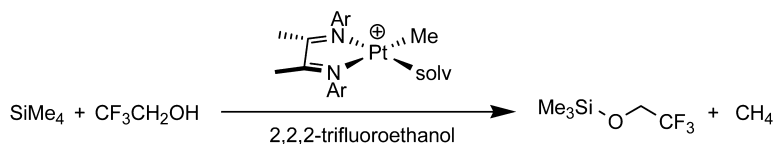


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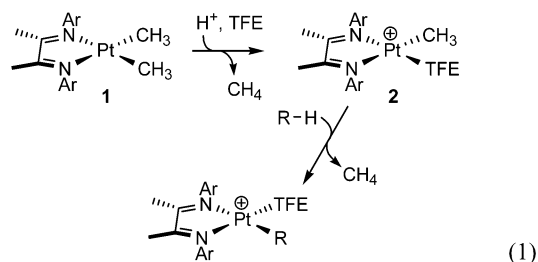
Catalytic Alcoholysis of Tetramethylsilane via Pt-Mediated C–H Bond Activation

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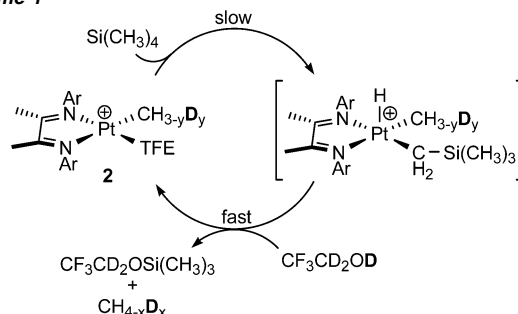
Square-planar, d^8 complexes of platinum have received considerable attention as potential catalysts in selective alkane oxidation schemes.¹ Cationic platinum(II) complexes of the general formula $[(NN)PtMe(TFE)]^+$ (NN = a chelating α -diimine ligand; TFE = 2,2,2-trifluoroethanol), generated by protonolysis of the corresponding neutral dimethyl $(NN)PtMe_2$ (**1**) in TFE, have been particularly useful as mechanistic probes for individual steps of the catalytic oxidation.² Ongoing studies into the rate- and selectivity-determining C–H activation step (Eq 1) have provided a working mechanistic model, the details of which continue to evolve. As part of a study into the kinetic and thermodynamic preferences for aliphatic C–H bond activation, we examined the reaction of tetramethylsilane (TMS) with $[(NN)PtMe(TFE)][X]$ (**2**; NN = 2,3-bis(3,5-dimethylphenylimino)butane; $X = [(CF_3CH_2O)B-(C_6F_5)_3]^-$, $B[C_6H_3(CF_3)_2]_4^-$). Although reaction at a C–H bond of TMS apparently occurs, the initial C–H activation product proved to be unstable, and catalytic conversion of TMS and TFE solvent to methane and $Me_3SiOCH_2CF_3$ was observed. We report here our preliminary studies of this novel transformation.



Solutions of **2** in TFE- d_3 were readily generated upon dissolution of **1** and either $H(OEt_2)_2[B(C_6H_3(CF_3)_2)_4]$ or $B(C_6F_5)_3$.³ Following addition of TMS (0.35 mmol, 0.52 M, 36 equiv relative to **2**) to a TFE- d_3 solution of **2**, the signature 1H NMR resonance for TMS decayed with concomitant growth of a new signal at δ 0.18. Integration ratios in the 1H NMR spectrum indicated 75% consumption of TMS after 18 h at 26 °C. Throughout the reaction, 1H NMR signals for **2** were unchanged except for diminution of the resonance for the platinum-bound methyl group accompanied by the appearance of upfield multiplets for the Pt- CH_2D and Pt- CHD_2 isotopomers of platinum cation **2**. After 18 h, integration of ligand backbone resonances indicated that over 75% of **2** remained; 0.29 mmol of gas (30 equiv relative to **2**, TOF = 1.6 h^{-1}) was then collected from the reaction solution by Toepler pump and was identified as a mixture of methane isotopomers by gas-phase IR spectroscopy.⁴

