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# Activation of Si−C or C−H Bonds in Tetramethylsilane: Evidence from Protonolysis of (Trimethylsilyl)methyl−Platinum Bonds

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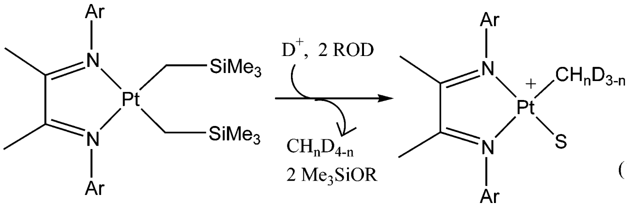
*Summary: Protonolysis of the (trimethylsilyl)methyl−platinum bonds in* $[Pt(CH_2SiMe_3)_2(NN)]$ *(NN = 4,4′-di-tert-butyl-2,2′-bipyridine) and in* $[Pt(CH_2SiMe_3)(NNC)]$ *(NNC =* $C_6H_4$*-2-CH=N-trans-*$C_6H_{10}$*-2-N=CHPh) is suggested to occur by protonation at platinum to give a 16-electron hydridoplatinum(IV) intermediate, followed by either rapid, concerted rearrangement to give a methyl(trimethylsilyl)platinum(IV) complex intermediate or reductive coupling to form tetramethylsilane (TMS). The direct characterization of (trimethylsilyl)platinum(IV) complex intermediates, such as* $[PtBrMe_2(SiMe_3)(NN)]$*, proves that the α-migration of the trimethylsilyl group from carbon to a cationic platinum center is easy and suggests that Si−C bond activation by electrophilic platinum(II) complexes may be an alternative to C−H activation.*

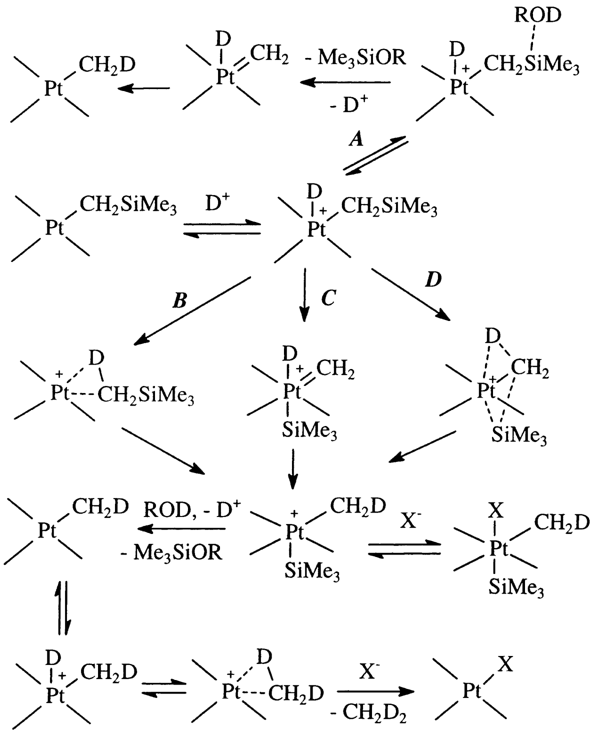
While studying of the activation of C−H bonds by electrophilic platinum complexes,[1] Heyduk, Labinger, and Bercaw recently discovered the catalytic alcoholysis of tetramethylsilane with ROH (R = $CF_3CH_2$) to give methane and $Me_3SiOR$.[2] To gain insight into the mechanism of this interesting catalytic reaction, the protonolysis of (trimethylsilyl)methyl−platinum(II) bonds was studied and shown to occur according to eq 1. No tetramethylsilane, the expected product of simple protonolysis, was formed. The similar reaction with $D^+$/ROD gave $Me_3SiOR$, with no deuterium incorporation into the MeSi groups, and a mixture of all isotopomers $CH_nD_{4-n}$.



