Kinetic and Computational Study of Dissociative Substitution and Phosphine Exchange at Tetrahedrally Distorted *cis*-Pt$(SiMePh_2)_2(PMe_2Ph)_2$

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The substitution kinetics of Me_2PhP in *cis*-Pt$(SiMePh_2)_2(PMe_2Ph)_2$ (**1**) by the chelating ligand bis(diphenylphosphino)ethane has been followed at 25.0 °C in dichloromethane by stopped-flow spectrophotometry. Addition of the leaving ligand causes mass-law retardation compatible with a dissociative process via a three-coordinate transition state or intermediate. Exchange of Me_2PhP in **1** has been studied by variable-temperature magnetization transfer ^{1}H NMR in toluene-d_8, giving $k_{ex}^{326} = 1.76 \pm 0.12$ s^{-1}, $\Delta H^‡ = 117.8 \pm 2.1$ kJ mol^{-1}, and $\Delta S^‡ = 120 \pm 7$ J K^{-1} mol^{-1}. An exchange rate constant independent of the concentrations of free phosphine, a strongly positive $\Delta S^‡$, and nearly equal exchange and ligand dissociation rate constants also support a dissociative process. Density functional theory (DFT) calculations for a dissociative process give an estimate for the Pt−P bond energy of 98 kJ mol^{-1} for $R = R' = Me$, which is in reasonable agreement with the experimental activation energy given the differences between the substituents used in the calculation and those employed experimentally. DFT calculations on *cis*-Pt$(PR_3)_2(SiR'_3)_2$ (R = H, CH_3; R′ = H, CH_3) are consistent with the experimental molecular structure and show that methyl substituents on the Si donors are sufficient to induce the observed tetrahedral twist. The optimized Si−Pt−Si angle in *cis*-Pt$(SiH_3)_2(PH_3)_2$ is not significantly altered by changing the P−Pt−P angle from its equilibrium value of 104° to 80° or 120°. The origin of the tetrahedral twist is therefore not steric but electronic. The Si−Pt−Si angle is consistently less than 90°, but the Si−Si distance is still too long to support an incipient reductive elimination reaction with its attendant Si−Si bonding interaction. Instead, it appears that four tertiary ligands introduce a steric strain which can be decreased by a twist of two of the ligands out of the plane; this twist is only possible when two strong σ donors are cis to each other, causing a change in the metal's hybridization.

Introduction

Substitution reactions in square-planar d^8 complexes usually involve associative activation through five-coordinate transition states.[1−3] The search for factors promoting dissociative behavior has focused on steric blocking of the pseudooctahedral positions and/or ground-state destabilization by use of ligands with a high trans influence.[4,5] The first convincing evidence of a dissociative mode of activation was given by the substitution of sulfoxides or thioethers in some platinum(II) complexes of the type *cis*-PtR_2L_2, where R is a carbon σ-donor ligand.[6] Dissociative behavior was first attributed to the ground-state destabilization by the trans ligand, but it was later shown that the cis ligands also play a crucial role for the electronic properties of the metal center and the blocking of the associative attack that are necessary to promote ligand dissociation.[7]

Silyl complexes of d^8 metal ions have received attention because of their role in catalytic hydrosilylation, and reductive elimination and insertion reactions have been studied in platinum(II) silyl complexes.[8−10] Silyl ligands are known to have a higher ground-state trans influence than σ-bonded carbon donor ligands.[11−14] We recently reported the first kinetic study of substitution reactions trans to triphenylsilyl in a platinum(II) complex, indicating that silyl ligands also have a very large trans effect, comparable to ethene and methyl isocyanide and, as expected, larger than that of σ-bonded carbon donor ligands.[15] Although the substitution mechanism trans to silyl could be characterized as an interchange with negative volumes and entropies of activation, it was obvious that the nature of the

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leaving ligand had an unusually large influence on the rate of reaction.[15] On the basis of these results, a study of substitution reactions in bis(silyl) complexes seemed worthwhile in order to gain further insight into the factors promoting dissociative activation.

