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Cis and Trans Isomers of $Pt(SiHAr_2)_2(PR_3)_2$ (R = Me, Et) in the Solid State and in Solutions

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Summary: trans-$Pt(SiHPh_2)_2(PMe_3)_2$ (**1**) *is prepared from the reaction of* H_2SiPh_2 *with cis-*$PtEt_2(PMe_3)_2$ *and is characterized by X-ray crystallography. Dissolution of* **1** *in THF-*d_8 *or* CD_2Cl_2 *causes its isomerization into cis-*$Pt(SiHPh_2)_2(PMe_3)_2$*, which is equilibrated to* **1** *in the solutions. Temperature-dependent* ^1H *NMR spectra of a mixture of the isomers provided thermodynamic parameters for the trans to cis isomerization,* $\Delta H° = 5.7(3)$ kJ mol^{-1} *and* $\Delta S° = 6.7(7)$ J mol^{-1}K^{-1} *in* CD_2Cl_2 *and* $\Delta H° = 3.8(2)$ kJ mol^{-1} *and* $\Delta S° = 3.5(6)$ J mol^{-1}K^{-1} *at 298 K in THF-*d_8*, respectively. The reactions of* H_2SiAr_2 *with* $Pt(PEt_3)_4$ *give cis-*$Pt(SiHAr_2)_2(PEt_3)_2$ (**2**, *Ar* = C_6H_5; **3**, *Ar* = C_6H_4F*-p), which are considerably more stable than the trans isomers in* CD_2Cl_2 *(ca. 96:4 in an equilibrated* CD_2Cl_2 *solution of* $Pt(SiHPh_2)_2(PEt_3)_2$ *at room temperature).*

Introduction

Platinum complexes with organosilyl ligands[1−7] have been widely studied because the complexes are often involved as crucial intermediates in Pt complex catalyzed synthetic reactions such as hydrosilylation of alkenes,[8] bissilylation of alkenes and dienes,[9] and dehydrocoupling of organosilanes to form Si−Si or Si−C bonds.[10] Most of the mononuclear bis(organosilyl)platinum complexes and alkyl- or hydrido(organosilyl)platinum(II) complexes bearing two phosphine ligands

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(1) Bis(silyl)platinum(II) complexes: (a) Chatt, J.; Eaborn, C.; Ibekwe, S. *J. Chem. Soc., Chem. Commun.* **1966**, 700. (b) Chatt, J.; Eaborn, C.; Kapoor, P. N. *J. Chem. Soc. (A)* **1970**, 881. (c) Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. (A)* **1970**, 1343. (d) Holmes-Smith, R. D.; Stobart, S. R.; Cameron, T. S.; Jochem, K. *J. Chem. Soc., Chem. Commun.* **1981**, 937. (e) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411. (f) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. (g) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447. (h) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227. (i) Grundy, S. L.; Holmes-Smith, R. D.; Stobart, S. R.; Williams, M. A. *Inorg. Chem.* **1991**, *30*, 3333. (j) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917. (k) Michalczyk, M. J.; Recatto, C. A.; Calabrese, J. C.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7955. (l) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1993**, *115*, 2373. (m) Ozawa, F.; Kamite, J. *Organometallics* **1997**, *17*, 55630. (n) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1997**, *17*, 55599.

(2) Alkyl(silyl)platinum(II) complexes: (a) Ozawa, F.; Hikida, T.; Hayashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2844. (b) Ozawa, F.; Hikida, T. *Organometallics* **1996**, *15*, 4501. (c) Ozawa, F.; Hikida, T.; Hasebe, K.; Mori, T. *Organometallics* **1998**, *17*, 1018. (d) Gilges, H.; Kickelbick, G.; Schubert, U. *J. Organomet. Chem.* **1997**, *548*, 57. (e) Gilges, H.; Schubert, U. *Organometallics* **1998**, *17*, 4760.

(3) Silyl(germyl)platinum(II) complexes: Glockling, F.; Hooton, K. A. *J. Chem. Soc. (A)* **1967**, 1066.

