Oxidative Addition of Silicon−Halogen Bonds to Platinum(0) Complexes and Reactivities of the Resulting Silylplatinum Species

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Oxidative addition of the silicon−halogen bonds of halosilanes R_3Si-X ($X = Cl$, Br, I) to platinum(0) complexes PtL_n ($L =$ tertiary phosphine) yielded *trans*-$R_3SiPtXL_2$ species. Halosilanes exhibited the following orders of reactivities: for Me_3SiX, $X = Cl$ (no reaction) $<<$ Br $<$ I, and for $Me_{4-n}SiCl_n$, $n = 1$ (no reaction) $<< 2 < 3$. The reactivities of platinum complexes increased in the order of $Pt(PPh_3)_4$, $Pt[Ph_2P(CH_2)_2PPh_2]_2$ (no reactions) $<<$ $Pt(PMe_2Ph)_4 < Pt(PMe_3)_4 < Pt(PEt_3)_4$. Coordinately unsaturated $Pt(PEt_3)_3$ was more reactive than $Pt(PEt_3)_4$. $Me_3SiSiMe_2I$ also underwent addition at the Si−I bond to $Pt(PEt_3)_3$ with the Si-Si bond being intact to form *trans*-$Me_3SiMe_2SiPtI(PEt_3)_2$. Treatment of *trans*-$Me_3SiPtBr(PEt_3)_2$ (**2a**) with a phosphine (PEt_3, PPh_3) resulted in reductive elimination of Me_3SiBr. The reaction of **2a** with styrene gave $PhCH{=}CHSiMe_3$, although the major part of the Me_3Si moiety was eliminated as Me_3SiBr. Silyl group exchange of **2a** or *trans*-$Me_3SiPtI(PEt_3)_2$ cleanly took place upon treatment with the hydrosilane R_3SiH (Me_2PhSiH, $MePhSiH_2$) to provide *trans*-$R_3SiPtX(PEt_3)_2$ ($X =$ Br, I). Transmetalation between **2a** and Et_2Zn or Ph_2Hg respectively yielded Me_3SiEt or Me_3SiPh in a smooth reaction. ^1H, ^{13}C, ^{29}Si, ^{31}P, and ^{195}Pt NMR spectra of the resulting silylplatinum species are discussed in terms of the trans and cis influences and the electronegativity of the ligated groups.

Introduction

Organosilane, organogermane, and organostannane compounds have attracted growing interest for their utility as versatile synthetic reagents and for their intriguing physicochemical properties, especially those of relevant polymers.[1] In this context, new efficient catalyses to prepare or to transform these heteroatom compounds are increasingly required, considering the important role played by catalytic reactions for the advancement of organic chemistry in the past decades. For the development of new catalyses, oxidative addition of these group 14 element−halogen bonds to transition metals is one of the most important key elemental reactions, since it offers the possibility of realizing a variety of catalytic reactions similar to those of organic halides that are widely used in organic synthesis.[2] However, the reactivities of silicon, germanium, and tin halides toward transition-metal complexes have not been fully elucidated as yet.[3] To our knowledge, unequivocal examples of oxidative addition have been limited to those of some silicon−halogen bonds toward iridium[4−6] or platinum[7−9] complexes and some germanium−halogen[9−11] or tin−halogen[9,12−14] bonds toward platinum complexes. We have already disclosed that oxidative addition of silicon-halogen (I, Br, and Cl) bonds to platinum(0) complexes proceeds to give the corresponding halogeno(silyl)platinum complexes.[8] Herein are reported the details of the reaction, including the reactivities and the NMR spectra of the resulting silylplatinum species.

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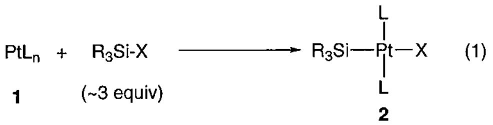
Table 1. Reactions of Platinum(0) Complexes with Halosilanes[a]

complex	halosilane	temp (°C)	time	product	yield[b] (%)
$Pt(PPh_3)_4$ (**1a**)	Me_3SiX (X = Cl, Br, I)	120	15 h	no reactn	
$Pt(dppe)_2$[c] (**1b**)	Me_3SiX (X = Cl, Br, I)	120	15 h	no reactn	
$Pt(PEt_3)_4$ (**1c**)	Me_3SiBr	90	1 h	*trans*-$Me_3SiPtBr(PEt_3)_2$ (**2a**)	~35
			4 h	**2a**	~65
			15 h	**2a**	~80
$Pt(PEt_3)_3$ (**1d**)	Me_3SiBr	90	4 h	**2a**	~95
	Me_3SiI	90	~5 min	*trans*-$Me_3SiPtI(PEt_3)_2$ (**2b**)	~100
	Me_3SiCl	120	15 h	no reacn	
	$MePh_2SiCl$	120	15 h	no reacn	
	Ph_3SiCl	120	15 h	no reacn	
	Me_2SiCl_2	120	1 h	*trans*-$Me_2ClSiPtCl(PEt_3)_2$ (**2c**)	~90
	$MeSiCl_3$	90	15 min	*trans*-$MeCl_2SiPtCl(PEt_3)_2$ (**2d**)	~100
$Pt(PMe_3)_4$ (**1e**)	Me_3SiBr	120	18 h	*trans*-$Me_3SiPtBr(PMe_3)_2$ (**2e**)	~50
	Me_3SiI	90	1 h	*trans*-$Me_3SiPtI(PMe_3)_2$ (**2f**)	~90
$Pt(PMe_2Ph)_4$ (**1f**)	Me_3SiX (X = Cl, Br)	120	15 h	no reacn	
	Me_3SiI	120	13 h	*trans*-$Me_3SiPtI(PMe_2Ph)_2$ (**2g**)	~70
1d	$Me_3SiSiMe_2I$	90	10 min	*trans*-$Me_3SiMe_2SiPtI(PEt_3)_2$ (**2h**)	~100

[a] Conditions: complex (0.075−0.30 mmol, ca. 0.4−0.5 M), halosilane (~3 equiv), benzene-d_6 (0.20−0.60 mL). [b] Estimated by ^1H NMR. [c] dppe = $Ph_2P(CH_2)_2PPh_2$.