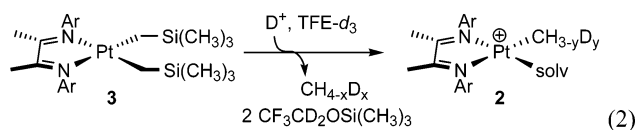
Methane formation in tandem with TMS consumption suggests that **2** catalyzes Si–C bond alcoholysis to produce Me_3SiOCH_2-

Scheme 1



CF_3 . The ^{13}C NMR spectrum of the reaction solution exhibited a new Si– CH_3 resonance at δ -0.7 and a new CF_3 resonance at δ 126.1 ppm ($^1J_{CF} = 277$ Hz); an independently prepared sample of $Me_3SiOCH_2CF_3$ ⁵ exhibited the same 1H and ^{13}C NMR signals. Combined with the above-noted H/D exchange between Pt– CH_3 and CF_3CD_2O-D , these observations suggest that a rate-determining C–H activation step,⁶ analogous to previously reported arene activation reactions, initiates a rapid solvolysis reaction (Scheme 1).^{7,8}

Protonolysis reactions of $(NN)Pt(CH_2SiMe_3)_2$ (**3**) were used to probe the mechanism of the fast, product-forming step of Scheme 1. The reaction of *cis/trans*- $PtCl_2(SMe_2)_2$ with $Li(CH_2SiMe_3)$ at low temperature followed by addition of 1,2-bis(3,5-dimethylphenylimino)butane afforded dark purple **3** as a semicrystalline solid (see Supporting Information for details). **3** dissolved slowly into TFE- d_3 containing excess $B(C_6F_5)_3$ to afford 2 equiv of $Me_3SiOCD_2CF_3$ and one equivalent each of methane and **2**, both partially deuterated (eq 2). No free TMS was observed and no deuterium incorporation was observed in the methyl groups of the silyl ether product.

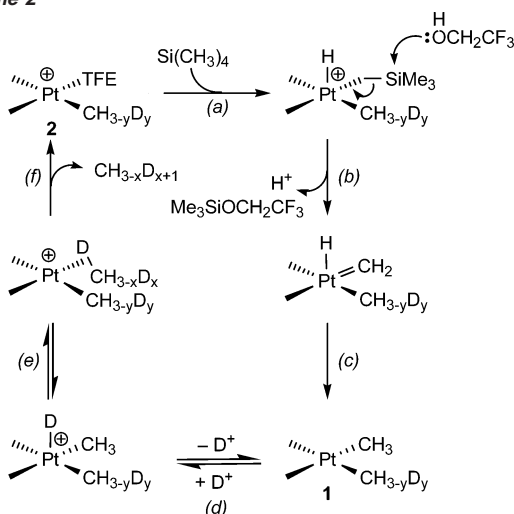


The same results were obtained for the protonation of **3** at -80 °C with $D(OEt_2)_2[B(3,5-C_6H_3(CF_3)_2)_4]$ in THF- d_8 containing TFE- d_3 ($[TFE-d_3] = 0.2-1.1$ M), except that **2** formed as the THF adduct. Significantly, addition of excess TMS to this reaction afforded no additional silyl ether, indicating that the THF adduct of **2** was not reactive toward TMS. Hence, both equivalents of $Me_3SiOCD_2CF_3$ must be produced directly from protonolysis of **3** rather than by liberation and subsequent activation of TMS. Finally, solutions of **3** in THF containing TFE produced no silyl ether without acid addition.

These results appear to be most consistent with the mechanism presented in Scheme 2 for the catalytic functionalization of TMS.

