Transition Metal-Catalyzed Silanone Generation

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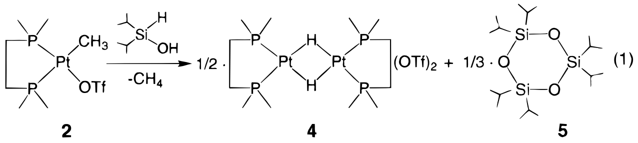
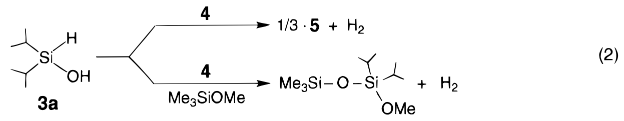
The generation of compounds containing multiply bonded silicon is of much current interest.[1,2] Silanones (i.e., compounds containing a silicon−oxygen double bond), although not isolated, are being generated as short-lived intermediates, normally using elaborate procedures for preparation and decomposition of suitable precursors.[2] Since the trapping of the generated silanones and their incorporation into other molecules may be a synthetically very useful approach in organosilicon chemistry, we chose to study the possibility of generation of silanones from relatively simple starting materials under mild conditions using transition metal complexes.

We report here a new type of homogeneous catalytic reaction that generates silanones from secondary silanols under extremely mild conditions. Platinum complexes are used as catalysts. We elucidated the mechanism of the reaction, isolated active intermediates, and characterized them by spectroscopy and X-ray diffraction. This reaction is formally analogous to (although mechanistically different from) the well-known catalytic dehydrogenation of alcohols[3] that leads to ketones.

The platinum complex (dmpe)Pt(Me)(OTf) (**2**)[4,5] (dmpe = $Me_2PCH_2CH_2PMe_2$, OTf = OSO_2CF_3, triflate) was synthesized by selective protonolysis of one methyl group of the dimethyl precursor (dmpe)$PtMe_2$ (**1**).[4,5] This, in turn, is readily made from (1,5-cyclooctadiene)$PtMe_2$.

When 1 equiv of the silanol $^iPr_2SiHOH$ (**3a**)[6] is added at room temperature to a colorless acetone solution of **2**, the solution immediately becomes red. The ^{31}P NMR spectrum of the reaction mixture indicates the disappearance of **2** and the formation of a new dimeric hydrido-bridged complex [(dmpe)-PtH]$_2$(OTf)$_2$ (**4**).[4,5] The ^1H NMR spectrum shows that methane was liberated (eq 1). Upon addition of 50 equiv of **3a** to the red solution of **4**, subsequent ^1H and ^{29}Si NMR and mass spectroscopic analyses of the mixture indicated that under these very mild conditions **3a** was *catalytically* converted into the known cyclic trimer of diisopropylsilanone ($^iPr_2SiO)_3$ (**5**)[7] (70% yield, 35 turnovers, by ^1H NMR after 3 h at room temperature) and free H_2 (detected by ^1H NMR) (eq 2), while **4** was not consumed as evident from ^{31}P NMR. The same reaction, carried out in the presence of an excess of the silanone trap Me_3SiOMe, resulted in the formation of the expected trapping product $Me_3SiOSi^iPr_2(OMe)$ (eq 2), identified unambiguously by its mass spectrum.[8] These results constitute strong evidence of the possibility to catalytically generate silanones from secondary silanols in room temperature homogeneous reactions.





Our rationalization of the mechanism of this novel catalytic process is presented in Figure 1. Complex **2**, acting as a catalyst precursor, oxidatively adds the Si−H bond of **3a**[9] leading, after reductive elimination of methane, to the platinasilanol intermediate **6a** which enters the catalytic cycle. Complex **6a** decomposes by *β*-hydrogen elimination from Si−OH[10] resulting in the liberation of the silanone and the formation of (dmpe)Pt(H)(OTf) (**7**) which is probably in equilibrium with its dimer **4**.[11] Complex **7** adds another molecule of **3a**, and after H_2 reductive elimination, regenerates complex **6a** thereby completing the catalytic cycle. Complexes analogous to **4** and **7** are known.[12]