(4) Hydrido(silyl)platinum(II) complexes: (a) Baird, M. C. *J. Inorg. Nucl. Chem.* **1967**, 367. (b) Eaborn, C.; Pidcock, A.; Ratcliff, B. *J. Organomet. Chem.* **1972**, *43*, C5. (c) Eaborn, C.; Tune, D. J.; Walton, D. R. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2255. (d) Eaborn, C.; Ratcliff, B.; Pidcock, A. *J. Organomet. Chem.* **1974**, *65*, 181. (e) Azizian, H.; Dixon, K. R.; Eaborn, C.; Pidcock, A.; Shuaib, N. M.; Vinaixa, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1020. (f) Latif, L. A.; Eaborn, C.; Pidcock, A. P.; Weng, N. S. *J. Organomet. Chem.* **1994**, *474*, 217. (g) Ebsworth, E. A. V.; Marganian, V. M.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 1167. (h) Koizumi, T.; Osakada, K.; Yamamoto, T. *Organometallics* **1997**, *16*, 6014. (i) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635.

(5) Halogeno(silyl)platinum(II) and alkoxo(silyl)platinum complexes: (a) Yamashita, H.; Hayashi, T.; Kobayashi, T.; Tanaka, M.; Goto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4417. (b) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1993**, *12*, 988. (c) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1989**, *8*, 1369. (d) Goikhman, R.; Aizenberg, M.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 10894.

(6) Other mononuclear silylplatinum complexes: (a) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667. (b) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517. (c) Levy, C. J.; Puddephatt, R. J.; Vittal, J. J. *Organometallics* **1994**, *13*, 1559 (d) Levy, C. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 2108. (e) Shimada, S.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8289.

(7) Dinuclear Pt complexes with bridging silyl or silylene ligands: (a) Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murray, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 659. (b) Ciriano, M.; Green, M,; Howard, J. A. K.; Proud, J.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1978**, 801. (c) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068. (d) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1989**, 577. (e) Anderson, A. B.; Shiller, P.; Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *Organometallics* **1989**, *8*, 2320. (f) Braunstein, P.; Knorr, M.; Hirle, B.: Reinhard, G.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1583. (g) Knorr, M.; Braunstein, P.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1995**, *14*, 4910. (h) Knorr, M.; Hallauer, E.; Huch, V.; Veith, M.; Braunstein, P. *Organometallics* **1996**, *15*, 3868. (i) Braunstein, P.; Knorr, M. *J. Organomet. Chem.* **1995**, *500*, 21.

(8) Reviews: (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25. (b) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (c) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253. (d) *Comprehensive Handbook on Hydrosilylation;* Marciniec, B., Ed.; Pergamn Press: Oxford, 1992.

(9) (a) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31. (b) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280. (c) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992**, *11*, 2353. (d) Sakaki, S.; Ogawa, M.; Musashi, Y. *J. Organomet. Chem.* **1997**, *535*, 25. See also: Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. Tamao, K.; Okazaki, S.; Kumada, M.; *J. Organomet. Chem.* **1978**, *146*, 87. Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. Sakurai, H.; Eriyama, Y.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1984**, *264*, 229. Seyferth, D.; Goldman, E. W.; Escudié, J. *J. Organomet. Chem.* **1984**, *271*, 337. Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948. Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495.

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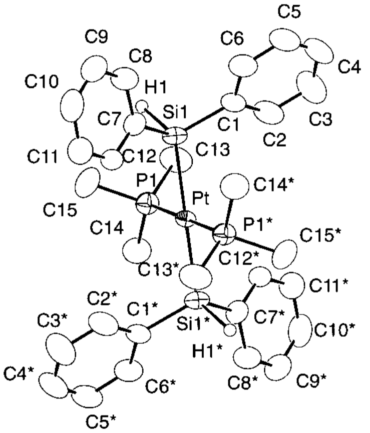
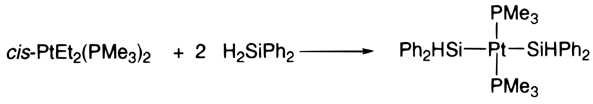