We report kinetics and a mechanism for the reaction of *cis*-$Pt(SiMePh_2)_2(PMe_2Ph)_2$ (**1**) with the chelating bis(diphenylphosphino)ethane (dppe) in dichloromethane and for the phosphine exchange in toluene, together with a series of quantum chemical density functional theory (DFT) calculations. DFT has been shown to give a good description of associatively activated exchange at Pd(II) and Pt(II) centers.[16,17] Here, it is used to investigate both the structure of **1** and the dissociative mechanism of phosphine exchange. The crystal and molecular structures of the compound have been reported earlier first by us[18,19] and later by Tsuji et al.[20] The two structure determinations are virtually identical.

Experimental Section

General Procedures and Materials. The complex *cis*-$Pt(SiMePh_2)_2(PMe_2Ph)_2$ (**1**) was prepared according to the literature.[21] Its ^1H and ^{31}P NMR spectra were satisfactory. Dichloromethane was flushed with argon for at least 30 min prior to use in the stopped-flow experiments. Toluene-d_8 (Acros) was freeze−pump−thaw degassed, dried, and stored over 4 Å activated molecular sieves. All other solvents and chemicals were used as received. Magnetic susceptibility measurements were performed at room temperature on a Sherwood Scientific magnetic susceptibility balance. UV/vis spectra were recorded on a Milton Roy 3000 diode array spectrophotometer.

NMR Measurements. NMR spectra were recorded on a Varian UNITY 300 spectrometer, working at 299.79 (^1H) or 121.36 (^{31}P) MHz. The temperature was measured using the temperature-dependent shifts of the CH_2 and OH protons of ethylene glycol. T_1 for the Me protons was determined in free Me_2PhP using the inversion−recovery technique. T_2* was determined from the line widths at room temperature. Chemical shifts are given in ppm downfield from TMS using $CD_2HC_6D_5$ (^1H NMR δ 2.08) or H_3PO_4 (^{31}P NMR δ 0) as internal and external references, respectively. Samples were prepared in a glovebox by weighing the platinum complex in an NMR tube (2−3 mg), adding toluene-d_8 and free Me_2PhP (Strem), and sealing the tube. In the magnetization transfer experiments performed between 38.6 and 73.8 °C, the peak from the methyl protons of the free phosphine was selectively inverted using the DANTE pulse sequence[22] and, after a variable pulse-mixing time, *t*, an FID was recorded with a nonselective $\pi/2$ pulse. For the duration of the FID, ^{31}P decoupling was applied.

Peak heights were used in the kinetic evaluation because the peak widths showed no systematic change during an experiment. Spectra were collected as 4 repetitions with a 40 s (4−5 × T_1) relaxation delay. In the line-broadening experiments at 73.8 °C, spectra were collected as 16 repetitions with a 20 s relaxation delay. The temperature dependencies of the chemical shifts were determined in the slow-exchanging region.

Stopped-Flow Measurements. The stopped-flow experiments were performed at 25.0 °C under anaerobic conditions on an Applied Photophysics Bio Sequential SX-17 MX stopped-flow spectrofluorimeter.[23] The substitution of Me_2PhP in **1** with dppe was studied in dichloromethane under pseudo-first-order conditions by observing the decrease in absorbance at 380 nm. The metal solution (approximately 0.15 mM), containing at least a 20-fold excess of free Me_2PhP, was prepared using standard Schlenk techniques. The ligand solution was prepared using deoxygenated dichloromethane but without taking any further precautions to exclude air. It was shown with ^{31}P NMR spectroscopy that such a solution contained less than 2% phosphine oxide after 24 h of storage. Rate constants are given as an average of at least three runs.

Computational Details. The DFT calculations employed the Amsterdam Density Functional (ADF) program suite version 2.3.0.[24] Geometries were optimized at the local density approximation (LDA) level[25] and included scalar relativistic corrections.[26,27] The basis sets were uncontracted triple-ζ Slater-type orbital expansions with additional polarization functions on all atoms (ADF basis sets IV). The frozen core approximation[28] (up to 5p on Pt, up to 2p on Si and P, and 1s on C) was used throughout. The correlation part of the LDA used the formulation of Vosko et al.[29] All energies were computed at the LDA-optimized geometries, using the gradient-corrected functionals of Becke[30] and Perdew[31] for exchange and correlation, respectively.