Results and Discussion

Reactions of Platinum(0) Complexes with Si−X (X = Cl, Br, I) Bonds. The reaction of a platinum(0) complex with a halosilane (ca. 3 equiv) was carried out in a sealed NMR tube using benzene-d_6 or benzene as solvent. The progress of the reaction was monitored by means of ^1H and/or ^{31}P NMR. As summarized in eq 1



$$PtL_n + R_3Si\text{-}X \longrightarrow R_3Si{-}\overset{L}{\underset{L}{Pt}}{-}X \quad (1)$$

1 (~3 equiv) **2**

1a: $L_n = (PPh_3)_4$
1b: $L_n = (dppe)_2$
1c: $L_n = (PEt_3)_4$
1d: $L_n = (PEt_3)_3$
1e: $L_n = (PMe_3)_4$
1f : $L_n = (PMe_2Ph)_4$

2a: $R_3 = Me_3$, X = Br, L = PEt_3
2b: $R_3 = Me_3$, X = I, L = PEt_3
2c: $R_3 = Me_2Cl$, X = Cl, L = PEt_3
2d: $R_3 = MeCl_2$, X = Cl, L = PEt_3
2e: $R_3 = Me_3$, X = Br, L = PMe_3
2f : $R_3 = Me_3$, X = I, L = PMe_3
2g: $R_3 = Me_3$, X = I, L = PMe_2Ph

and Table 1, the reactions of $Pt(PPh_3)_4$ (**1a**) or $Pt(dppe)_2$ (**1b**; dppe = $Ph_2P(CH_2)_2PPh_2$) with Me_3SiX (X = Cl, Br, I) did not afford any silylplatinum species even under forcing conditions (heating up to 120 °C for 15 h). However, when $Pt(PEt_3)_4$ (**1c**) was treated with Me_3SiBr at 90 °C for 1 h, a new Me_3Si proton signal ascribable to *trans*-$Me_3SiPtBr(PEt_3)_2$ (**2a**) emerged at 0.42 ppm ($^3J_{PtH}$ = 25.4 Hz). The yield of **2a** was estimated at ~35% by ^1H NMR. The product appeared stable in the presence of excess halosilane, and prolonging the reaction time increased the yield of **2a** to ~65% (total heating time 4 h) and ~80% (15 h). Coordinately unsaturated $Pt(PEt_3)_3$ (**1d**) showed much higher reactivity than **1c**, and **2a** was formed in ~95% NMR yield after heating at 90 °C for 4 h. In a separate larger scale reaction of **1d** with Me_3SiBr (120 °C, 7 h), **2a** could be isolated as yellow needles in 59% yield after recrystallization from pentane. Its NMR and IR spectra and elemental analysis were quite consistent with the proposed structure. The NMR and IR spectra were similar to those of the known complex *trans*-$Me_3SiPtCl(PEt_3)_2$, which was prepared separately by the reaction of *cis*-$PtCl_2(PEt_3)_2$ with $(Me_3Si)_2Hg$.[15] The structure of **2a** was finally confirmed by X-ray diffraction analysis.[8a,16] Thus, oxidative addition of the Me_3Si−Br bond to **1c** or **1d** was unequivocally verified to proceed.

The iodosilane Me_3SiI reacted with **1d** much more readily than Me_3SiBr to give *trans*-$Me_3SiPtI(PEt_3)_2$ (**2b**) nearly quantitatively by heating at 90 °C for ~5 min. In a separate reaction at 80 °C for 50 min, **2b** could be isolated in 82% yield after recrystallization from pentane. In contrast with Me_3SiX (X = Br, I), no reactions took place between **1d** and monochlorosilanes such as Me_3SiCl, $MePh_2SiCl$, and Ph_3SiCl (heating up to 120 °C). The dichlorosilane Me_2SiCl_2, however, could react at the Si-Cl bond to give *trans*-$Me_2ClSiPtCl(PEt_3)_2$ (**2c**) in ~90% NMR yield (120 °C, 1 h). In addition, the more chlorinated halosilane $MeSiCl_3$ underwent the addition to **1d** at a much higher rate to give *trans*-$MeCl_2SiPtCl(PEt_3)_2$ (**2d**) in ~100% NMR yield (90 °C, 15 min).[17] Noteworthy is that activation of the Si−Cl bonds of industrially produced chlorosilanes was achieved under relatively mild conditions. In separate reactions under similar conditions, reasonably pure **2c** and **2d** were easily obtained by removal of volatiles from the reaction mixtures in vacuo. Silyl species **2b**−**d** were identified by ^1H, ^{13}C, ^{29}Si, ^{31}P, and ^{195}Pt NMR (vide infra) and IR and/or elemental analysis.

Besides the PEt_3 complexes **1c**,**d**, $Pt(PMe_3)_4$ (**1e**) also reacted with Me_3SiBr to give the corresponding silylplatinum species *trans*-$Me_3SiPtBr(PMe_3)_2$ (**2e**), although **1e** was much less reactive than **1c**; the NMR yield of **2e** was ~50% (120 °C, 18 h), while the yield of **2a** in the reaction of **1c** was ~80% (90 °C, 15 h). The reaction of **1e** with Me_3SiI proceeded more readily, as in the reaction of **1d**, to form *trans*-$Me_3SiPtI(PMe_3)_2$ (**2f**) in ~90% yield (90 °C, 1 h). In addition, $Pt(PMe_2Ph)_4$ (**1f**) reacted with Me_3SiI at 120 °C over 13 h to give *trans*-$Me_3SiPtI(PMe_2Ph)_2$ (**2g**) in ~70% yield, whereas **1f** did not react with Me_3SiBr up to 120 °C. For species **2e**−

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(15) (a) Glockling, F.; Hooton, K. A. *J. Chem. Soc. A* **1967**, 1066. Generally, $R_3SiPtXL_2$ (X = halogen, L = phosphine) species were prepared by treating PtX_2L_2 with R_3SiLi or with R_3SiH and Et_3N or by treating $PtHXL_2$ with R_3SiH. For instance, see: (b) Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343 and references cited therein. (c) Ebsworth, E. A. V.; Edward, J. M.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1976**, 1673 and references cited therein.

(16) The silicon atom coordinates to the platinum atom directly. The coordination geometry around the platinum atom is that of a square plane, and the phosphine ligands are located at positions trans to each other. The accuracy in the X-ray analysis was not particularly high but was sufficient to elucidate these important structural characteristics. The crystallographic parameters have been deposited with the Cambridge Crystallographic Data Centre; REFCODE:GETPIE.