(1)

These observations were interpreted in terms of the mechanism ***A*** (Scheme 1), which involves nucleophilic attack at silicon to cleave the Si−$CH_2$ bond in a cationic 16-electron hydridoplatinum(IV) intermediate. It was argued that mechanism ***B***, involving reductive coupling followed by α-migration of the $Me_3Si$ group, would lead to formation of some tetramethylsilane and probably to deuterium incorporation into the product $Me_3SiOR$ and that mechanism ***C***, involving earlier α-migration, would give a high-energy intermediate.[2,3]

**Scheme 1**



We have independently (Scheme 2) studied reactions of acids with the complexes $[Pt(CH_2SiMe_3)_2(NN)]$ (**2**; NN = 4,4′-di-*tert*-butyl-2,2′-bipyridine) and $[Pt(CH_2SiMe_3)(NNC)]$ (**4**; NNC = $C_6H_4$-2-CH=N-*trans*-$C_6H_{10}$-2-N=CHPh) and with the methylplatinum(II) analogues **1** and **3**,[4] and we suggest that the reactions occur by mechanism ***D***, in which the major product is formed by the concerted migration of hydride to carbon and of silicon to platinum. The evidence is outlined below.

The reaction of complex **4** with HCl in moist $CD_2Cl_2$ or $CD_2Cl_2/CD_3CN$ (1:1) occurred to give [PtCl(NNC)]

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(1) Recent references: (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (b) Iverson, C. H.; Carter, C. A. G.; Baker, R. T.; Scollard, J. D.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 12674. (c) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804. (d) Iron, M. A.; Lo, H. C.; Martin, J. M. L.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 7041. (e) Vedernikov, A. N.; Caulton, K. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 4102. (f) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7249. (g) Ong, C. M.; Jennings, M. C.; Puddephatt, R. J. *Can. J. Chem.* **2003**, *81*, 1196.

(2) Heyduk, A. F.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 6366.

(3) The short-lived platinum(IV) complex $[PtHMe_2\{C_3H_2N_2(CH_2\text{-}2\text{-}py)_2\}]^+$, with a stabilized Arduengo carbene ligand, has been reported recently: Prokopchuk, E. M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 563.

(4) (a) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (b) Baar, C. R.; Jenkins, H. A.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 2805.

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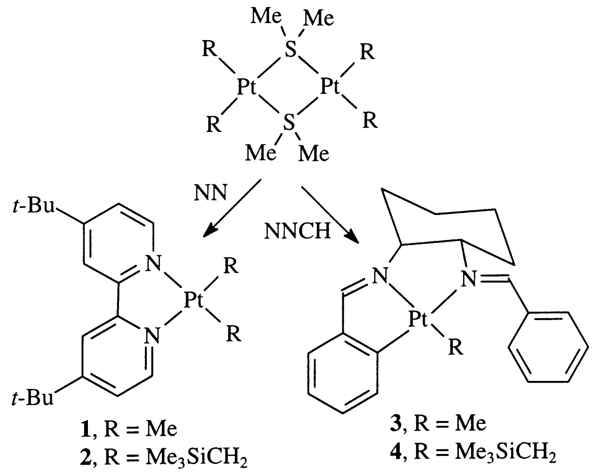
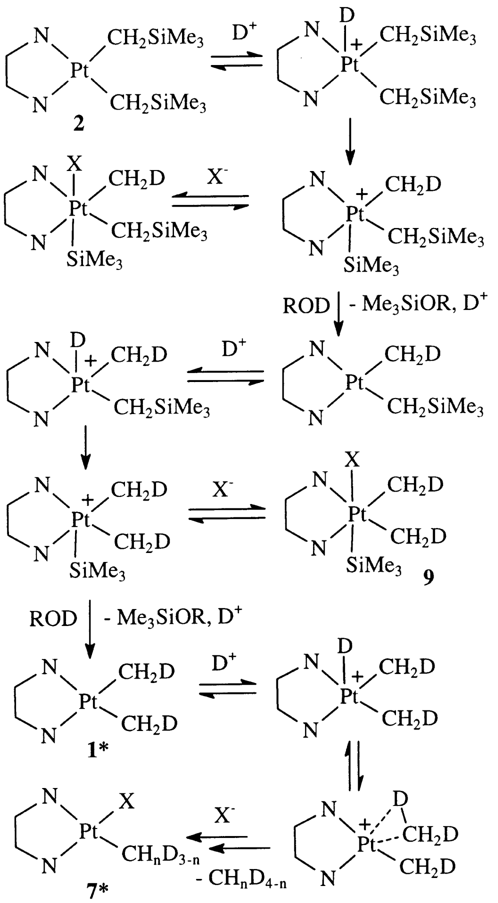
**Scheme 2**