Geometries were computed for the complexes *cis*-$Pt(SiR'_3)_2(PR_3)_2$ (R = H, Me; R′ = H, Me) under C_2 symmetry, where the axis bisects the P−Pt−P angle. The structures of *cis*-$Pt(SiMe_3)_2(PR_3)$ (R = H, Me) were constrained to C_s symmetry, where the plane contains the Pt, P, and both of the Si atoms. Default self-consistent field and geometry optimization convergence criteria were used.

Results

Synthesis. For the synthesis of **1**, we employed the method of Eaborn et al.,[21] starting from the carbonato complex of Pt(II) and the silyl hydride. Bis(silyl) compounds are known to undergo reductive elimination of disilanes,[8] but no such reactions could be detected in the present system. The complex is diamagnetic with a molar magnetic susceptibility of -2.4×10^{-4} cgsu.

Substitution of Me_2PhP in 1 with dppe. Reaction 1 was

$$cis\text{-}Pt(SiMePh_2)_2(PMe_2Ph)_2\ (\mathbf{1}) + dppe \rightarrow cis\text{-}Pt(SiMePh_2)_2(dppe)\ (\mathbf{2}) + 2PMe_2Ph \quad (1)$$

studied in dichloromethane at 25.0 °C. The ^{31}P NMR spectrum of **1** is a singlet with platinum satellites (δ −6.5 ppm, $^1J_{Pt-P}$ = 1563 Hz). The low value of the coupling constant is due to the large trans influence of the silyl ligand and confirms that the cis geometry is maintained in solution. On addition of 1.1 equiv of dppe, the peak at −6.5 ppm starts to disappear, whereas two new peaks (apart from the dppe peak) grow in: one from **2** (δ 56.0 ppm, $^1J_{Pt-P}$ = 1389 Hz) and one from free dimethylphenylphosphine (δ −43.8 ppm). After 0.5 h, the reaction is complete, and all of **1** has been converted to **2**. The reaction is thus irreversible. During the reaction, no other P-containing species could be detected. Other chelating incoming ligands with

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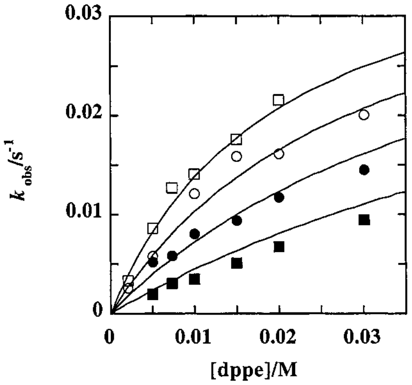

Figure 1. Observed pseudo-first-order rate constants of reaction 1 at 25 °C as a function of dppe concentration at different concentrations of methyldiphenylphosphine [(□) 2.99 mM, (○) 4.50 mM, (●) 7.03 mM, (■) 12.3 mM]. Equation 2 was fitted simultaneously to all of the data using a single set of parameters and the computer program MATLAB. The solid lines denote the best fit.

S and N donors were also tried, but no reaction was observed. Tsuji et al. report **1** to be fluxional in solution.[20] This process, however, is fast at room temperature and does not influence the NMR spectra at this temperature. Furthermore, it does not involve any breaking of the Pt−P bond.

Reaction 1 was followed by the use of stopped-flow spectrophotometry as a function of both leaving and incoming ligand concentration. The kinetic traces fitted well to a single exponential. Figure 1 is a plot of k_{obsd} versus [dppe] at different [Me_2PhP], showing that the addition of a free leaving ligand causes mass-law retardation. A global nonlinear least-squares fit of the rate law of eq 2 to all of the data simultaneously using the

$$k_{obsd} = \frac{a[\mathrm{dppe}]}{b[\mathrm{Me_2PhP}] + [\mathrm{dppe}]} \qquad (2)$$

computer program MATLAB[32] gives the best values of $a = 0.042 \pm 0.004\ s^{-1}$ and $b = 6.8 \pm 0.8$. Values of k_{obsd} as a function of [dppe] and [Me_2PhP] are given in the Supporting Information (Table S1).