Figure 1. ORTEP drawing of *trans*-$Pt(SiHPh_2)_2(PMe_3)_2$ (**1**) (50% probability). The molecule has a crystallographic point of symmetry at the Pt center position. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected bond lengths (Å) and angles (deg): Pt−P1 2.287(2), Pt−Si1 2.407(2), P1−Pt−P1* 180.0, P1−Pt−Si1 86.97(8), P1*−Pt−Si1 93.03(8), Si1−Pt−Si1* 180.0.

favor cis structure of the square-planar coordination. There have been only a few exceptional complexes such as *trans*-$PtH(SiXH_2)\{P(C_6H_{11})_3\}(X = H, Cl)^{4g}$ and *trans*-$PtMe(SiPh_3)L_2$ (L = PMe_2Ph, $PMePh_2$),[2a−c] the latter of which are readily turned, upon reaction with CO, into the thermodynamically more stable cis isomer. Preferential cis geometry of the bis(organosilyl)platinum complexes was attributed to a large trans effect of the organosilyl ligand,[1a] while precise determination of relative thermodynamic stability between cis and trans isomers has not been reported so far. Here we report isolation and crystal structure of *trans*-$Pt(SiHPh_2)_2(PMe_3)_2$ as well as its trans−cis isomerization in solutions.

Results and Discussion

H_2SiPh_2 reacts with *cis*-$PtEt_2(PMe_3)_2$ in a 2:1 molar ratio to give *trans*-$Pt(SiHPh_2)_2(PMe_3)_2$ (**1**) at room temperature accompanied by evolution of ethane. Complex **1** is isolated by recrystallization of the product and characterized by X-ray crystallography. The molecule has a square-planar coordination around the Pt center with two mutually trans $SiHPh_2$ ligands, as shown in Figure 1. The Pt−Si bond is elongated (2.407(2) Å) by a large trans influence of an $SiHPh_2$ ligand at the trans position. The reactions of diorganosilanes with dialkylpalladium and -platinum complexes with phosphine ligands also gave bis(organosilyl) complexes of the group 10 metals but with cis geometry.[11,12] The ^1H and $^{31}P\{^1H\}$ NMR spectra of **1** in benzene-d_6 contain signals


$$cis\text{-}PtEt_2(PMe_3)_2 + 2\ H_2SiPh_2 \longrightarrow Ph_2HSi-\overset{PMe_3}{\underset{PMe_3}{Pt}}-SiHPh_2 \quad (1)$$

(**1**, isolated)

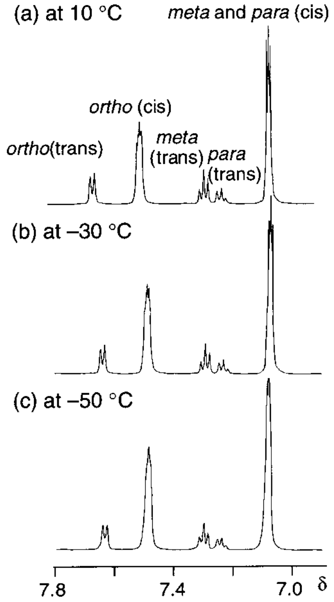
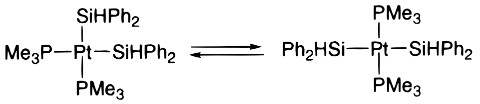


Figure 2. Temperature-dependent change of the ^1H NMR spectra (phenyl hydrogen region) of the equilibrated mixture of *cis*- and *trans*-$Pt(SiHPh_2)_2(PMe_3)_2$ in THF-d_8.

