Reversible Water and Methanol Activation at the Pd═Sn Bond[1]

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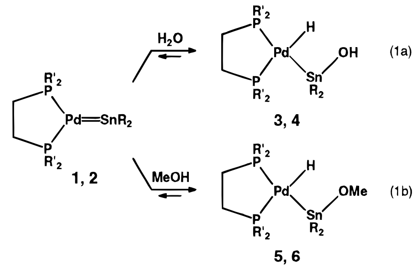
Water, alkanol, and amine activation reactions of transition metals may lead to complexes in which a hydro substituent is paired with an hydroxy, alkoxy, or amide substituent, all of which are potential reactive sites.[2] Well-studied examples are the d^6 Ir(III) *cis* hydro hydroxy complexes $[(Me_3P)_4Ir(H)OH]^+PF_6^{-}$ [3a] (ionic; stable at 100 °C) and $(R_3P)_3Ir(H)OH(Cl)$ (R = Me, Et; neutral; reversible water elimination at 20 °C).[3b] Of the d^{10} metal complexes, $\{(c\text{-}C_6H_{11})_3P\}_2Pt$ oxidatively adds phenols (ArOH; Ar = C_6H_5, C_6F_5) at 20 °C to afford stable *trans*-$\{(c\text{-}C_6H_{11})_3P\}_2Pt(H)OAr$.[4] Similarly, $(^iPr_3P)_2Pt$ reacts with H_2O to give thermally unstable *trans*-$(^iPr_3P)_2Pt(H)OH$.[5a,b] In contrast, $(^iPr_3P)_2Pd$ does not react with water at 20 °C.[5c] Furthermore, the stannylene SnR_2 (R = $CH(SiMe_3)_2$)[6a] is reported to decompose in water and alkanol.[6b,c] As we have recently discovered, the adducts $L_2Pd(0){=}SnR_2$ (L_2 = chelating bidentate phosphane)[7] undergo reversible oxidative additions of water and methanol.[8]

When deoxygenated water is added at 20 °C to the red THF solutions of the complexes $(R'_2PC_2H_4PR'_2)Pd{=}SnR_2$ [R′ = ^{i}Pr (**1**), ^{t}Bu (**2**)], the color fades immediately. After evaporation of the solvent and recrystallization (pentane), colorless crystals of the bimetallic hydro hydroxy complexes $(R'_2PC_2H_4PR'_2)Pd(H)Sn(OH)R_2$ [R′ = ^{i}Pr (**3**), ^{t}Bu (**4**)] are isolated (90%; eq 1a). Similarly, complexes **1** and **2** react with methanol to afford the hydro methoxy complexes $(R'_2PC_2H_4PR'_2)Pd(H)Sn(OCH_3)R_2$ [R′ = ^{i}Pr (**5**), ^{t}Bu (**6**)] (eq 1b). When D_2O and CD_3OD are reacted, the partially deuterated derivatives $(d^ippe)Pd(D)Sn(OD)R_2$ (**3**-d_2) and $(d^ippe)Pd(D)Sn(OCD_3)R_2$ (**5**-d_4) are obtained. The reactions of **1** and **2** with water and methanol also proceed at −40 °C within a few minutes; however, no reaction of **1** and **2** occurs with NH_3. The melting points of **3**−**6** are well above 100 °C, and prior to melting, discoloration to red is observed due to partial formation of **1** and **2**. The d^tbpe complexes are more stable than the d^ippe derivatives.

