Reaction Mechanism of Transmetalation between Tetraorganostannanes and Platinum(II) Aryltriflate Complexes. Mechanistic Model for Stille Couplings

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The complexes *trans*-[PtPh(OTf)(PMe_2Ph)$_2$] (**1**) and *trans*-[PtPh(OTf)(PPh_3)$_2$] (**4**) were synthesized from the corresponding chloro complexes in moderate yields. Complex **1** is slowly hydrolyzed in solution, giving the dinuclear hydroxo-bridged complex [Pt(μ-OH)(PMe_2Ph)$_2$]$_2$(CF_3SO_3)$_2$ (**6**), which was characterized by X-ray crystallography. In solution **1** and **4** undergo fast solvolysis to give the corresponding solvento cations. The reactivities of **1** and **4** with Me_3SnPh were investigated in different solvents, and with **1** two products, *trans*-[$PtPh_2$(PMe_2Ph)$_2$] (**8**) and *cis*-[$PtPh_2$(PMe_2Ph)$_2$] (**9**), were always formed simultaneously. In THF an intermediate, *trans*-[PtPhMe(PMe_2Ph)$_2$] (**14**), was characterized on the path to **9**. The kinetics for these reactions were evaluated numerically, and on the basis of rate laws, activation parameters, and reactivity trends a mechanism involving parallel equilibria to **8** and **9** with associative activation in all steps is proposed. In this mechanism the initial attack always takes place trans to the phenyl group, giving **8** and **14**, respectively, via an open transition state. In a subsequent reaction, **14** reacts with another molecule of stannane, giving **9** as the final product via a cyclic transition state. Complex **4** gives exclusive formation of cis products: *cis*-[PtPhMe(PPh_3)$_2$] (**12**) and *cis*-[$PtPh_2$(PPh_3)$_2$] (**13**). These results are discussed in relation to the reaction mechanism of the transmetalation step in the Stille reaction.

Introduction

In the Stille coupling reaction a palladium catalyst is used to couple aryl halides with organotin nucleophiles and generate carbon−carbon bonds. It has become an attractive method in modern organic synthesis.

The mechanism originally proposed for the Stille reaction considered a Pd(0)/Pd(II) catalytic cycle with four consecutive reaction steps (oxidative addition, transmetalation, trans-to-cis isomerization, and reductive elimination), in which the transmetalation step was suggested to be rate-determining.[1] Recent work has provided a greater mechanistic understanding of the catalytic cycle and the individual steps therein,[2] and it has become apparent that the reaction conditions used strongly influence the mechanism.[3] However, due to its intrinsic complexity, the transmetalation reaction is still the most poorly understood step in the catalytic cycle and is therefore a matter of intense study.[4]

Many different model systems have been used to study the transmetalation step.[5] The high tolerance toward air and moisture of the reagents in the Stille reaction mainly stems from the low polarity of the Sn−C bond, and this property is perhaps mostly pronounced in the transmetalation step. Thus, the mechanistic insight gained from studies of transmetalation from organotin reagents are also relevant in other processes involving M−C bonds of moderate polarity: e.g., Suzuki and Hiyama coupling.[6] Also, phosphapalladacycles including PCP pincer complexes have become known as very promising catalysts for C−C bond formation reactions.[7] Although these types of complexes are not very commonly used in the Stille coupling, examples have appeared, from which some mechanistic insight into the transmetalation reaction has been generated.[8]

From a mechanistic standpoint, the use of platinum instead of palladium should make the complexes less prone to reductive

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elimination of the coupling product, and this could possibly aid in the detection of intermediates from the different reaction steps in the Stille coupling reaction. A system where the active metal center is platinum(II) instead of palladium(II) therefore seemed to be a good choice for a thorough kinetic and mechanistic investigation of the transmetalation step in the Stille reaction.

A number of investigations on the reaction between tetraorganotin compounds and different platinum complexes have been reported in the literature.[9] As stoichiometric probes of transmetalation in d^8 complexes, we have studied the reactions of *trans*-[PtPhX(L)$_2$] (X = F, OTf; L = PPh_3, PMe_2Ph, $AsPh_3$) with tetraorganostannanes, such as Me_3SnPh and Bu_3Sn(vinyl).[10,11] Here we report a kinetic study of the transmetalation reaction between *trans*-[PtPh(OTf)(PMe_2Ph)$_2$] (**1**) and Me_3SnPh in different solvents. The effects on the reactivity, as well as the product distribution, in the transmetalation reaction in terms of the nature of the leaving group and the ancillary phosphine ligands are discussed, and a mechanistic picture, including the characterization of an intermediate, is reported.

Experimental Section

General Procedures and Materials. All experiments involving air-sensitive compounds were carried out using standard high-vacuum-line or Schlenk techniques or in a glovebox under nitrogen. If nothing else is stated, all reagents and solvents were of the best quality available and were used as received from Aldrich. The complexes *trans*-[PtPhCl(PMe_2Ph)$_2$] (**2**) and *trans*-[PtPhCl(PPh_3)$_2$] (**3**) were prepared according to the literature.[10,12] Elemental analyses was performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Fast atom bombardment (FAB) mass spectroscopic data were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as the matrix. Conductivity measurements were performed using a Metrohm 644 conductometer. The cell constant was determined to be 0.87 cm^{-1}.

NMR Measurements. ^1H, ^{31}P, and ^{19}F NMR spectra were recorded on a Varian Unity 300 or a Varian Unity Inova 500 spectrometer. Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^1H and ^{13}C NMR) or H_3PO_4 (^{31}P NMR δ 0) and $CFCl_3$ (^{19}F NMR δ 0) as external references. The temperature was measured using the temperature-dependent shift of the CH_2 and OH protons of ethylene glycol.

