Equilibria, Kinetics, and Mechanism for Rapid Substitution Reactions *Trans* to Triphenylsilyl in Platinum(II) Complexes

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Fast substitution of chloride for bromide and iodide *trans* to triphenylsilyl in *trans*-$PtCl(SiPh_3)(PMe_2Ph)_2$ has been studied by stopped-flow spectrophotometry in acetonitrile solution. Substitution is reversible with an observable solvent path via the solvento complex *trans*-$[Pt(SiPh_3)(MeCN)(PMe_2Ph)_2]^+$, which has also been synthesized and characterized in solution. Rate constants for the forward and reverse direct substitution pathways are 2900 ± 100 and 7500 ± 300 for bromide and 14300 ± 1100 and 81000 ± 11000 M^{-1} s^{-1} for iodide as nucleophile. The solvento complex reacts ca. 10^3 times faster with iodide than the parent chloride complex, and its reactivity is some 2 orders of magnitude higher than the most reactive solvento species of platinum(II) studied so far. Halide substitution occurs with negative volumes and entropies of activation, but the nucleophilic discrimination is low, and the leaving ligand plays the most important role in the activation process, indicating an I_d mechanism. Triphenylsilyl has a very high *trans* effect, comparable to that of ethene and methylisocyanide, due to extensive bond-weakening in the ground state, probably enforced by π-acception in the transition state. Due to electronic and solvational effects the platinum(II) silyl moiety acts as a hard or borderline metal center in acetonitrile, the thermodynamic stability sequence of its halide complexes being Cl > Br > I, *i.e.* the reverse of what is usually observed for platinum(II) complexes.

Introduction

Rates of substitution reactions in square-planar platinum(II) complexes vary largely dependent on the electronic properties of the ligand *trans* to the coordination site where substitution takes place. For instance, the half-life for acid hydrolysis *trans* to the aqua ligand in $PtCl_3(H_2O)^-$ is ca. 290 days, *trans* to dimethyl sulfoxide in $PtCl_3(Me_2SO)^-$ 7 s, and *trans* to ethene in Zeise's anion probably ca. 50 μs.[1] Similarly, the large reactivity ratio of 11 orders of magnitude observed for solvent exchange at $Pt(H_2O)_4^{2+}$ and $Pt(MeNC)_4^{2+}$ can partly be rationalized by differences in the *trans* effect.[2,3] This kinetic effect is high for ligands which are good σ-donors and/or π-acceptors,[4,5] whereas the ground-state *trans* influence seems to follow the σ-donicities of the ligands fairly well.[6]

It was established already in the late sixties that silyl ligands have an unusually high ground-state *trans* influence,[7,8] and recent structural studies have confirmed that alkyl- or arylsilyl ligands have the highest *trans* influence observed in platinum chemistry so far.[9] Thus, chemical bonds *trans* to silyl in platinum(II) complexes are extremely long and weak. It was therefore considered to be of interest to study the kinetics and mechanism for the very rapid substitution processes that could be expected to occur *trans* to silyl in such complexes.

Silyl complexes of d^8 metals have received some attention due to their role in catalytic hydrosilylation reactions.[10] In this context reductive elimination and insertion reactions in silyl complexes of platinum(II) have been studied,[11,12] but we are not aware of any quantitative studies of substitution reactions *trans* to silyl. Reaction between *trans*-$PtCl(SiPh_3)(PMe_2Ph)_2$ and various nucleophiles has been reported to result in substitution *trans* to silyl,[13] but this early report contains no kinetic or mechanistic information.

To determine the *trans* effect of silyl ligands and to elucidate the mechanism by which substitution takes place in platinum(II) silyl complexes we have investigated the kinetics for the reaction of *trans*-$PtCl(SiPh_3)(PMe_2Ph)_2$ with bromide and iodide in acetonitrile and for the iodide anation reaction of the corresponding solvento complex, *trans*-$[Pt(SiPh_3)(MeCN)(PMe_2Ph)_2]^+$.