**Scheme 3**



(**5a**) and $Me_3SiOH/CH_4$ (85−90%) and $Me_4Si$ (10−15%).[5−7] When a similar reaction was carried out in $CD_2Cl_2/CD_3OD$ or $CD_2Cl_2/CD_3CN/CD_3OD$ (1:1:1), the corresponding products were **5a** and $Me_3SiOCD_3/CH_2D_2$ (85−90%, with a minor amount of $CH_3D$ but no $CHD_3$) and $Me_3SiCH_2D$ (10−15%, with a minor amount of $Me_4Si$). The reactions were similar using triflic acid, except that the organoplatinum product was $[PtS(NNC)]^+$ (**6**; S = $CD_3CN$), as the triflate salt. With $H[BF_4]$, the major difference was that $Me_3SiF$ was formed in place of $Me_3SiOH$ or $Me_3SiOCD_3$.[5] There are strong similarities and also some key differences compared to the previously studied system.[2] Most obvious is the formation of $Me_4Si$ as a minor product in the reactions of complex **4**, whereas none was observed in the reaction of eq 1.[2] Also, in the reactions with **4**, the reductive coupling to give methane or $Me_4Si$ appears irreversible, and so the reactions with $DX/CD_3OD$ give mostly the isotopomers $CH_2D_2$ and $Me_3SiCH_2D$. It is significant that the partition between the products $CH_4/Me_3SiY$ and $Me_4Si$ was largely independent of the acid or solvent used. The product of simple reductive elimination, $Me_4Si$, will be formed in a unimolecular step from a coordinatively unsaturated hydrido(alkyl)platinum(IV) intermediate, $[PtH(CH_2SiMe_3)(NNC)]^+$,[1−3] whereas in mechanism ***A*** (Scheme 1) the product $Me_3SiY$ is formed in a bimolecular reaction involving, for example, attack by ROH at silicon, to give $Me_3SiOR$ in the product-determining step. Hence, the partition between $Me_3SiOR$ and $Me_4Si$ should be dependent on the concentration of ROH or $H_2O$ or on the nucleophilic nature of the solvent medium. The present observations are most easily rationalized if the product-determining steps in both reaction paths are unimolecular.

Reaction of complex **2** with HCl or HBr in moist solvent $CD_2Cl_2$ or $CD_2Cl_2/CD_3CN$ at room temperature gave [PtXMe(NN)] (**7a**, X = Cl; **7b**, X = Br) with the major products $Me_3SiOH/CH_4$ and minor product $Me_4Si$ (major:minor = ca. 90:10).[5−7] Similar reactions with $CF_3SO_3H$ or $HBF_4$ in $CD_2Cl_2/CD_3CN$ at room temperature gave $[PtSMe(NN)]^+$ (**8**; S = $CD_3CN$) with the major products being $Me_3SiOH/CH_4$ using $CF_3SO_3H$ or $Me_3SiF/CH_4$ using $HBF_4$ and the minor product being $Me_4Si$ in each case. The reactions with acids DX in the solvent $CD_2Cl_2/CD_3OD$ gave the range of isotopomers $CH_nD_{4-n}$ and $[PtX(CH_nD_{3-n})(NN)]$ or $[PtS(CH_nD_{3-n})(NN)]^+$, but the TMS was formed as $Me_3SiCH_2D$ only, indicating that the reductive coupling to give coordinated methane is reversible in this case but that reductive coupling to give TMS is irreversible (Scheme 3).[8]