***trans*-[PtPh(OTf)(PMe_2Ph)$_2$] (1).** A Schlenk flask was charged with 208 mg (0.356 mmol) of complex **2** dissolved in 15 mL of dichloromethane. While the mixture was stirred, 103 mg (0.402 mmol) of AgOTf (Acros Organics, 99+%), dissolved in 5 mL of acetone, was added and the reaction solution was shielded from light. After 48 h at room temperature the solution was filtered before the solvent was removed. The crystals were dried under vacuum for 2 h. To eliminate residual silver metal and triflate, the product was dissolved in benzene and placed at 4 °C for 2 h before another filtration was performed and the solvent removed. The off-white product was washed with petroleum ether and recrystallized from dichloromethane−petroleum ether. The yield was 137 mg (0.197 mmol, 55%). Anal. Calcd for $C_{23}H_{27}F_3O_3P_2PtS$: C, 39.60; H, 3.90. Found: C, 39.50; H, 4.02. ^1H NMR ($CDCl_3$): δ 1.56 (t, 12H, $^2J_{P-H}$ = 3.6 Hz, $^3J_{Pt-H}$ = 27 Hz), 6.54−6.84 (m, 5H), 7.32−7.44 (m, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 1.09 (s, $^1J_{Pt-P}$ = 2929 Hz). ^{19}F NMR ($CDCl_3$): δ 0.47 (s, 3F).

***trans*-[PtPh(OTf)(PPh_3)$_2$] (4).** An 81.6 mg portion (0.098 mmol) of **3** was dissolved in 5 mL of dichloromethane in a Schlenk flask. A 30.5 mg portion (0.119 mmol) of AgOTf was dissolved in 2 mL of acetone and added to the dichloromethane solution. After 48 h at room temperature with shielding from light, the solution was filtered and the solvent removed under reduced pressure. A brownish oil was formed, which was dissolved in benzene and filtered through a 1 cm layer of Celite, giving a yellow solution. After evaporation a yellow oil containing white crystals was achieved. The product was dissolved in a minimum of dichloromethane, which was allowed to evaporate under atmospheric pressure before the white crystals were washed with pentane. The yield was 51.6 mg (0.056 mmol, 57%). Anal. Calcd for $C_{43}H_{35}F_3O_3P_2PtS$: C, 54.60; H, 3.73. Found: C, 54.52; H, 3.82. ^1H NMR (C_6D_6): δ 6.08 (t, 2H, $^3J_{H-H}$ = 7.50 Hz, *m*-H, Pt−*Ph*), 6.35 (t, 1H, $^3J_{H-H}$ = 7.01 Hz, *p*-H, Pt−*Ph*), 6.70 (d, 2H, $^3J_{H-H}$ = 7.50 Hz, *o*-H, Pt−*Ph*), 7.02−7.05 (m, 12H), 7.41−7.48 (m, 6H), 7.62−7.67 (m, 12H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 28.2 (s, $^1J_{Pt-P}$ = 3201 Hz). MS (FAB^+): *m*/*z* 796 [PtPh(PPh_3)$_2^+$]. MS (FAB^-): *m*/*z* 149[$OSO_2CF_3^-$].

Me_3Sn(OTf) (5). The following synthesis is a modification of a procedure already described in the literature.[13] A 100 mL round-bottom flask, connected to a swivel frit, was charged with 0.534 g (2.08 mmol) of AgOTf and 0.634 g (2.60 mmol) of Me_3SnBr. Approximately 20 mL of THF was vacuum-transferred from Na/Ph_2CO into the flask under reduced pressure before the reaction solution was stirred at room temperature for 2 h. The reaction solution was filtered, and the solvent was evaporated under reduced pressure, giving a white product which was stored under N_2(g) at −20 °C. The yield was 0.416 mg (1.33 mmol, 64%). ^1H NMR ($CDCl_3$): δ 0.78 (s, $^2J_{Sn-H}$ = 64.0)[14] (assignment of the ^1H NMR signal was confirmed by a $^1H\{^{13}C\}$ HSQC NMR experiment).

Reaction of 1 and 4 with Stannane. In a typical experiment, a J. Young NMR tube was loaded with the aryltriflate platinum(II) complex and solvent. The reaction mixture was thermostated prior to addition of an excess of the tin compound, and the reaction was monitored using ^{31}P NMR spectroscopy. In most cases the products were not separated and isolated but characterized in situ. In addition, some qualitative measurements were performed in the presence of $Bu_4N(PF_6)$, Bu_4N(OTf), or free PMe_2Ph. In these cases the reagents were administered as stock solutions in dichloromethane-d_2.

Data Analysis. A kinetic model was fitted to the measured concentration vs time data by nonlinear least-squares (NLLS) regression using the program Pro-KII.[15] The observed data were arranged into the matrix **C**, where each column of **C** contained the time-dependent concentration profile of a particular species. A proposed kinetic model was entered into the software program using an intelligent model parser, which extracts the number of species,

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species names, their corresponding stoichiometric coefficients, and the number of reactions. The program produces a list of parameters (rate constants) with their reaction coefficients and constructs a system of simultaneous ordinary differential equations (ODEs) that describe the change in concentration of each species with time.[16] With knowledge of the initial concentrations of the species in the chemical model, the differential equations were integrated to yield calculated concentrations of each species at the same times as the measured data. The calculated concentration data were arranged into a matrix of concentration profiles, $\hat{\mathbf{C}}$.

A matrix of residuals, $\hat{\mathbf{R}}$, representing the difference between the measured and calculated concentration data, was calculated according to eq 1. The rate constants of the kinetic model were

$$\hat{\mathbf{R}} = \mathbf{C} - \hat{\mathbf{C}} \tag{1}$$

then refined by NLLS regression until a best fit was found between $\mathbf{C}$ and $\hat{\mathbf{C}}$ (as measured by the sum of the squared residuals). The NLLS algorithm used was the Levenburg−Marquardt algorithm.[17]

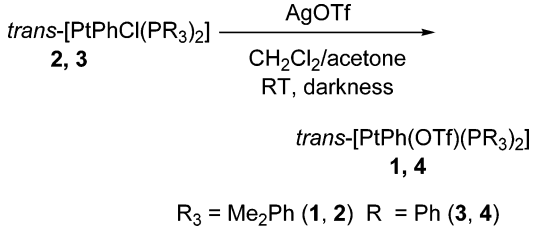
As a comparison the commercially available FACSIMILE chemical modeling package, implemented on a PC, was also used.