Experimental Section

General Procedures and Materials. The complex *trans*-$PtCl(SiPh_3)(PMe_2Ph)_2$ (**1**) was prepared from $PtCl_2(PMe_2Ph)_2$ and Ph_3SiH in benzene/triethylamine according to the literature, and its ^{1}H- and ^{31}P-NMR spectra agreed satisfactory with those reported.[14] It has a ν(Pt−Cl) of 238 cm^{-1}. The solvento complex, *trans*-$[Pt(SiPh_3)(MeCN)(PMe_2Ph)_2]^+$ (**2**), was prepared in solution by adding a stoichiometric amount of silver triflate (1.67 mg, 6.50 μmol) to a 0.702 mM solution of **1** in MeCN (9.26 mL, 6.50 μmol) and filtering through a cotton plug. The cotton plug was rinsed with MeCN, and the resulting clear solution was immediately diluted to the concentration required for the experiments (10^{-4} M or less). In more concentrated solutions, the solvento complex decomposes with time. Tetraethylammonium chloride (Janssen Chimica 99%) and bromide (Merck z S) were

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recrystallized and dried over P_2O_5 *in vacuo*. Tetrabutylammonium iodide (Merck z S), sodium iodide (Merck pa), acetonitrile (Labscan AR), and all other solvents were used as received. IR spectra were recorded as polyethylene pellets on a Bio-Rad FTS 6000 FT-IR spectrometer.

NMR Measurements. NMR spectra were recorded on a Varian UNITY 300 spectrometer working at 64.15–64.37 (^{195}Pt), 121.36 (^{31}P), or 299.96 (^{1}H) MHz. WALTZ-16 ^{1}H-decoupling was used in the non-^{1}H nuclei experiments. Chemical shifts are given in ppm downfield from TMS, H_3PO_4, or K_2PtCl_6. $CD_2\mathit{H}CN$ (δ 2.05), $H_3\mathit{P}O_4$, and $K_2\mathit{Pt}Cl_4$ (δ −1639) were used as internal and external references, respectively. Samples were prepared by mixing a stock solution of **1** or **2** in CH_3CN/CD_3CN with solutions of tetraethylammonium bromide, tetraethylammonium chloride, or sodium iodide. ^{1}H-NMR samples were prepared similarly in neat CD_3CN.

Kinetics. The stopped-flow experiments were performed on an Applied Photophysics Bio Sequential SX-17 MX stopped-flow spectrofluorometer. The substitution of chloride in **1** by bromide or iodide was studied in acetonitrile by observing the increase in absorbance at 285 and 310 nm, respectively. The complex solution ($(1-2) \times 10^{-4}$ M) contained excess chloride ($(1-10) \times 10^{-3}$ M) and was mixed with at least a 10-fold excess of incoming ligand ($(2-100) \times 10^{-3}$ M), ensuring pseudo-first-order conditions. The kinetic traces were fitted to single exponentials using the software provided by Applied Photophysics.[15] This gave observed rate constants at different concentrations of leaving and incoming ligands. Rate constants are given as an average of at least 5 runs. Variable-temperature experiments were performed between 283 and 303 K. Variable-pressure measurements were made between 1 and 1500 bar on a Hi-Tech high-pressure stopped-flow spectrophotometer, HPSF-56, connected to a Hi-Tech high-performance hydraulic pressurizing system (Hydratron) with digital recording of the pressure and with water as pressurizing medium.[16] No free chloride was added in the high-pressure measurements to ensure a large absorbance change. This caused no observable deviation from first-order behavior.

Due to the high rates of reaction 1 the observed pseudo-first-order rate constants in all these experiments usually varied between ca. 70 and 500 s^{-1}. The dead-time of the stopped-flow instruments used is ca. 1.5 ms. Thus, the most rapid reactions were not observable until after 1–2 half-lives. Platinum concentrations were therefore chosen sufficiently large to allow observation during several half-lives. The high rates, low equilibrium constants, and the necessity to produce a sufficiently large equilibrium displacement of reaction 1 also led to restrictions as to the choice of free ligand concentrations. Complete data are given in the Supporting Information tables.

The reaction of the solvento complex **2** with iodide is too fast for pseudo-first-order conditions, and it was followed in the stopped-flow instrument under second-order conditions at 298.2 K using solutions with equal concentrations of complex and ligand ($(0.25 \text{ or } 0.5) \times 10^{-4}$ M). At each concentration 10 runs were performed. These are summarized in a Supporting Information table.