(17) Clark et al. briefly mentioned the formation of *trans*-$(PhCl_2Si)PtCl(PCy_3)_2$ (Cy = cyclohexyl) by oxidative addition of $PhSiCl_3$ to $Pt(PCy_3)_2$, although no experimental details were given.[7]

g, pure samples have not been obtained because of the difficulty of removing unidentified phosphorus-containing impurities and/or separating the products from the unreacted starting complexes. However, NMR observations evidenced the identity of species **2e**−**g**. Thus, relatively pure **2e**−**g** clearly displayed the ^{1}H, ^{13}C, and ^{29}Si NMR signals of the M_3Si-Pt moieties with expected coupling patterns (vide infra). In addition, ^{31}P and ^{195}Pt NMR of **2e**−**g** at low temperatures (−20 to −60 °C) unambiguously revealed the existence of *trans*-bis(phosphine)platinum structures, although those resonances were significantly broadened at room temperature, presumably because of the phosphorus-containing impurities.

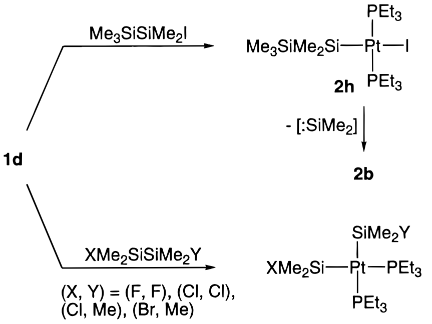
The geometry of the silylplatinum species obtained in the foregoing reactions was determined to be trans, as judged from the relatively large values of $^1J_{PtP}$ ranging from 2516 to 2914 Hz (vide infra).[18] In the case of **2a**, the trans structure was determined by X-ray crystallography.[8a,16] The preference for the trans geometry is the same as in the oxidative addition of carbon−halogen bonds to zerovalent phosphine complexes of group 10 metals.[19]

On the basis of the reaction conditions and the NMR yields of the silylplatinum species (Table 1), the reactivities of silicon−halogen bonds are estimated to increase in the following order: for Me_3SiX, X = Cl (no reaction) << Br < I, and for $Me_{4-n}SiCl_n$, n = 1 (no reaction) << 2 < 3. The trend of the reactivity in the series of Me_3SiX seems to reflect the dissociation energies of the Me_3Si-X bonds (98, 76, and 57 kcal/mol for X = Cl, Br, and I, respectively[20]); halosilanes with weaker silicon−halogen bonds are more favorable for the oxidative addition. On the other hand, the reactivities of platinum(0) complexes increased in the order of L = PPh_3, dppe (no reactions) << PMe_2Ph < PMe_3 < PEt_3. The order for monodentate phosphines is the reverse of that of the electronic parameters (ν)[21] of phosphines (ν = 2068.9, 2065.3, 2064.1, and 2061.7 for PPh_3, PMe_2Ph, PMe_3, and PEt_3, respectively); electron-donating phosphines enhance the susceptivity to the oxidative addition. This indicates that the reaction proceeds via electrophilic interaction of halosilanes with platinum(0) complexes. The dissociation of the phosphine L from PtL_4 also seems to be a crucial step, since the coordinately unsaturated **1d** exhibited significantly higher reactivity than **1c**.

On the basis of the thermochemical considerations of the reactions between platinum(0) species and group 14 metal halides R_3EX (E = Sn, Ge, Si; X = Br, Cl), Eaborn et al. previously proposed that the E−C bonds are more easily cleaved than the E−X bonds.[12a] Indeed, R_3SnX (R = Ph, X = I, Br, Cl; R = Me, X = Br, Cl) were reported to react with $Pt(CH_2{=}CH_2)(PPh_3)_2$ at the Sn−R bonds to form *cis*-$R_2XSnPtR(PPh_3)_2$ species.[12] The present study, however, demonstrates that halosilanes Me_3SiX (X = I, Br) undergo oxidative addition at the silicon−halogen bonds with silicon−carbon bonds intact. The reaction manners of Me_2SiCl_2 and $MeSiCl_3$ are similar to those of Me_2SnX_2 (X = Br, Cl) and $MeSnCl_3$, manifesting the preferential formation of E−Pt−X (E = Si, Sn; X = Br, Cl) species.

For the reactivities of halosilanes toward palladium(0) or platinum(0) complexes, it was reported that Me_3SiCl reacted with **1b**[22] or $Pd(PPh_3)_4$[23] to provide a disilane ($Me_3SiSiMe_3$) along with the corresponding metal dichloride ($PtCl_2$(dppe) or $PdCl_2(PPh_3)_2$). The disilane might be formed via sequential reactions of the 2 equiv of the Me_3Si-Cl bond with the metal species. However, formation of disilanes was not observed in the foregoing reactions.

In addition to halomonosilanes, an iododisilane, $Me_3SiSiMe_2I$, also reacted with **1d** at the Si−I bond to give *trans*-$Me_3SiMe_2SiPtI(PEt_3)_3$ (**2h**) nearly quantitatively (90 °C, 10 min; eq 2, Table 1). In a separate reaction (60 °C, 1 h), **2h** was obtained as yellow cubic crystals in 68% yield by recrystallization from pentane. The isolated **2h** showed satisfactory NMR (vide infra), IR, and analytical data. As we reported previously, other halogenated disilanes, such as $XMe_2SiSiMe_2Y$ for (X, Y) = (F, F), (Cl, Cl), (Cl, Me), and (Br, Me), underwent the selective cleavage of the Si−Si bonds with the silicon−halogen bonds intact to provide *cis*-$(XMe_2Si)(YMe_2Si)Pt(PEt_3)_2$ species.[8b] The reactivities of halodisilanes seem to be associated with the dissociation energies of the Me_3Si-X bonds (57, 68, 76, 98, and 141 kcal/mol for X = I, $SiMe_3$, Br, Cl, and F);[20] weaker bonds are more reactive for the oxidative addition. Complex **2h** was stable in benzene-d_6 solution for at least several weeks at room temperature. However, when the solution stood (in a sealed NMR tube) for 2.5 years, decomposition of **2h** into **2b** occurred (≥80% NMR yield, see Experimental Section). We have already observed the analogous conversion of a disilanylplatinum (*cis*-$(Me_3SiClMeSi)Pt(SiMe_2Cl)(PEt_3)_2$) into a silylplatinum species (*cis*-$(ClMe_2Si)_2Pt(PEt_3)_2$) in the presence of a silylene trapping agent (benzil).[24] The formation of **2b** would be best explained by α-migration of the Me_3Si group of the $SiMe_2SiMe_3$ ligand, giving a $Pt({=}SiMe_2)(SiMe_3)$ intermediate and subsequent extrusion of $SiMe_2$ species. A similar mechanism was previously proposed in the



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[18] For examples of ^{31}P NMR of *trans*-bis(phosphine)platinum species, see: (a) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, Germany, 1979. (b) Duncan, W.; Anderson, W.; Ebsworth, E. A. V.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1973**, 2370.