not only of **1** but also of its isomer generated in the solution. The isomer is assigned to *cis*-$Pt(SiHPh_2)_2(PMe_3)_2$ on the basis of a larger $J(HPt)$ of the SiH hydrogen signal (74 Hz) and a smaller $J(PtP)$ (1659 Hz) value than **1** ($J(HPt) = 25$ Hz, $J(PtP) = 2402$ Hz) as well as the $J(PtP)$ similar to those of already reported *cis*-$Pt(SiR_3)_2(PR'_3)_2$ type complexes.[1c,d,h] Although a benzene-d_6 solution of $Pt(SiHPh_2)_2(PMe_3)_2$ contains almost equal amounts of trans and cis isomers, the ^1H NMR spectra of the complex in THF-d_8 and in CD_2Cl_2 exhibit the presence of a larger amount of the cis isomer than **1** (ca. 77:23 in CD_2Cl_2 and 74:26 in THF-d_8 at 25 °C). The ^1H NMR spectra of the mixture at −50 to 10 °C in THF-d_8 show a temperature-dependent change in relative peak intensities between the isomers, as depicted in Figure 2, indicating that the cis and trans isomers are equilibrated as shown in eq 2. The equilibration of the trans and cis form of $Pt(SiHPh_2)_2(PMe_3)_2$ is observed also in CD_2Cl_2, whereas a benzene solution of the complex shows negligible temperature-dependent change in the signal intensity possibly due to slow isomerization and/or a small $\Delta G°$ of the reaction in benzene. Figure 3 summarizes the equilibrium constants of the reaction in the temperature range −50 to 10 °C, which provides the thermodynamic parameters of $\Delta H° = 5.7(3)$ kJ mol^{-1} and $\Delta S° = 6.7(7)$ J mol^{-1} K^{-1} in CD_2Cl_2 and $\Delta H° = 3.8(2)$ kJ mol^{-1} and $\Delta S° = 3.5(6)$ J mol^{-1} K^{-1} at 298 K in THF-d_8, respectively.


$$Me_3P-\overset{SiHPh_2}{\underset{PMe_3}{Pt}}-SiHPh_2 \rightleftharpoons Ph_2HSi-\overset{PMe_3}{\underset{PMe_3}{Pt}}-SiHPh_2 \quad (2)$$

1

Trans−cis isomerization of square-planar organopalladium(II) and -platinum(II) complexes has been reported to occur via dissociation of auxiliary phosphine ligands and ensuing isomerization of three-coordinated intermediates or an associative pathway involving Berry's pseudorotation.[13−15] Addition of PMe_3 to a CD_2Cl_2

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[10] (a) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1970**, *23*, C7. (b) Uchimaru, Y.; Mouneer, A.; Sayed, M. E.; Tanaka, M. *Organometallics* **1993**, *12*, 2065. (c) Uchimaru, Y.; Brandl, P.; Tanaka, M.; Goto, M. *J. Chem. Soc., Chem. Commun.* **1993**, 744.

[11] Eaborn, C.; Pidcock, A.; Ratcliff, B. *J. Organomet. Chem.* **1974**, *66*, 23.

[12] Schubert, U.; Müller, C. *J. Organomet. Chem.* **1989**, *373*, 165.

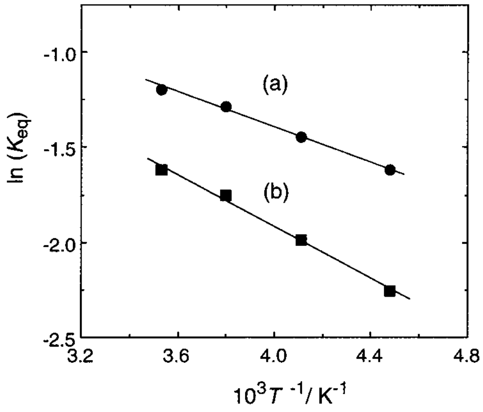
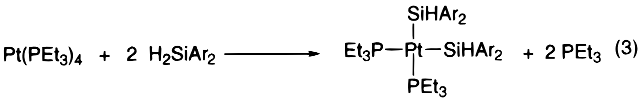


Figure 3. van't Hoff plots of isomerization of **1** to *cis*-Pt$(SiHPh_2)_2(PMe_3)_2$ (a) in THF-d_8 and (b) in CD_2Cl_2.

solution of $Pt(SiHPh_2)_2(PMe_3)_2$ (PMe_3:Pt = ca. 1:1) led to broadening of the $^{31}P\{^1H\}$ NMR signals. Although the ^1H NMR signal of SiH hydrogens of the trans and cis isomers lost P−H coupling, neither broadening nor coalescence of the signals was observed at the temperature range −30 to 30 °C. Thus, the trans−cis isomerization is not significantly accelerated by addition of PMe_3 and probably does not involve the associative pathway.