UV/Vis Equilibrium Measurements. UV/vis spectra were recorded on a Milton Roy 3000 diode array spectrophotometer. The equilibrium absorbance at 310 nm in the reaction between **1** and iodide was measured at a constant chloride concentration of 1.29 mM and different temperatures and [I$^-$]. For the reaction between **1** and bromide, the equilibrium absorbance at 285 nm was derived from the amplitude of the kinetic traces at different [Cl$^-$] and [Br$^-$]. In this case the absorbances are given as an average of at least 5 runs. Complete data are given in Supporting Information tables.

Results

Equilibria. Reaction 1 was studied in MeCN with bromide and iodide as incoming ligands giving **3** (X = Br) and **4** (X = I) as products. The ^{31}P-NMR of **1** is a singlet with ^{195}Pt satellites (δ −0.48 ppm, $^{1}J_{Pt-P}$ = 2789 Hz), and its ^{1}H-NMR spectrum consists of a triplet with ^{195}Pt satellites in the methyl region (δ 1.40 ppm, $^{2}J_{P-H}$ = 7.2 Hz, $^{3}J_{Pt-H}$ = 30.3 Hz), all indicating that it has a *trans* geometry in solution. The virtual coupling that gives rise to the triplet instead of the expected doublet is typical of *trans*-bis(phosphine) complexes.[17] The addition of iodide gives a new peak in the ^{31}P-spectrum (δ −6.39 ppm, $^{1}J_{Pt-P}$ = 2787 Hz); it grows in as more iodide is added, and finally the peak from **1** disappears completely. The ^{1}H-NMR spectrum of **4** is similar to that of **1** with three triplets centered at 1.52 ppm ($^{2}J_{P-H}$ = 7.2 Hz, $^{3}J_{Pt-H}$ = 31.2 Hz). The ^{195}Pt-NMR spectrum of **1** is a triplet centered at −3400 ppm ($^{1}J_{Pt-P}$ = 2778 Hz), whereas **4** gives a triplet at −3477 ppm ($^{1}J_{Pt-P}$ = 2770 Hz). Similarly, addition of bromide to a solution of **1** gives a ^{31}P-NMR peak at −2.62 ppm ($^{1}J_{Pt-P}$ = 2791 Hz) that grows with growing bromide concentration. (Approximate values of the equilibrium constants K_{eq} for X = Br and I can be roughly estimated from these ^{31}P-NMR spectra: $K_{eq,I} \approx 0.6$, $K_{eq,Br} \approx 0.3$.)

$$\underset{\mathbf{1}}{trans\text{-PtCl(SiPh}_3\text{)(PMe}_2\text{Ph)}_2} + X^- \rightleftharpoons \underset{\mathbf{3},\,\mathbf{4}}{trans\text{-Pt(SiPh}_3\text{)X(PMe}_2\text{Ph)}_2} + Cl^- \qquad (1)$$

The equilibrium constants for reaction 1 were determined using spectrophotometry. Equation 2 was fitted to data of

$$A = \frac{A_0[Cl^-] + \epsilon_b K_{eq}[X^-]C_{Pt}}{[Cl^-] + K_{eq}[X^-]} \qquad (2)$$

equilibrium absorbances A at different concentrations of leaving and incoming ligands to give the equilibrium constants, K_{eq}. A_0 denotes the absorbance before reaction, C_{Pt} the total concentration of platinum, and ϵ_b the molar extinction coefficient for the product at the path length used. A plot of absorbance versus concentration for X = Br is given in Figure 1. For X = I, K_{eq} was determined at different temperatures and eq 3 was fitted to

$$\ln(K_{eq}) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R}\frac{1}{T} \qquad (3)$$

these data giving ΔS° and ΔH° for the overall process. The resulting equilibrium constants and thermodynamic parameters are reported in Tables 1 and 2. Equilibrium constants derived from the kinetics as the ratio between rate constants are in satisfactory agreement; they are also given in Table 1.