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Scheme 2



An initial, rate-determining C–H activation of TMS by **2** (step a) reflects the established reactivity pattern of these platinum cations with hydrocarbon substrates.² Protonolysis reactions of **3** support a subsequent solvolytic cleavage of the Si–C bond via nucleophilic attack by TFE (step b). Two factors suggest that this nucleophilic attack at silicon must be fast relative to both reductive coupling⁹ and alkane elimination:^{10,11} (1) protonation of **3** in the presence of TFE gave no TMS, but rather 2 equiv of the silyl ether product, and (2) incorporation of deuterium was not observed in the SiMe₃ group under any circumstances. Elimination of the silyl ether in step b would produce a transient, neutral methylidene hydride complex that rearranges to **1** by an α -hydrogen migration (step c). In an acidic environment, **1** readily loses methane (with isotopic scrambling; steps d and e) to regenerate the catalyst resting state, **2**.

Nucleophilic attack at the silicon of cationic [Pt^{IV}–CH₂SiMe₃] is reminiscent of the established reactivity of silyl groups β to an electropositive carbon center.¹² A related mechanism, in which the alcohol adds across the Si–C bond via a four-centered transition state, is also consistent with our observations. Two other mechanisms for the Si–C bond cleavage have precedent. β -methyl migration from the activated silane to platinum¹³ followed by addition of TFE to the coordinated silylene¹⁴ may be ruled out, since this would incorporate deuterium into the methyl groups of the silyl ether product. A rapid α -silyl migration^{15,16} to give a Pt^{IV}-(silyl)methylidene species does not account for the observed reactivity: if it follows alkane elimination, the protonolysis of **3** would give TMS (not observed), whereas if it precedes alkane elimination, the putative intermediate would require Pt^{VI}; moreover, **3** does not react with TFE to extrude the silyl ether product in the absence of added acid.

While stoichiometric cleavage of unactivated alkyl–Si bonds by transition metal centers, including platinum, have been reported,^{13,15–17} to our knowledge this is the first example of a catalytic Si–C bond cleavage and functionalization catalyzed by a transition metal complex.¹⁸ The coupling of C–H activation to nucleophilic attack at the activated alkylsilane affords a novel route for selective functionalization at the silicon center. We are currently exploring the scope and synthetic utility of this transformation.

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Supporting Information Available: Detailed experimental procedures including the synthesis and spectroscopic characterization of **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (3) B(C₆F₅)₃ dissolves in TFE to afford an acidic solution capable of protonating **1** to release methane and form **2**. Isotopic scrambling patterns are inconsistent with methide abstraction from **1**. Heyduk, A. F.; Labinger, J. A.; Bercaw, J. E., manuscript in preparation.
- (4) Isotopomers were readily observed in the C–H bending region of the IR spectrum: 1302 (CH₄), 1157 (CH₃D), 1090 (CH₂D₂), and 1034 (CHD₃) cm⁻¹.
- (5) Prepared by the reaction of Me₃SiCl with TFE in the presence of base.
- (6) Alternatively, a C–Si bond activation could initiate the solvolysis of TMS; however, based on the established reactivity of cationic platinum complexes with hydrocarbons and the reactivity of the putative [Pt–CH₂–SiMe₃] species (vide infra), we currently favor an initial, rate-determining C–H bond activation.
- (7) The persistence of **2** as well as its formation in stoichiometric reactions strongly suggests that it, rather than an impurity or decomposition product, participates in the catalytic cycle. Control experiments comprising solutions of TMS and B(C₆F₅)₃ in TFE-*d*₃, or of TMS in the presence of Zeise's dimer, H₂PtCl₆ or platinum metal, did not lead to formation of Me₃SiOCH₂CF₃.
- (8) At longer reaction times (after ca. 90% consumption of the TMS) secondary activation is observed, forming Me₂Si(OCH₂CF₃)₂ and another equivalent of methane.
- (9) Here, reductive coupling is used to describe the conversion of a platinum(IV) alkyl hydride species to a platinum(II) alkane σ species; a mechanism that could lead to isotope scrambling into the SiMe₃ group.
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