Spectroscopic Characterization. In the EI mass spectrum of the d^ippe-derived hydro hydroxy complex **3** (80 °C), the molecular ion is observed. Fragmentation proceeds both by elimination of water and by destruction of the SnR_2 group, affording $[(d^ippe)Pd]^+$ as the base peak. For **4** (120 °C) and the hydro methoxy complexes **5** (60 °C) and **6** (110 °C), the largest ions observed are $[(d^ippe)Pd{=}SnR_2]^+$ ($\mathbf{1}^+$) and $[(d^tbpe)Pd{=}SnR_2]^+$ ($\mathbf{2}^+$), and these fragment further to yield the base peaks $[(d^ippe)Pd]^+$ and $[(d^tbpe)Pd]^+$, respectively. In the IR spectrum, complexes **3** and **5** give rise to a Pd−H stretching band at about 1890 cm^{-1} (**4**, **6**, 1860 cm^{-1}).[9a] Sharp bands at 3649 cm^{-1} (**3**) and 3666 cm^{-1} (**4**) are attributed to SnOH. The C−H stretching bands of $SnOCH_3$ (expected at 2900 cm^{-1}) are largely overlapped by phosphane modes, but a prominent $SnOCH_3$ overtone vibration is observed at 2776 cm^{-1} (**5**).[9b] According to ^{1}H NMR spectroscopy the complexes are defined by high-field resonances for PdH (**3**, δ_H −4.25; **4**, δ_H −5.42) and SnOH (**3**, δ_H −0.55; **4**, δ_H −0.35). For PdH, the couplings $^2J(PH)_{trans}$ (160−173 Hz) and $^2J(PH)_{cis}$ (9−15 Hz) are as expected, and the coupling $^2J(SnH)_{cis}$ is rather small (**3**, **5**, **6**: 15−45 Hz) or even not observed (**4**). The ^{31}P NMR spectra show that in THF-d_8 solution complex **3** is pure and **5** (<1%, **1**) is almost pure but **4** (>1%, **2**) and **6** (8%, **2**) are markedly dissociated due to the equilibria of eq 1. Sharp signals indicate that H_2O or MeOH exchange reactions between **1** or **2** and **3**−**6** are slow with respect to the ^{31}P NMR time scale.



R = $CH(SiMe_3)_2$; **1, 3, 5**: R′ = ^{i}Pr ; **2, 4, 6**: R′ = ^{t}Bu

Molecular Structure of 3. The X-ray structure[10] of **3** (Figure 1) reveals that the geometry at Pd(II) is distorted *SP*-4 (the hydride has not been located). The main structural features are similar to those of the related pallada(II)stanna(II)cyclobutene $(d^ippe)Pd(CH{=}CH)SnR_2$ (Pd−Sn) (**7**).[7] In **3** the deviations from the rectangular arrangement (P2−Pd1−Sn1 108.9°; P1−Pd1−Sn1 162.7°) are obviously due to the small size of the hydride ligand, whereas similar distortions in **7** (P_{cis}−Pd−Sn 113.0°; P_{trans}−Pd−Sn 158.5°) arise from the strained four-membered ring. For both complexes, the bond Pd−P_{trans} (to Sn) is shorter than Pd−P_{cis} (to Sn), although the difference for **3** (2.29, 2.32 Å) is less than for **7** (2.29, 2.34 Å). Other structural data of **3** are intermediate between those of the Pd(0)═SnR_2 complex **1**[7] (from which **3** is formed) and **7**. This is the case for the angle P−Pd−P [**1**, 89.0; **3**, 87.5; **7**, 86.2°], the relatively short Pd−Sn bond [**1**, 2.48; **3**, 2.58; **7**, 2.67 Å], the distances Sn−C [**1**, 2.21; **3**, 2.22 (mean); **7**, 2.24 Å (mean)], and the angle C−Sn−C [**1**, 98.8; **3**, 99.6; **7**, 105.0°]. The plane Pd1,Sn1,O1 forms an angle of only 27.3° to the mean Pd(II) coordination plane (P1,P2,Pd1,Sn1) with the hydroxy group (O1) at Sn(II) opposite to the calculated hydride position.

Reactivity. When **3** (100 °C) and **5** (70 °C) are heated under vacuum, they slowly eliminate water and methanol, respectively,

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[1] Abbreviations: d^ippe, bis(diisopropylphosphino)ethane, $^iPr_2PC_2H_4P{}^iPr_2$; d^tbpe, bis(di-*tert*-butylphosphino)ethane, $^tBu_2PC_2H_4P{}^tBu_2$.