There is no solvolysis of **1** upon dissolution. Addition of an excess of chloride causes no effect in the ^{31}P-NMR spectrum. The precipitation of chloride with silver, however, gives a new ^{31}P-NMR shift of −2.99 ppm ($^{1}J_{Pt-P}$ = 2647 Hz), corresponding to the solvento complex, **2**. Addition of 1.5 equiv of iodide again gives the spectrum of complex **4**, without any sign of reversibility, reaction 4.

$$\underset{\mathbf{2}}{trans\text{-[Pt(SiPh}_3\text{)(MeCN)(PMe}_2\text{Ph)}_2]^+} + I^- \xrightarrow{k_3} \underset{\mathbf{4}}{trans\text{-[PtI(SiPh}_3\text{)(PMe}_2\text{Ph)}_2]} + \text{MeCN} \qquad (4)$$

Kinetics. Reaction 1 was studied at different concentrations of leaving and incoming ligands. Plots of k_{obsd} vs [X$^-$] for different concentrations of chloride are linear with intercepts

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(15) Applied Photophysics Bio Sequential SX-17MV Stopped Flow ASVD Spectrofluorimeter, software manual, Applied Photophysics Ltd. 203/205 Kingston Road, Leatherhead KT22 7PB, U.K.

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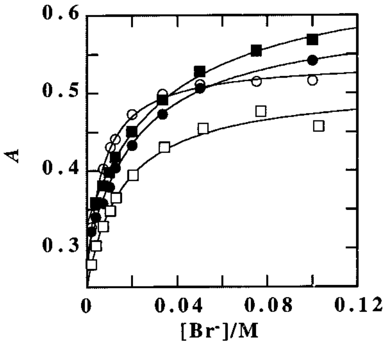


Figure 1. Equilibrium absorbance at 285 nm as a function of bromide concentration at different chloride and complex concentrations. (T = 298.2 K): (○) [Cl$^-$] = 2.00 mM, [Pt] = 0.26 mM; (□) [Cl$^-$] = 4.00 mM, [Pt] = 0.25 mM; (●) [Cl$^-$] = 5.60 mM, [Pt] = 0.29 mM; (■) [Cl$^-$] = 10.0 mM, [Pt] = 0.33 mM. The solid lines denote the best fit of eq 2.

Table 1. Rate and Equilibrium Constants for the Reaction of **1** (Reaction 1) with Various Nucleophiles at 25 °C in MeCN

	nucleophile	
	Br$^-$	I$^-$
a/s^{-1} [a]	36 ± 7	89 ± 15
$10^{-6}k_3$/M^{-1} s^{-1}		7 ± 1
$10^{-3}k_2$/M^{-1} s^{-1}	2.9 ± 0.1	7.5 ± 0.3
$10^{-3}k_{-2}$/M^{-1} s^{-1}	14.3 ± 1.1	81 ± 11
K_{eq}	0.27 ± 0.03[b]	0.082 ± 0.007[b]
K_{eq}	0.20 ± 0.02[c]	0.092 ± 0.014[c]

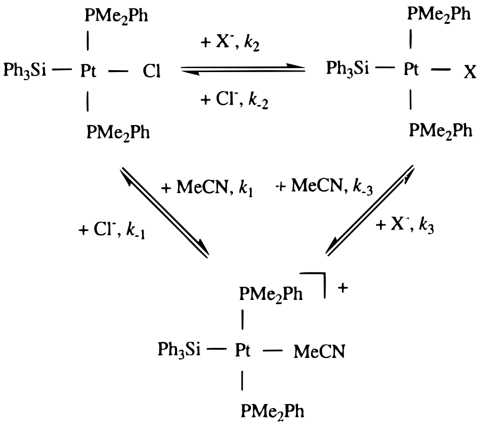
[a] As defined by eq 5. [b] Determined by spectrophotometry. [c] Calculated from the rate constants as the ratio k_2/k_{-2}.

Table 2. Activation and Thermodynamic Parameters for the Reaction of **1** (Reaction 1) with Iodide at 25 °C in MeCN.

	$\Delta H^{\neq}$/ kJ/mol	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\neq}$/ cm^3 mol^{-1}	$\Delta H°$/ kJ/mol[a]	$\Delta S°$/J K^{-1} mol^{-1} [a]
k_2 path	24.3 ± 1.2	−89 ± 4	−3.2 ± 1.2	−5.1 ± 0.4	−38.0 ± 1.2
k_{-2} path	28 ± 4	−57 ± 12			

[a] Determined from eq 3.