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[5] Organosilicon compounds were identified by spiking the NMR solutions with authentic compounds and checking that the chemical shifts were identical. Chemical shifts for $\delta$(MeSi): TMS, 0.00; $Me_3SiOH$, 0.10; $(Me_3Si)_2O$, 0.06; $Me_3SiF$, 0.20 (d, $J$(HF) = 7.5 Hz); $Me_3SiOCD_3$, 0.05. (a) Schmidbaur, H. *Chem. Ber.* **1964**, *97*, 830. (b) Schmidbaur, H. *J. Am. Chem. Soc.* **1963**, *85*, 2336. (c) Ostdick, T.; McCusker, P. A. *Inorg. Chem.* **1967**, *6*, 98. Chemical shifts for $Me_3SiCH_2D$: $\delta$(MeSi) −0.002, 9H; $\delta(CH_2D)$ −0.02, 2H, 1:1:1 triplet, $^2J$(HD) = 2 Hz. No $SiCHD_2$ resonance was detected, and the integration of $Me:CH_2D$ = 9:2 indicated that no significant amount of $Me_2Si(CH_2D)_2$ was present; when $Me_4Si$ was also formed, its $^1H$ resonance was just resolved at $\delta$(MeSi) 0.00.

[6] The final organoplatinum products were isolated and fully characterized. Several are known compounds, and there was good agreement with published NMR data.[4,7] The complex [PtClMe(NN)] was also characterized crystallographically: $C_{19}H_{27}ClN_2Pt$, fw = 513.97, $T$ = 296(2) K, $\lambda$ = 0.710 73 Å, monoclinic, $P2_1/c$, $a$ = 7.535(1) Å, $b$ = 19.176(4) Å, $c$ = 12.991(3) Å, $\beta$ = 96.55(3)°, $V$ = 1864.9(6) $Å^3$, $Z$ = 4, $d$(calcd) = 1.831 $Mg/m^3$, R1($I > 2\sigma(I)$) = 0.048, wR2(all data) = 0.116.

[7] (a) Levy, C. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 2108. (b) Levy, C. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 10127. (c) Levy, C. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 4115. The oxidative addition of $Me_3SiX$ to complex **1** is thermodynamically favorable for X = I, Br but not for X = Cl, and the trend is determined by the relative Pt−X vs Si−X bond energies.[7b] By extension, it is clear that the reaction is unfavorable for X = F ($D$(SiF) = 665 kJ $mol^{-1}$) or OH ($D$(Si−OH) = 536 kJ $mol^{-1}$).

[8] Reversibility of the reductive coupling to form a TMS complex, coupled with easy PtH for PtD exchange of the hydridoplatinum intermediate, would give $Me_3SiCHD_2$ and, if exchange between coordinated $CH_3Si$ and $CH_2DSi$ groups occurs, $Me_2Si(CH_2D)_2$ and more highly deuterated isotopomers. Also, D incorporation into the MeSi groups of the products $Me_3SiY$ would occur.