Structure Determination of 6. Single crystals of the dinuclear complex $[Pt(\mu\text{-}OH)(PMe_2Ph)_2]_2(CF_3SO_3)_2$ (**6**) suitable for X-ray diffraction were obtained after thawing a benzene-d_6 stock solution of **1** that had been stored at −20 °C. The intensity data set was collected at 293 K with a Bruker SMART CCD system using ω scans and a rotating anode with Mo Kα radiation (λ = 0.710 73 Å).[18] The intensities were corrected for Lorentz, polarization, and absorption effects using SADABS.[19] The first 50 frames were collected again at the end to check for decay; no decay was observed. All reflections were integrated using SAINT.[20] The structure was solved by Patterson methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL 5.1.[21] Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model. The crystals were fairly weak scatterers, giving rise to a high R_{int} value.[22] The data are more than 99% complete out to θ = 29°. The benzene solvent molecule displayed a large disorder, and to resolve this, the ring was constrained to be a planar hexagon with identical C−C distances.

Results

Synthesis and Characterization. Complexes **1** and **4** were synthesized by chloride for triflate substitution as described earlier for similar Pd complexes[4c] (cf. Scheme 1). This reaction operates in moderate yields and gives a reaction mixture with residual silver metal, which made the purification difficult. However, repeated filtration and recrystallization gave pure products that were characterized by NMR spectroscopy and elemental analysis.

Scheme 1



The $^{31}P\{^1H\}$ NMR spectrum of **1** in chloroform solvent is a singlet with platinum satellites ($^1J_{Pt-P}$ = 2929 Hz), which confirms the trans configuration. The virtual triplet at δ 1.56 ($^2J_{P-H}$ = 3.6 Hz) for the methyl protons on the phosphorus ligands, as seen in the ^1H NMR spectrum, also indicates a trans configuration. Similarly, **4** displays a $^1J_{Pt-P}$ coupling constant of 3201 Hz, which is consistent with a trans geometry.

From a benzene-d_6 solution of **1** single crystals of the dinuclear complex $[Pt(\mu\text{-}OH)(PMe_2Ph)_2]_2(CF_3SO_3)_2$ (**6**) were formed after several weeks. The molecular structure is given in Figure 1 together with selected bond distances and angles. Crystal data and details of the data collection are given in Table 1. The coordination geometry around the Pt(II) atoms is distorted square planar, with two bridging hydroxo ligands. This gives rise to a cis arrangement between the phosphine ligands and a four-membered ring where the O−Pt−O and Pt−O−Pt angles are 79.2(3) and 100.7(2)°, respectively. Hydroxo-bridged dinuclear complexes of palladium and platinum are far from unusual, and several crystal structures of tetraphosphine compounds are known, including the cation of complex **6**; it was earlier solved in the space group $P\bar{1}$ with nitrate as the counteranion.[23] Although the angles in the reported nitrate complex are similar to those in **6**, packing effects are far from negligible, since all the distances in the coordination sphere of the present triflate crystals are substantially longer.

Most reasonably, the formation of **6** takes place via protonolysis (by adventitious water) of the phenyl group of **1** in solution. It is known that coordination of a water molecule, by displacement of the triflate, renders it acidic enough to explain the protonolysis, although Pt−C bonds are normally stable toward water.[24] In the presence of hydroxide, formed in the protonolysis, dicationic bis(phosphine) complexes are known to form hydroxo-bridged dinuclear complexes.[23] In addition, the lability of coordinated triflate anions has been used in developing facile routes to ligand-bridged, dinuclear transition-metal complexes.[25]

All crystallographic data in the CIF format are given in the Supporting Information.

A modified procedure[13] to synthesize compound **5** was developed, using dry conditions and THF as solvent instead of benzene. The ^1H and ^{13}C NMR spectroscopic data of the crude product were in good agreement with the literature data, and no further purification or characterization was done.

Solvolysis. Even though **1** obviously undergoes a slow protonolysis reaction in solution, the general stability to air and moisture is good and in the solid state the compound can be kept at ambient temperature and under air for a very long time. Since the triflate ligand is known to be a good leaving group

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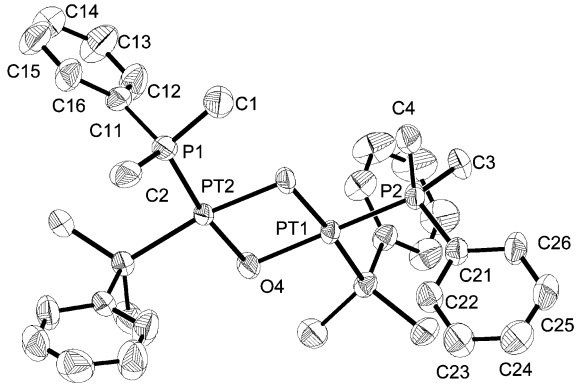


Figure 1. Diamond drawing with atomic numbering of the molecular structure of complex **6**. The ellipsoids denote 30% probability. Bond distances (Å) and angles (deg) with estimated standard deviations: Pt1−O4 = 2.122(5), Pt1−P2 = 2.260(2), Pt2−O4 = 2.117(5), Pt2−P1 = 2.258(2); O4−Pt1−O4 = 79.2(3), O4−Pt1−P2 = 170.26(17), 93,64(16), P2−Pt1−P2 = 94.18(12), O4−Pt2−O4 = 79.5(3), P1−Pt2−P1 = 94.38(12), O4−Pt2−P1 = 170.83(16), 93.32(16), Pt1−O4−Pt2 = 100.7(2).