[19] For instance, see: (a) Reference 2, p 306. (b) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434.

[20] Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 9, p 6.

[21] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[22] Glockling, F.; Hooton, K. A. *J. Chem. Soc. A* **1968**, 826.

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[24] Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1995**, *14*, 530.

photochemical conversion of $Cp(CO)_2FeSiMe_2SiMe_3$ into $Cp(CO)_2FeSiMe_3$.[25]

Besides the silicon−halogen bonds, the reactivities of the Si−S and Si−N bonds have been examined under similar conditions. However, monitoring the reactions of **1d** with $Me_3Si-SPh$, $Me_3Si-N(CH_2)_4$ (*N*-(trimethylsilyl)pyrrolidine), and Me_3Si-N_3 by ^1H and/or ^{31}P NMR did not reveal any recognizable Me_3Si-Pt proton signals up to 120 °C.

Reactivities of *trans*-Halogeno(silyl)bis(phosphine)platinum Species. There have been a few limited investigations on the reactivities of *trans*-$R_3SiPtClL_2$ (R = Me, Ph; L = PEt_3, $PPhMe_2$) complexes toward water,[15a] hydrogen,[15a] 1,2-dichloroethane,[15a] organoalkali and organoalkaline earth metals (aryllithium, arylmagnesium bromide),[26] metal salts (iodides, thiocyanates, and azides of alkali metals),[26] and some unsaturated compounds (phenylacetylene, tetracyanoethylene, etc.).[15a,26] However, the reactivities of the silylplatinum species have not been fully clarified as yet. In order to learn other aspects of the reactivities and/or to find a clue for the development of new catalyses, we have examined the reactivities of the silyl species **2a**,**b** toward phosphines, organometallics (organomercury, organozinc, etc.), hydrosilanes, and olefinic compounds.

(a) Reactions with Phosphines. Treatment of **2a** with PEt_3 (2 equiv) in benzene-d_6 below 90 °C did not cause any significant change in the NMR. However, heating the mixture at 120 °C for 3 h formed Me_3SiBr (~50% yield) and $Pt(PEt_3)_3$ with consumption of **2a** (~60% conversion)[27] (eq 3). Further heating for 2 h hardly changed the product distribution. When PPh_3 was used in place of PEt_3, the reaction took place more readily to give a higher yield of Me_3SiBr (~80%) with a higher conversion of **2a** (~90%) (120 °C, 5 h). Unless the extra phosphines were present, the reaction was considerably slow to proceed; the yield of Me_3SiBr was only ~10% with ~25% conversion of **2a** (120 °C, 5 h). These results clearly indicate that oxidative addition of the Si−Br bond to platinum(0) species is reversible and reductive elimination of the Si−Br bond occurs in the presence of extra phosphines. Higher conversion of **2a** in the presence of PPh_3 is probably associated with a lower rate of the reverse reaction; $Pt(PEt_3)_p(PPh_3)_q$ species, which are likely to be formed from **2a** and PPh_3, seem to be less reactive for oxidative addition than $Pt(PEt_3)_m$, judging from the result that **1c**,**d** exhibited much higher reactivity toward halosilanes than **1a**.

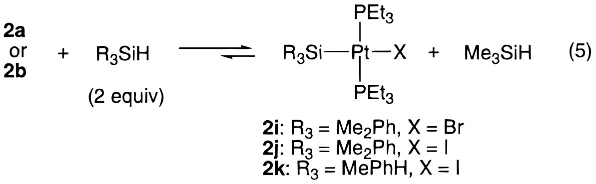
$$\mathbf{2a} + \underset{\substack{(2\ \text{equiv})\\ L\,=\,PEt_3,\ PPh_3}}{L} \rightleftharpoons Me_3SiBr + Pt(PEt_3)_mL_n \qquad (3)$$

(b) Reactions with Organometallics. Silylplatinum species **2a** was inert toward Ph_4Sn (2 equiv) in benzene-d_6 even at 90 °C. In contrast, **2a** smoothly reacted with Et_2Zn (1 equiv) at room temperature for ~10 min to provide Me_3SiEt in ≥90% yield with ≥95% conversion of **2a** (eq 4). Likewise, the reaction of **2a** with Ph_2Hg (1 equiv) at 60 °C over 40 min produced Me_3SiPh in ~90% yield with almost complete consumption of **2a**. Me_3SiBr itself did not react with R_2M (Et_2Zn, Ph_2Hg) under comparable conditions, indicating that a pathway involving reductive elimination of Me_3SiBr and its interaction with R_2M to give Me_3SiR was not likely. Accordingly, the formation of Me_3SiR would be best explained by the reaction sequence of transmetalation between **2a** and R_2M, forming a Me3Si-Pt-R intermediate,[28] and subsequent reductive elimination of Me_3SiR.

$$\mathbf{2a} + R_2M \longrightarrow [Me_3SiPtR(PEt_3)_2] \longrightarrow Me_3SiR \qquad (4)$$

$$R_2M = Et_2Zn,\ Ph_2Hg$$

(c) Reactions with Hydrosilanes. Heating a mixture of **2a** and Me_2PhSiH (2 equiv) in benzene-d_6 at 60 °C for 10 min caused partial silyl group exchange to give *trans*-$Me_2PhSiPtBr(PEt_3)_2$ (**2i**) and Me_3SiH (eq 5). The reaction proceeded cleanly without formation of other platinum species. The ratio of the remaining **2a**/**2i** was estimated to be ~90/10 by ^1H NMR. When the mixture was heated to 90 °C, the ratio of **2a**/**2i** changed to ~15/85 (10 min) and to ~5/95 (30 min). Reductive elimination of Me_3SiBr from **2a** did not significantly take place in the reaction (yield of Me_3SiBr ≤ 0.5%).



$$\begin{matrix}\mathbf{2a}\\ \text{or}\\ \mathbf{2b}\end{matrix} + \underset{(2\ \text{equiv})}{R_3SiH} \rightleftharpoons R_3Si-\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{\overset{|}{\underset{|}{Pt}}}}-X + Me_3SiH \qquad (5)$$