[2] Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

[3] (a) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387. (b) Blum, O.; Milstein, D. *Angew. Chem.* **1995**, *107*, 210; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 229. (c) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582.

[4] Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006.

[5] (a) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027. (b) Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191. (c) The formation of intermediate complexes [*trans*-$(R_3P)_2Pd(H)OH$] has been suggested on the basis of a slow $(Et_3P)_3Pd$-catalyzed H/D exchange of $PhCOCH_3$ and D_2O (80 °C, 20 h, 37%).[5a] When water is added to a THF-d_8 solution of $(^iPr_3P)_2Pd$, no change of the ^{1}H and ^{31}P NMR signals is observed between −50 and 30 °C.

[6] (a) Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 317. Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (b) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275. (c) For the reaction of the Ge analogue of SnR_2, $Ge\{CH(SiMe_3)_2\}_2$, with water and alcohol, see: Lappert, M. F.; Miles, S. J.; Atwood, J. L.; Zaworotko, M. J.; Carty, A. J. *J. Organomet. Chem.* **1981**, *212*, C4.

[7] (a) Krause, J.; Pluta, C.; Pörschke, K.-R.; Goddard, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1254. (b) Krause, J.; Haack, K.-J.; Pörschke, K.-R.; Gabor, B.; Goddard, R.; Pluta, C.; Seevogel, K. *J. Am. Chem. Soc.* **1996**, *118*, 804.

[8] (a) Schager, F. Diplomarbeit, Universität Düsseldorf, 1995. (b) Schager, F.; Pörschke, K.-R. *GECOM-CONCOORD 1995,* St Jacut de la Mer (France). (c) Schager, F. Planned Dissertation.

[9] (a) The corresponding Pd−D stretching bands [**3**-d_1 (PdD), **3**-d_2, **4**-d_2, **5**-d_1, **5**-d_4] are obscured by phosphane bands. (b) Additional analytically significant bands attributable to $SnOCH_3$ are found for **5** at 1437 (CH_3 deformation) and 1057 cm^{-1} (C−O stretching). Full IR spectroscopic characterization of all compounds is given in the Supporting Information.

[10] For **3**: triclinic, $P\bar{1}$ [No. 2]; a = 12.748(3), b = 17.199(1), and c = 20.190(2) Å, α = 99.46(1), β = 93.29(2), and γ = 91.65(2)°; Z = 4; R = 0.062, R_w = 0.179 [$w = 1/\sigma^2(F_o)$], max. shift/error = 0.94, final difference Fourier ρ = 1.50 e Å^{-3}. Both crystallographically independent molecules are identical in the framework of the heavier elements but differ slightly in the orientation of the $SiMe_3$ groups and in one of the bridging carbons of the chelating phosphane.

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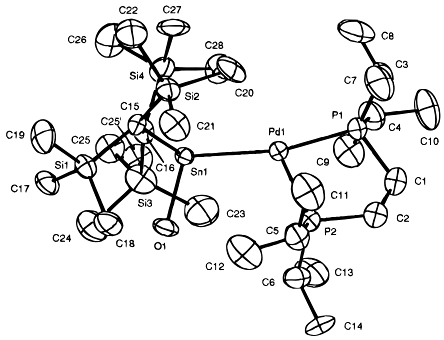
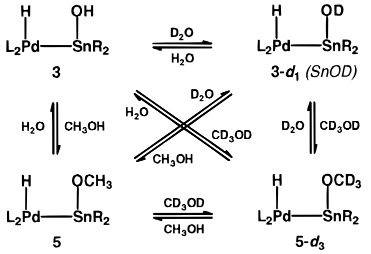


Figure 1. Molecular structure of **3** (molecule 1), showing 30% probability ellipsoids. Selected bond distances (Å): Pd1−Sn1, 2.575(1); Pd1−P1, 2.294(2); Pd1−P2, 2.322(2); Sn1−O1, 2.037(5); Sn1−C15, 2.211(7); Sn1-C16, 2.231(7). Selected bond angles (deg): P1−Pd1−P2, 87.5(1); P1−Pd1−Sn1, 162.7(1); P2−Pd1−Sn1, 108.9(1); C15−Sn1−C16, 99.6(3); Pd1−Sn1−C15, 123.9(2); Pd1−Sn1−C16, 118.8(2); Pd1−Sn1−O1, 107.6(2).