Exchange of Me_2PhP in 1. Phosphine exchange of the type shown in eq 3 (n = 1, 2) can easily be studied by means of

$$\begin{aligned} &cis\text{-Pt(SiMePh}_2)_2(\mathrm{PMe_2Ph})_2 + n{*}\mathrm{PMe_2Ph} \rightleftharpoons \\ &\quad cis\text{-Pt(SiMePh}_2)_2(\mathrm{PMe_2Ph})_{2-n}({*}\mathrm{PMe_2Ph})_n + n\mathrm{PMe_2Ph} \quad (3) \end{aligned}$$

NMR. The stopped-flow experiments indicate that the rate would be too low for line-broadening experiments and for magnetization transfer at room temperature. Reaction 3 was therefore studied by use of magnetization transfer as a function of temperature and free phosphine concentration in toluene-d_8, a solvent that allows variation of the temperature in combination with inertness and reasonable solubility properties. A ^{31}P-decoupled ^{1}H NMR spectrum of a mixture of **1** and Me_2PhP in toluene consists of a singlet with Pt satellites (δ 0.60 ppm, $^3J_{Pt-H}$ = 16.5 Hz) from the coordinated phosphine and a singlet (δ 1.06 ppm) from free phosphine. In this region of the spectrum, there is also a peak from the protons in the *Me*Ph_2Si ligand (δ 0.85 ppm, $^3J_{Pt-H}$ = 30.9 Hz), but it is unaffected during the experiments.

In an experiment, the peak from the free phosphine was selectively inverted, and the peak heights of the two types of phosphines were recorded as a function of pulse-mixing time.

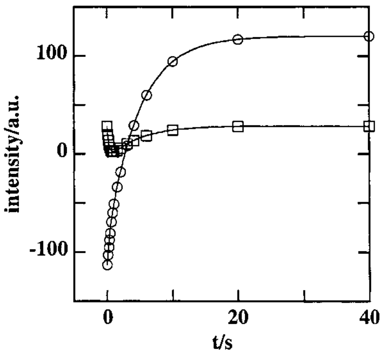

Figure 2. Magnetization of free (○) and coordinated (□) phosphine in reaction 4 as a function of pulse-mixing time. The solid lines denote the best fit using the computer program CIFIT. [Pt] = 5.0 m*m*, [Me_2PhP] = 41.8 m*m*, T = 316.7 K, $k_{ex} = 3.46\ s^{-1}$, T_{1F} = 12.5 s, and T_{1C} = 1.0 s (cf. Table S3).

Table 1. Total Exchange Rate Constants at 326.3 K, k_{ex}, for Phosphine Exchange at **1** in Toluene-d_8 at Different [Me_2PhP]

[Me_2PhP]/ m*m*	k_{ex}/ s^{-1}
20.8	1.67 ± 0.05
41.8	1.74 ± 0.11
63.7	1.79 ± 0.08
81.7	1.94 ± 0.17
107	1.65 ± 0.14

The reaction was then treated as a two-site exchange according to eq 4. The return of magnetization to equilibrium is governed

$$\mathrm{P_{free}} \underset{k_C}{\overset{k_F}{\rightleftharpoons}} \mathrm{P_{coord}} \qquad (4)$$

by the exchange rate constants, k_F and k_C, and the relaxation rate constants, $1/T_{1F}$ and $1/T_{1C}$.[33] Taking into account the fact that $k_F = k_C([\mathrm{P_{coord}}]/[\mathrm{P_{free}}])$ (because the system is at equilibrium), we fitted this model iteratively to the time-dependent magnetization data using the computer program CIFIT.[34] The value of k_C thus obtained will be the rate constant for exchange of a specific phosphine. Figure 2 shows an example of such a fit. Assuming a mechanism in which ligand dissociation is rate determining gives the expression of eq 5 for the total rate of exchange, R_{ex}, where k_{ex} denotes the overall exchange rate constant.