Table 1. Crystal Data and Details of Data Collection and Refinement for Compound 6

chem formula	$C_{46}H_{58}F_6O_8P_4Pt_2S_2$
mol wt	1431.10
cryst syst	monoclinic
space group	*C*2/*c*
a/Å	25.078(5)
b/Å	13.604(3)
c/Å	18.511(4)
β/deg	110.12(3)
V/Å^3	5930(2)
Z	4
D_{calcd}/g cm^{-3}	1.603
μ/mm^{-1}	4.954
θ range/deg	1.73−32.01
no. of collected rflns	28 702
no. of unique rflns	8972 (R_{int} = 0.128)
no. of params	298
$R(F)$,[a] $R_w(F^2)$[b] ($I > 2\sigma(I)$)	0.0589, 0.1155
$R_w(F^2)$ (all data)	0.1402
S[c]	0.995

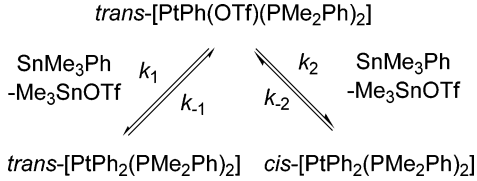
[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. [c] $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

and is often used to activate metal complexes, one of our first goals was to investigate whether solvolysis of the triflate ligand in **1** occurs in solution. Our results point to a fast solvolysis of the triflate ligand. Dissolving **1** in CD_2Cl_2 gives only one (apart from coupling) sharp resonance in both ^{31}P and ^{19}F NMR spectroscopy. Upon addition of LiOTf or Bu_4N(OTf) to the solution, the ^{19}F NMR data gave no additional signal, indicating that there is only free triflate present in solution. Addition of Et_4NBF_4, on the other hand, results in an additional signal at higher field, corresponding to the BF_4^- anion. Similar results were obtained in other solvents. In addition, conductivity measurements were performed on dichloromethane solutions of **1**, **2**, Bu_4N(OTf), and Bu_4NCl. The molar conductivities are given in the Supporting Information, and they support the occurrence of solvolysis of the triflate ligand, where the molar conductivity of the solution of **1** is much higher than that of the corresponding solution of **2**. We cannot fully exclude the possibility of a very fast exchange between free and coordinated triflate, but there is no sign of any broadening of the signals in the NMR spectra, and substitution reactions of similar compounds are known to be slow on the NMR time scale.[26]

The lability of the triflate ion was further demonstrated by the fact that addition of free PMe_2Ph or chloride (in the form of Et_4NCl) to a CD_2Cl_2 solution of **1** gave instant formation of $[PtPh(PMe_2Ph)_3]^+$ (**7**) and **2**, respectively (cf. Table 2). The reactions take place with equal amounts, as well as an excess, of the entering ligands.

Transmetalation Reactions. The reaction of complex **1** with Me_3SnPh was studied in CD_2Cl_2, acetone-d_6, and THF at room temperature by ^{31}P NMR spectroscopy (cf. Scheme 2).

Scheme 2



Complex **1** reacts with Me_3SnPh, and there is a conversion into two different products, *trans*-[$PtPh_2(PMe_2Ph)_2$], (**8**) and *cis*-[$PtPh_2(PMe_2Ph)_2$], (**9**). The products were characterized by NMR spectroscopy and display $^1J_{Pt-P}$ values of 2899 and 1755 Hz, typical of trans and cis configurations, respectively. The chemical shifts for the cis product were confirmed by comparison with a complex synthesized elsewhere.[27] An independent synthesis of **8** by the addition of the Grignard reagent BrMgPh to a THF solution of **2** was attempted. Instantly, only compound **9** was formed, as seen by ^{31}P NMR spectroscopy. However, if the THF solvent was removed and CH_2Cl_2 was added, **8** was also formed within 2 days at room temperature. In this Grignard synthesis two additional species were also observed, identified as *trans*-[$PtPhBr(PMe_2Ph)_2$] (**10**) and *trans*-[$PtBr_2(PMe_2Ph)_2$] (**11**), respectively.[28] **10** and **11** were characterized by ^{1}H and ^{31}P NMR spectroscopy (cf. Table 2).

The initial formation of **8** is faster than the formation of **9**, regardless of reaction conditions. The reactivity and the product distribution ratio vary depending on the amount of added tin compound, reaction temperature, and solvent. Moreover, in CD_2Cl_2 and acetone there is always **1** left when the reaction is over. This indicates that the reaction in Scheme 2 is reversible, at least under certain conditions.

To verify this reversibility, the equilibrium was accessed also from the product side in separate experiments. To a solution of **1** and Me_3SnPh in dichloromethane-d_2, considered to be at equilibrium, **5** was added in a 1:1 molar ratio with respect to the platinum complex. This caused a small change of the compound distribution in solution in favor of compound **1**. Leaving the reaction solution for 20 h at room temperature gave no further changes. However, when an additional amount of **5** was added, the reaction was shifted further to the left, making **1** the most abundant platinum compound. The uncatalyzed cis−trans isomerization is very slow, and addition of free PMe_2Ph to a solution of only **9** resulted in no changes even after several days, although free phosphines are known to catalyze such isomerizations.[29] The reversible nature of the transmetalation

(26) (a) Alibrandi, G.; Romeo, R.; Monsù Scolaro, L.; Tobe, M. L. *Inorg. Chem.* **1992**, *31*, 5061. (b) Romeo, R.; Arena, G.; Monsù Scolaro, L.; Plutonia, M. R. *Inorg. Chim. Acta* **1995**, *240*, 81.

(27) Wendt, O. F. Platinum(II) and Palladium(II) Complexes with Group 14 and 15 Donor Ligands. Synthesis, Structure and Substitution Mechanisms. Thesis, Lund University, Lund, Sweden, 1997.

(28) No references for the NMR data were found in the literature. However, the assignment was based on the fact that PR_3 is known to have a higher trans influence than Br. For references concerning analogous platinum(II) complexes, see for example ref 9g and: Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667. Rahn, J. A.; O'Donnell, D. J.; Palmer, A. R.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 2631.