With **3a** as a substrate, no intermediates, except for complex **4**, are detected by NMR. However, the use of the bulkier ditertbutylsilanol $^tBu_2SiHOH$ (**3b**)[6] allowed us to observe two stoichiometric steps. We were also able to isolate and fully characterize by spectroscopy and X-ray crystallography the platinasilanol **6b** (as the acetone solvate),[13] which is the analog

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[1] For recent reviews, see (a) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (b) Hemme, I.; Klingebiel, U. *Adv. Organomet. Chem.* **1996**, *39*, 159. (c) Dreiss, M. *Adv. Organomet. Chem.* **1996**, *39*, 193. (d) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 232. (e) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (f) Zybill, C. E.; Liu, C. *Synlett.* **1995**, 687. (g) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; pp 257−263, 324−341.

[2] (a) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 2, Chapter 17. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

[3] This process was first described in (a) Charman, H. B. *J. Chem. Soc. B* **1967**, 629. (b) Charman, H. B. *J. Chem. Soc. B* **1970**, 584. See also: (c) Dobson, A.; Robinson, S. D. *Inorg. Chem.* **1977**, *16*, 137. (d) Critchlow, P. B.; Robinson, S. D. *Inorg. Chem.* **1978**, *17*, 1902. (e) Matsubara, T.; Saito, Y. *J. Mol. Catal.* **1994**, *92*, 1 and references therein.

[4] Selected NMR data (the solvent used is $(CD_3)_2CO$ unless otherwise specified). For **1**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 25.2 (s, $^1J_{Pt,P} = 1735$ Hz); ^1H NMR (C_6D_6) δ 1.21 (dd, $^3J_{P_1,H} = 7.4$, $^3J_{P_2,H} = 8.2$, $^2J_{Pt,H} = 69.0$ Hz, Pt-$(CH_3)_2$). For **2**: $^{31}P\{^1H\}$ NMR δ 15.5 (s, $^1J_{Pt,P} = 4305$ Hz, 1P trans to O), 41.1 (s, $^1J_{Pt,P} = 1828$ Hz, 1P trans to C); ^1H NMR δ 0.22 (d, $^3J_{P_{trans},H} = 6.3$, $^2J_{Pt,H} = 45.8$ Hz, $PtCH_3$). For **4**: $^{31}P\{^1H\}$ NMR δ 48.5 (s, $^1J_{Pt,P} = 2855$, $^3J_{Pt,P} = 142$, $^4J_{P,P} = 53.5$ Hz); ^1H NMR δ −4.87 (broad t with ^{195}Pt satellites of doubled intensity, $^2J_{P,H} = 60$, $^1J_{Pt,H} = 560$ Hz, Pt−H−Pt). For **6b**: ^{31}P-$\{^1H\}$ NMR δ 11.2 (s, $^1J_{Pt,P} = 4355$ Hz, 1P trans to O), 54.3 (s, $^1J_{Pt,P} = 1168$ Hz, 1P trans to Si); ^1H NMR δ 1.05 (s, $(CH_3)_3Si$, 18H), 1.63 (d, $^2J_{P,H} = 8.9$, $^3J_{Pt,H} = 10.5$ Hz, $(CH_3)_2PPtSi$, 6H), 2.02 (d, $^2J_{P,H} = 12.8$, $^3J_{Pt,H} = 62.4$ Hz, $(CH_3)_2PPtO$, 6H).

[5] See Supporting Information.

[6] The silanols used were prepared from the corresponding commercially available chlorosilanes using the general procedure described by Sommer (Sommer, L. H.; Tyler, L. J. *J. Am. Chem. Soc.* **1954**, *76*, 1030). For the individual silanols, see: (**3a**) Gilman, H.; Clark, R. N. *J. Am. Chem. Soc.* **1947**, *69*, 1499. (**3b**) Barton, T. S.; Tully, C. R. *J. Organomet. Chem.* **1979**, *172*, 11. ($^iPr_2Si(OH)_2$) Eaborn, C. *J. Chem. Soc.* **1952**, 2840.