$$R_{ex} = k_{ex}[\mathrm{Pt}] \qquad (5)$$

Because, according to eq 6,

$$R_{ex} = k_C[\mathrm{P_{coord}}] = 2k_C[\mathrm{Pt}] \qquad (6)$$

this means that $2k_C = k_{ex}$. The exchange rate constants, k_{ex}, at different [Me_2PhP] are given in Table 1. The relaxation times were typically 0.9−1.4 s for coordinated phosphine and 9−13 s for free phosphine. The temperature dependence of k_{ex} was determined at a single [Me_2PhP] and gave a perfectly linear Eyring plot between 311 and 347 K. Values of k_{ex} at different temperatures are given in the Supporting Information (Table S2). Activation parameters are $\Delta H^\ddagger = 117.8 \pm 2.1$ kJ mol^{-1} and $\Delta S^\ddagger = 120 \pm 7$ J K^{-1} mol^{-1}. At the highest temperature (347 K), there is a broadening of the lines, because of exchange. This line-broadened spectrum was compared with spectra simulated by the computer program DNMR5,[35] giving an

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Table 2. Calculated Structural Parameters, Dihedral Angles τ, and Total Binding Energies of Four-Coordinate Complexes *cis*-$Pt(SiR'_3)_2(PR_3)_2$ (R = H, Me; R′ = H, Me)

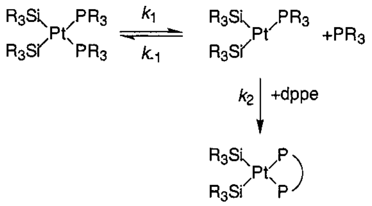
complex	Pt−P/Å	Pt−Si/Å	P−Pt−P/deg	Si−Pt−Si/deg	τ/deg	E_b/(kJ mol^{-1})
$Pt(SiH_3)_2(PH_3)_2$	2.37	2.35	103	80	12	−6 409
$Pt(SiH_3)_2(PH_3)_2$	2.40	2.34	106	77	45[a]	−6 394
$Pt(SiMe_3)_2(PH_3)_2$	2.43	2.35	103	87	36	−15 983
$Pt(SiH_3)_2(PMe_3)_2$	2.36	2.36	95	80	16	−15 947
$Pt(SiMe_3)_2(PMe_3)_2$	2.41	2.36	95	87	38	−25 508

[a] τ fixed at 45°.

Table 3. Calculated Structural Parameters and Total Binding Energies of Three-Coordinate Complexes $Pt(PR_3)(SiMe_3)_2$

complex	Pt−P/Å	Pt−Si_{cis}/Å	Pt−Si_{trans}/Å	P−Pt−Si_{cis}/deg	P−Pt−Si_{trans}/deg	Si−Pt−Si/deg	E_b/(kJ mol^{-1})
$Pt(SiMe_3)_2(PH_3)$	2.41	2.29	2.33	102	170	88	−14 489
$Pt(SiMe_3)_2(PMe_3)$	2.42	2.29	2.34	101	171	87	−19 226

Scheme 1



exchange rate constant of 29 s^{-1}, in fairly good agreement with the value of 22.8 s^{-1} from the magnetization transfer experiments. The latter value was used in the Eyring plot.

DFT Calculations. Selected calculated structural parameters and total binding energies for the four-coordinate complexes are collected in Table 2. For *cis*-$Pt(SiH_3)_2(PH_3)_2$, fixing the dihedral angle, τ, between the PtP_2 and $PtSi_2$ planes at 45° generated a structure only 15 kJ mol^{-1} higher than that of the ground state ($\tau = 12°$), showing that the tetrahedral twist is a low-energy process. Further calculations with fixed P−Pt−P angles are described below. Structural parameters and binding energies for the three-coordinate *cis*-$Pt(SiMe_3)_2(PR_3)$ complexes are given in Table 3. The structures of isolated PH_3 and PMe_3 are as reported elsewhere with binding energies of −1464 and −6184 kJ mol^{-1}, respectively.[36] Complete sets of Cartesian coordinates for all of the Pt complexes described here are given as Supporting Information (Table S4).