Scheme 1



depending on [Cl$^-$]; *cf.* Figure 2. The data can be fitted to a rate law of the form of eq 5, where k_2 and k_{-2} are rate constants

$$k_{obsd} = a + k_2[X^-] + k_{-2}[Cl^-] \tag{5}$$

defined in Scheme 1 and a is a constant. For iodide as an incoming ligand, enthalpies and entropies of activation were determined by fitting the Eyring equation to k_2 and k_{-2}. The volume of activation for the reaction path described by k_2 was determined by fitting eq 6, where k_0 denotes the rate constant

$$\ln k_2 = \ln k_0 - \frac{\Delta V^{\ddagger}}{RT}P \tag{6}$$

at zero pressure, to k_2 at different pressures. k_2 was obtained as slopes from plots of the observed rate constants vs concentration of iodide at different temperatures and pressures. Values of k_{-2} were calculated from k_2 by means of the thermodynamic parameters for reaction 1, except for T = 298.2 K, where it was determined directly from the fit of eq 5. Values of all rate constants and activation parameters are given in Tables 1 and 2.

The halide anation reaction of the solvento complex, eq 4, is too fast to be studied under pseudo-first-order conditions. For iodide as nucleophile the second-order kinetic traces recorded were fitted to eq 7,[18] giving an average value of the rate constant k_3 defined in Scheme 1 of (7 ± 1) × 10^6 M^{-1} s^{-1} at 298.2 K.

$$A_t = \frac{A_0 - A_\infty}{1 + k_3A_0t} + A_\infty \tag{7}$$

Discussion

Rate Laws. Reaction 1 is reversible, and the forward and reverse reactions contribute to the overall rate expression. The experimental rate law of eq 5 indicates that the stoichiometric mechanism involves an additional parallel path via a solvento complex according to Scheme 1. From the NMR spectra it is clear that a solution of **1** contains no detectable amounts of the solvento species **2**. This species has also been shown to have a very high reactivity. Since steady-state conditions for the solvento species **2** are fulfilled, the following rate law can be deduced:

$$k_{obsd} = k_2[X^-] + k_{-2}[Cl^-] + \frac{k_{-3}k_{-1}[Cl^-] + k_1k_3[X^-]}{k_{-1}[Cl^-] + k_3[X^-]} \tag{8}$$

This rate law is compatible with the experimental one in eq 5, if the third term is approximately constant for the experimental conditions used. In each series of experiments [Cl$^-$] was kept constant, whereas [X$^-$] varied; *cf.* Figure 2. This means that both numerator and denominator of the third term increase with increasing [X$^-$], resulting in an approximately constant value. Values of ($k_{obsd} - k_2$ [X$^-$] $- k_{-2}$ [Cl$^-$]) are randomly distributed around a mean value equal to a in eq 5. By use of different assumptions this constant can be identified as k_1, k_{-3}, or different expressions involving these constants, but none of these assumptions can be validated on the basis of the present experiments, and we can only state that a in eq 5 is a constant with unknown mechanistic significance.

The high rate of the halide anation reaction, eq 4, prohibits a detailed study of its mechanism. However, the experiments performed under second-order conditions indicate a rate law according to eq 9, consistent with a direct associative attack by

$$rate = k_3[Pt][I^-] \tag{9}$$

iodide at the solvento complex. The solvento complex reacts 10^3 times faster with iodide than does the parent chloride complex (*cf.* k_2 and k_3 in Table 1). The instability of the solvento complex in more concentrated solutions precludes a study of its solvent exchange.