Although isolation of *cis*-$Pt(SiHPh_2)_2(PMe_3)_2$ as single crystals was not feasible, *cis*-$Pt(SiHAr_2)_2(PEt_3)_2$ (**2**, Ar = C_6H_5, **3**; Ar = C_6H_4F-*p*) were obtained from the reaction of H_2SiAr_2 with $Pt(PEt_3)_4$, as shown in eq 3 and characterized by X-ray crystallography and NMR spectroscopy. Figure 4 depicts the molecular structure of **2**,



$$Pt(PEt_3)_4 + 2\ H_2SiAr_2 \longrightarrow Et_3P{-}\overset{\displaystyle SiHAr_2}{\underset{\displaystyle PEt_3}{Pt}}{-}SiHAr_2 + 2\ PEt_3 \quad (3)$$

2: Ar = C_6H_5;
3: Ar = C_6H_4F-*p*

which has a distorted square-planar coordination around the metal center with two diphenylsilyl ligands at cis positions. Complex **3** has similar cis coordination around the Pt center. The NMR spectra of **2** and **3** contain the signals of their trans isomers in a small intensity. The ^1H NMR signal ratios of the *trans*- and *cis*-$Pt(SiHPh_2)_2(PEt_3)_2$ are 4:96 to 6:94 in the temperature range −30 to 25 °C. Precise equilibrium constants and thermodynamic parameters were not obtained due to small peak intensity of the signal of the trans isomer.

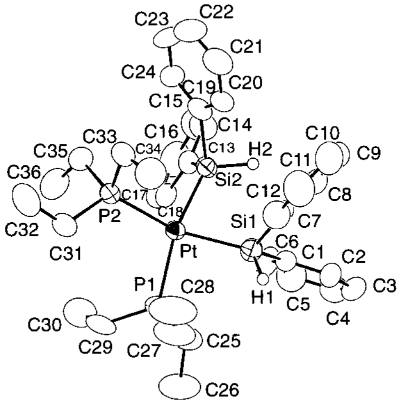


Figure 4. ORTEP drawing of *cis*-$Pt(SiHPh_2)_2(PEt_3)_2$ (**2**) (50% probability). Selected bond lengths (Å) and angles (deg): Pt−P1 2.362(3), Pt−P2 2.355(3), Pt−Si1 2.374(3), Pt−Si2 2.359(3), P1−Pt−P2 103.9(1), P1−Pt−Si1 87.9(1), P1−Pt−Si2 157.1(1), P2−Pt−Si1 156.6(1), P2−Pt−Si2 94.0(1), Si1−Pt−Si2 80.7(1). Selected bond lengths (Å) and angles (deg) of **3**: Pt−P1 2.373(3), Pt−P2 2.356(3), Pt−Si1 2.355(3), Pt−Si2 2.369(3), P1−Pt−P2 99.4(1), P1−Pt−Si1 94.74(9), P1−Pt−Si2 165.48(9), P2−Pt−Si1 162.2(1), P2−Pt−Si2 88.7(1), Si1−Pt−Si2 79.91(9).

The present study has provided crystallographic results of *cis*- and *trans*-$Pt(SiHAr_2)_2(PR_3)_2$ type complexes as well as their equilibrium in solutions. *cis*-$Pt(SiHPh_2)_2(PEt_3)_2$ is much more stable than the trans isomer. Use of PMe_3 as the auxiliary ligand has resulted in a reduction of difference in thermodynamic stability between the cis and trans isomers and enabled isolation and full characterization of **1** having the trans structure.

Experimental Section

General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under argon or nitrogen atmosphere. *cis*-$PtEt_2(PMe_3)_2$ and $Pt(PEt_3)_4$ were prepared according to the literature method.[16] NMR spectra (^1H, 400 MHz; ^{31}P, 160 MHz; ^{13}C, 100 MHz) were recorded on a JEOL EX-400 spectrometer. Peak positions of the ^{31}P NMR were referenced to external 85% H_3PO_4. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder and with a Yanaco YS-10 ion chromatograph.

