Platinum Bis(tricyclohexylphosphine) Silyl Hydride Complexes

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A series of platinum metal silyl hydride complexes, *cis*-$Pt(PCy_3)_2(H)(SiR_2R')$ (SiR_2R' = $SiPh_2H$, $SiEt_2H$, $SiPh_3$, $SiEt_3$, $SiMe_2(OSiHMe_2)$, $Si(OSiMe_3)_2Me$, $SiMe_2(CH_2CH{=}CH_2)$, $SiMe_2Et$, $SiMe_2[OCH_2C(Me){=}CH_2]$, $Si(OMe)_2(CH_2CH{=}CH_2)$, $SiPh_2(OSiPh_2H)$), have been prepared in solution by reaction of $Pt(PCy_3)_2$ with the appropriate silane, $HSiR_2R'$. The complex *cis*-$Pt(PCy_3)_2(H)(HSiPh_2)$ (**1-cis**) has been characterized by X-ray crystallography at −100 °C. The platinum center exhibits a distorted-square-planar geometry with angles P(1)−Pt−P(2) = 113.55(3)°, P(1)−Pt−Si = 146.83(3)°, and P(2)−Pt−Si = 99.37(3)°. The reaction of $Pt(PCy_3)_2$ with chlorinated hydrosilanes at −78 °C yields the analogous complexes *cis*-$Pt(PCy_3)_2(H)(SiR_2R')$ (SiR_2R' = $SiMe_2Cl$, $SiMeCl_2$, $SiCl_3$), which isomerize to their trans isomers on warming to room temperature. The complex **1-cis** and several analogues convert to the trans isomers photochemically at room temperature. Ready silane exchange is demonstrated by the reaction of $HSiPh_3$ with *cis*-$Pt(PCy_3)_2(D)(SiPh_3)$ and by the reaction of H_2SiPh_2 with *cis*-$Pt(PCy_3)_2(H)(SiPh_3)$. These experiments also revealed the relative thermodynamic stability of some of the platinum silyl complexes, of which the most stable was *cis*-$Pt(PCy_3)_2(H)(SiPh_2H)$. NMR spectroscopy demonstrates that the inequivalent phosphine ligands of the cis isomers undergo *intramolecular mutual* exchange on the NMR time scale. In competition with this process, the complexes undergo reversible reductive elimination of silane. Analysis of the NMR spectra yields the thermodynamic data for dissociation of silanes for SiR_2R' = $SiPh_3$, $SiMe_2Et$. Rate constants for phosphine exchange were calculated via line-shape analysis of ^1H NMR spectra. Rate constants for reductive elimination of silane in *cis*-$Pt(PCy_3)_2(H)(SiR_2R')$ (SiR_2R' = $SiPh_2H$, $SiMe_2Et$, $SiPh_3$) were calculated via ^1H EXSY measurements. The three distinct reaction pathways, photochemical cis−trans isomerization, intramolecular thermal phosphine site exchange, and reductive elimination, are shown to involve three distinct transition states. The transition states for the independent processes of phosphine site exchange and for reductive elimination must retain substantial Pt−H and Pt−Si interactions, while there is also significant Si−H bond formation. This situation can therefore be described as involving $Pt(\eta^2\text{-}H{-}SiR_3)$ interactions.

Introduction

Silylmetal complexes are known for nearly all of the transition metals[1,2] and have been shown to play a key role in many metal-catalyzed silylation reactions.[3] The oxidative addition of a Si−H bond to a coordinatively unsaturated metal complex has proved to be a very versatile method for their synthesis. Indeed, the activation of Si−H bonds is featured in the industrial processes hydrosilylation, dehydrogenative silylation, and polysilane production.[4] The silyl ligand exerts a high trans influence, which is manifested in NMR spectra as well as in metal−ligand bond lengths. Silyl hydrides may also bind in the η^2-Si−H mode, and complexes containing this grouping are becoming increasingly important. Metal η^2-Si−H complexes are also thought to be involved in the oxidative addition and reductive elimination of Si−H bonds.[2,5] Recent investigations of the dynamics of metal η^2-silane hydride complexes have shown the importance of metal silyl dihydrogen isomers in fluxional behavior.[6] In this paper, we are concerned with the oxidative addition of Si−H bonds at platinum and the dynamics of the resulting complexes.

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In the late 70s Ebsworth et al. reacted *trans*-Pt(PCy_3)$_2$(H)$_2$ with the series of silanes SiH_4, SiH_3Cl, and Si_2H_6 to form the corresponding complexes *trans*-Pt(PCy_3)$_2$(H)(SiH_2R) (R = H, Cl, SiH_3).[7] Their studies revealed a six-coordinate trihydride platinum(IV) species of the type *trans*-Pt(PCy_3)$_2$(H)$_3$(SiH_2R) formed by the oxidative addition of the silane to the *trans*-dihydride platinum complex at −80 °C. When it was warmed to room temperature, the trihydride platinum species lost H_2 to form *trans*-Pt(PCy_3)$_2$(H)(SiH_2R).

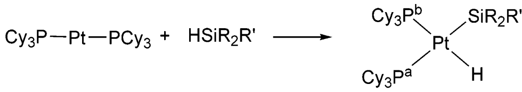
Trogler and co-workers examined the photochemical reactions of complexes of $Pt(C_2O_4)L_2$ and $Pd(C_2O_4)L_2$ (L = tertiary phosphine).[8] Their observations point to formation of highly reactive 14-electron ML_2 species that undergo oxidative addition reactions with organosilanes to yield platinum(II) or palladium(II) derivatives. They derived a photocatalyst for hydrosilation from this system by supporting it on silica via the functional ligand L = $(OMe)_3Si(CH_2)_2PEt_2$.[9] Complexes of the type *cis*-Pt(PEt_3)$_2$(H)(SiR_3) have also been made by silane transfer from a rhodium complex.[10]

Ozawa and co-workers have proposed that Si−C bond formation during hydrosilation can occur via both reductive elimination and silyl migration in the same system.[11] They reported that *cis*-PtL_2(Me)($SiPh_3$) complexes (L = $PMePh_2$, PMe_2Ph) readily afford $MeSiPh_3$ in solution[12,13] and studied the kinetics of $MeSiPh_3$ formation in the presence of diphenylacetylene. They also examined the thermolysis reaction of *cis*-Pt(PMe_2Ph)$_2$(R)($SiPh_3$) complexes in solution.[14] The thermolysis reactions were found to involve two additional processes: reversible β-hydrogen elimination from the alkyl ligand and isomerization of *cis*-Pt(PMe_2Ph)$_2$(R)($SiPh_3$) to *cis*-Pt(PMe_2Ph)$_2$(Ph)($SiRPh_2$).

An early example of the observation of a mutual phosphine exchange process was noted by Pidcock et al. for *cis*-Pt(PPh_3)$_2$(H)($SiPh_3$).[15] Their ^1H NMR spectra revealed behavior indicative of phosphine dissociation rather than reversible addition−elimination of the silane ligand. Clark and Hampden-Smith later found that the analogous compound *cis*-Pt(PCy_3)$_2$(H)($SiPh_3$)[16,17] undergoes both intramolecular phosphine interchange and reversible addition−elimination of silane. They proposed that a complex containing an η^2-silane ligand enabled mutual phosphine exchange to occur via rotation about the Si−H bond.

Recently, Boyle et al. have described the oxidative addition of tertiary silanes to [Pd($Cy_2PCH_2CH_2PCy_2$)]$_2$, yielding Pd($Cy_2PCH_2CH_2PCy_2$)(SiR_3)H, and have shown that equilibria are established between the resulting complexes in the presence of different silanes.[18] They have also shown that the phosphorus nuclei undergo dynamic exchange and use a temperature-dependent kinetic isotope effect as evidence to support a Pd(η^2-silane) intermediate in the fluxional process.

Scheme 1. Preparation and Numbering of *cis*-Pt(PCy_3)$_2$(H)(SiR_2R')



	SiR_2R'		
1-*cis*	$SiPh_2H$	**7-*cis***	$SiPh_2OSiPh_2H$
2-*cis*	$SiEt_2H$	**8-*cis***	$SiMe_2OSiMe_2H$
3-*cis*	$SiEt_3$	**9-*cis***	$SiMe(OSiMe_3)_2$
4-*cis*	$SiMe_2Et$	**10-*cis***	$SiMe_2[OCH_2C(Me)=CH_2]$
5-*cis*	$SiPh_3$	**11-*cis***	$Si(OMe)_2CH_2(CH=CH_2)$
6-*cis*	$SiMe_2(CH_2CH=CH_2)$		

Our studies expand the earlier work of Clark and Hampden-Smith into new silyl hydride complexes of the form *cis*-Pt(PCy_3)$_2$(H)(SiR_2R'). We examine the reactivity of Pt(PCy_3)$_2$ toward a variety of silanes and characterize the products by extensive NMR studies. Competition experiments and deuterium labeling have been employed to follow silane exchange at *cis*-Pt(PCy_3)$_2$(H)($SiPh_3$). These experiments also serve to demonstrate the relative stability of different species of this class. Several complexes of the type *cis*-Pt(PCy_3)$_2$(H)(SiR_2R') undergo photochemical cis−trans isomerization, but those with R or R′ = Cl isomerize thermally. The dynamic behavior of the complexes where SiR_2R' = $SiPh_2H$, $SiPh_3$, $SiMe_2Et$ has been studied by line-shape analysis and EXSY spectroscopy.[19] Intramolecular phosphine site exchange competes with a second process involving reductive elimination−oxidative addition of silane that renders the phosphorus centers equivalent.

Results and Discussion

Preparation of *cis*-Pt(PCy_3)$_2$(H)(SiR_2R') Complexes. The 14-electron complex[20] Pt(PCy_3)$_2$ reacts with a variety of silanes, $HSiR_2R'$, to form Si−H bond activation products, Pt(PCy_3)$_2$(H)(SiR_2R') (Scheme 1), which can be isolated as white solids in moderate yields (40−50%) in favorable cases. The characterization of the most stable product in this series, *cis*-Pt(PCy_3)$_2$(H)($SiPh_2H$) (**1-cis**), is now discussed as the example that includes crystallographic data. Tables 1 and 2 contain essential NMR features for cis and trans products, respectively.