(29) Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Longman: New York, 1999.

Table 2. NMR Data for Compounds 7−11

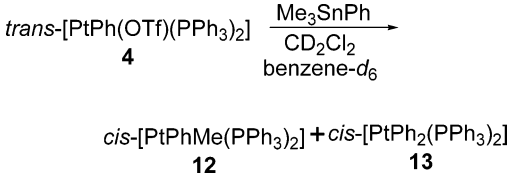
compd	nucleus	chem shift/δ (multiplicity, coupling const/Hz, assign[a])
7	^{1}H	1.15 (d, 12H, $^2J_{P-H}$ = 8.79, $^3J_{Pt-H}$ = 26.0), 1.30 (t, 6H, $^2J_{P-H}$ = 4.03, $^3J_{Pt-H}$ = 24.9), 6.93−7.00 (m, 3H, Pt−*Ph*), 7.07−7.14 (m, 2H, Pt−*Ph*), 7.27−7.49 (m, 15H, P−*Ph*)
	^{31}P{^{1}H}	−5.69 (d, $^1J_{Pt-P}$ = 2658, $^2J_{P-P}$ = 21.9), −15.16 (t, $^1J_{Pt-P}$ = 1748, $^2J_{P-P}$ = 22)
8[b]	^{1}H	1.50 (vt, 12H, $^2J_{P-H}$ = 3.66, $^3J_{Pt-H}$ = 17.2)
	^{31}P{^{1}H}	−5.76 (s, $^1J_{Pt-P}$ = 2899)
9	^{1}H	1.10 (d, 12H, $^2J_{P-H}$ = 7.49, $^3J_{Pt-H}$ = 28.8), 6.63−6.71 (m, 4H), 6.84−6.92 (m, 6H), 7.28−7.50 (m, 10H)
	^{31}P{^{1}H}	−14.8 (s, $^1J_{Pt-P}$ = 1755)
10	^{1}H	1.50 (t, 12H, $^2J_{P-H}$ = 3.66, $^3J_{Pt-H}$ = 32.6), 6.76−6.82 (m, 3H, Pt−*Ph*), 7.08−7.11 (m, 2H, Pt−*Ph*), 7.34−7.40 (m, 6H, P−*Ph*), 7.63−7.68 (m, 4H, P−*Ph*)
	^{31}P{^{1}H}	−5.10 (s, $^1J_{Pt-P}$ = 2840)
11	^{1}H	0.96 (t, 12H, $^2J_{P-H}$ = 5.49, $^3J_{Pt-H}$ = 68.12), 7.33−7.42 (m, 6H), 7.62−7.69 (m, 4H)
	^{31}P{^{1}H}	−15.9 (s, $^1J_{Pt-P}$ = 1929)

[a] The assignment is only displayed for clarification when necessary. In all cases the solvent has been CD_2Cl_2. [b] Not all protons could be assigned due to interference with protons from the Me_3SnPh compound.

thus implies that the organotin reagents are catalysts for cis−trans isomerization. On the basis of the Grignard experiment this seems to be true also for organomagnesium reagents.

The reaction of complex **4** with Me_3SnPh was investigated in CD_2Cl_2 and benzene-d_6 at room temperature using ^{1}H and ^{31}P NMR spectroscopy (cf. Scheme 3). Complex **4** reacts with Me_3SnPh, and within 6 h there is a complete conversion into one product, identified as *cis*-[PtPhMe(PPh_3)$_2$] (**12**) by NMR spectroscopy. After 18 h also *cis*-[$PtPh_2(PPh_3)_2$] (**13**) was identified in the reaction mixture, and the molar ratio between **12** and **13** was about 7:3. Over the course of another 48 h no further changes were seen, making compound **12** the dominant transmetalation product of the reaction in Scheme 3. Similar observations were done in both CD_2Cl_2 and benzene-d_6. Complexes **12** and **13** have been identified elsewhere, giving the same NMR signatures as observed here.[30]

Scheme 3



As noted, triflate ions are easily substituted in solution by, for example, chloride or free phosphine, which are typically present in catalytic mixtures. This prompted us to investigate the reactivity toward transmetalation also for complexes **2** and **7**, respectively. Addition of Me_3SnPh or $Bu_3Sn(CH{=}CH_2)$ to a solution of **2** in CD_2Cl_2 clearly showed that no transmetalation reaction occurs between **2** and either stannane. Complex **7** displayed the same inertness against transmetalation reactions with Me_3SnPh. The transmetalation reaction in both cis and trans positions is obviously facilitated by the lability of the triflate ligand. Espinet and co-workers[4c] have shown that the formation of *trans*-[$Pd(C_6Cl_2F_3)Cl(PPh_3)_2$] (upon addition of LiCl to the reaction solution) gives a retardation of the transmetalation rate in comparison to the case when no free Cl^- is used. Since the stability of a Pt−Cl bond is even higher than that of the corresponding Pd−Cl bond, the total inertness toward transmetalation in our system is in agreement with this. Also the inertness of complex **7** can be explained by thermodynamic considerations. Early, qualitative observations on Pt(II) systems in transmetalation reactions concluded that strong σ-donors dramatically slow the reaction rate.[4c,9d−h] Hence, the additional coordination of a phosphine ligand, which is a relatively strong σ-donor and a π-acceptor, hampers the transmetalation reaction for complex **7**. The question remains, though, why the presence of strongly bonded ligands with a good bridging ability affects the cis transmetalation so dramatically.

(30) For NMR characterization data of **12**, see ref 10, and for complex **13**, see ref 9g.