Preparation of *trans*-$Pt(SiHPh_2)_2(PMe_3)_2$ (1). To a hexane (6 mL) solution of *cis*-$PtEt_2(PMe_3)_2$ (522 mg, 1.3 mmol) was added H_2SiPh_2 (498 mg, 2.7 mmol) at room temperature. A colorless solid began to precipitate after 1 h. Stirring of the reaction mixture was continued for 12 h. The resulting solid was collected by filtration, washed with hexane, and dried in vacuo. Recrystallization from toluene−hexane gave **1** as colorless crystals (827 mg, 90%). The NMR data were obtained in a mixture of **1** and its cis isomer (ca. 50:50 in benzene-d_6, 23:77 in CD_2Cl_2, and 26:74 in THF-d_8 at 25 °C). ^1H NMR (benzene-d_6, 25 °C): δ 0.95 (br, PMe_3 (cis)), 1.16 (br, PMe_3 (trans), J(PtH) = 29 Hz), 5.29 (t, SiH (trans), J(PH) = 13 Hz, J(PtH) = 25 Hz), 5.60 (apparent triplet due to multispin system, SiH (cis), J(PtH) = 74 Hz), 7.13−7.22 (m, meta (trans and cis) and para (cis)), 7.30 (t, para (trans), J(HH) = 7 Hz), 7.88 (d, ortho (cis), J(HH) = 7 Hz), 7.94 (d, ortho (trans), J(HH) = 7 Hz); (CD_2Cl_2, 25 °C) δ 1.29 (br, PMe_3 (trans)), 1.35 (br, PMe_3 (cis)), 4.81 (t, SiH (trans), J(PH) = 13 Hz, J(PtH) not determined due to overlapping with the signal of cis isomer), 4.90 (apparent triplet due to multispin system, SiH (cis), J(PtH) = 76 Hz), 7.14 (m, meta and para (cis)), 7.27 (t, para (trans), J = 7 Hz), 7.32 (t, meta (trans), J = 7 Hz), 7.52 (m, ortho (cis)), 7.67 (d, ortho (trans), J = 7 Hz); (THF-d_8, 25 °C) δ 1.36 (br, PMe_3 (cis and trans)), 4.90 (SiH (trans), J not

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(13) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185.

(14) (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *J. Organomet. Chem.* **1979**, *168*, 375. (b) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457. (c) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (d) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (e) Alibrandi, G.; Scolaro, L. M.; Romeo, R. *Inorg. Chem.* **1991**, *30*, 4007. (f) Minniti, D. *Inorg. Chem.* **1994**, *33*, 2631. (g) Casado, A. L.; Casares, J. A.; Espinet, P. *Organometallics* **1997**, *16*, 5730.

(15) Bis(triorganostanyl)platinum complexes and hydrido(triarylsilyl)platinum complexes with two phosphine ligands were reported to undergo rapid intramolecular exchange of the two stannyl or two phosphine ligands via a tetrahedral transition state. Although the transition state may also cause intramolecular cis−trans isomerization, the trans−cis isomerization was not observed in the complexes. See: ref 4e and Obora, Y.; Tsuji, Y.; Nishiyama, K.; Ebihara, M.; Kawamura, T. *J. Am. Chem. Soc.* **1996**, *118*, 10922.

(16) (a) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411. (b) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 122.