2i: $R_3 = Me_2Ph$, X = Br
2j: $R_3 = Me_2Ph$, X = I
2k: $R_3 = MePhH$, X = I

The iodide complex **2b** reacted with Me_2PhSiH more readily to give *trans*-$Me_2PhSiPtI(PEt_3)_2$ (**2j**) and Me_3SiH; the ratios of **2b**/**2j** were ~10/90 (60 °C, 10 min) and ~5/95 (30 min). These reactions were reversible, and further heating did not substantially change the ratios of **2a**/**2i** and **2b**/**2j**. The dihydrosilane $MePhSiH_2$ exhibited much higher reactivity than the monohydride Me_2PhSiH. Thus, **2b** smoothly reacted with $MePhSiH_2$ even at room temperature to provide *trans*-$MePhHSiPtI(PEt_3)_2$ (**2k**) and Me_3SiH with almost complete consumption of **2b** (4 h, **2b**/**2k** = ~0/100). In the reaction of **2b** with Me_2PhSiH or $MePhSiH_2$, formation of Me_3SiI was not observed by NMR. The reaction was generally clean, and each silylplatinum product was isolated in good yield (**2i**, 69%; **2j**, 86%; **2k**, 93%) by evaporation of volatiles followed by recrystallization from pentane, offering a convenient method to prepare various halogeno(silyl)bis(phosphine)platinum complexes.

The present silyl group exchange is likely to proceed via oxidative addition of the Si−H bonds of the hydrosilanes to **2a** or **2b**, forming hexacoordinate bis(silyl)platinum(IV) species (**3**), and subsequent reductive elimination of Me_3SiH, providing the silylplatinums **2i**−**k**. A similar addition−elimination process was previously proposed in the reactions of platinum(II) hydrides with hydrosilanes, affording silylplatinum(II) species

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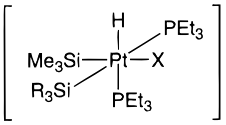
[25] (a) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. P. *Organometallics* **1986**, 5, 1056. (b) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777.

[26] Chatt, J.; Eaborn, C.; Kapoor, P. N. *J. Organomet. Chem.* **1970**, *23*, 109.

[27] In the reactions of **2a** with phosphines or styrene, some amounts of $(Me_3Si)_2O$ (10−35%) were also formed, although the origin of the oxygen was ambiguous.

[28] For examples of transmetalation between halogenometal species and organometallics, see ref 2, p 704.

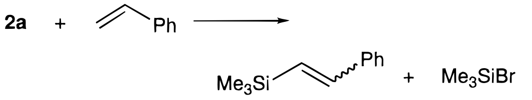


3

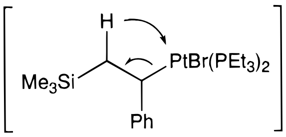
along with hydrogen.[29] In the foregoing reactions, formation of the thermodynamically more stable R$_3$Si−Pt (R$_3$ = Me$_2$Ph, MePhH) bond as compared with the Me$_3$Si−Pt bond would be a driving force. On the basis of the ratios of **2b**/**2j** and **2b**/**2k**, the strength of R$_3$Si-Pt bonds is estimated to increase in the order of R$_3$Si = Me$_3$Si < Me$_2$PhSi < MePhHSi. This sequence is consistent with the suggestion that electronegative groups at silicon atoms stabilize the silicon−metal bonds.[30] On the other hand, no intermediate species were observed in NMR monitoring of the reactions, suggesting that oxidative addition of the Si−H bond was the rate-determining step. The iodide ligand has weaker electronegativity than the bromide ligand and would be favorable for oxidative addition of the Si−H bond, resulting in a higher rate of the exchange reaction.[31] In addition, the strong trans influence of the iodide ligand compared with that of the bromide ligand would also promote the reaction by facilitating the cleavage of the Si−Pt bond.

Assuming that **3** is involved as an intermediate, it seems possible to get a bis(silyl) species, (Me$_3$Si)(R$_3$Si)-Pt(PEt$_3$)$_2$, by removal of the hydrogen halides HX from the platinum(IV) species **3** using appropriate bases. However, addition of Et$_3$N (2 equiv) did not affect the product distribution in the reaction of **2a** with Me$_2$-PhSiH.

(d) Reactions with Olefinic Compounds. Silyl species **2a** did not react with isoprene in benzene-d_6 up to 60 °C. The reaction with styrene (2 equiv) did not take place up to 90 °C either. However, when the mixture of **2a** and styrene was heated at an elevated temperature (120 °C) for 4 h, PhCH=CHSiMe$_3$ (~5%, $E/Z \approx 8/1$) was obtained along with Me$_3$SiBr (~50%) and recovered **2a** (~10%)[27] (eq 6). The reaction in the presence of Et$_3$N (5 equiv) at 120 °C over 5.5 h also provided PhCH=CHSiMe$_3$ (~2% yield, $E/Z \approx 4/1$) along with a larger amount of Me$_3$SiBr (~75%) and unreacted **2a** (≤5%).[32] The formation of the styrylsilane would be best explained by styrene insertion into the Si−Pt bond of **2a**,[33] giving a (1-phenyl-2-silylethyl)platinum species (**4**), followed by β-hydride elimination from the 2-silylethyl moiety of **4**.[34,35] A similar reaction sequence was previously suggested for group 8 or 9 metal-catalyzed dehydrogenative silylation of olefins with hydrosilanes.[36] In addition, we have observed that a bis(silyl)platinum species, *cis*-(Me$_2$PhSi)$_2$Pt(PMePh$_2$)$_2$, reacts with styrene to yield a styrylsilane, presumably via similar elemental steps (eq 7).[35a] These results could be successfully applied to the development of novel catalyses, such as in a palladium-catalyzed Heck-type reaction of Me$_3$SiI with olefins[32] (eq 8) and a platinum-catalyzed reaction of disilanes with olefins,[37] both of which provided alkenylsilanes.