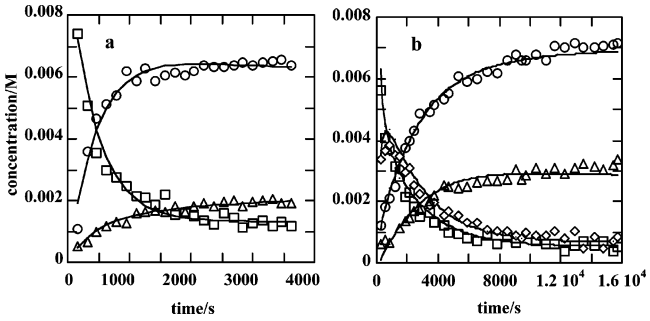


Figure 2. Observed concentrations of reactant (□), intermediate (◇), trans (○), and cis (△) product as a function of time: (a) [**1**] = 9.6 mM, [Me_3SnPh] = 414 mM in CD_2Cl_2 at 25 °C (solid lines denote the best fit using FACSIMILE); (b) [**1**] = 11.0 mM, [Me_3SnPh] = 388 mM in THF/THF-d_8 at 50 °C (solid lines denote the best fit using Pro-KII).

Table 3. Activation Parameters and Rate Constants for the Different Pathways of the Proposed Equilibrium in Scheme 2 in CD_2Cl_2 at 25 °C

pathway	10^3k/M^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
k_1	3.4 ± 0.3	36 ± 4	−178 ± 13
k_{-1}	42 ± 11	31 ± 4	−176 ± 13
k_2	1.3 ± 0.3	55 ± 4	−123 ± 14
k_{-2}	20 ± 5	19 ± 4	−221 ± 13

Kinetic Analysis. To understand the mechanism of these transmetalation reactions, we performed a detailed kinetic study of the equilibrium in Scheme 2. In this way it was possible to study the transmetalation in both the cis and trans positions. It was soon clear to us that any closed-form solution of a kinetic scheme involving two equilibria would be excessively complicated, and we turned to numerical fittings of the concentration−time data. The reactions were always followed with the tin compound in large excess compared to the concentration of **1**. This pushed the equilibrium to the right to a convenient extent. Typical kinetic traces for the reaction are shown in Figure 2. Two different kinetic modeling programs were used to fit the experimental data to different mechanisms; very good correlation between the programs was seen, and reasonably good fits were obtained (cf. Figure 2). Experimental results are summarized in Tables 3 and 4, and complete data are reported as Supporting Information.

Table 4. Rate Constants (10^3 M^{-1} s^{-1}) for the Different Pathways of the Proposed Mechanism in Scheme 4 in THF at 50 °C[a]

pathway					
k_3	k_{-3}	k_4	k_{-4}	k_5	k_{-5}
1.8 ± 0.4	4.8 ± 2.2	5.4 ± 0.9	330 ± 130	1.0 ± 0.3	18 ± 9

[a] The platinum(II) complex was *trans*-[PtPh(OTf)(PMe_2Ph)$_2$] (**1**). The errors are given as 1 standard deviation.

In THF and acetone an intermediate is observed, and this of course provided us with additional information when defining the reaction mechanism. Starting with the data for THF solutions, we tested a number of mechanisms (see the Supporting Information) and the best agreement was obtained with a scheme consisting of two parallel and reversible reaction paths leading to **8** and **9** with no uncatalyzed interconversion of **8** and **9** on the time scale of the reaction. The results from our fitting procedure strongly suggest that the long-lived intermediate is on the reaction path to **9** only. Cases where the intermediate is on the reaction path to **8**, or common to the paths to both products, were considered. In these cases, and especially in the former one, the results displayed a low significance in some of the determined rate constants as well as large errors, which indicates that these models can be discarded. In THF, we were able to identify the intermediate by ^{31}P and ^{1}H NMR spectroscopy. In the ^{31}P spectrum it has a chemical shift of -4.1 ppm and a $^{1}J_{Pt-P}$ value of 2960 Hz. This strongly suggests a Pt(II) trans species. In the ^{1}H NMR spectrum a transient peak at -0.19 ppm was observed ($^{2}J_{P-H} = 6.5$ Hz, $^{2}J_{Pt-H} = 49$ Hz). Taken together, these data are compatible with the intermediate being *trans*-[PtMePh(PMe_2Ph)$_2$] (**14**), and chemical shifts and coupling constants agree with those reported.[10]

In CD_2Cl_2 no intermediate was observed, and the best fit was obtained with two parallel reversible pathways leading to cis and trans products. The fitting suggests that there is no common intermediate in this case either, but of course one cannot exclude the existence of intermediates in steady-state concentrations along one or both pathways. In all cases, the adopted models were fitted at various concentrations of [Me_3SnPh] and [Pt], giving good agreement for the calculated parameters in most cases.

Activation parameters were determined for the reaction in CD_2Cl_2 by fitting the Eyring equation to the rate constants at different temperatures, and they are given in Table 3.

Equilibrium constants were calculated from the determined rate constants, and these agree with the qualitative estimations: i.e., the reaction in Scheme 2 is an equilibrium in CD_2Cl_2, whereas it goes more or less to completion in THF. In CD_2Cl_2 the calculated equilibrium constants for formation of **8** and **9** were 0.081 ± 0.023 and 0.065 ± 0.023, respectively. The final thermodynamic product distribution was determined at room temperature in CD_2Cl_2. The molar ratios for **1**, **8**, and **9** changed from being 49:48:3 after 100 min to 6:35:59 after 6 days. No further changes were observed even after several more days. This indicates that **9** is slightly more stable than **8**, which is somewhat off the calculated ratio based on the equilibrium constants from kinetics, which indicate a slightly higher stability for the trans compound **8**. It is clear that when the kinetic runs were terminated, equilibrium was not yet established.

Salt Effects. The ionic strength effects during transmetalation in CD_2Cl_2 were also investigated. They were adjusted in two different ways, with the addition of $Bu_4N(PF_6)$ or $Bu_4N(OTf)$. In this way we were able to distinguish between proper salt effects and reagent concentration effects. Furthermore, the salt effects can be divided into two categories: one thermodynamic, where the final distribution between the reactant and the products is changed, and one kinetic, where the initial rates of formation of the different products are affected. All these results are qualitative in nature.