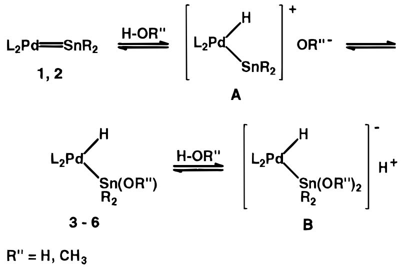
Scheme 1[16]



to form **1** (*ca.* 35% conversion of **3** in 1 h).[11] Thus, the oxidative addition of water or methanol to **1** and **2** to afford **3**−**6** is reversible and methanol elimination proceeds more readily than water elimination.

When D_2O is added to a THF solution of **3**, the hydroxy group exchanges for OD and pure (d^{i}ppe)Pd(H)Sn(OD)R_2 (**3**-d_1 SnOD) is obtained.[12] Similarly, **3**-d_2 reacts with H_2O to afford (d^{i}ppe)Pd(D)Sn(OH)R_2 (**3**-d_1 PdD). When complex **5** is dissolved in CD_3OD/THF, the methoxy group exchanges for OCD_3 to yield mainly (d^{i}ppe)Pd(H)−Sn(OCD_3)R_2 (**5**-d_3) and **5**-d_4 as a minor product. However, when **5**-d_4 is reacted with CH_3OH, the major product formed is (d^{i}ppe)Pd(D)Sn(OCH_3)R_2 (**5**-d_1) with a minor amount of **5** (Scheme 1, horizontal reactions). Upon addition of H_2O to a THF solution of **5**, the methoxy substituent rapidly exchanges for hydroxy to give **3**. On the other hand, when MeOH is added to a THF solution of **3**, only a partial hydroxy/methoxy exchange occurs to afford **5** (50%). These reactions show that the hydroxy complexes are thermodynamically more stable than the methoxy derivatives (vertical reactions). Finally, the reactions of **3** with CD_3OD (equilibrium reaction to afford 50% of **5**-d_3 and minor amounts of **5**-d_4 and **3**-d_1/d_2) and of **5** with D_2O [rapid and quantitative conversion into **3**-d_1 (SnOD)] and the reverse reactions have been studied (diagonal reactions). The exchange reactions of the d^{i}ppe complexes **3** and **5** and their partially deuterated derivatives with *water* (D_2O or H_2O) proceed without any detectable H/D exchange at the Pd(II) center (reactions studied over a week) and may thus be considered to be clean nucleophilic substitution reactions of hydroxide at the Sn(II) center. The related exchange reactions with *methanol* (CD_3OD or CH_3OH) do involve partial Pd−H/D exchange and presumably proceed both by a reductive elimination (water or methanol)/oxidative addition (methanol) sequence at the Pd═Sn bond and by a nucleophilic substitution reaction of methoxide at the Sn(II) center. The reductive elimination/oxidative addition reaction of complexes **3**−**6**, as a competing reaction to the nucleophilic substitution at the Sn(II) center, is preferred by exchanging the Pd(II) d^{i}ppe ligands for d^{t}bpe[13] and the Sn(II) OH^- substituents for OMe^-; it is thus not detected for **3** and fastest for **6**.

Scheme 2



So far we have not succeeded in inserting unsaturated substrates into the Pd−H function of **3**. No reaction is observed at 20 °C between **3** and butadiene, CO, or CO_2 in the course of 1 d. However, when **3** is reacted with HC≡CH, MeC≡CMe, or C_2F_4, the Pd−Sn bond is slowly cleaved to afford (d^{i}ppe)Pd(HC≡CH)[14], (d^{i}ppe)Pd(MeC≡CMe),[8a,b] or (d^{i}ppe)Pd(C_2F_4),[8c] respectively, together with SnR_2/H_2O.