(6)



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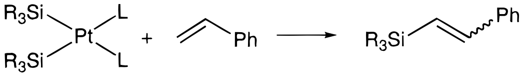
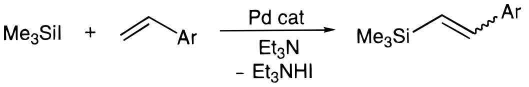


(7)

R$_3$Si = Me$_2$PhSi, L = PMePh$_2$



(8)

In contrast with styrene, we have found that acetylenes RC≡CR (R = Ph, Pr) smoothly insert into the Si−Pt bonds of **2a**,**b** at 90−120 °C to give the corresponding (β-silylvinyl)platinum species in high yields (≥90%).[38] High reactivities of acetylenes as compared with olefins have been generally observed in reactions with other silylplatinum complexes.[39]

NMR Spectra of *trans*-Halogeno(silyl)bis(phosphine)platinum Species. ^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{195}Pt NMR spectral data of the resulting platinum species **2a**−**k** and *trans*-Me$_3$SiPtCl(PEt$_3$)$_2$[15a] are summarized in Tables 2−4. All the complexes show satisfactory NMR spectra for the proposed structures.

The ^{1}H and ^{13}C NMR signals of the PEt$_3$ and PMe$_3$ ligands have virtual coupling with the trans phosphines, as has been observed for other *trans*-bis(phosphine)-platinum(II) complexes.[40] Other characteristic features of the chemical shifts and the coupling constants in the series of *trans*-Me$_3$SiPtX(PEt$_3$)$_2$, *trans*-Me$_{3-n}$Cl$_n$SiPtCl-

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(29) Bentham, J. E.; Cradock, S.; Ebsworth, E. A. V. *J. Chem. Soc. A* **1971**, 587.

(30) For instance, see ref 3b, pp 28, 84.

(31) We thank a reviewer for providing an instructive suggestion.

(32) Preliminary results were reported: Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1991**, 761.

(33) For examples of olefin insertion into silicon-metal bonds, see ref 3d.

(34) For examples of β-hydride elimination, see ref 2, p 386.

(35) For alkenylsilane formation in the reaction of silicon-metal bonds with olefins, see: (a) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. (b) Thorn, D. L.; Harlow, R. L. *Inorg. Chem.* **1990**, *29*, 2017.

(36) For instance, see: Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748 and references cited therein.

(37) Hayashi, T.; Kawamoto, A. M.; Kobayashi, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1990**, 563.

(38) (a) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1993**, *12*, 988. See also ref 26. (b) Oxidative addition of the Si−I bond of an iodosilane to a palladium complex and subsequent C≡C bond insertion into the resulting Si−Pd species were proposed as key elemental steps in the palladium-catalyzed three-component coupling of an iodosilane (R$_3$SiI), an acetylene (R′C≡CH), and an organometallic (R″SnBu$_3$, R″$_2$-Zn), giving an alkenylsilane derivative (R$_3$SiCH=CR′R″). See: Chatani, N.; Amishiro, N.; Murai, S. *J. Am. Chem. Soc.* **1991**, *114*, 7779. Chatani, N.; Amishiro, N.; Takaya, M.; Yamashita, T.; Murai, S. *J. Org. Chem.* **1995**, *60*, 1834.

(39) (a) Reference 26. (b) Reference 35a. (c) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *428*, 1.

(40) For instance, see: (a) Duddell, D. A.; Evans, J. G.; Goggin, P. L.; Goodfellow, R. J.; Rest, A. J.; Smith, J. G. *J. Chem. Soc. A* **1969**, 2134. (b) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457. (c) Rieger, A. L.; Carpenter, G. B.; Rieger, P. H. *Organometallics* **1993**, *12*, 842 and references cited therein.

Table 2. ^{1}H NMR of 2[a]

complex	δ(H$_3$CSiPt)	$^3J_{\mathrm{PtH}}$ (Hz)	δ(others)
trans-Me$_3$SiPtCl(PEt$_3$)$_2$	0.51	25.3	0.99,[b] 1.92[c] ($^3J_{\mathrm{PtH}} = 22.2$ Hz)
trans-Me$_3$SiPtBr(PEt$_3$)$_2$ (**2a**)	0.45	25.5	0.97,[b] 1.96[c] ($^3J_{\mathrm{PtH}} = 22.5$ Hz)
trans-Me$_3$SiPtI(PEt$_3$)$_2$ (**2b**)	0.45	24.9	0.96,[b] 2.02[c] ($^3J_{\mathrm{PtH}} = 23.1$ Hz)
trans-Me$_2$ClSiPtCl(PEt$_3$)$_2$ (**2c**)	0.90	21.7	0.96,[b] 1.97[c] ($^3J_{\mathrm{PtH}} = 21.4$ Hz)
trans-MeCl$_2$SiPtCl(PEt$_3$)$_2$ (**2d**)	1.17	14.6	0.94,[b] 2.00[c] ($^3J_{\mathrm{PtH}} = 21.0$ Hz)
trans-Me$_3$SiPtBr(PMe$_3$)$_2$ (**2e**)[d,e]	0.47	26.9	1.28[f] ($^3J_{\mathrm{PtH}} = 30.5$ Hz)
trans-Me$_3$SiPtI(PMe$_3$)$_2$ (**2f**)[d,g]	0.40	26.7	1.37[f] ($^3J_{\mathrm{PtH}} = 31.1$ Hz)
trans-Me$_3$SiPtI(PMe$_2$Ph)$_2$ (**2g**)[d,h]	0.14	~23	1.86[i] (br, $^3J_{\mathrm{PtH}} \approx 20$ Hz, 12H, PCH$_3$), 6.8−7.3 and 7.5−7.8 (each m, 10H, C$_6$H$_5$)
trans-Me$_3$SiMe$_2$SiPtI(PEt$_3$)$_2$ (**2h**)	0.51	33.6	0.25 (s, 9H, H$_3$CSiSi), 0.97,[b] 2.06[c] ($^3J_{\mathrm{PtH}} = 20.3$ Hz)
trans-Me$_2$PhSiPtBr(PEt$_3$)$_2$ (**2i**)	0.64	27.0	0.95,[b] 1.84[c] ($^3J_{\mathrm{PtH}} = 21.7$ Hz), 7.09−7.27 and 7.75−7.83 (each m, 5H, C$_6$H$_5$)
trans-Me$_2$PhSiPtI(PEt$_3$)$_2$ (**2j**)	0.62	26.5	0.93,[b] 1.87[c] ($^3J_{\mathrm{PtH}} = 22.2$ Hz), 7.07−7.23 and 7.68−7.77 (each m, 5H, C$_6$H$_5$)
trans-MePhHSiPtI(PEt$_3$)$_2$ (**2k**)	0.82[j]	33.2	0.88,[b] 1.90−2.12 (m), 4.21(qt, $^3J_{\mathrm{HH}} = 4.0$ Hz, $^3J_{\mathrm{PH}} = 14.0$ Hz, $^2J_{\mathrm{PtH}} = 63.6$ Hz, 1H, HSi), 7.11−7.28 and 7.79−7.87 (each m, 5H, C$_6$H$_5$)