Characterization of *cis*-Pt(PCy_3)$_2$(H)($SiPh_2H$) (1-cis). Reaction of Pt(PCy_3)$_2$ with H_2SiPh_2 in hexane in the absence of light yields a single white product that was recrystallized from hexane/toluene at −30 °C. The ^1H NMR spectrum of this product in [$^2H_8$]toluene contains a hydride resonance at δ −3.1 (1H) that

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Table 1. ^{1}H and ^{31}P NMR Data (295 K) for the Complexes *cis*-Pt(PCy$_3$)$_2$(H)(SiR$_2$R′) (1-cis−14-cis)

complex, T (K)	^{1}H NMR hydride,[c] δ (J, Hz)	^{31}P NMR,[d] δ (J, Hz)
Pt(PCy$_3$)$_2$(H)(SiPh$_2$H) (**1-cis**),[a] 293	−3.1 (J(PH)$_{cis}$ = 24.5, J(PH)$_{trans}$ = 138.4, J(PtH) = 838)	38.5 (P^b), 46.2 (P^a) (J(PP) = 11.6, J(PtP^b) = 2632, J(PtP^a) = 1675)
Pt(PCy$_3$)$_2$(H)(SiEt$_2$H) (**2-cis**),[a] 293	−3.4 (J(PH)$_{cis}$ = 25, J(PH)$_{trans}$ = 142, J(PtH) = 873)	42.8 (P^b), 50.8 (P^a) (J(PP) = 11.6, J(PtP^b) = 2687, J(PtP^a) = 1540)
Pt(PCy$_3$)$_2$(H)(SiEt$_3$) (**3-cis**),[a] 243	−3.6 (J(PH)$_{cis}$ = 26, J(PH)$_{trans}$ = 146, J(PtH) = 823)	42.9 (P^b), 43.1 (P^a) (J(PP) = 12, J(PtP^b) = 2721, J(PtP^a) = 1368)
Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) (**4-cis**),[a] 250	−3.5 (J(PH)$_{cis}$ = 26, J(PH)$_{trans}$ = 141, J(PtH) = 858)	42.2(P^b), 43.1 (P^a) (J(PP) = 12, J(PtP^b) = 2704, J(PtP^a) = 1387)
Pt(PCy$_3$)$_2$(H)(SiPh$_3$) (**5-cis**),[a] 250	−4.0 (J(PH)$_{cis}$ = 23, J(PH)$_{trans}$ = 142, J(PtH) = 784)	37.3(P^b), 41.1 (P^a) (J(PP) = 13, J(PtP^b) = 2642, J(PtP^a) = 1560)
Pt(PCy$_3$)$_2$(H){SiMe$_2$CH$_2$(CH=CH$_2$)} (**6-cis**),[a] 250	−3.5 (J(PH)$_{cis}$ = 26, J(PH)$_{trans}$ = 141, J(PtH) = 853)	41.6 (P^b), 42.8 (P^a) (J(PP) = 12, J_H(PtP) = 2677, J(PtP^a) = 1420)
Pt(PCy$_3$)$_2$(H)(SiPh$_2$OSiPh$_2$H) (**7-cis**),[b] 295	−4.0 (J(PH)$_{cis}$ = 27, J(PH)$_{trans}$ = 141, J(PtH) = 851)	43.4 (P^b), 43.1 (P^a) (J(PP) = 15, J(PtP^b) = 2612, J(PtP^a) = 1428)
Pt(PCy$_3$)(H)(SiMe$_2$OSiHMe$_2$) (**8-cis**),[a] 268	−4.2 (J(PH)$_{cis}$ = 27, J(PH)$_{trans}$ = 141, J(PtH) = 912)	43.0 (P^b), 43.2 (P^a) (J(PP) = 13, J(PtP^b) = 2656, J(PtP^a) = 1320)
Pt(PCy$_3$)$_2$(H){SiMe(OSiMe$_3$)$_2$} (**9-cis**),[a] 225	−3.8 (J(PH)$_{cis}$ = 28, J(PH)$_{trans}$ = 138, J(PtH) = 912)	46.9(P^b), 45.5 (P^a) (J(PP) = 13, J(PtP^b) = 2594, J(PtP^a) = 1280)
Pt(PCy$_3$)$_2$(H)(SiMe$_2$OCH$_2$C(Me)=CH$_2$) (**10-cis**),[a] 240	−4.2 (J(PH)$_{cis}$ = 28, J(PH)$_{trans}$ = 141, J(PtH) = 889)	41.9 (P^b), 42.0 (P^a) (J(PP) = 13, J(PtP^b) = 2658, J(PtP^a) = 1369)
Pt(PCy$_3$)$_2$(H)(SiOMe$_2$CH$_2$CH=CH$_2$) (**11-cis**),[b] 295	−4.0 (J(PH)$_{cis}$ = 28, J(PH)$_{trans}$ = 142, J(PtH) = 883)	41.9 (P^b), 42.4 (P^a) (J(PP) = 14, J(PtP^b) = 2638, J(PtP^a) = 1408)
Pt(PCy$_3$)$_2$(H)(SiMe$_2$Cl) (**12-cis**),[b] 295	−4.8 (J(PH)$_{cis}$ = 24, J(PH)$_{trans}$ = 136, J(PtH) = 957)	38.2 (P^b), 36.5 (P^a) (J(PP) = 18, J(PtP^b) = 2716, J(PtP^a) = 1520)
Pt(PCy$_3$)$_2$(H)(SiCl$_2$Me) (**13-cis**),[a] 260	−4.5 (J(PH)$_{cis}$ = 22, J(PH)$_{trans}$ = 135, J(PtH) = 895)	34.0 (P^b), 36.0 (P^a), (J(PP) = 14, J(PtP^b) = 2628, J(PtP^a) = 1800)
Pt(PCy$_3$)$_2$(H)(SiCl$_3$) (**14-cis**),[a] 260	−4.4 (J(PH)$_{cis}$ = 19, J(PH)$_{trans}$ = 133, J(PtH) = 826)	35.6 (P^b), 33.3 (P^a) (J(PP) = 14, J(PtP^b) = 2594, J(PtP^a) = 2055)

[a] In [^{2}H$_8$]toluene. [b] In C$_6$D$_6$. [c] All hydride signals appears as doublets of doublets, except those for **1-cis** and **2-cis**, which show additional 3.4 Hz couplings to the SiH proton. [d] See Schemes 1 and 2 for labels.

Table 2. ^{1}H and ^{31}P NMR Data for the Complexes *trans*-Pt(PCy$_3$)$_2$H(SiR$_2$R′) (1-trans−14-trans)

complex	^{1}H NMR hydride,[c] δ (J, Hz)	^{31}P NMR, δ (J, Hz)
Pt(PCy$_3$)$_2$(H)(SiPh$_2$H) (**1-trans**)[a]	−1.3 (J(PH) = 16, J(PtH) = 666)	39.9 (J(PtP) = 2657)
Pt(PCy$_3$)$_2$(H)(SiEt$_2$H) (**2-trans**)[a]	−1.3 (J(PH) = 18, J(PtH) = 616)	42.8 (J(PtP) = 2714)
Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) (**4-trans**)[a]	−2.9 (J(PH) = 19, J(PtH) = 552)	43.4 (J(PtP) = 2772)
Pt(PCy$_3$)$_2$(H)(SiPh$_3$) (**5-trans**)[a]	−3.0 (J(PH) = 17, J(PtH) = 584)	37.5 (J(PtP) = 2656)
Pt(PCy$_3$)$_2$(H){SiMe$_2$CH$_2$(CH=CH$_2$)} (**6-trans**)[a]	−2.6 (J(PH) = 18, J(PtH) = 561)	43.5 (J(PtP) = 2747)
Pt(PCy$_3$)$_2$(H)(SiMe$_2$Cl) (**12-trans**)[b]	−3.9 (J(PH) = 17, J(PtH) = 646)	40.0 (J(PtP) = 2677)
Pt(PCy$_3$)$_2$(H)(SiCl$_2$Me) (**13-trans**)[a]	−4.5 (J(PH) = 15, J(PtH) = 628)	35.5 (J(PtP) = 2627)
Pt(PCy$_3$)$_2$(H)(SiCl$_3$) (**14-trans**)[a]	−5.5 (J(PH) = 14, J(PtH) = 695)	34.0 (J(PtP) = 2560)

[a] In [^{2}H$_8$]toluene. [b] In C$_6$D$_6$. [c] No hydride coupling to the SiH proton is visible in **1-trans** and **2-trans**; all hydride resonances, therefore, appear as simple triplets.

appears as a doublet of doublets of doublets (ddd) with ^{195}Pt satellites and another ddd feature at δ 5.4 (1H) due to a new silyl hydride group. These two proton resonances are linked by a 3.4 Hz coupling. The associated ^{31}P{^{1}H} NMR spectrum contains two mutually coupled resonances, each with ^{195}Pt satellites, at δ 38 and 46. It has been shown previously that the magnitude of a Pt−P coupling decreases as the trans influence of the ligand trans to phosphine increases.[21,22] In the complex **1-cis**, the values of J(PtP) are substantially different, with the lower value being indicative of the phosphorus center that is trans to silicon rather than hydride, as is confirmed by ^{1}H−^{31}P HMQC experiments. These data are consistent with a higher trans influence for the silyl group than for hydride.

The characterization of this complex was further facilitated by a series of heteronuclear multiple quantum ^{1}H−^{29}Si (Figure 1) and ^{1}H−^{195}Pt correlation experiments. In the ^{1}H−^{29}Si-HMQC experiment, active couplings to ^{29}Si enable us to produce a map that contains passive H−^{31}P and H−^{195}Pt couplings. In this way, the ^{1}H−^{29}Si correlation locates a ^{29}Si signal at δ 3.4 with ^{195}Pt satellites, which connects to both the Si−H and Pt−H signals with additional couplings to phosphorus.

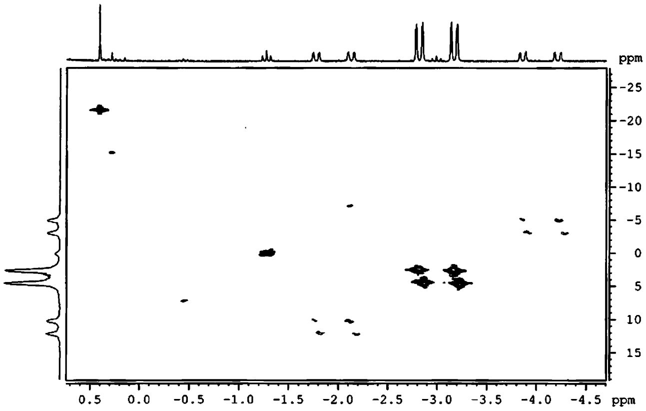

Figure 1. ^{1}H−^{29}Si 2D-HMQC correlation spectrum of *cis*-Pt(PCy$_3$)$_2$(H)(SiPh$_2$H) (**1-cis**) with projections of the 2D spectrum in the ^{29}Si and ^{1}H dimensions plotted along the horizontal (δ(^{1}H)) and vertical (δ(^{29}Si)) axes. The ^{1}H spectrum shows a triplet at δ −1.33 for *trans*-Pt(PCy$_3$)$_2$(H)(SiPh$_2$H) and a triplet at δ −3.2 for *trans*-Pt(PCy$_3$)$_2$(H)$_2$.

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Table 3. NMR Data for 1-cis (δ; *J*, Hz)[a]

X	*Pt*	Si	H^a	H^b	P^a	P^b
δ	−5370	3.43	−3.09	5.37	46.2	38.5
J_{X-Pt}		1206	838	15	1675	2632
J_{X-Si}			10	164	154	12.4
J_{X-H^a}				3.4	24.5	138
J_{X-H^b}					17.6	7.3
J_{X-P^a}						11.6

[a] See Scheme 1 for labels. H^a is the hydride bound to Pt, and H^b is bound to Si.