Discussion

Reaction 1 is proposed to take place according to Scheme 1 involving a 14-electron three-coordinate intermediate, which is too reactive to be detected by NMR. Using the steady-state approximation for this intermediate gives the rate expression of eq 7, which is consistent with the experimental rate law of

$$k_{obsd} = \frac{k_1[\text{dppe}]}{\dfrac{k_{-1}}{k_2}[\text{Me}_2\text{PhP}] + [\text{dppe}]} \qquad (7)$$

eq 2, if $a = k_1$ and $b = k_{-1}/k_2$. The mechanism in Scheme 1 is further supported by the phosphine exchange experiments. In reaction 3, there is no contribution from a [Me_2PhP]-dependent path (cf. Table 1), and the activation entropy is highly positive. These facts together support a mechanism in which the rate-determining step is the breaking of a Pt−P bond.

Another characteristic of dissociative reactions is that the rate is independent of the nature of the incoming ligand; that is, k_1 in reaction 1 should be the same as k_{ex} in reaction 3. Recalculating k_{ex} to 298 K gives a value of 0.025 s^{-1} as compared to that of k_1^{298} (0.042 s^{-1}). This difference is well within what one would expect on going from toluene to dichloromethane, with its superior solvational properties.[6a]

Although substitution reactions in d^8 square-planar systems are known normally to be associative, it is not surprising that **1**, with two ligands of high trans influence, undergoes dissociative substitution; complexes with carbon σ-donor ligands of the type *cis*-PtR_2L_2 (R = Ph, Me; L = R_2S, R_2SO) react dissociatively as well.[37] There are examples of phosphine dissociation at platinum being the rate-determining step in, for example, β-hydride elimination and isomerization,[38,39] but none have been reported for pure substitution reactions.

Ozawa and Kamite recently reported that **1** undergoes insertion of phenylacetylene into the Pt−Si bond.[40] On the basis of the rate law, they proposed a mechanism involving initial phosphine dissociation, but no activation parameters were given for the individual steps. A recalculation of our phosphine exchange rate constant to the temperature at which the acetylene insertion was studied gives a good agreement between the two dissociation rate constants, thus corroborating the proposed mechanism for insertion.[40]

Using phosphines as incoming nucleophiles toward the above-mentioned aryl and alkyl complexes with sulfur donors results in parallel associative and dissociative pathways.[41] For complex **1**, on the other hand, only the dissociative pathway is observed. This means that silyl ligands are even more effective in blocking associative attack, in keeping with their better σ-donor properties and higher trans influence (vide supra). The three-coordinate intermediate has a substantial lifetime as seen from its discriminative ability; the reactivity ratio between Me_2PhP and dppe is 6.8, although the nucleophilicity difference between these two phosphines is small. In fact, the discriminating ability of the intermediate is approximately equal to that of a four-coordinate complex, assuming equal properties of dppe and $MePh_2P$.[42]

The trans effect in square-planar associative reactions depends on both the σ-base and π-acid properties of the trans ligand,[2] whereas the trans effect of a ligand in a dissociative reaction is expected to depend only on the σ-donor properties and thus should parallel the ground-state trans influence. Comparing the present data with rate constants for ligand dissociation from

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Table 4. Rate Constants for Dissociation of Me_2SO or Me_2PhP at 303.2 K

substrate complex	10^3k_1 /s^{-1}	solvent	ref
cis-Pt$(C_6F_5)_2(Me_2SO)_2$	0.89^a	toluene	43
cis-Pt$(C_6H_5)_2(Me_2SO)_2$	14^a	benzene	6a
cis-Pt(*p*-tolyl)$_2(Me_2SO)_2$	16^a	benzene	6a
cis-Pt$(CH_3)_2(Me_2SO)_2$	11^a	benzene	44
cis-Pt$(CH_3)_2(Me_2SO)_2$	40^b	benzene	6b
cis-Pt$(MePh_2Si)_2(Me_2PhP)_2$	56^b	toluene	this work