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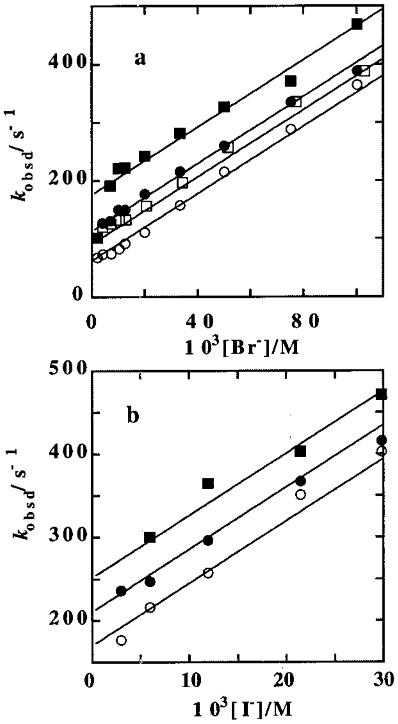

Figure 2. Observed pseudo-first-order rate constants for reaction 1 as a function of concentration of incoming ligand at different chloride concentrations ($T = 298.2$ K). (a) X = Br: (○) $[Cl^-] = 2.00$ mM, (□) $[Cl^-] = 4.00$ mM, (●) $[Cl^-] = 5.60$ mM, (■) $[Cl^-] = 10.0$ mM. (b) X = I: (○) $[Cl^-] = 1.00$ mM, (●) $[Cl^-] = 1.50$ mM, (■) $[Cl^-] = 2.00$ mM. The solid lines denote the best fit of eq 5.

Transition State. Silyl ligands have for a long time been known to have a very high ground state *trans* influence, as displayed by *e.g.* low Pt−Cl stretching frequencies and long Pt−Cl distances in the solid state.[9,14] The recent determination of the crystal structure of **1** in this laboratory revealed a Pt−Cl distance of 2.465 Å,[9] one of the longest such distances measured, indicating, as expected, that Ph_3Si^- has an even higher *trans* influence than carbon σ-donor ligands.[19] In spite of the very weak Pt−Cl bond there is no evidence for any 3-coordinate intermediate in reaction 1; the rate law and the entropy and volume of activation are consistent with a transition state of increased coordination number, *i.e.* an I_a process. However, it is obvious that the leaving ligand plays the most important role in the activation process: for the reactions of **4** and **3** with Cl^- (rate constants k_{-2} in Table 1) the reactivity ratio is 5.7, whereas the ratio between Br^- and I^- as nucleophiles toward **1** (rate constants k_2 in Table 1) is only 2.6. This higher sensitivity to the nature of the leaving ligand is usually taken as evidence for an I_d mechanism. It has earlier been found that two strong σ-donor ligands are needed to partially or totally block the associative attack at platinum(II),[20,21] and these dissociative systems often show a low reactivity.[22] The present complexes react several orders of magnitude faster than $Pt(SiMePh_2)_2(PMe_2Ph)_2$, which follows a clear-cut D mechanism.[23] In view of these observations it seems reasonable to conclude that reaction 1 proceeds *via* a 5-coordinate transition state in which bond-breaking is more important than bond-making, and thus that the reaction should be classified as an I_d process in spite of the negative entropies and volumes of activation. Noteworthy, however, 5-coordinate transition states are common to all I_d, I_a, and A mechanisms and the reactivity of the triphenylsilyl complexes is therefore probably best discussed within the framework of other such reactions.

***trans*-Effect of Triphenylsilyl.** Having established the nature of the transition state, one can determine the relative strength of the *trans* effect of the triphenylsilyl group. Complexes **1**−**4** have an equally high or higher reactivity than the most reactive Pt(II) complexes studied so far.[3,24,25] Analogous complexes with other strong σ-donor ligands such as Me^-, H^-, and Me_3P react orders of magnitude slower than **1**.[26,27] Only very strongly π-accepting ligands such as C_2H_4 and MeNC have *trans* effects comparable to silyl. An approximate series of decreasing *trans* effect including ligands high in the series would then be as follows:[3,19,24−28]

$$Ph_3Si^-, C_2H_4, MeNC \gg Ph_3P, CN^- > H^- > Me^- > Ph^- \tag{10}$$

In this context it can be noted that very high reactivities have been observed *trans* to carbon in solvento complexes, but still the reactivity of the solvento complex **2** is some 2 orders of magnitude higher than that of for instance a cyclometalated solvento species reported recently.[29] One obvious reason for the very high *trans* effect of silyl is the high ground-state *trans* influence resulting in a very weak bond to the leaving ligand, but it cannot be ruled out that the triphenylsilyl ligand also operates as a π-acceptor in the 5-coordinate transition state, thus further enhancing its over-all *trans* effect. The *trans* effect of phosphines relies on their σ-donor properties but to some extent also on their π-acceptor capability, and if the isoelectronic R_3Si^- and R_3P ligands are assumed to have π^*-orbitals of similar energy,[30] it is reasonable to expect that π-back-donation from platinum to silyl is also feasible.