[a] In C$_6$D$_6$ at 20−25 °C. [b] tt, $^3J_{\mathrm{HH}} \approx {}^1/_2|^3J_{\mathrm{PH}} + {}^5J_{\mathrm{PH}}| \approx 7.8$ Hz, 18H, PCCH$_3$. [c] qt, $^3J_{\mathrm{HH}} \approx |^2J_{\mathrm{PH}} + {}^4J_{\mathrm{PH}}| \approx 7.8$ Hz, 12H, PCH$_2$. [d] Small amounts of phosphorus-containing impurities were present. [e] In C$_6$D$_5$CD$_3$ at −30 °C. [f] t, $|^2J_{\mathrm{PH}} + {}^4J_{\mathrm{PH}}| \approx 6.6$ Hz, 18 H, PCH$_3$. [g] In C$_6$D$_5$CD$_3$ at −20 °C. [h] In C$_6$D$_5$CD$_3$ at −60 °C. [i] The $|^2J_{\mathrm{PH}} + {}^4J_{\mathrm{PH}}|$ value was not confirmed. [j] $^3J_{\mathrm{HH}} = 4.0$ Hz.

Table 3. ^{13}C NMR of 2[a]

complex	δ(CSiPt)	$^2J_{\mathrm{PtC}}$ (Hz)	$^3J_{\mathrm{PC}}$ (Hz)	δ(others)
trans-Me$_3$SiPtCl(PEt$_3$)$_2$	8.1	78.4	3.2	8.7 ($^3J_{\mathrm{PtC}} = 28.8$ Hz, PC*C*), 16.8[c] (t, $J_{\mathrm{PC}}{}^b = 16.8$ Hz, $^2J_{\mathrm{PtC}} = 42.0$ Hz, PC)
trans-Me$_3$SiPtBr(PEt$_3$)$_2$ (**2a**)	8.1	77.8	3.4	8.8 ($^3J_{\mathrm{PtC}} = 28.3$ Hz, PC*C*), 17.8 (t, $J_{\mathrm{PC}}{}^b = 16.9$ Hz, $^2J_{\mathrm{PtC}} = 42.9$ Hz, PC)
trans-Me$_3$SiPtI(PEt$_3$)$_2$ (**2b**)	8.1	75.0	3.8	8.9 ($^3J_{\mathrm{PtC}} = 27.9$ Hz, PC*C*), 19.4 (t, $J_{\mathrm{PC}}{}^b = 17.0$ Hz, $^{2J}{}_{\mathrm{PtC}} = 44.0$ Hz, PC)
trans-Me$_2$ClSiPtCl(PEt$_3$)$_2$ (**2c**)	12.8	112	~2	8.7 ($^3J_{\mathrm{PtC}} = 26.5$ Hz, PC*C*), 16.3 (t, $J_{\mathrm{PC}}{}^b = 17.5$ Hz, $^2J_{\mathrm{PtC}} = 36.6$ Hz, PC)
trans-MeCl$_2$SiPtCl(PEt$_3$)$_2$ (**2d**)	18.1	154	~1	8.5 ($^3J_{\mathrm{PtC}} = 24.5$ Hz, PC*C*), 16.1 (t, $J_{\mathrm{PC}}{}^b = 17.4$ Hz, $^2J_{\mathrm{PtC}} = 33.9$ Hz, PC)
trans-Me$_3$SiPtBr(PMe$_3$)$_2$ (**2e**)[c,d]	7.3	78.1	3.8	16.6 (t, $J_{\mathrm{PC}}{}^b = 19.1$ Hz, $^2J_{\mathrm{PtC}} = 47.4$ Hz, PC)
trans-Me$_3$SiPtI(PMe$_3$)$_2$ (**2f**)[c,e]	7.0	73.9	4.2	18.1 (t, $J_{\mathrm{PC}}{}^b = 19.3$ Hz, $^{2J}{}_{\mathrm{PtC}} = 49.5$ Hz, PC)
trans-Me$_3$SiPtI(PMe$_2$Ph)$_2$ (**2g**)[c,f]	6.3	~65	~4	19.0 (t, $J_{\mathrm{PC}}{}^b = 19.3$ Hz, PC)[g]
trans-Me$_3$SiMe$_2$SiPtI(PEt$_3$)$_2$ (**2h**)	6.4	42.0	4.6	1.0 ($^3J_{\mathrm{PtC}} = 12.1$ Hz, CSiSiPt), 9.0 ($^3J_{\mathrm{PtC}} = 29.5$ Hz, PC*C*), 19.4 (t, $J_{\mathrm{PC}}{}^b = 17.2$ Hz, $^2J_{\mathrm{PtC}} = 43.5$ Hz, PC)
trans-Me$_2$PhSiPtBr(PEt$_3$)$_2$ (**2i**)	6.9	76.0	3.0	8.8 ($^3J_{\mathrm{PtC}} = 27.6$ Hz, PC*C*), 17.5 (t, $J_{\mathrm{PC}}{}^b = 17.1$ Hz, $^2J_{\mathrm{PtC}} = 40.1$ Hz, PC), 127.5 (*m*-C), 128.0 (*p*-C), 134.6 ($^3J_{\mathrm{PtC}} = 21.8$ Hz, *o*-C), 148.2 (t, $^3J_{\mathrm{PC}} = 3.3$ Hz, ^2JPtC ≈ 56 Hz, *ipso*-C)
trans-Me$_2$PhSiPtI(PEt$_3$)$_2$ (**2j**)	6.7	73.1	3.1	9.0 ($^3J_{\mathrm{PtC}} = 27.1$ Hz, PC*C*), 19.2 (t, $J_{\mathrm{PC}}{}^b = 17.3$ Hz, $^2J_{\mathrm{PtC}} = 41.3$ Hz, PC), 127.6 (*m*-C), 128.0 (*p*-C), 134.4 ($^3J_{\mathrm{PtC}} = 19.2$ Hz, *o*-C), 147.8 (t, $^3J_{\mathrm{PC}} = 3.8$ Hz, $^2J_{\mathrm{PtC}} \approx 56$ Hz, *ipso*-C)
trans-MePhHSiPtI(PEt$_3$)$_2$ (**2k**)	-0.4	58.0	~1	8.6 ($^3J_{\mathrm{PtC}} = 27.3$ Hz, PC*C*), 17.7 (t, $J_{\mathrm{PC}}{}^b = 17.9$ Hz, $^2J_{\mathrm{PtC}} = 35.8$ Hz, PC), 127.7 (*m*-C), 128.4 (*p*-C), 135.3 ($^3J_{\mathrm{PtC}} = 27.2$ Hz, *o*-C), 143.4 (t, $^3J_{\mathrm{PC}} = 1.8$ Hz, $^2J_{\mathrm{PtC}} \approx 88$ Hz, *ipso*-C)