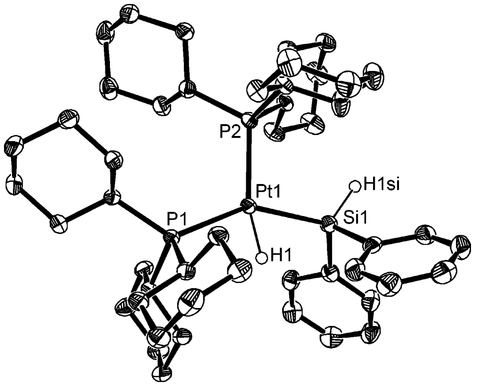

Figure 2. Crystal structure (ORTEP digram) of *cis*-Pt-$(PCy_3)_2(H)(SiPh_2H)$ (**1**). Hydrogen atoms bonded to carbon are not shown. Ellipsoids are at the 50% level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for *cis*-$Pt(PCy_3)_2H(SiPh_2H)$ (1-cis)

Bond Lengths			
Pt−P(1)	2.3493(8)	Pt−H(1)	1.44(3)
Pt−P(2)	2.3127(8)	Si−H(1SI)	1.42(3)
Pt−Si	2.3311(9)		
Bond Angles			
Si−Pt−P(1)	146.83(3)	P(1)−Pt−P(2)	113.55(3)
Si−Pt−P(2)	99.37(3)		

A $^1H-^{195}Pt$ NMR spectrum revealed the platinum chemical shift and passive hydride−^{29}Si coupling. The NMR data are fully consistent with the structure *cis*-$Pt(PCy_3)_2(H)(SiPh_2H)$ (**1-cis**). A complete set of chemical shifts and couplings for Pt, Si, P, and the two hydridic protons is given in Table 3.

The value $^1J(SiH) = 164$ Hz for the directly bonded SiH group contrasts with the value $^2J(SiH) = 10$ Hz for the HPtSi linkage, providing a very clear distinction between the bonding interactions of silicon to these two hydridic protons. Furthermore, we tested for magnetization transfer between these two protons in an EXSY experiment and found no evidence of exchange at room temperature. These data allow us to exclude an η^2-silane moiety in the ground state, since we would expect to find intermediate values of *J*(SiH).[1,5] The complex **1-cis** is fluxional above room temperature: its dynamic behavior is described below.

X-ray Structure Determination of *cis*-$Pt(PCy_3)_2$-(H)($SiPh_2H$) (1-cis). Crystals of *cis*-$Pt(PCy_3)_2(H)$-$(SiPh_2H)\cdot 1.5$(toluene) suitable for X-ray analysis were grown from a hexane/toluene solution at −20 °C. The structure determined at −100 °C (see Table 4 and Figure 2) reveals that the $PtSiP_2$ unit is close to planar with cis phosphine ligands. The platinum hydride and the silicon hydride were located via a difference map. The Pt−H distance of 1.44(3) Å is somewhat short, corresponding to the 14th percentile of Pt−H distances in the Cambridge Structural Database.[23] The P(1)−Pt−P(2) angle is 113.55(3)°, while the P(1)−Pt−Si and P(2)−Pt−Si angles are 146.83(3) and 99.37(3)°. Thus, the angles at platinum are far from the ideal 90° of a square-planar arrangement. The platinum atom lies 0.0619 Å from the P(1)P(2)Si plane. The length of the Pt−P bond approximately trans to silicon (Pt−P(1) = 2.3493(8) Å) is greater than the Pt−P bond approximately cis to silicon (Pt−P(2) = 2.3127(8) Å). There are two published structures of complexes with the same coordination set at platinum: *cis*-$Pt(PEt_3)_2(H)(SiPh_3)$ and *cis*-$Pt(PPh_3)_2(H)(SiPh_3)$. In both cases, the P(1)−Pt−P(2) angles (107.2(1) and 108.05(9)°, respectively) and the P−Pt−Si angles are smaller than ours.[10,24] The P(1)−Pt−P(2) angle is slightly larger in our complex than in the ruthenium(II) complexes containing cis PCy_3 groups, $Ru(PCy_3)_2(H)_2\{[\eta^2\text{-}HSiMe_2]_2X\}$, where it is typically 108−109°.[5]

Reaction of $Pt(PCy_3)_2$ with Other Silanes $HSiR_2R'$. The reactions of $Pt(PCy_3)_2$ with the silanes H_2SiEt_2, $HSiEt_3$, $HSiMe_2Et$, $HSiPh_3$, $HSiMe_2(CH_2CH{=}CH_2)$, $HMe_2SiOSiMe_2H$, $HSiPh_2OSiPh_2H$, $HSiMe(OSiMe_3)_2$, $HSiMe_2OCH_2C(Me){=}CH_2$, and $HSi(OMe)_2CH_2CH{=}CH_2$ were followed by NMR spectroscopy in a similar way. Samples were prepared at −78 °C as described in the Experimental Section. The corresponding low-temperature ^1H NMR spectra of the products formed in these reactions (**2-cis**−**11-cis**, Scheme 1) contain hydride resonances that appear as undistorted doublets of doublets, indicative of a cis ligand arrangement with ^{195}Pt satellites at −25 °C (Table 1). The products of these reactions, *cis*-$Pt(PCy_3)_2(H)(SiR_2R')$, are highly fluxional, as described later, and many contain relatively labile silanes. Consequently, only the complexes formed from H_2SiPh_2 and $HSiPh_3$ have been isolated in analytically pure form.

Reactions with Hydrochlorosilanes. We have also explored the reactivity of $Pt(PCy_3)_2$ toward the hydrochlorosilanes $HSiMe_2Cl$, $HSiMeCl_2$, and $HSiCl_3$. When these reactions are carried out at −78 °C, the cis complexes **12-cis**, **13-cis**, and **14-cis** were formed together with minor amounts of *trans*-$Pt(PCy_3)_2(H)(Cl)$. Comparison of the platinum−phosphorus coupling constants for the series of complexes *cis*-$Pt(PCy_3)_2(SiMe_{3-x}Cl_x)H$ ($x = 1-3$) reveals that $J(PtP^a)$, where P^a lies trans to silicon, grows linearly with x.[25] When they were warmed to 20 °C, the complexes rearranged to their trans counterparts **12-trans**, **13-trans**, and **14-trans** (Scheme 2). NMR data for cis and trans complexes are presented in Tables 1 and 2, respectively.

Photochemical Reactions of *cis*-$Pt(PCy_3)_2(H)$-(SiR_2R'). Clark et al. found that the complex *cis*-Pt-$(PCy_3)_2(H)(SiPh_3)$ (**5-cis**) undergoes quantitative cis−trans isomerization when irradiated by a weak UV source to yield *trans*-$Pt(PCy_3)_2(H)(SiPh_3)$.[17] In our studies, we have found that the complexes *cis*-$Pt(PCy_3)_2(H)$-

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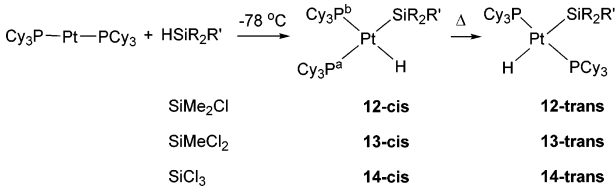
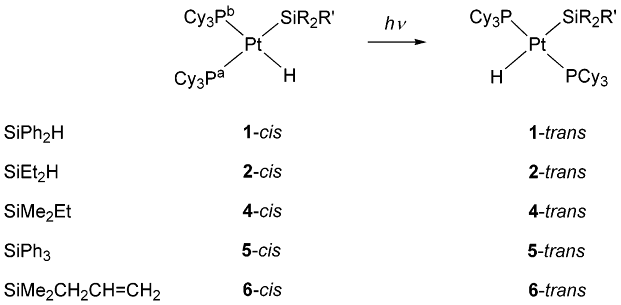
[24] Latif, L. A.; Eaborn, C.; Pidcock, A. P.; Weng, N. S. *J. Organomet. Chem.* **1994**, *474*, 217.

[25] (a) Lemke, F. R.; Chaitheerapapkul, C. *Polyhedron* **1996**, *15*, 2559. (b) Lemke, F. R.; Galat, K. J.; Wiley, J. Y. *Organometallics* **1999**, *18*, 1419. (c) Freeman, S. T. N.; Lofton, L. L.; Lemke, F. R. *Organometallics* **2002**, 21, 4776. (d) Freeman, S. T. N.; Petersen, J. L.; Lemke, F. R. *Organometallics* **2004**, 23, 1153.

Scheme 2. Reaction of Pt(Cy$_3$)$_2$ with Hydrochlorosilanes

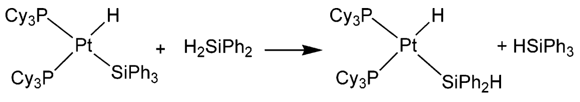


Scheme 3. Photochemical Isomerization of Pt(PCy$_3$)$_2$(SiR$_2$R′)H



(SiR$_2$R′) (**1-cis**, **2-cis**, **4-cis**, **5-cis**, and **6-cis**) also undergo quantitative cis−trans isomerization when photolyzed with UV light at room temperature to form *trans*-Pt(PCy$_3$)$_2$(H)(SiR$_2$R′) (**1-trans**−**6-trans**) (Scheme 3). For example, the hydride of *trans*-Pt(PCy$_3$)$_2$(H)(SiPh$_2$H) is characterized by a triplet with Pt satellites in the ^{1}H NMR spectrum (δ −1.33, J(PH) = 16, J(PtH) = 666 Hz). The ^{31}P NMR spectrum shows a singlet at δ 39.9 (J(PtP) = 2657 Hz). The ^{29}Si spectrum exhibits a triplet at δ 0.26 (J(SiP) = 9.7 Hz), while the ^{195}Pt chemical shift is δ −5359 (see the Experimental Section). When the complex **1-cis** was prepared in the absence of light, only the cis isomer was observed, but without such precautions some trans isomer was detected. No attempt was made to isolate the trans complexes. Table 2 summarizes NMR data for *trans*-Pt(PCy$_3$)$_2$(H)(SiR$_2$R′).

Competition Reaction between *cis*-Pt(PCy$_3$)$_2$(H)(SiPh$_2$H) (1-cis) and *cis*-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) (5-cis). To explore the relative stabilities of **1-cis** and **5-cis**, a sample of **5-cis** was prepared in [^{2}H$_8$]toluene and 1 equiv of H$_2$SiPh$_2$ added at low temperature. The corresponding ^{1}H and ^{31}P{^{1}H} NMR spectra, recorded immediately at 273 K, revealed that complete silane exchange had occurred (Figure 3a,b). There was no further change on warming to room temperature (Figure 3c). We can therefore conclude that {**1-cis** + HSiPh$_3$} is far more stable than {**5-cis** + H$_2$SiPh$_2$} (eq 1). Similar results were obtained when H$_2$SiEt$_2$ was added to **5-cis**: thus, {**2-cis** + HSiPh$_3$} proved more stable than {**5-cis** + H$_2$SiEt$_2$}.