Direct evidence for α-migration was obtained by monitoring the reactions by low-temperature $^1$H NMR. Thus, for the reaction of complex **2** with HBr in moist $CD_2Cl_2$, the spectra at −80 to −50 °C were broad and indicated the presence of more than one compound but, at −30 °C, the spectrum was sharp and the major organoplatinum product was clearly identified as $[PtBrMe_2(SiMe_3)(NN)]$ (**9b**) by comparison of its spectrum with that of an authentic sample prepared by oxidative addition of $Me_3SiBr$ to complex **1**.[7] Key resonances were $\delta$(PtMe) 1.27 (s, 6H, $^2J$(PtH) = 64 Hz) and $\delta$(MeSi) −0.28 (s, 9H, $^3J$(PtH) = 19 Hz), with the coupling of the methylsilicon protons to $^{195}$Pt being definitive.[7] At room temperature, complex **9b** had decomposed to give **7b**. A similar reaction of complex **2** with HCl gave $[PtClMe_2(SiMe_3)(NN)]$ (**9a**), and this is particularly significant, since **9a** is a new complex that cannot be prepared by oxidative addition of $Me_3SiCl$ to complex **1**.[7] Complex **9a** could not be isolated, but it was characterized at −30 °C by the similarity of its NMR parameters, $\delta$(PtMe) 1.06 (s, 6H, $^2J$(PtH) = 64 Hz) and $\delta$(MeSi) −0.37 (s, 9H, $^3J$(PtH) = 19 Hz) to those of **9b**. In the reaction with HCl, minor resonances due to the hydridoplatinum(IV) complex $[PtHClMe_2(NN)]$[3] were observed at −30 °C at $\delta$(PtMe) 1.23 (s, 6H, $^2J$(PtH) = 67 Hz) and $\delta$(PtH) −21.80 (s, 1H, $^1J$(PtH) = 1590 Hz), and these grew in intensity at −20 °C as complex **9a** decomposed before decaying again as the final product **7a** was formed. Finally, the reaction at low temperature of **2** with either triflic acid or tetrafluoroboric acid in $CD_2Cl_2/CD_3CN$ gave the cation $[PtMe_2(SiMe_3)S(NN)]^+$ (**10**; S = $CD_3CN$), which has NMR parameters, $\delta$(PtMe) = 0.87 (s, 6H, $^2J$(PtH) = 66 Hz) and $\delta$(MeSi) = −0.41 (s, 9H, $^3J$(PtH) = 19 Hz) similar to those of **9a** and **9b**. The cationic complex **10** decomposed on warming to give $[PtMeS(NN)]^+$, and $Me_3SiOH$ or $Me_3SiF$. Since these organosilicon products, with strong Si−O or Si−F bonds, will not undergo oxidative addition to complex **1**, it is clear that complex **10** must be formed during the protonolysis of complex **2**.[7]

The concerted mechanism ***D*** (Scheme 1) is consistent with the present observation that an α-migration occurs to give a (trimethylsilyl)platinum(IV) intermediate and with the deduction by Heyduk, Labinger, and Bercaw that α-migration does not occur before or after reductive coupling.[2] If the approximate bond energies (kJ mol$^{-1}$) Pt−H = 213, Si−C = 374, Pt−Si = 233, and C−H = 420 are assumed,[7,9] then the rearrangement of $[PtH(CH_2SiMe_3)(NNC)]^+$ to $[PtMe(SiMe_3)(NNC)]^+$ can be estimated to have $\Delta H$ = ca. −71 kJ mol$^{-1}$, and hence the rearrangement will not be easily reversed under the mild conditions used. If the trimethylsilyl group is anti to the migrating hydride, it will rock toward the platinum atom and so Pt···Si bond formation can occur easily, so that a low activation energy for the reaction is likely.[10] It follows from microscopic reversibility that the activation of TMS by electrophilic platinum(II) complexes may occur through an intermediate similar to that shown in mechanism ***D*** of Scheme 1 and may be considered to involve Si−C bond activation following initial complexation of TMS to platinum via a C−H bond.

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**Supporting Information Available:** Text giving experimental procedures and tables giving X-ray data for [PtClMe-(NN)]. This material is available free of charge via the Internet at http:/pubs.acs.org.

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[9] Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000.

[10] One possible rationalization for the partition between the two reaction paths leading to $Me_4Si$ or $Me_3SiY$ is that there is a dependence on the conformation of the $Me_3SiCH_2$ group with respect to the hydride ligand in the 16-electron hydridoplatinum(IV) intermediate when the hydride migration to carbon begins. If the $Me_3Si$ group is anti to the hydride, then α-migration to platinum occurs to ultimately yield $Me_3SiY$, but if it is syn to the hydride, then it cannot migrate at an early stage and so reductive coupling to give TMS is preferred. A reviewer points out that the distinction between mechanisms ***B*** and ***D*** may be subtle and that the mechanism proposed here may not apply when no TMS is formed, as in the system of ref 2. We note that silyl migration reactions are often much faster than the corresponding alkyl migrations[9] and that platinum is a particularly good silyl acceptor. (a) Braunstein, P.; Boag, N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2427. (b) Braunstein, P.; Knorr, M.; Reinhard, G.; Schubert, U.; Stahrfeldt, T. *Chem. Eur. J.* **2000**, *6*, 4265.