Table 1. Crystallographic Data and Details of Refinement of 1−3

	1	**2**	**3**
chemical formula	$C_{30}H_{40}P_2PtSi_2$	$C_{36}H_{52}P_2PtSi_2$	$C_{36}H_{48}F_4P_2PtSi_2$
fw	713.52	797.59	869.59
cryst syst	monoclinic	triclinic	triclinic
space group	*C*2/c (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	23.027(5)	12.168(4)	11.581(2)
b, Å	8.957(4)	16.896(6)	16.895(2)
c, Å	15.943(6)	9.952(4)	9.866(1)
α, deg		90.12(3)	96.63(1)
β, deg	108.51(2)	113.75(2)	93.39(1)
γ, deg		92.97(3)	86.28(1)
V, $Å^3$	3117(1)	1869(1)	1910.9(5)
Z	4	2	2
μ, cm^{-1}	47.41	39.61	38.95
F(000)	1424	808	872
D_{calcd}, g cm^{-3}	1.521	1.418	1.512
crystal size, mm × mm × mm	0.5 × 0.7 × 0.9	0.5 × 0.6 × 0.8	0.3 × 0.4 × 0.6
2*θ* range, deg	5.0−55.0	5.0−50.0	5.0−55.0
no. of unique reflns	3804	5785	6734
no. of used reflns ($I \geq 3\sigma(I)$)	2459	4366	5942
no. of variables	160	370	406
$R\ (F_o)^a$	0.032	0.045	0.044
$R_w\ (F_o)^a$	0.036	0.042	0.058

[a] Weighting scheme, $[\{\sigma(F_o)\}^2]^{-1}$.

estimated due to overlapping with the SiH signal of trans isomer), 5.00 (br, SiH (cis), *J*(PtH) = 75 Hz), 7.04 (m, meta and para (cis)), 7.20 (t, para (trans), *J*(HH) = 7 Hz), 7.26 (t, meta (trans), *J*(HH) = 7 Hz), 7.49 (d, ortho (cis), *J*(HH) = 7 Hz), 7.64 (d, ortho (trans), *J*(HH) = 7 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): *δ* 18.6 (br, $P(CH_3)_3$), 127.2 (ortho (cis), *J*(PtC) = 29 Hz), 127.5 (para (cis)), 127.6 (ortho (trans), *J*(PtC) = 22 Hz), 137.2 (meta (cis), *J*(PC) = 13 Hz), 143.1 (ipso (cis), *J*(PC) and *J*(PtC) not determined); (benzene-d_6, 25 °C) *δ* 18.0 (br, $P(CH_3)_3$), 127.3 (para (cis and/or trans), 137.3 (meta (trans), *J*(PtC) = 15 Hz), 137.5 (meta (cis), *J*(PC) = 13 Hz), 143.2 (ipso (cis), *J*(PC) = 16 Hz), 145.3 (ipso (trans), *J* (PtC) = 24 Hz). Several signals were not observed due to overlapping with those of the solvent or low peak intensity. $^{31}P\{^1H\}$ NMR (benzene-d_6, 25 °C): *δ* −24.0 (trans, *J*(Pt−P) = ca. 2400 Hz), −17.0 (cis, *J*(PtP) = ca. 1640 Hz); (CD_2Cl_2, 25 °C) *δ* −22.8 (trans, *J*(Pt−P) = 2402 Hz), −15.8 (cis, *J*(PtP) = 1659 Hz). Anal. Calcd for $C_{30}H_{40}P_2Si_2Pt$: C, 50.48; H, 5.65. Found: C, 50.17; H, 5.53.