(1)

5-*cis* **1-*cis***

Deuterium labeling has also been used to learn about the reactivity of these systems.[5] When DSiPh$_3$ was added to Pt(PCy$_3$)$_2$, *cis*-Pt(PCy$_3$)$_2$(D)(SiPh$_3$) (**5-cis-D**) was formed in quantitative yield, as shown by NMR spectroscopy. Addition of 1 equiv of either H$_2$SiPh$_2$ or H$_2$SiEt$_2$ to **5-cis-D** resulted in the immediate formation of undeuterated **1-cis** or **2-cis**, respectively. Further evidence of exchange was obtained by addition of HSiPh$_3$ to a sample of *cis*-Pt(PCy$_3$)$_2$(D)(SiPh$_3$) (**5-cis-D**). These exchange experiments may be compared with the exchange of hydrosilanes with *trans*-Pt(PEt$_3$)$_2$(SiMe$_3$)X (X = Br, I).[26]

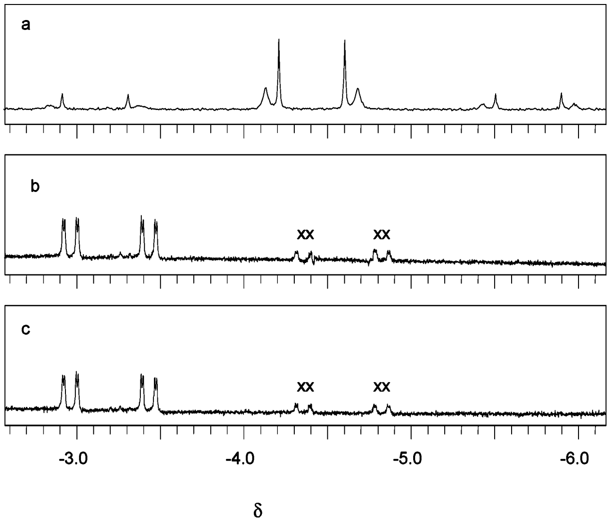
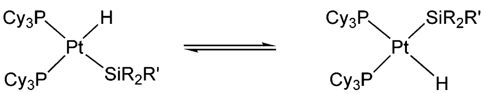


Figure 3. ^{1}H NMR spectra (300.13 MHz) in [^{2}H$_8$]toluene: (a) *cis*-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) (**5-cis**) at 273 K; (b) **5-cis** and H$_2$SiPh$_2$ at 273 K (×× denotes Pt satellites); (**c**) **5-cis** and H$_2$SiPh$_2$ at 293 K.

Thermal Decomposition of 1-cis. An NMR tube containing **1-cis** and its trans isomer **1-trans** in [^{2}H$_8$]toluene was prepared in order to follow their thermal decomposition. The complexes are stable at 295 K, but 20% of both are converted to *trans*-Pt(PCy$_3$)$_2$H$_2$ after 1 h at 343 K. At higher temperatures, the dihydride complex rapidly became the major product (δ_H = −3.2, J(PH) = 17.6, J(PtH) = 793 Hz; δ_P 53.5, J(PtP) = 2872 Hz; δ_{Pt} = −5481). The silicon products were not identified. The same dihydride was observed on decomposition of other silyl hydride complexes, as is illustrated for the complex **2-cis** (Figure 4). Thermal decomposition of **5-cis-D** yielded *trans*-Pt(PCy$_3$)$_2$D$_2$ (^{31}P δ 51.5 with J(PtP) = 2872 Hz).

Dynamic Behavior of *cis*-Pt(PCy$_3$)$_2$(H)(SiR$_2$R′). We have already alluded to the observation that the shapes of the hydride resonances for complexes **1-cis**−**11-cis** are temperature dependent. This effect is observed for **1-cis**, **7-cis**, **8-cis**, **9-cis**, and **11-cis** above room temperature but is readily discernible for the others at lower temperatures. It manifests itself in the gradual decrease in intensity of the outer lines of the hydride pattern as the temperature increases, while the inner lines remain sharp with constant separation, as shown for **5-cis** in Figure 5. The observation that only the outer lines collapse indicates that the phosphine ligands undergo mutual exchange while retaining P−H spin correlation; i.e., the mechanism of the underlying phosphorus exchange is intramolecular (eq 2).[27] Moreover, the appearance of such spectra depends on the



(2)

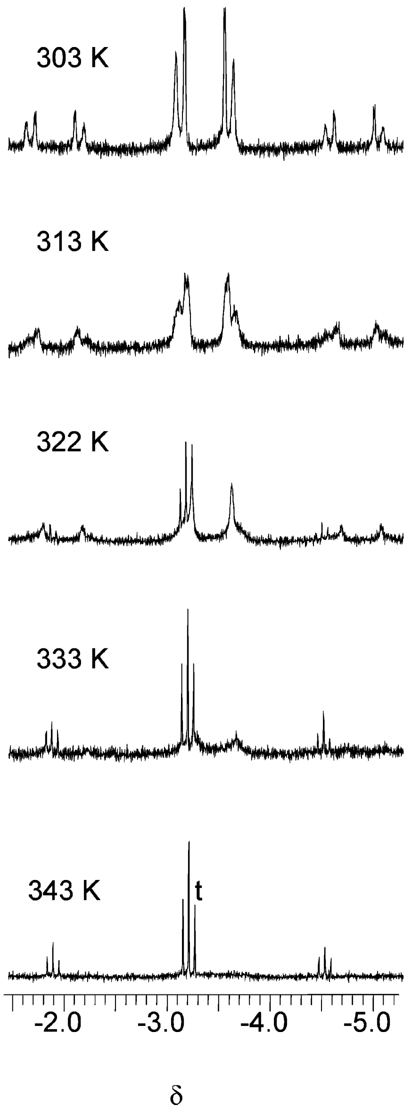


Figure 4. ^{1}H NMR spectra (300.13 MHz) showing effect of heating *cis*-Pt(PCy_3)$_2$(H)($SiEt_2H$) (**2-cis**) in [$^2H_6$]benzene (t denotes *trans*-Pt(PCy_3)$_2H_2$).

relative signs of the phosphorus hydride couplings, with the broadening of the outer lines indicating that $^2J(PH)_{trans}$ and $^2J(PH)_{cis}$ have opposite signs. When it is the inner lines that broaden selectively, the signs are the same. The separation of the inner lines is given by $\{|^2J(PH)_{trans}| - |^2J(PH)_{cis}|\}$.[28]

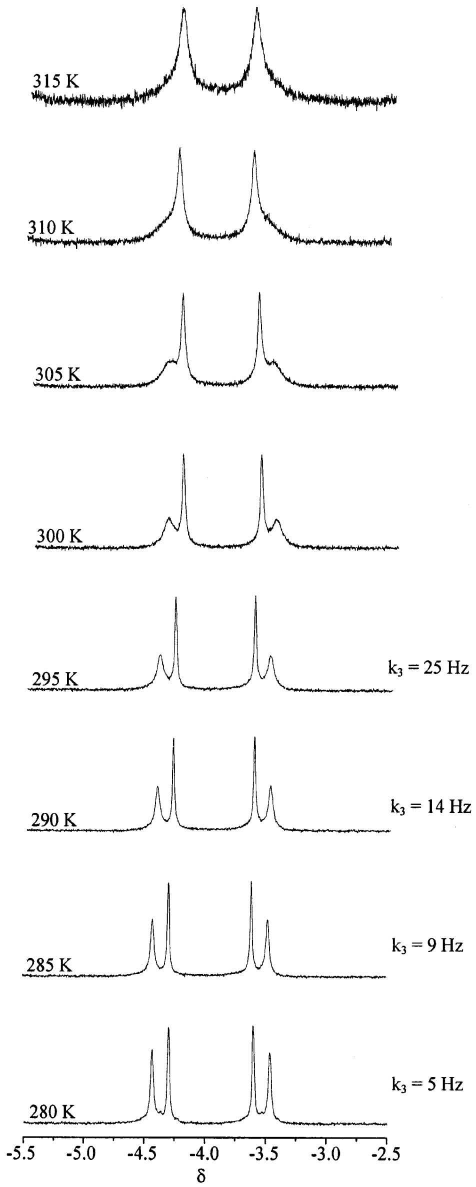
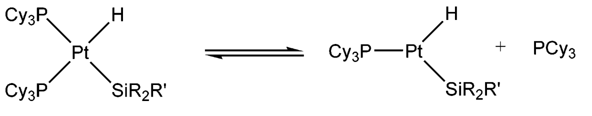
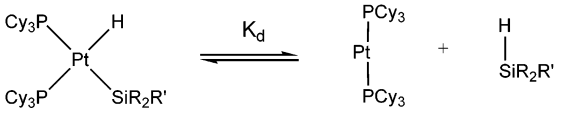


Figure 5. ^{1}H NMR spectra (500.13 MHz) of the hydride region of the spectrum of *cis*-Pt(PCy_3)$_2$(H)($SiPh_3$) (**5-cis**) in [$^2H_8$]toluene.

At higher temperatures, more general broadening occurs but no central resonance develops. This behavior can be readily understood if a second dynamic process competes with the intramolecular phosphine exchange. This second process must be intermolecular and requires the loss of P−H coupling. It is consistent with dissociative exchange between *cis*-Pt(PCy_3)$_2$(H)(SiR_3) and free phosphine (eq 3), dissociative exchange between *cis*-Pt(PCy_3)$_2$(H)(SiR_3) and free silane (eq 4), or a combination of the two.



(3)



(4)

Variable-temperature ^{31}P NMR spectra are consistent with ^{1}H NMR data for phosphine exchange; for instance, the spectrum of **6-cis** is at the low-temperature limit at 250 K but each of the resonances and their satellites broadens up to ca. 290 K. At higher temperature the two ^{31}P resonances coalesce, so that the room-temperature spectrum is very broad indeed. In the corresponding ^{31}P EXSY measurements, cross-peaks connected phosphorus centers within specific platinum isotopomers, confirming the intramolecularity of phosphorus site exchange.

The processes in eqs 3 and 4 involve the disruption of the spin−spin coupling between the phosphorus

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[27] Jesson, J. P.; Muetterties, E. L. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 279.

[28] Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1998**, *37*, 2422.

Table 5. Thermodynamic Parameters for the Reductive Elimination of $HSiR_2R'$ from *cis*-$Pt(PCy_3)_2(H)(SiR_2R')$ in $[^2H_8]$Toluene[a]

complex	$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J K^{-1} mol^{-1}	$\Delta G°_{300}$, kJ mol^{-1}
cis-$Pt(PCy_3)_2(H)(SiMe_2Et)$ (**4-cis**)	32 ± 2	117 ± 8	−2.9 ± 0.4
cis-$Pt(PCy_3)_2(H)(SiPh_3)$ (**5-cis**)	64 ± 9	207 ± 30	1.9 ± 0.2

[a] Error bars as 95% probability on least-squares fit.

atoms and the hydride. Clark and Hampden-Smith have suggested that silane reductive elimination occurs as in eq 4.[16] We report several pieces of evidence to support this conclusion. When **6-cis** is dissolved in C_6D_6, at 295 K, detectable amounts of free silane and $Pt(PCy_3)_2$ are observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, although no free phosphine is detected. When an NMR sample of **6-cis** was prepared at low temperature in $[^2H_8]$toluene and $^{31}P\{^1H\}$ NMR spectra were subsequently measured at 250 K, only signals due to **6-cis** were observed. However, when the sample was warmed to 290 K a signal corresponding to $Pt(PCy_3)_2$ was detected. The establishment of a similar equilibrium process was demonstrated for the complex **5-cis**: free silane is detected at 315 K but is absent at 280 K. In none of these experiments was free phosphine evident, nor was *trans*-$Pt(PCy_3)_2(SiR_2R')H$ formed. Furthermore, the competition and H/D exchange experiments can be explained by rapid reductive elimination of $HSiPh_3$ or H_2SiEt_2. Evidence for silane exchange was also revealed by spin saturation transfer methods.[29] When the hydride resonance was irradiated selectively, the intensity of the ^1H Si−H resonance of free silane decreased markedly. These effects appeared to be independent of the concentration of silane, thus excluding a mechanism involving a Pt(IV) complex.