Nucleophilic discrimination has been used as one criterion for discriminating σ-donor and π-acceptor properties, the argument being that strong σ-donors give rise to open transition states and a low nucleophilic discrimination, whereas the opposite should be true for strong π-acceptors.[31] Thus it has been observed that ligands which deduce their *trans* effect solely from σ-donation, *e.g.* phenyl or ethyl, lower the nucleophilic discrimination to the extent where the solvent path becomes totally dominant.[26,32] This is obviously not the case in the present system. However, iodide, in its reaction with **1**, is a better nucleophile as compared to bromide by a factor of 2.6 only, as compared to the factor of 30 derived from the n^0_{Pt} values.[33] The solvent is an inefficient nucleophile in the present system probably because the anionic nucleophiles are less solvated in acetonitrile than in *e.g.* methanol (in which solvent

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investigations of n^0_{Pt} values and the σ-carbon systems have been performed), and therefore comparatively better nucleophiles. In conclusion, the nucleophilic discrimination is low, compatible with a strong σ-*trans* effect of triphenylsilyl, and in accordance with what was concluded earlier about the intimate mechanism (being I_d). However, the question of the σ-donor/π-acceptor properties of the silyl ligand cannot be solved definitely upon the basis of the present experimental material.

Thermodynamic Stability. The single silyl ligand is not capable of inducing a turnover to a D mechanism, but it does increase the effect of the leaving ligand on the expense of the incoming one. As far as thermodynamics is concerned, this results in an unexpected conclusion. Normally platinum(II) acts as a typical soft metal center; *i.e.*, the stability of its complexes increases in the order Cl < Br < I.[34] For the present complexes the trend is the reverse; *i.e.*, the iodide complex **4** is less stable than the bromide complex **3** that is less stable than the chloride complex **1**, implying that the platinum center in these complexes is hard or borderline in character (equilibrium data in Table 1). As noted previously, iodide is a slightly better nucleophile than bromide, and the reason for the reverse stability sequence is the higher lability of the iodo and bromo complexes, which could be explained by a greater sensitivity of these ligands to the *trans* influence. The silyl ligand deprives the hybrid orbital of the platinum−halogen bond of some of its s-character, thus making the interaction more ionic, which disfavors iodide more than chloride.

An alternative explanation is possible. Changing the solvent from water to acetonitrile changes the stability sequence of copper(I) in the same manner as observed here for the silyl complexes.[35] This change can be rationalized using the same argument as in the discussion above on nucleophilic discrimination; chloride is much more strongly solvated than iodide in more protic media, whereas in acetonitrile the difference is smaller. It is thus reasonable to conclude that the solvent and the silyl ligand cooperate to render the platinum its hardness in the present complexes.

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Supporting Information Available: Observed pseudo-first-order rate constants for reaction 1 (X = Br) at 25 °C in acetonitrile at different concentrations of incoming and leaving ligands (Table S1), observed pseudo-first-order rate constants for reaction 1 (X = I) at 25 °C in acetonitrile at different concentrations of incoming and leaving ligands (Table S2), observed pseudo-first-order rate constants for reaction 1 (X = I) in acetonitrile at different temperatures and iodide concentrations (Table S3), observed pseudo-first-order rate constants for reaction 1 (X = I) in acetonitrile at different pressures and iodide concentrations (Table S4), second-order rate constants for reaction 4 (Table S5), equilibrium absorbances for reaction 1 (X = Br) at 25 °C in acetonitrile at different concentrations of bromide and chloride (Table S6), and equilibrium absorbances for reaction 1 (X = I) in acetonitrile at different temperatures and iodide concentrations (Table S7) (5 pages). Ordering information is given on any current masthead page.

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