Table 5. Qualitative Influences on the Initial Rate of Reactant Decay and Product Formation in the Reaction Depicted in Scheme 2 upon Addition of Different Salts to the Reaction Solution[a]

			influence on the reacn rate		
entry[b]	additive	[additive]/mM	**1**	**8**	**9**
1	$Bu_4N(PF_6)$	8.92	+	+	−
2	$Bu_4N(PF_6)$	89.2	+	+	−
3	$Bu_4N(OTf)$	8.43	none	none	−
4	$Bu_4N(OTf)$	84.3	−	−	−

[a] All comparisons refer to when no additive is used. All reactions were done in dichloromethane-d_2 solvent at room temperature with [**1**] = 10.5−14.3 mM and [Me_3SnPh] = 204−208 mM.

Addition of both the hexafluorophosphate and triflate salts to the reaction solution favors the formation of products in Scheme 2. This is most reasonably a consequence of an increased stabilization of the products: e.g., the tin triflates. One can also note that **9** is favored compared to **8**, when neutral salt is added, and this most probably has its origin in the higher charge separation in solution, favoring the product with higher dielectricity constant. With increased free triflate concentration, **8** is instead the favored product.

The qualitative influences on the reaction rate, corresponding to the reactant decay and the product formation, are depicted in Table 5. For the hexafluorophosphate the overall effect is that the rate of reactant decay and the formation of **8** are increased, whereas the rate of formation of **9** is decreased. When the triflate salt is added, the trend is instead a retardation of the reaction rate for all species involved (at lower concentrations this concentration effect seems to be counterbalanced by the "salt" effect that triflate also gives rise to). This observation goes well in line with our suggestion of the necessity of a solvolysis prior to transmetalation, and the presence of triflate ions in solution probably disfavors the formation of the solvated complex.

Discussion

Much effort has been devoted to the elucidation of the mechanism of transmetalation reactions in the Stille coupling. It has been concluded that both the outcome of the reaction and the reaction mechanism are strongly dependent on the reaction conditions used. Our observations are no exception, but we will try to present a unified picture that explains most of our observations. The present investigation was not complicated by a consecutive reductive elimination reaction, as is usually the case when palladium complexes are used. On the other hand, one can always question the relevance of using platinum when trying to understand palladium catalysis.

First of all, it seems clear that it is the solvento complex that is the reactive species in all cases in the current system. This is supported by a number of observations. First, we see a significant change of the reactivity and product distribution in different solvents and the reactivity follows the well-known coordinating ability of the different solvents, indicating that the solvent molecule is actually coordinated to the metal center and that this coordination plays a crucial role in the overall reaction. Without solvent coordination it is expected that the solvent with

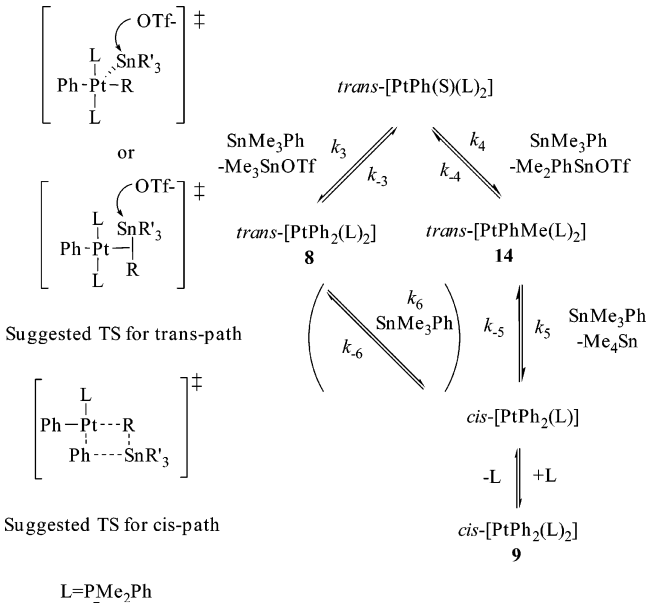
the highest dielectricity constant, acetone, would support the charge separation the best and give rise to the highest rate. Second, we see a retarding effect upon adding a triflate salt, in line with the formation of a less reactive neutral triflate complex. Third, the fact that no transmetalation reaction takes place on complex **2** or **7**, where a chloro or phosphine ligand is coordinated to the metal center, suggests that solvolysis and the lability of the leaving group are important for the reactivity. In addition, the conductivity measurements indicate the presence of a cationic complex in solution. It should be noted that all these effects apply to the reaction to both cis and trans products (vide infra).

All the elementary steps in the mechanistic models are bimolecular, first order in both platinum and stannane, and this together with the activation parameters strongly indicates an associatively activated reaction mode for the transmetalation reaction in Scheme 2. Also, the fact that we have a strong steric effect on the outcome of the transmetalation reaction indicates associatively activated reaction paths. The entropies of activation are all largely negative, and our values are in the same range as those derived earlier for different palladium(II) systems.[4c] It should be noted that the errors in the activation parameters are large and that one should not draw any far-reaching conclusions on the basis of their numerical values.

It has been claimed that increased bridging ability of the leaving ligand in transmetalation reactions should increase the formation of the cis product, due to the enhanced possibility for formation of a cyclic transition state.[31] Recently we investigated the reactivity of a platinum(II)−fluoro complex.[10] Our results displayed an exclusive formation of trans products, which was somewhat surprising in view of the good bridging ability of the fluoro ligand. In addition, we were also able to identify transmetalation over an Sn−C(sp^3) bond, which was rationalized in terms of steric demands of the ancillary phosphine ligands. Thus, in the current system, where the leaving ligand has a lower bridging ability than fluoride, an exclusive trans product formation might also be expected. This is not the case, however, and we instead observe a mixed product distribution of cis and trans isomers when PMe_2Ph is used as ancillary ligand. In addition, and even more surprising, *only* cis products are formed in the case of the PPh_3 complex (Scheme 3). In this case the steric effect again directs the transmetalation to occur over the Sn−C(sp^3) bond rather than over the Sn−C(sp^2) bond.