Thermodynamic Parameters for the Free Silane Exchange Process in 1-cis, 5-cis, and 4-cis. Three complexes were chosen for detailed examination of kinetics and dissociation behavior: **1-cis**, **5-cis**, and **4-cis**. Of these, **5-cis** and **4-cis** exhibited equilibrium dissociation of silane (eq 4), while **1-cis** was too inert to attain equilibrium at temperatures below the decomposition point. The relative concentrations of *cis*-$Pt(PCy_3)_2(H)(SiR_2R')$, $HSiR_2R'$, and $Pt(PCy_3)_2$ for **5-cis** and **4-cis** were measured by quantitative ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and the equilibrium constant K_d was obtained (eq 5). The temperature dependence of the

$$K_d = \frac{[Pt(PCy_3)_2][HSiR_2R']}{[cis\text{-}Pt(PCy_3)_2(H)(SiR_2R')]} \qquad (5)$$

values of K_d (see the Supporting Information) was used to determine $\Delta H°$ and $\Delta S°$ for the dissociation (Table 5, Figure 6). The values of $\Delta H°$ and $\Delta S°$ for **5-cis** are both much larger than for complex **4-cis**, but the difference in $\Delta G°_{300}$ is slight.

Kinetics and Activation Parameters for the Dynamic Processes of *cis*-$Pt(PCy_3)_2(H)(SiR_2R')$. Scheme 4 illustrates the exchange processes that occur in **1-cis**−**7-cis**. The temperature-dependent line shape of the ^1H NMR spectra of *cis*-$Pt(PCy_3)_2(H)(SiR_2R')$ were simulated with *DNMR-SIM*[30] or *g-NMR*[31] up to those temperatures where the intermolecular exchange rate was significant compared to the intramolecular exchange; i.e., the inner lines remained sharp but the outer lines broadened. The programs were inappropriate at higher temperatures, since they could not simulate simultaneous intra- and intermolecular processes quantitatively. These simulations yielded k_3 for complexes **1-cis**, **4-cis**, and **5-cis**.

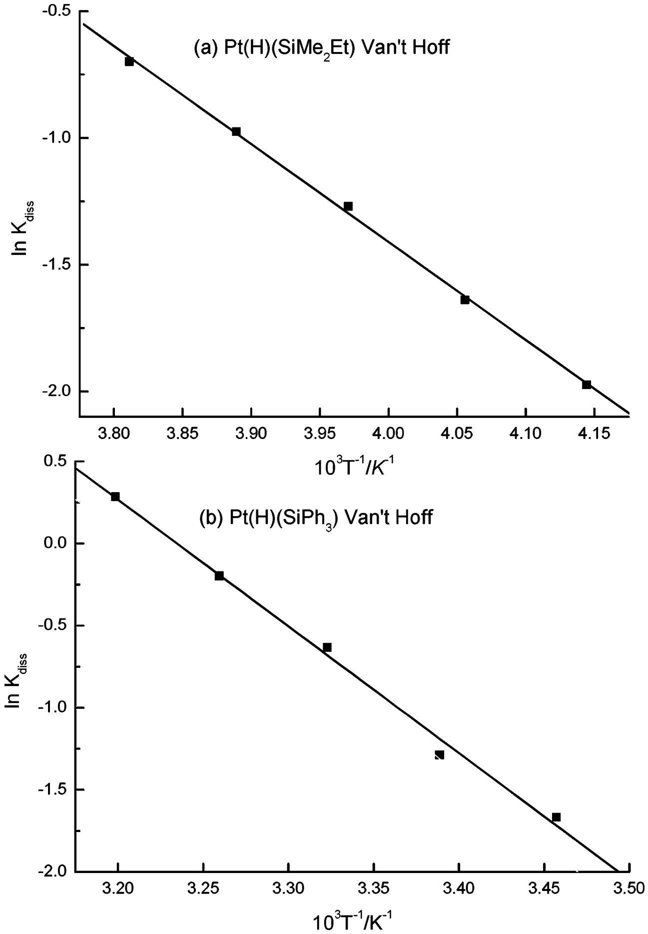
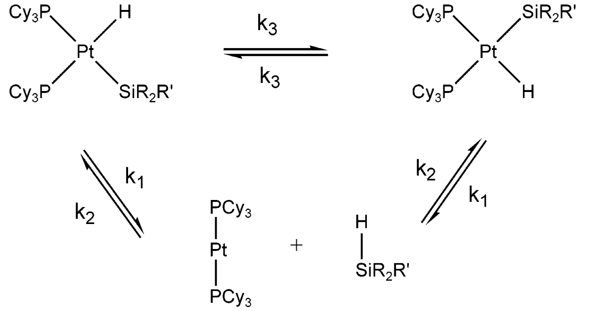


Figure 6. van't Hoff plots for (a) *cis*-$Pt(PCy_3)_2(H)(SiMe_2Et)$ (**4-cis**) and (b) *cis*-$Pt(PCy_3)_2(H)(SiPh_3)$ (**5-cis**).

Scheme 4. Dynamic Exchange Processes of *cis*-$Pt(PCy_3)_2(H)(SiR_2R')$



In addition to line-shape analysis, we employed ^1H and ^{31}P EXSY spectroscopy to measure rate constants.[32]

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[32] Meier, B. H.; Ernst, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 6441.

Table 6. Activation Parameters for the Complexes 1-cis, 5-cis, and 4-cis in [$^2H_8$]Toluene[a]

complex	rate process[b]	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	$\Delta G^\ddagger_{300}$, kJ mol^{-1}
cis-Pt(PCy$_3$)$_2$(SiPh$_2$H)H (**1-cis**)	k_1, s^{-1}	87 ± 5	24 ± 15	80.1 ± 0.4
	k_2, dm^3 mol^{-1} s^{-1}	*c*	*c*	*c*
	k_3, s^{-1} EXSY	87 ± 3	50 ± 10	72.3 ± 0.1
	k_3, s^{-1} (line shape)	90 ± 8	53 ± 26	74.1 ± 0.7
cis-Pt(PCy$_3$)$_2$(SiMe$_2$Et)H (**4-cis**)	k_1, s^{-1}	62 ± 4	12 ± 15	58.6 ± 0.7
	k_2, dm^3 mol^{-1} s^{-1}	31 ± 4	−104 ± 15	61.3 ± 0.8
	k_3, s^{-1}	52 ± 3	−19 ± 11	57.4 ± 0.6
cis-Pt(PCy$_3$)$_2$(SiPh$_3$)H (**5-cis**)	k_1, s^{-1}	77 ± 5	34.7 ± 19	66.4 ± 0.4
	k_2, dm^3 mol^{-1} s^{-1}	13 ± 5	−173 ± 19	64.5 ± 0.3
	k_3, s^{-1}	60 ± 5	−16 ± 16	64.5 ± 0.2

[a] Error bars quoted as 95% probability on least-squares fit. [b] k_1 from EXSY, k_2 from combination of k_1 and K_d, k_3 from line-shape analysis and from EXSY for **1-cis**. [c] Not determined.

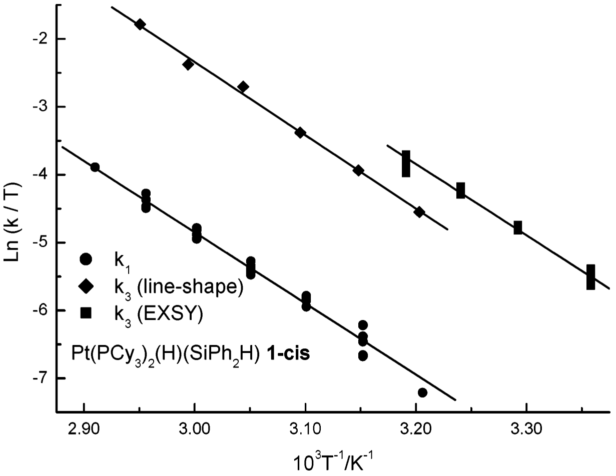

Figure 7. Eyring plots of k_1 (●) and k_3 (◆, line-shape analysis; ■, EXSY) for *cis*-Pt(PCy$_3$)$_2$(H)(SiPh$_2$H) **1-cis**.

For EXSY measurements, samples were made up containing a 12−14-fold excess of silane, so that the rate of oxidative addition was high compared to the rate of reductive elimination. This concentration also ensures that any silane released has a low probability of recombining with the same molecule it came from. The transfer of magnetization was examined from hydride to free silane by ^{1}H EXSY spectroscopy over the following temperature ranges: 310−340 K for **1-cis**, 270−312 K for **5-cis**, and 242−265 K for **4-cis**. The results were analyzed to yield k_1 by numerical solution of the differential equations with the aid of a version of EXCEL adapted for kinetic simulation. The values of the rate constant for oxidative addition, k_2, were calculated by employing the values of k_1 and K_d, and $k_2 = k_1/K_d$. Eyring plots of ln(k/T) vs T^{-1} yielded activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger_{300}$ (Figures 7−9, Table 6).

We also used the EXSY experiments to examine the possibility of exchange between the Si*H* and Pt*H* protons of **1-cis**. No such exchange was detected in the presence of a large excess of silane, but some magnetization transfer was observed when the silane concentration was reduced to ca. 5−10 times the concentration of **1-cis**. The rate of this exchange is so low that it can be explained entirely by reductive elimination and recombination of the same molecule of silane.

Rate constants for mutual phosphine exchange (k_3) for **1-cis** were also calculated by ^{31}P EXSY methods. The 2D-EXSY spectra were recorded as a function of mixing time in order to determine the rate for the exchange process in d_8-toluene for **1-cis** from 297 to 313 K. For an uncoupled system of spins A and B with equal populations and equal spin−lattice relaxation times, $T_{1A} = T_{1B} = T_1$, the rate of phosphorus exchange, k_{obsd}/s^{-1}, may be determined for a mixing time τ_m using eq 6, where $I = (I_{AA} + I_{BB})/(I_{AB} + I_{BA})$ compares the

$$k = \frac{1}{\tau_m} \ln \frac{I+1}{I-1} \tag{6}$$

volumes of the diagonal peaks and cross-peaks.[30,31,33,34] In this analysis, the forward and reverse rate constants are averaged.

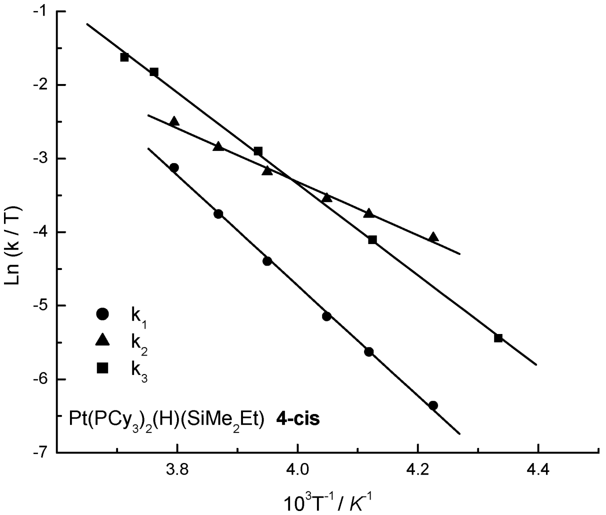

Figure 8. Eyring plots of k_1 (●), k_2 (▲), and k_3 (■) for *cis*-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) (**4-cis**).