[a] From ligand substitution experiments. [b] Calculated from the temperature dependence. k_1 derived from k_{ex}, the total rate of exchange, in the NMR magnetization transfer experiments.

the literature (cf. Table 4), we can deduce the following trans effect series for dissociative processes at platinum(II):[6a,43,44]

$$Ph_2MeSi > p\text{-tolyl} \approx Ph \approx Me > C_6F_5 \qquad (8)$$

Taking into account that the leaving group is Me_2SO in all cases but **1**, where it is Me_2PhP, the difference between the silyl and the carbon-bonding ligands is probably even larger than it appears from the data in Table 4.

The Ph_2MeSi ligand introduces a substantial ground-state destabilization of its trans ligands. The observed Pt−P distances in **1** are very long (2.359 Å)[19,20] compared to Pt−P distances trans to chloride (2.258 Å)[45] or methyl (2.284 Å),[46] and the only longer Pt−P distances found in the literature are also trans to silicon, e.g., in a bis(phosphinoethylsilyl) complex (2.374 Å).[47] Similarly, the calculated Pt−P distance of 2.41 Å in the all-methyl complex is consistent with the large trans influence of the silyl ligands, while the $^1J_{Pt-P}$ coupling constant is also on the extreme: 1563 Hz in **1** compared to 1736 Hz in *cis*-$PtPh_2(PMe_2Ph)_2$ and 3547 Hz in *cis*-$PtCl_2(PMe_2Ph)_2$.[19] As has been pointed out earlier, such a ground-state destabilization does not seem to be sufficient to accomplish dissociative activation. It is also necessary to block associative attack with excess electron density on the metal.[7]

The DFT dissociation energy of 98 kJ mol^{-1} for breaking a Pt−PMe_3 bond in *cis*-Pt$(SiMe_3)_2(PMe_3)_2$ is in reasonable agreement with the experimental value of 117.8 kJ mol^{-1} given the difference between the substituents. The calculations have not been corrected for zero-point energies or the effect of temperature, but substantial cancellation of errors is expected.[17] However, the DFT estimate is sensitive to the nature of the ligand substituents and changes from 30 kJ mol^{-1} for the Pt−PH_3 bond energy in *cis*-Pt$(SiMe_3)_2(PH_3)_2$ to 98 kJ mol^{-1} for PMe_3 exchange at *cis*-Pt$(SiMe_3)_2(PMe_3)_2$. Even closer agreement might be obtained if the actual phenyl-substituted ligands were also employed in the calculations, but this is computationally prohibitive. Nevertheless, we conclude that DFT gives a consistently semiquantitative description for the energetics of these reactions.

The most obvious explanation for the tetrahedral twist in the ground-state structure[19,20] is that the steric congestion arising from putting four tertiary ligands on platinum forces two of the coordinated atoms out of the plane. This is the explanation offered by Tsuji and co-workers for the twist in **1** and an analogous tin complex;[20,48] a similar explanation has been provided for *cis*-Pt$(GeMe_2Cl)_2(PMe_2Ph)_2$.[49] However, on the basis of our calculations and the findings of Ozawa and Kamite,[40] this appears to be only part of the story.

Table 5. Calculated Bond Angles for *cis*-Pt$(SiH_3)_2(PH_3)_2$

P−Pt−P	Si−Pt−Si	P−Pt−P	Si−Pt−Si
80^a	80	120^a	76
103	80		

[a] Indicates constrained angle.