Discussion. With respect to the mechanism of the *reversible water and methanol addition* to the Pd═Sn bond (eq 1), it is noteworthy that the propensity of uncoordinated SnR_2 to form weak solvates[6b] is lost when it is coordinated to a strongly back-bonding metal center as for complexes ($R'_2PC_2H_4PR'_2$)M═SnR_2 (M = Ni, Pd, Pt).[15] On the other hand, the otherwise unreactive Pd(0) center is easily protonated when coordinated by SnR_2. Apparently, the nucleophilicity of Pd(0) is enhanced by the donor function of the SnR_2 ligand and, conversely, upon forming Pd(II) by protonation, Pd → Sn(II) back-bonding is weakened to such an extent that the SnR_2 substituent is now able to coordinate OR''^- (R'' = H, Me). Thus, disregarding a concerted mechanism, it appears likely that H−OR″ addition reactions to the Pd(0)═Sn(II) bond in **1** or **2** are initiated by electrophilic attack of a proton at the Pd atom to afford an intermediate Pd(II) cation $[(R'_2PC_2H_4PR'_2)Pd(H)SnR_2]^+$ (**A**, Scheme 2) to which OR''^- subsequently coordinates at Sn(II) to give the products **3**−**6**. Reductive elimination of water or methanol from complexes **3**−**6** proceeds by the mechanistic reverse. However, the *base exchange at the Sn(II) center* presumably proceeds associatively by an S_N2-type mechanism through intermediate **B**. This explains why the Pd−H(D) function is not at all affected in the base exchange reactions of the d^{i}ppe complexes with water and only slightly affected in the corresponding reactions with methanol. Preliminary experiments have shown that similar to **1**, the Ni analogue (d^{i}ppe)Ni═SnR_2[7b] reacts with water to afford (d^{i}ppe)Ni(H)Sn(OH)R_2 (**8**) which is presently studied in detail.

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Supporting Information Available: Experimental details on the synthesis and spectroscopical characterization of the new compounds, including details on the structure analysis of **3** (12 pages). See any current masthead page for ordering and Internet access instructions.

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[11] The solid d^{t}bpe complexes **4** and **6** eliminate water and methanol under vacuum (to give **2**) at a higher temperature (>100 °C) as compared to the d^{i}ppe derivatives.

[12] Typically, about 1 mmol of complex is reacted with the 10-fold excess of water or methanol in concentrated THF solution at 20 °C. The reactions proceed instantaneously.

[13] Similar as for **3** and **5**, the d^{t}bpe complexes **4** and **6** react with water (D_2O) by a fast (no more than a few minutes) and complete nucleophilic exchange at the Sn(II) center to afford **4**-d_1 (SnOD). However, in contrast to **3**-d_1 (SnOD), complex **4**-d_1 (SnOD) undergoes a slow Pd−H/D exchange to afford **4**-d_2 (60% after 1 week and 100% after 2 weeks; by NMR) due to a reductive elimination/oxidative addition mechanism.

[14] Krause, J.; Bonrath, W.; Pörschke, K.-R. *Organometallics* **1992**, *11*, 1158.

[15] (a) For complexes ($R'_2PC_2H_4PR'_2$)M═SnR_2 (see Table 1 of ref 7b), no solvent (THF and toluene) or temperature dependence of the NMR resonances has been found. Furthermore, attempts to isolate donor adducts were unsuccessful.[8c] Donor adducts are also not formed by $(CO)_5$M═SnR_2 (M = Cr, Mo).[6b] (b) In contrast, for $(C_2H_4)_2$Ni═SnR_2, various adducts $(C_2H_4)_2$Ni−SnR_2(donor) [donor = THF, NH_3, py, $(Me_2N)_3PO$] have either been isolated or detected by NMR. Pluta, C.; Pörschke, K.-R.; Mynott, R.; Betz, P.; Krüger, C. *Chem. Ber.* **1991**, *124*, 1321.

[16] Exchange H/D for the interconversion of **3**-d_2, **3**-d_1 (PdD), **5**-d_4, and **5**-d_1.