In THF solution we observe that **14** is an intermediate on the path to the cis product, and it therefore seems reasonable that the initial attack on the triflate/solvento platinum compound always takes place trans to the phenyl ligand. We propose that this is true also in dichloromethane, although we cannot observe any intermediate in this case and the kinetic modeling cannot distinguish between a mechanism where **14** is present in steady-state concentrations and where there is no intermediate. If the initial attack takes place trans to the phenyl and the solvent is always the leaving group, most of our observations are explained. A comprehensive mechanism is given in Scheme 4. The rate constants defined in Scheme 4 refer to the measurements in THF. It is a well-known fact that it is the nature of the trans ligand that, apart from steric reasons, dictates the reactivity in square-planar complexes, and thus it is very difficult to comprehend the lower reactivity of the THF complex and **2** and **7** also in the cis position if phosphine is the leaving group. Especially chloride, with a low steric demand and good bridging properties, would be expected to be a good cis ligand. The

Scheme 4



presence of a chloride or a THF molecule, instead of a dichloromethane, would therefore hamper the reactivity in the trans position, whereas the cis effect would be minor. Still, we see an almost equal effect in both the cis and trans positions, and this is easily rationalized if **14** is an intermediate on the path to **9**, also in dichloromethane. This is also in line with the notion put forward by Espinet and co-workers that transmetalations are similar to nucleophilic substitutions.[4c] Reacting **1** with chloride exclusively gives **2**, and reacting **2** with iodide exclusively results in substitution of chloride.[10] From our work on fluoro complexes where trans complexes are exclusively formed, we know that these can be transformed into cis products also with exchange of alkyl/aryl ligands.[10] The fact that we see more isomerization in the present system can probably be explained by the large excess of organotin reagent used here. The salt effects are also in agreement with the proposed mechanism; neutral salt facilitates the initial formation of trans product, whereas the isomerization to the cis product is less influenced, as expected for a nonpolar transition state. The organotin-catalyzed isomerization from **8** to **9** (k_6 path in Scheme 4) was considered as an alternative to the intermediacy of **14**. In the end, this was not the best model, but it seems likely that this pathway is operating, at least to some extent.

We suggest open transition states for the formation of trans products, as shown in Scheme 4. We cannot distinguish between the existence of a so-called σ-complex where the triflate (or solvent) attacks the coordinated stannane and releases the R_3-SnX and an oxidative path where there is oxidation over the Sn−C bond to form a Pt(IV) intermediate from which the R_3-Sn group is reductively eliminated. For the formation of the cis product it seems most likely that we have a cyclic transition state of the type pictured in Scheme 4. This would directly lead to the cis configuration.[4c,e] Such a reaction would be favored for bulkier phosphine ligands and could explain why the PPh_3 complexes give exclusive formation of cis complexes.

Overall, it is difficult to know how relevant these results are for transmetalation reactions of palladium complexes. A retardation of the reaction rate is often observed when free neutral ligand is added to a reaction solution in the Stille coupling reaction,[4a,b] and one explanation that has been offered is the formation of a tris(phosphine) complex with lower reactivity.[4c] This explanation is clearly substantiated by our finding that the

(31) (a) Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129. (b) Reference 4c.

tris(phosphine) complex is completely unreactive. Also, it is clear that if reductive elimination operates on a cis compound the reversible nature of these reactions could easily funnel all product out via the cis complex, even if substantial amounts of trans compound are formed initially. The transformation of *trans*-bis(phosphine) to *cis*-bis(phosphine) complexes mediated by organotin compounds is evidently a possibility also in palladium chemistry. In fact, isomerization reactions via bridging hydrocarbyl complexes have been considered before.[32]

Conclusion

By choosing platinum(II) instead of palladium(II), we could successfully perform a thorough kinetic and mechanistic investigation of the transmetalation reaction with organotin reagents, having reasonable reaction rates and no subsequent reductive elimination. The transmetalation reaction between *trans*-[PtPh(OTf)(PMe_2Ph)$_2$] (**1**) and Me_3SnPh was investigated, and we always observe two products, *trans*-[$PtPh_2$(PMe_2Ph)$_2$] (**8**) and *cis*-[$PtPh_2$(PMe_2Ph)$_2$] (**9**), formed simultaneously. In THF we were able to characterize, by NMR spectroscopy, an intermediate, *trans*-[PtPhMe(PMe_2Ph)$_2$] (**14**), on the path to **9**. We evaluated the kinetics for these reactions numerically and propose a mechanism involving parallel equilibria to **8** and **9** with associative activation in all steps. In this mechanism the initial attack always takes place trans to the phenyl group, giving **8** and **14**, respectively, via an open transition state. In a subsequent reaction, **14** (and possibly **8**) reacts with another molecule of stannane and gives **9** as the final product via a cyclic transition state. Initial reaction taking place in the trans position only explains the reactivity trends, where the reactivities to both cis and trans products are found to be extremely sensitive to the leaving-group ability of the ligand trans to the phenyl group. Implications for the Stille reaction are further substantiation for the retardation by added free ligand based on the formation of unreactive tris(phosphine) complexes. Also, the reversibility of the transmetalation reactions means that all organic product could be funneled out via a cis complex, although there are substantial amounts of trans complex initially. In essence, the stannanes catalyze the cis−trans isomerization.

Acknowledgment. We thank Mr. Felix Plamper for great assistance with the synthesis of the triphenylphosphine complex. Financial support from the Swedish Research Council, the Crafoord Foundation, the Knut and Alice Wallenberg Foundation, and the Royal Physiographic Society in Lund is also gratefully acknowledged.

Supporting Information Available: Tables giving detailed crystallographic data, atomic positional parameters, and bond lengths and angles in the CIF format, tables of all observed rate constants as a function of temperature and concentration, and primary data from the mechanistic fitting. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051021A

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