Preparation of *cis*-Pt(SiHAr$_2$)(PEt$_3$)$_2$ (2, Ar = Ph; 3, Ar = C$_6$H$_4$F-*p*). To a pentane (5 mL) solution of $Pt(PEt_3)_4$ (1.39 g, 2.1 mmol) was added H_2SiPh_2 (777 mg, 4.2 mmol) at room temperature. The yellow solution turned colorless within a short time, and a colorless solid was soon generated on stirring. After 3 h the resulting solid product was collected by filtration, washed with pentane, and dried in vacuo (1.54 g, 93%). The NMR spectrum of the product contained signals of trans and cis isomers in a 6:94 ratio. Recrystallization from toluene−hexane afforded single crystals of *cis*-$Pt(SiHPh_2)_2(PEt_3)_2$ (**2**). ^1H NMR (benzene-d_6): *δ* 0.75−0.82 (m, 18H, *J*(PH) = 16 Hz, *J*(HH) = 7 Hz, P−CH_2−C*H*$_3$, (cis and trans)), 1.58−1.66 (m, 12H, P−C*H*$_2$−CH_3, (cis)), 1.86−1.88 (m, 12H, P−C*H*$_2$−CH_3 (trans)), 5.46 (t, 2H, SiH (trans), *J*(PH) = 11 Hz), 5.70 (apparent triplet due to multispin system, 2H, Si−H (cis), *J*(PH) = 16 Hz, *J*(PtH) = 69 Hz), 7.12−7.20 (m, 12H, meta and para (cis) and meta (trans)), 7.30 (t, 4H, para (trans), *J*(HH) = 7 Hz), 7.80 (d, 8H, *J*(HH) = 7 Hz, ortho (cis)), 7.96 (d, 8H, *J*(HH) = 7 Hz, ortho (trans)). $^{13}C\{^1H\}$ NMR (benzene-d_6, signals of cis form): *δ* 8.6 (CH_3, *J*(PtC) = 15 Hz), 18.2 (CH_2, dd, *J*(PC) = 13 and 2 Hz), 127.2 (ortho), 127.4 (para), 137.4 (meta, *J*(PtC) = 20 Hz), 143.3 (ipso, *J*(PC) = 4 Hz). $^{31}P\{^1H\}$ NMR (benzene-d_6): *δ* 15.7 (cis, *J*(PtP) = 1710 Hz) and 6.77 (trans, *J*(PtP) = 2441 Hz). Anal. Calcd for $C_{36}H_{52}P_2Si_2Pt$: C, 54.18; H, 6.56. Found: C, 53.80; H, 6.28.

Complex **3** was prepared analogously (86%). ^1H NMR (benzene-d_6, signals of cis form): *δ* 0.71 (td, 18H, *J*(PH) = 15 Hz, *J*(HH) = 7 Hz, P−CH_2−C*H*$_3$), 1.53 (m, 12H, P−C*H*$_2$−CH_3), 5.45 (apparent triplet due to multispin system, 2H, *J*(PtH) = 69 Hz, Si−H), 6.86 (dd, 8H, *J*(HH) = 8 Hz, *J*(FH) = 8 Hz, meta), 7.52 (dd, 8H, *J*(HH) = 8 Hz, *J*(FH) = 7 Hz, ortho). $^{31}P\{^1H\}$ NMR (benzene-d_6): *δ* 15.3 (cis, *J*(PtP) = 1694 Hz) and 6.6 (trans, *J*(PtP) = 2418 Hz). Anal. Calcd for $C_{36}H_{48}F_4P_2Si_2Pt$: C, 49.70; H, 5.56; F, 8.74. Found: C, 49.65; H, 5.65; F, 8.44.

Equilibrium Constants Measurement. A sealable NMR tube was charged with complex **1** (ca. 25 mg). CD_2Cl_2 (ca. 0.40 mL) was vacuum transferred to the tube. After three freeze−pump−thaw cycles the tube was sealed. The NMR spectra were recorded at −50, −30, −10, and 10 °C. Molar ratios of **1** and its cis isomer in equilibrated mixtures were determined by comparison of the peak area of the ortho phenyl hydrogens. *K* = [**1**]/[*cis*-$Pt(SiHPh_2)(PMe_3)_2$] = 0.105 (−50 °C), 0.136 (−30 °C), 0.173 (−10 °C), and 0.198 (10 °C). Equilibrium constants in THF-d_8 were estimated similarly; *K* = 0.198 (−50 °C), 0.235 (−30 °C), 0.277 (−10 °C), and 0.302 (10 °C).

Crystal Structure Determination. Crystals of **1**−**3** suitable for X-ray diffraction study were obtained by recrystallization from toluene−pentane and mounted in glass capillary tubes under argon. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo Kα radiation (λ = 0.71069 Å) and the ω−2θ scan method, and an empirical absorption correction (Ψ scan) was applied. Calculations were carried out by using a program package TEXSAN on a DEC Micro VAX-II computer. Atomic scattering factors were obtained from the literature.[17] A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotoropic thermal parameters. Positions of the SiH hydrogens were determined by the difference Fourier technique, while the other hydrogens were located by assuming the ideal geometry. The hydrogens were included in the structure calculation without further refinement of the parameters. Crystallograhic data and details of refinement are summarized in Table 1.

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Supporting Information Available: Crystallographic data of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980939H

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[17] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.