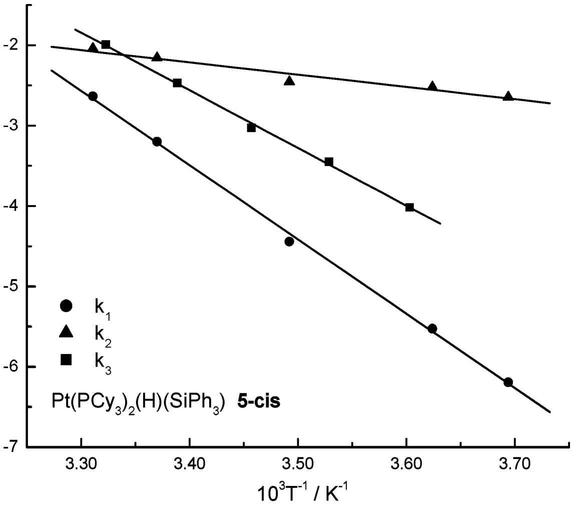

Figure 9. Eyring plots of k_1 (●), k_2 (▲), and k_3 (■) for *cis*-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) (**5-cis**).

These experiments yielded the rate constant, k_{obsd}, for magnetization leaving a phosphorus site. Since magnetization can be transferred both directly by mutual phosphine exchange and indirectly by silane reductive elimination−oxidative addition, both k_3 and k_1 contribute to the value of k_{obsd}. When a silane undergoes reductive elimination, it may recombine with the same nuclear configuration of the phosphines (P^a and P^b retain their identity) or the opposite (P^a and P^b reversed). The contribution to k_{obsd} from silane elimination does not require the same molecule of silane to add as eliminate. Because we use excess silane, addition of silane is fast compared to reductive elimination and there is no contribution from k_2 to the rate expression. As a result of the equal probability of addition in the two configurations, k_{obsd} is related to k_3 and k_1 by $k_{obsd} = k_3 + {}^1/_2k_1$. The value of k_3 is derived accordingly, and the activation parameters were obtained from the Eyring plot (Table 6). The values of the activation parameters obtained by EXSY spectroscopy are better determined than those obtained by line-shape analysis. The activation parameters determined by the two methods overlap when 95% confidence limits are included, although there are differences in the absolute rate constants.

Discussion

Energetics and the Structure of *cis*-Pt(PCy$_3$)$_2$(SiR$_2$R′)H. The products of reaction of Pt(PCy$_3$)$_2$ with hydrosilanes are cis platinum silyl hydride complexes for all silanes reported in this paper. Only with a chlorinated silyl group have we observed thermal cis to trans isomerization. For these complexes, we can be sure that the trans complex is thermodynamically more stable than the cis complex for SiMe$_2$Cl, SiMeCl$_2$, and SiCl$_3$ substituents. For the remaining complexes, we observe the cis isomer as the kinetic product and heating leads to silane exchange and decomposition but not isomerization. The cis isomer can be converted to the trans isomer photochemically in each case that we have attempted. Thus, the trans isomers are also kinetically stable, but we cannot be sure that they are thermodynamically more stable than the cis isomers. For comparison, it is worth noting that *cis*-Pt(PEt$_3$)$_2$(H)(SiPh$_3$) appears to be more stable than its trans analogue.[35]

An examination of the crystal structure of cis-Pt(PCy$_3$)$_2$(H)(SiPh$_2$H) shows that the angles at platinum are far from ideal. The angles between the cis ligands are 99.4 and 113.5°, while the nominally “trans” ligands lie at 146.9° to one another. This arrangement must relieve the majority of the steric strain, and it is likely that the trans isomer is only favored strongly with a sterically undemanding silyl group. A cis arrangement of PCy$_3$ groups has also proved stable for Ru(PCy$_3$)$_2$(H)$_2${[η^2-HSiMe$_2$]$_2$X}.[5]

Our experiments also give information about the relative stability of complexes with different silyl groups. The effect of steric strain is apparent in the lower stability of {R$_2$SiH$_2$ + *cis*-Pt(PCy$_3$)$_2$(SiPh$_3$)H} as compared to the {Ph$_3$SiH + *cis*-Pt(PCy$_3$)$_2$(SiR$_2$H)H} (R = Ph, Et) complex.

The more sterically strained complexes are at equilibrium with Pt(PCy$_3$)$_2$ and free silane. We can use the experimental value of $\Delta H°$ and the bond enthalpy of the Si−H bond to estimate the sum of the Pt−Si and Pt−H bond enthalpies (assuming that the reorganization energy of Pt(PCy$_3$)$_2$ is negligible). Taking the Si−H bond enthalpy of Me$_2$EtSi−H as 396 kJ mol^{-1} (the published value for Me$_3$Si−H) and that of Ph$_3$Si−H as 371 kJ mol^{-1},[36] the sums of the Pt−Si and Pt−H bond enthalpies are 428 and 435 kJ mol^{-1} for **4-cis** and **5-cis**, respectively. If the Pt−H bond enthalpy is constant, it follows that the Pt−SiPh$_3$ bond is stronger than the Pt−SiMe$_2$Et bond.

Mechanisms of Reductive Elimination and Phosphine Site Exchange. The evidence for the reductive elimination of silane is compelling: line broadening, EXSY experiments, silane exchange, and isotope labeling all point in the same direction. The values obtained for $\Delta H^{\ddagger}$ show that the barrier to reductive elimination increases in the order SiMe$_2$Et < SiPh$_3$ < SiPh$_2$H. These values may be compared to those for $\Delta H°$ for the first two substituents of 32 and 64 kJ mol^{-1}. The values of $\Delta G^{\ddagger}$ follow the same pattern as the values of $\Delta H^{\ddagger}$. The enthalpy barrier, $\Delta H^{\ddagger}$, to silane reductive elimination is higher than the standard enthalpy of reductive elimination, $\Delta H°$. The values of $\Delta S^{\ddagger}$ are very small for a dissociative reaction, implying that dissociation is far from complete. Thus, the transition states for the reductive elimination process appear to be early and the Si−H bond formation must be incomplete in the transition state to account for the values of $\Delta H^{\ddagger}$.

The phosphine site exchange process, k_3, is demonstrated to be intramolecular by the selectivity of the line broadening. The barriers to phosphine site exchange follow the same order as for k_1: SiMe$_2$Et < SiPh$_3$ < SiPh$_2$H.

When we include the photoisomerization, our experiments point to the existence of two distinct transition states for isomerization and one for reductive elimination. (A) The transition state for photoisomerization leads to the trans isomer. It is likely that this TS is pseudo-tetrahedral, as has been postulated for other photoisomerization reactions at platinum(II).[37] (B) The transition state for phosphine site exchange does not lead to the trans complex, although the latter is kinetically stable. It must therefore have an alternative geometry, and it is most reasonable to postulate that this is an η^2-silane complex. Our magnetization transfer experiments indicate that exchange between Si−H and Pt−H in **1-cis** proceeds more slowly than phosphine site exchange. Thus, there cannot be any positional exchange of SiH groups in a putative Pt(PCy$_3$)$_2$(η^2-H−SiHPh$_2$) transition state. (C) The third transition state is distinct from the other two and leads to silane

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reductive elimination. If this is also described as an η^2-silane complex, its geometry must be distinct from the transition state for phosphine site exchange.

The transition state for mutual phosphine exchange could, in principle, involve a tetrahedral twist rather than an η^2-SiHR$_2$R′ complex. A twisted structure has been observed in the bis(silyl) complex Pt(PMe$_2$Ph)$_2$-(SiPh$_2$Me)$_2$; consequently, this complex exhibits a low barrier to ligand exchange via a twisting mechanism.[38] However, we exclude this mechanism for **1-cis** and related complexes, since **1-cis** exhibits almost planar coordination of platinum in the crystal structure. Moreover, a twisting motion may also be expected to yield a trans product for such a hindered complex.

Sakaki et al. have shown by theoretical treatments of oxidative addition of Si−H bonds to Pt(PH$_3$)$_2$ that these reactions proceed via an η^2-SiHR$_3$ (R = H, Cl, Me) transition state with a minimal activation energy (<13 kJ mol^{-1}). It is also significant that the precursor complex Pt(PH$_3$)$_2$(η^2-SiHR$_3$) was bound by only 9 kJ mol^{-1} with respect to the reactants.[39] These calculations might be regarded as models for transition state C, and they would suggest that $\Delta H°$ and $\Delta H^‡$ should be close to one another, which is not in accord with the experimental data.

Considering the stability of many metal−η^2-silane complexes, the pathway for reductive elimination may involve both an intermediate and a transition state of the type Pt(PCy$_3$)$_2$(η^2-SiHR$_3$). The same applies to the pathway for mutual phosphine exchange. However, we consider that the kinetic data are not sufficiently precise to warrant splitting either reaction pathway without independent evidence for a two-step process. We have recently shown that such evidence can be obtained if the molecular design introduces asymmetry between the rotamers of the M(η^2-H−SiR$_3$) complex. Thus, (η^5-C$_5$H$_5$)-Rh{Si(OMe)$_3$}(H)(η^2-C$_2$H$_3$CO$_2{}^t$Bu) exists as two interconverting rotamers in solution. However, the hydride resonances of the two rotamers broaden at different rates, because the barriers to the Rh{η^2-H−Si(OMe)$_3$} intermediate are different for the two rotamers.[40] These experiments raise the possibility of designing a platinum silyl hydride with the necessary asymmetry to detect the presence of an Pt(η^2-H−SiR$_3$) intermediate and hence obtain direct evidence for a two-step process.

Summary

Reaction of Pt(PCy$_3$)$_2$ with hydrosilanes yields *cis*-Pt-(PCy$_3$)$_2$(SiR$_2$R′)H for all silanes that we have examined, even with silanes capable of forming bidentate ligands. The X-ray structure determined for the SiPh$_2$H complex shows considerable distortion from the ideal square-planar geometry with a P−Pt−P angle of 113.54(3)°. For alkyl- and arylsilanes, the trans isomer is formed photochemically, but thermal reaction yields *trans*-Pt-(PCy$_3$)$_2$(H)$_2$. The silanes with chlorinated substituents yield both cis and trans products on low-temperature reaction. In these cases, heating results in cis−trans isomerization. The standard enthalpy of reductive elimination has been determined as 32 ± 2 and 64 ± 9 kJ mol^{-1} for SiMe$_2$Et and SiPh$_3$ substituents, respectively. Furthermore, the SiPh$_2$H and SiEt$_2$H complexes have been shown to be energetically more stable than the SiPh$_3$ complex. Reversible thermal reductive elimination of hydrosilane and intramolecular phosphine site exchange result in complex NMR dynamics. The barriers to reaction have been determined independently for these two processes: ^{1}H EXSY methods were employed for the former, while ^{1}H line-shape analysis and ^{31}P EXSY spectroscopy allowed determination of the latter. The barriers show substantial variation with substituents at silicon increasing in the order SiMe$_2$Et < SiPh$_3$ < SiPh$_2$H. The transition states for phosphine site exchange and reductive elimination of silane may both involve η^2-silane coordination but must be distinct. A third transition state, probably of tetrahedral geometry, is implicated in the photoisomerization.