Ozawa and Kamite note that the most sterically demanding ligands (the Ph_3Si ligands) do not give rise to the largest twist; instead, this is found in complex **1**.[40] The calculations for the present silyl species show that there is a small twist of about 12° when all of the substituents are hydrogens (Table 2) compared to a zero twist reported by Sakaki et al. on the basis of Hartree−Fock calculations.[50] With methyl groups only on the P donors, *cis*-Pt$(SiH_3)_2(PMe_3)_2$, the twist increases a little to 16°, but with methyls only on the Si donors, *cis*-Pt$(PH_3)_2(SiMe_3)_2$, it jumps to 36°. Assuming a similar bulk for PMe_3 and $SiMe_3$, the change in dihedral angles is clearly not purely steric in origin but is related to the greater electron donation and stronger binding of the $SiMe_3$ ligand compared to those of SiH_3, which is consistent with the Pt−P distances being some 0.05 Å longer trans to $SiMe_3$. Thus, it seems that the silyl ligands dominate the twist distortion, which clearly is not purely steric in origin.

The twist can be understood in terms of a simple MO picture, similar to the one offered by Ozawa and Kamite.[40] The four orbitals normally available for bonding at the platinum are the s, p_x, p_y, and $d_{x^2-y^2}$ orbitals. In an idealized square-planar geometry, **1** is of C_{2v} symmetry in which the s and $d_{x^2-y^2}$ orbitals have a_1 symmetry, whereas the p_x and p_y orbitals have b_1 and b_2 symmetries, respectively. In a normal hybridization scheme, all ligands will interact equally with the orbitals on the metal, but for the case where two of the ligands are much better σ donors, these will have a higher demand on the low energy a_1 orbitals. This will result in a corresponding decrease of the a_1 contribution to the bonding of their trans ligands. Thus, in the case of four ligands with equal or similar donor abilities, a twist out of the plane will result in a considerable decrease in orbital overlap. On the other hand, in the case where the two Pt−Si bonds have a very high s character, a tetrahedral twist of the two silyl ligands will not reduce the overlap to any large extent.

The other possibility is that the complex is partway toward a reductive elimination, which would certainly generate a formally d^{10} metal center. In fact, the Si−Pt−Si bond angle is consistently less than 90°, suggesting a degree of Si−Si attraction, but the distance in **1** is still very long (3.40 Å compared to the optimized distance of 2.34 Å in Si_2H_6), and any Si−Si bonding interaction must, at best, be quite weak. Nevertheless, we explored the origin of the Si−Pt−Si angle being less than 90° via a series of calculations where the P−Pt−P angle was fixed at 80° and 120°, i.e., at about 20° on either side of the equilibrium value of 103° (Table 5). Decreasing the P−Pt−P angle to 80°, thereby reducing the steric interactions between the PH_3 and SiH_3 groups, does not affect

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the Si−Pt−Si angle, whereas the P−Pt−P angle has to be increased to 120° before any appreciable compression of the Si−Pt−Si angle occurs. Apparently, the Si−Pt−Si angle has an inherent value determined by electronic effects connected with the Pt−Si bond. The angle is not determined by "passive" interactions such as VSEPR bond pair−bond pair repulsions because reducing the steric repulsions from the PH_3 groups did not allow the Si−Pt−Si angle to increase. Rather, it appears to involve an active interaction on the part of the Pt−Si bonds, which evidently imposes a bonding scheme on the metal center which results in an angle less than 90°.

To conclude, it seems that the four tertiary ligands in **1** introduce a steric strain which can be decreased by a twist of two of the ligands out of the plane; the twist is electronically possible because of the hybridization that occurs when two strong σ donors are cis to each other.

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Supporting Information Available: Observed pseudo-first-order rate constants for reaction 1 at 25.0 °C in dichloromethane at different incoming and leaving ligand concentrations (Table S1), exchange rate constants for reaction 4 in toluene-d_8 at different temperatures (Table S2), magnetization as a function of pulse-mixing time as given in Figure 2 (Table S3), and Cartesian coordinate files calculated for *cis*-$Pt(PR_3)_2(SiR'_3)_2$ (R = H, Me; R′ = H, Me), $Pt(PR_3)(SiMe_3)_2$ (R = H, Me), and *cis*-$Pt(PH_3)_2(CH_3)_2$ (Table S4). This material is available from the Internet at http://pubs.acs.org.

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