C, 40.43; H, 2.39; N, 3.43. ^1H NMR (NC_5F_5). δ 2.68 (s, 6H); 2.89 (s, 6H); 2.6–3.2 (m, 4H); 6.26 (t, 1H); 6.56 (t, 2H); 7.24 (sh, 1H, peak and Pt satellites obscured by BAR_f hydrogens); 7.26 (s, 4H); 7.67 (s, 8H).

(16) On heating a solution of **5** (0.05 mmol) and neopentane (1.5 mmol) in $\text{C}_5\text{F}_5\text{N}$ (0.5 mL), visible formation of Pt metal began almost immediately; after several hours at 85°C a sizable Pt mirror had formed. A similar reaction with benzene gave nearly complete conversion of **5** after 7 h at 115°C only a small amount of metallic Pt visible.

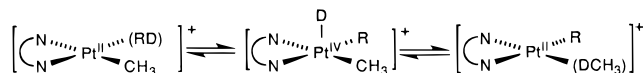


CH_4 , CH_3D , CH_2D_2 , and CHD_3 are observed by ^1H NMR after several days.¹⁷ Similar (multiple) H/D exchange observed in protonolysis of $(\text{tmeda})\text{Pt}(\text{CH}_3)_2(\text{H})\text{Cl}^3$ has been interpreted in terms of an equilibrium between Pt^{IV} dialkyl hydride and Pt^{II} σ -complex species (Scheme 2). The possibility that multiple exchange occurs via reversible loss and readdition of methane is ruled out by heating **5** with C_6D_6 under $^{13}\text{CH}_4$; no methane containing both ^{13}C and D is observed.

It should be noted that very similar activation of alkane and ether C–H bonds is observed for the Ir^{III} complexes $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{CH}_3)(\text{ClCH}_2\text{Cl})][\text{BARf}]$ and $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{CH}_3)(\text{OTf})$.¹⁸ A σ -bond metathesis mechanism has been offered as

(17) In a typical experiment, using C_6D_6 , the product distribution of CH_4 : CH_3D : CH_2D_2 was approximately 4:7:9 (by ^1H NMR), with a few percent of CHD_3 . The CH_4 probably arises from competing reaction and/or exchange with protonic impurities on glass surfaces and elsewhere, as prewashing the NMR tube with D_2O followed by thorough drying reduces the relative yield of CH_4 by half. Only a few percent of CH_4 is obtained in decomposition of $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{O}(\text{C}_2\text{D}_5)_2)][\text{BARf}]$.

Scheme 2



an alternative to oxidative addition as in Scheme 2, perhaps partly because of the unattractiveness of the Ir^{V} intermediate required for the latter.¹⁹ We cannot exclude σ -bond metathesis for reactions of **1** and **5**, although the multiple H/D exchange requires at a minimum that there be an intermediate, such as a σ complex (Scheme 2), with significant lifetime. Delineation of the various modes of C–H activation and their applicability to catalytic alkane functionalization remains the subject of further study.

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