Experimental Section

General Methods. All syntheses and manipulations were carried out under argon using standard Schlenk (vacuum 10^{-2} mbar) and high-vacuum techniques (10^{-4} mbar) or in an argon-filled glovebox. Toluene, benzene, hexane, and tetrahydrofuran (Fison AR or HPLC grade) were dried over sodium/benzophenone and distilled under argon. Ethanol (Fison AR grade) was dried over magnesium metal turnings and iodine and distilled under argon. The dried solvents were stored under argon in ampules fitted with a Young ptfe tap. All deuterated solvents, [^{2}H$_6$]benzene, and [^{2}H$_8$]toluene (Goss Scientific), were dried over potassium and vacuum-distilled prior to use. All NMR tubes (Wilmad 528-PP) were either fitted with a Young tap to allow sealing under argon atmosphere or were flame-sealed under vacuum. Mass spectra were measured in a VG Autospec mass spectrometer and are quoted for ^{196}Pt, and infrared spectra were recorded on a Mattson RS FTIR spectrometer.

Chemicals were obtained from the following sources. Tricyclohexylphosphine, triisopropylphosphine, 1-hexene, molecular sieves, potassium, styrene, and the following silanes were obtained from Aldrich: HSiEt$_3$, H$_2$SiPh$_2$, H$_2$SiEt$_2$, and HSiMe$_2$-Et. The following silanes came from Gelest: Me$_3$SiOSiHCH$_3$-OSiMe$_3$, Me$_2$SiHOSiHMe$_2$, Me$_2$HSiCl, MeHSiCl$_2$, (CH$_2$=CHSiMe$_2$)$_2$O, HSiMe$_2$CH$_2$CH=CH$_2$, and HSi(OMe)CH$_2$CH=CH$_2$. Me$_3$SiO(SiMeH)OSiMe$_3$ was a gift from Dow Corning. Sodium dispersion was obtained from Strem. Potassium tetrachloroplatinate was recovered from platinum residues by a standard procedure.

Photolysis (λ > 290 nm) of samples was carried out in Pyrex NMR tubes using a Philips HPK 125 W medium-pressure mercury lamp at room temperature equipped with a water filter.

NMR Measurements. NMR spectra were recorded on Bruker AC200 (^{1}H recorded at 200.13 MHz, ^{31}P at 81.015 MHz), Bruker MSL300 (^{1}H at 300.13 MHz, ^{31}P at 121.49 MHz), Bruker AMX500 (^{1}H at 500.13 MHz, ^{31}P at 202.46 MHz), and Bruker DRX400 spectrometers (^{1}H at 400.13 MHz, ^{31}P at 161.9 MHz, ^{29}Si at 79.46 MHz, ^{195}Pt at 86.024 MHz). All ^{31}P{^{1}H} spectra were referenced to external 85% H$_3$PO$_4$. The ^{195}Pt spectra were referenced relative to the absolute frequency of 86.024 MHz at δ 0. Temperature calibration was determined using an ethylene glycol chemical shift thermometer above room temperature and a methanol thermometer at low temperature.[41]

The spin−lattice relaxation values (T_1) were measured by the standard inversion recovery method with a variable delay

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d_1.[42] The results were analyzed using the 2D Bruker package, which fits the 1D peak integrals, I, to the expression $I(t) = I^0 + P^* \exp(-t/T_1)$, where P^* is a constant.[43] Quantitative ^{31}P-{^{1}H} NMR spectra were recorded using an inverse gated pulse sequence, with a delay period of at least 10 times the acquisition time.[44] The ^{1}H NMR resonance of the Si−H group on the free silane was found to have a relaxation time of up to 8 s at room temperature. A 60 s delay between acquisitions was therefore used to allow for reliable integration analysis of the proton spectrum.

2D EXSY spectra were recorded on a Bruker DRX400 spectrometer with the *noesygp* pulse program, which uses TPPI phase cycling to generate phase-sensitive spectra.[45] The EXSY spectra were recorded as a function of mixing time in order to determine the rate for the exchange process. EXSY experiments were recorded in [$^2H_8$]toluene at several values of τ_m (0.75, 0.5, 0.4, 0.3, 0.2, 0.1 s) for complexes **1-cis** and **5-cis** at different temperatures. Recycle times for EXSY pulse sequence were set to 5 times the measured T_1 values. The total acquisition time was approximately 15 to 20 h/experiment. The 2D spectra were phased in both dimensions. Exchange during the mixing period is detected in off-diagonal cross-peaks. The volume element was determined by integration under the peaks in both dimensions. The ^{31}P spin−lattice relaxation time (T_1) was determined by the inversion recovery pulse sequence, yielding values for the resonances of 1.5 s for one phosphorus ligand and 1.6 s for the other, for both **1-cis** and **5-cis**.

Exchange Process Monitoring. For processes involving the exchange of nuclei between sites, exact rate constants can then be determined via analysis of the intensity versus mixing time profile.[33] Integration of the excited peak and exchange peak areas was first completed to obtain the data necessary. A series of values were then calculated on the basis of a differential model for a given set of exchange rate constants as a function of reaction time using Microsoft Excel 97. The calculated peak intensities were then compared to the experimental values, noting the squares of the differences.[46] The rate constants were varied until the sum of the squares of the differences between measured and simulated points was minimized. Rate constants obtained in this way were multiplied by a factor of 2 to take into account the analysis method.[47]

X-ray Structure Determination of $Pt(PCy_3)_2(H)(SiPh_2H)\cdot 1.5$(toluene). Single crystals of **1** were obtained by slow cooling of a hexane/toluene solution. Details of the data collection are given in Table 7. Data were collected on a Bruker SMART 1000 CCD diffractometer (Mo Kα radiation, λ = 0.710 73 Å). The data were integrated and corrected for Lorentz and polarization effects using SAINT.[48] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[48] No significant crystal decay was observed during data collection. The structure was solved by direct methods and refined by full-matrix least squares against F^2 using all data, with the SHELXTL software package.[48] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on Pt and Si were located from difference maps and were refined as riding atoms. All other hydrogen atoms were placed geometrically and refined as riding atoms. The structure contains 1.5 toluene molecules of solvation. One toluene molecule is ordered; the half-molecule of toluene is disordered over a crystallographic special position. No hydrogen atoms have been fixed to the disordered toluene molecule.

Table 7. Crystal Data and Structure Refinement Details for *cis*-$Pt(PCy_3)_2H(SiPh_2H)\cdot 1.5C_7H_8$ (1-cis)

empirical formula	$C_{58.5}H_{90}P_2PtSi$
fw	1078.43
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	10.335(2)
b (Å)	12.915(3)
c (Å)	22.289(5)
α (deg)	77.357(4)
β (deg)	80.503(4)
γ (deg)	67.598(3)
V (Å^3)	2672.8(9)
Z	2
ρ_{calcd} (g/cm^3)	1.340
F(000)	1126
μ(Mo Kα) (mm^{-1})	2.743
temp (K)	150(2)
no. of measd rflns	32 707
no. of unique rflns	13 077
no. of unique rflns ($I > 2\sigma(I)$)	10 881
R_{int}	0.0524
no. of data/params	13 077/584
R1[a] ($I > 2\sigma(I)$)	0.0325
wR2[a] (all data)[a]	0.0551
GOF[b]	0.993
CCDC ref no.	235452

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of data and p is the number of parameters refined.

Syntheses. The complexes $Pt(PCy_3)_2$ and $Pt(P^iPr_3)_2$ were synthesized according to the literature procedures.[49] NMR data are given in the tables except where shown.

***cis*-$Pt(PCy_3)_2(H)(SiPh_2H)$ (1-cis).** $Pt(PCy_3)_2$ (0.10 g, 0.15 mmol) was dissolved in hexane (15 mL). To this was added a solution of diphenylsilane (0.024 g, 0.13 mmol) in hexane (10 mL) dropwise with stirring. The reaction mixture was then stirred in an ice bath for 30 min. The resulting white precipitate of *cis*-$(Pt(PCy_3)_2(H)(SiPh_2H)$ was collected and washed with 3 × 10 mL of cold hexane (yield 55%). The product was recrystallized by dissolving in toluene and layering with hexane. Anal. Found: C, 62.1; H, 8.8. Calcd for $C_{48}H_{78}PtP_2Si$: C, 61.32; H, 8.36. IR: KBr, 2051, 2039 cm^{-1}; THF, 2042, 2020 (sh) cm^{-1}; ν(PtH) and ν(SiH). MS (FAB): m/z 940 (M$^+$, 22%), 756 (M$^+$ − H_2SiPh_2, 100%). ^{1}H NMR (400.13 MHz, [$^2H_8$]toluene, 293 K): δ 1.2−2.8 (66H, m, C_6H_{11}), 7.21 (2H, m, p-Ph), 7.33 (4H, m, m-Ph), 8.08 (4H, m, o-Ph), 5.37 (1H, s with satellites, SiH, J(SiH) = 164 Hz).

***cis*-$Pt(PCy_3)_2(H)(SiEt_2H)$ (2-cis).** The complex **2-cis** was prepared using the same procedure as for **1-cis**. $Pt(PCy_3)_2$ (0.10 g. 0.15 mmol) was dissolved in hexane (15 mL), the silane H_2SiEt_2 solution (0.07 g, 0.193 mmol) was added, and the resulting solution was stirred in an ice bath for 2 h. The solvent was removed, the residue was dried under vacuum, and a white solid was obtained (yield, 40%). ^{1}H NMR spectrum (300.13 MHz, [$^2H_8$]toluene, 293 K): δ 1.12−2.65 (m, PC_6H_{11} and C_2H_5), 4.34 (1H, s with satellites, SiH, J(SiH) = 131 Hz).

***trans*-$Pt(PCy_3)_2(H)(SiPh_2H)$ (1-trans) and *trans*-$Pt(PCy_3)_2(H)(SiEt_2H)$ (2-trans).** *trans*-$Pt(PCy_3)_2(H)(SiPh_2H)$ (**1-trans**) and *trans*-$Pt(PCy_3)_2(H)(SiEt_2H)$ (**2-trans**) were formed by the photolysis of the corresponding cis complexes with UV light at room temperature. Samples were made up in C_6D_6 in an NMR tube. The reaction was followed by measurement of ^{1}H NMR spectra at 10 min intervals for the first 30 min of

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photolysis and then after 2 h photolysis. ^{1}H NMR of **1-trans** (300.13 MHz, [$^2H_8$]-toluene, 300 K): δ 0.9−2.5 (m, PC_6H_{11}), 5.68 (1H, s with satellites, Si*H*, *J*(SiH) = 124 Hz). ^{1}H NMR of **2-trans** (300.13 MHz, [$^2H_8$]toluene, 300 K): δ 0.5−2.4 (m, PC_6H_{11} and C_2H_5), 4.98 (1H, s with satellites, Si*H*, *J*(SiH) = 198 Hz).