[7] Graalman, O.; Klingebiel, U.; Clegg, W.; Haase, M.; Scheldrick, G. M. *Chem. Ber.* **1984**, *117*, 2988.

[8] MS (*m/e*, % rel. intensity): 219 ($M^+ - CH_3$, 4.5); 191 ($M^+ - C_3H_7$, 100); 163 ($M^+ - C_3H_7 - C_2H_4$, 50.7). An analogous fragmentation pattern was reported for the closest analog $Me_3SiOSi^tBu_2(OMe)$, see: Wiberg, N.; Preiner, G.; Schurz, K. *Chem. Ber.* **1988**, *121*, 1407.

[9] Oxidative addition of **3a** to an isoelectronic Ir(I) complex was reported by us, see: Goikhman, R.; Aizenberg, M.; Kraatz, H.-B.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 5865.

[10] *β*-Hydrogen elimination from analogous α-hydroxyalkyl intermediate complexes of Mn and Rh was proposed as the likely step leading to the formation of aldehydes and metal hydrides, see: (a) Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6768. (b) Milstein, D.; Fultz, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1336.

[11] Hydrido-bridged dimers of platinum(II) are known to undergo dissociation in an acetone solution, see: Carmona, D.; Thouvenot, R.; Venanzi, L. M.; Bachechi, F.; Zambonelli, L. *J. Organomet. Chem.* **1983**, *250*, 589.

[12] Analogs of **4** and **7** containing bulkier chelating bis-phosphines are fully characterized by NMR and X-ray analyses, see: (a) Mole, L.; Spencer, J. L.; Kitster, S. A.; Redhouse, A. D.; Carr, N.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1996**, 2315. (b) Carr, N.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 2653.

[13] There is only one additional platinasilanol complex known, see: Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219.

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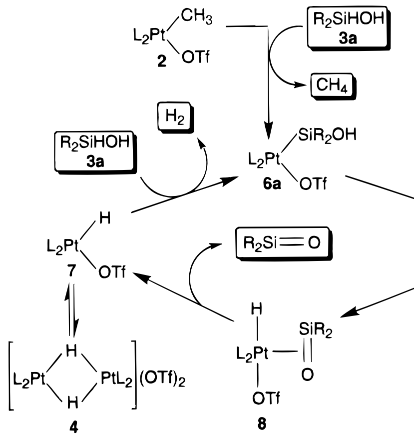


Figure 1. Catalytic cycle for dehydrogenation of **3a** (L_2 = dmpe).

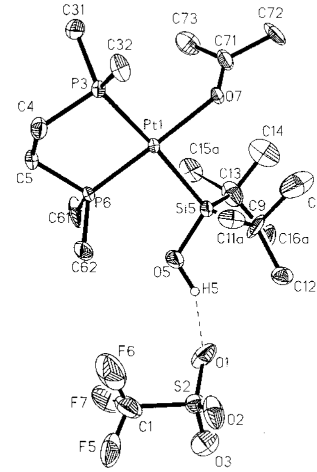
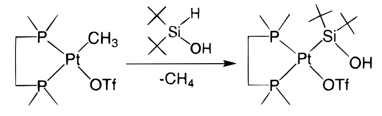


Figure 2. Perspective view of the acetone solvate of platinasilanol **6b**. Bond distances (Å) and angles (deg): Pt(1)−P(3) = 2.381(2); Pt(1)−P(6) = 2.192(2); Pt(1)−Si(5) = 2.401(3); Pt(1)−O(7) = 2.137(5); Si(5)−O(5) = 1.661(8); H(5)−O(5) = 1.04(3); H(5)···O(1) = 1.80(3); O(7)−C(71) = 1.224(12); P(3)−Pt(1)−Si(5) = 167.44(10); P(6)−Pt(1)−O(7) = 177.3(2).

of the postulated central intermediate **6a**. Complex **6b** results from the reaction of **2** with 1 equiv of **3b** (eq 3). The solution