***cis*-Pt(PCy$_3$)$_2$(H)(SiEt$_3$) (3-cis).** The complex was prepared in situ in an NMR tube by reacting $Pt(PCy_3)_2$ (0.023 g) with an excess of $HSiEt_3$, in [$^2H_8$]toluene at −78 °C, and following the reaction by low-temperature NMR spectroscopy. ^{1}H NMR spectrum (300.13 MHz, [$^2H_8$]toluene, 243 K): δ 0.9−1.9 (m, PC_6H_{11} and C_2H_5).

***cis*-Pt(PCy$_3$)$_2$(H)(SiMe$_2$Et) (4-cis) and *cis*-Pt(PCy$_3$)$_2$(H)-[SiMe$_2$OCH$_2$C(Me)=CH$_2$] (10-cis).** The complexes **4-cis** and **10-cis** were prepared in situ in an NMR tube by reacting $Pt(PCy_3)_2$ with an excess of silane in [$^2H_8$]toluene at −78 °C. Attempts to obtain a solid product only yielded an oily residue. ^{1}H NMR (500.13 MHz, [$^2H_8$]toluene, 240 K) of **4-cis**: δ 0.85 (6H, d, $SiCH_3$, ^4J(PH) = 1.6 Hz, ^3J(PtH) = 26.7 Hz), 1.10−2.40 (m, PC_6H_{11} and C_2H_5). ^{1}H NMR of **10-cis** (500.13 MHz, [$^2H_8$]toluene, 250 K): δ 1.16 (6H, s, $SiCH_3$, ^3J(PtH) = 29.9 Hz), 1.20−2.40 (69H, m, PC_6H_{11}, $CH_2C(CH_3)$=CH_2), 4.52 (2H, br, $SiOCH_2$), 5.24 (1H, br, $C(CH_3)$=CH_2), 5.51 (1H, br, $C(CH_3)$=CH_2).

***cis*-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) (5-cis).** $Pt(PCy_3)_2$ (0.10 g, 0.15 mmol) was dissolved in pentane (15 mL). Triphenylsilane (0.07 g, 0.26 mmol) in pentane (10 mL) was added dropwise with stirring. The reaction mixture was stirred in an ice bath for 2 h, and a white precipitate was formed. The white solid **5-cis** was collected and washed with 3 × 10 mL of cold pentane (yield 0.70 g, 47%) Anal. Found: C, 63.8; H, 8.1. Calcd for $C_{54}H_{82}P_2SiPt$: C, 63.1; H, 8.1. MS (FAB): *m/z* 1016 {M^+, 79%}. ^{1}H NMR (500.13 MHz, [$^2H_8$]toluene, 250 K): δ 1.12−2. 50 (66H, m, PC_6H_{11}), 7.20−8.40 (15H, m, C_6H_5). ^{195}Pt NMR spectrum (86.024 MHz, 295 K): δ −5205 (dd, J_{PtP^a} = 1555, J_{PtP^b} = 2650 Hz (see Scheme 1)). IR (KBr): ν(PtH) 2078 cm^{-1}.

***cis*-Pt(PCy$_3$)$_2$(H)(SiMe$_2$CH$_2$CH=CH$_2$) (6-cis).** **6-cis** was prepared using the same procedure as for *cis*-$Pt(PCy_3)_2(H)(SiPh_3)$. $Pt(PCy_3)_2$ (0.43 g, 0.57 mmol) and $HSiMe_2CH_2CH$=CH_2 (0.33 μL, 2.27 mmol) were dissolved in hexane and stirred in an ice bath for 5 h. The white solid that formed was collected and washed with 3 × 10 mL of cold hexane (yield 0.20 g, 41%). MS (FAB): *m/z* 855 {M^+, 79%}. ^{1}H NMR (500.13 MHz, [$^2H_8$]toluene, 240 K): δ 1.05 (6H, d, $SiCH_3$, ^4J(PH) = 1.6 Hz, ^3J(PtH) = 26.5 Hz), 1.10−2.30 (66H, m, PC_6H_{11}), 2.41 (2H, d, $SiCH_2CH$=CH_2, *J*(HH) = 8.3 Hz, ^3J(PtH) = 30.8 Hz), 5.16 (1H, m, $SiCH_2CH$=CH_2), 5.25 (1H, m, $SiCH_2CH$=CH_2), 6.52 (1H, m, $SiCH_2CH$=CH_2). IR (KBr): ν(PtH) 2085 cm^{-1}.

***trans*-Pt(PCy$_3$)$_2$(H)(SiPh$_3$) and *trans*-Pt(PCy$_3$)$_2$(H)-(SiMe$_2$CH$_2$CH=CH$_2$) (5-trans and 6-trans).** The photolysis reactions were carried out as for **1-trans**, but the photolysis was carried out at 195 K and the spectra were recorded at 250 K after 4 h of irradiation.

***cis*-Pt(PCy$_3$)$_2$(H)(SiPh$_2$OSiPh$_2$H) (7-cis).** **7-cis** was prepared by reacting $Pt(PCy_3)_2$ and $HSiPh_2OSiPh_2H$ in a 1:1 ratio in C_6D_6 in an NMR tube at room temperature. ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ 0.71−2.79 (66H, m, PC_6H_{11}), 6.06 (1H, s, with satellites, Si*H*, *J*(SiH) = 213 Hz), 7.04−7.15 (20H, m, SiC_6H_5). When a 2:1 ratio of $Pt(PCy_3)_2$ and $HSiPh_2OSiPh_2H$ was used in the reaction, **7-cis** was again the only product. Chelated disilyl complexes or dimeric species were not detected.

***cis*-Pt(PCy$_3$)$_2$(H)(Me$_2$SiOSiHMe$_2$) (8-cis) and *cis*-Pt(PCy$_3$)$_2$(H){SiMe(OSiMe$_3$)$_2$} (9-cis).** **8-cis** and **9-cis** were prepared by reacting $Pt(PCy_3)_2$ (0.026 g) and 1 equiv of $Me_2HSiOSiHMe_2$ and $HSiMe(OSiMe_3)_2$ in [$^2H_8$]toluene in an NMR tube at −15 °C. ^{1}H NMR of **8-cis** (300.13 MHz, [$^2H_8$]toluene, 268 K): δ 0.43 (6H, d, 6 Hz, $SiHMe_2$), 0.8−2.5 (m, PC_6H_{11} and CH_3), 5.29 (1H, m with satellites, Si*H*, *J*(SiH) = 198 Hz). ^{1}H NMR of **9-cis** (300.13 MHz, [$^2H_8$]toluene, 225 K): δ 0.48 (s, 9H, $Si(CH_3)_3$), 0.8−2.1 (m, PC_6H_{11} and CH_3).

***cis*-Pt(PCy$_3$)$_2$(H)[Si(OMe)$_2$CH$_2$CH=CH$_2$] (11-cis).** **11-cis** was prepared by reacting $Pt(PCy_3)_2$ and excess $HSi(OMe)_2CH_2CH$=CH_2 in C_6D_6 in an NMR tube at room temperature. Attempts to isolate this product only produced an oily residue. ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ 0.80−2.77 (66H, m, PC_6H_{11}), 2.40 (2H, d, $SiCH_2CH$=CH_2, *J*(HH) = 8.9 Hz), 3.84 (6H, s, $Si(OCH_3)$), 5.13−5.30 (2H, m, $SiCH_2CH$=CH_2), 6.50 (1H, m, $SiCH_2CH$=CH_2).

***cis*-Pt(PCy$_3$)$_2$(H)(SiR$_2$R′) (12-cis−14-cis).** The cis platinum silyl hydride complexes **12-cis−14-cis** were prepared by the reaction of $Pt(PCy_3)_2$ with chlorosilanes in [$^2H_8$]toluene. In a typical reaction, excesses of $HSiMe_2Cl$, $HSiMeCl_2$, and $HSiCl_3$ were added by vacuum transfer to cold (195 K) solutions of $Pt(PCy_3)_2$ in NMR sample tubes. When these samples were warmed, white precipitates formed of the *trans*-$Pt(PCy_3)_2(H)(SiR_2R')$ complexes **12-trans−14-trans**. ^{1}H NMR (300.13 MHz, [$^2H_8$]toluene, 295 K) for **12-cis**: δ 0.7−2.1 (m, PC_6H_{11} and CH_3). ^{1}H NMR (300.13 MHz, [$^2H_8$]toluene, 235 K) for **13-cis**: δ 1.1−2.5 (m, PC_6H_{11} and CH_3). ^{1}H NMR (300.13 MHz, [$^2H_8$]toluene, 270 K) for **14-cis**: δ 0.6−2.5 (m, PC_6H_{11}).

^{1}H NMR (300.13 MHz, [$^2H_8$]toluene, 295 K) for **12-trans**: δ 0.7−2.6 (m, PC_6H_{11} and CH_3). ^{1}H NMR (300.13 MHz, [$^2H_8$]toluene, 295 K) for **13-trans**: δ 1.2−3.0 (m, PC_6H_{11} and CH_3). ^{1}H NMR (300.13 MHz, [$^2H_8$]toluene, 295 K) for **14-trans**: δ 1.2−3.1 (m, PC_6H_{11}).

Deuterated Triphenylsilane. The compound was prepared with a slight variation from the literature procedure.[50] Triphenylchlorosilane (0.5 g) was dissolved in 50 mL of dry ether in a three-necked flask equipped with a reflux condenser, mechanical stirrer, and argon inlet, and a suspension of $LiAlD_4$ (0.15 g) in dry ether was added dropwise over a period of 30 min. When the addition was complete, the mixture was stirred and heated to reflux. Dry benzene was added dropwise to the reaction flask, and simultaneously ether was distilled off until the distillation temperature reached 351 K. The mixture was allowed to settle, and benzene was siphoned off under argon pressure. The solvent was pumped off from the benzene solution, and the residue was dried under vacuum to give $DSiPh_3$. Full deuteration was indicated by the total disappearance of the Si−H septet at δ 5.5 and the shift of the ν(Si−H) band from 2124 to 1546 cm^{-1}.

Measurement of Equilibrium Parameters for Silane Dissociation: 5-cis, 6-cis, and 4-cis. NMR samples of **5-cis**, **6-cis**, and **4-cis** were prepared in [$^2H_8$]toluene and kept in ice prior to recording the NMR spectra. This precaution was required to prevent excessive decomposition to *trans*-$Pt(PCy_3)_2(H)_2$, which occurs at room temperature. Quantitative ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded initially at 290 K and subsequently at 5 K intervals to 310 K. The relative concentrations of **5-cis**, [$HSiPh_3$], and [$Pt(PCy_3)_2$] were obtained from the integrals of the hydride resonance of **5-cis**, the Si−H resonance of $HSiPh_3$ in the ^{1}H NMR spectra, and the integrals of the phosphorus resonance of **5-cis** and $Pt(PCy_3)_2$. The equilibrium constants for the dissociation of **5-cis** and **6-cis** were calculated, and the thermodynamic parameters were determined. An NMR sample of *cis*-$Pt(PCy_3)_2(H)(SiMe_2Et)$ (**4-cis**) was prepared by adding a slight excess of the silane $HSiMe_2Et$ to a [$^2H_8$]toluene solution of $Pt(PCy_3)_2$, where the SiH:Pt ratio was 1.06:1.00. Equilibrium constants for dissociation were obtained for **4-cis**, as for **5-cis** and **6-cis**.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray study, and bond distances and angles for **1-cis**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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