2 **6b** (3)

NMR spectral data of complex **6b**[4,5] are unambiguous and consistent with the coordination geometry found in the crystal structure (Figure 2).[5,14] The presence of the very strong (silyl) and the very weak (acetone) trans-directors located trans to the phosphorus atoms of the dmpe ligand is clearly evident in the greatly differing values of the Pt−P bond lengths (2.381(2) and 2.192(2) Å) and the $^1J_{\mathrm{Pt,P}}$ coupling constants (1168 and 4355 Hz). It should be noted that the reaction of **2** with silanols **3a** and **3b** results in selective C−H reductive elimination, while analogous reactions with other silanes, such as Et_3SiH, $^iPr_2SiHCl$, and $^iPr_2SiHF$, lead to products of both C−H and C−Si coupling. The latter reactions are in accord with the known relative ease of C−Si reductive elimination from platinum,[15] while the exclusive C−H bond formation with the silanols is indicative of the important role the OH group plays in the selectivity of the process we observe. Significantly, although the cationic complex **6b** is stabilized in the solid state by acetone coordination and by hydrogen bonding between the OH group and the triflate anion (Figure 2), it is not stable in solution at room temperature. It decomposes in acetone with a half-life of about 3 h selectively producing the hydrido complex **4** in accord with the proposed mechanism. Regarding the reactivity of **4** (or its monomer **7**) toward **3a**, we are confident that it involves Si−H rather than O−H oxidative addition as a first step. Initial intermolecular O−H activation was excluded by the complete absence of reactivity of **4** toward silanols lacking Si−H bonds, namely Et_3SiOH and $^iPr_2Si(OH)_2$,[6] and toward methanol.[16] Taken together, the results above provide strong support for the proposed catalytic sequence presented in the Figure 1.

There are important aspects of this reaction which deserve further comment.

The efficiency of the catalysis reported here is probably not the highest that can be achieved. Complex **4** remained unchanged after the consumption of diisopropylsilanol, indicating a reasonable stability for the catalytic system. When optimized, the full synthetic potential of this approach could be realized and, with more sophisticated trapping agents, possibly lead to organosilicon compounds not readily accessible using conventional routes. These studies are now underway.

Intermediate **8** in Figure 1 represents a silanone bound to a transition metal center. Our results constitute strong evidence of the involvement of such an intermediate in the catalysis we have described. We hope that by modifying the metal center and the silanol ligand, stabilization of the silicon−oxygen double bond by coordination may be achieved.[17]

In conclusion, this paper describes the catalytic generation of the silicon−oxygen double bond using a transition metal complex. The reaction, which involves platinum-catalyzed silanol dehydrogenation, proceeds efficiently in solution under very mild conditions (room temperature). The mechanism of this unprecedented form of catalysis has been elucidated, including isolation and structural characterization of a key intermediate.

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Supporting Information Available: Details of preparation and characterization of complexes **1**, **2**, **4**, and **6b**, procedures of catalytic and trapping experiments, full X-ray data of complex **6b** (16 pages). See any current masthead page for ordering and Internet access instructions.

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[14] X-ray structure of **6b**: $C_{18}H_{41}F_3O_5P_2PtSSi$, colorless, monoclinic, $P2(1)/n$ (No. 14), $a = 8.333(2)$ Å, $b = 21.514(4)$ Å, $c = 15.910(3)$ Å, $\beta = 97.07(3)°$, $T = 110$ K, $V = 2830.6(10)$ Å^3, $Z = 4$, R_1 (on F^2) = 0.0633 ($I > 2\sigma(I)$), GOF (on F^2) = 1.141.

[15] Ozawa, F.; Hikida, T.; Hayashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2844.

[16] No reactions of these substrates with **4** took place after 2 h both at room temperature and at 40 °C as observed by ^1H NMR.

[17] An iridium silanone intermediate was postulated in siloxane disproportionation: Curtis, M. D.; Greene, J. *J. Am. Chem. Soc.* **1978**, *100*, 6362.