[a] In C$_6$D$_6$ at 20−25 °C. [b] $J_{\mathrm{PC}} = {}^1/_2|^1J_{\mathrm{PC}} + {}^3J_{\mathrm{PC}}|$. [c] Small amounts of phosphorus-containing impurities were present. [d] In C$_6$D$_5$CD$_3$ at −30 °C. [e] In C$_6$D$_5$CD$_3$ at −20 °C. [f] In C$_6$D$_5$CD$_3$ at −60 °C. [g] The $^3J_{\mathrm{PtC}}$ value of the methyl carbon and the chemical shifts of the phenyl carbons in the PMe$_2$Ph ligand were not confirmed.

Table 4. ^{29}Si, ^{31}P, and ^{195}Pt NMR of 2[a]

complex	δ(^{29}Si)	δ(^{31}P)	δ(^{195}Pt)	$^1J_{\mathrm{PtSi}}$ (Hz)	$^2J_{\mathrm{PSi}}$ (Hz)	$^1J_{\mathrm{PtP}}$ (Hz)
trans-Me$_3$SiPtCl(PEt$_3$)$_2$	−15.6	21.0	−4985	1256	10.3	2859
trans-Me$_3$SiPtBr(PEt$_3$)$_2$ (**2a**)	−12.2	19.2	−5015	1248	9.7	2864
trans-Me$_3$SiPtI(PEt$_3$)$_2$ (**2b**)	−8.0	16.3	−5039	1215	8.8	2869
trans-Me$_2$ClSiPtCl(PEt$_3$)$_2$ (**2c**)	23.0	20.6	−4860	1614	10.3	2674
trans-MeCl$_2$SiPtCl(PEt$_3$)$_2$ (**2d**)	18.6	20.1	−4779	2135	12.3	2516
trans-Me$_3$SiPtBr(PMe$_3$)$_2$ (**2e**)[b,c]	−11.4	−11.9	−5001	1227	10.3	2772
trans-Me$_3$SiPtI(PMe$_3$)$_2$ (**2f**)[b,d]	−7.1	−14.2	−5040	1192	9.6	2781
trans-Me$_3$SiPtI(PMe$_2$Ph)$_2$ (**2g**)[b,e]	−8.2	−1.1	−5136	1130[f]	9.3	2914
trans-Me$_3$SiMe$_2$SiPtI(PEt$_3$)$_2$ (**2h**)	−20.8 (Si$^\alpha$Pt), −17.9 (Si$^\beta$SiPt)	15.4	−5096	1198 (Si$^\alpha$), 119 (Si$^\beta$)	9.2 (Si$^\alpha$), ~0 (Si$^\beta$)	2820
trans-Me$_2$PhSiPtBr(PEt$_3$)$_2$ (**2i**)	−12.6	17.1	−5042	1336	10.0	2780
trans-Me$_2$PhSiPtI(PEt$_3$)$_2$ (**2j**)	−10.9	14.2	−5065	1296	9.1	2796
trans-MePhHSiPtI(PEt$_3$)$_2$ (**2k**)	−22.7	12.8	−5244	1318	11.0	2614

[a] In C$_6$D$_6$ at 20−25 °C. [b] Small amounts of phosphorus-containing impurities were present. [c] In C$_6$D$_5$CD$_3$ at −30 °C. [d] In C$_6$D$_5$CD$_3$ at −20 °C. [e] In C$_6$D$_5$CD$_3$ at −60 °C. [f] At 20 °C. The $^1J_{\mathrm{PtSi}}$ value was not confirmed at −60 °C.

(PEt$_3$)$_2$, *trans*-R$_2$MeSiPtI(PEt$_3$)$_2$, and *trans*-Me$_3$SiPtIL$_2$ are as follows.

(a) *trans*-Me$_3$SiPtX(PEt$_3$)$_2$. The ^{29}Si resonances shift downfield with a decrease in the electronegativity of the halogen atom, while the tendencies for the $^1J_{\mathrm{PtSi}}$ and $^2J_{\mathrm{PSi}}$ values are similar to those reported for *trans*-Ph$_3$SiPtX(PMe$_2$Ph)$_2$ (X = Cl, Br, I).[41] The trend for ^{31}P and ^{195}Pt resonances and $^1J_{\mathrm{PtP}}$ is also similar to that manifested in the *trans*-MePtXL$_2$ (X = Cl, Br, I; L = PMe$_2$Ph, PEt$_3$) species.[42]

(b) *trans*-Me$_{3-n}$Cl$_n$SiPtCl(PEt$_3$)$_2$. The ^{29}Si NMR is contrasted with that reported for some Me$_{3-n}$Cl$_n$Si-M (M = Fe, Ru, Os) species,[43] the ^{29}Si NMR chemical shifts of which linearly increase in the order $n = 0 < 1 < 2$. Meanwhile, the $^3J_{\mathrm{PtH}}$(MeSiPt) value follows the sequence $n = 0 > 1 > 2$, which is similar to that reported for Me$_{3-n}$Cl$_n$E−Pt species (E = Ge, Sn; $n = 0, 1$).[10,13] In contrast, the $^2J_{\mathrm{PtC}}$, $^1J_{\mathrm{PtSi}}$, and $^2J_{\mathrm{PSi}}$ values adopt the

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[41] Latif, L. A. *J. Chem. Res., Miniprint* **1995**, 1568.

[42] For instance, see: Kennedy, J. D.; McFarlane, W.; Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1976**, 874 and references cited therein.

[43] Krentz, R.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2976.

reverse order, $n = 0 \leq 1 < 2$, which seems to be reasonable, since an increase in the number of electronegative substituents at silicon atoms is likely to shorten silicon-metal bonds[30] to result in larger coupling constants. The correlations regarding the ^{195}Pt resonance and $^1J_{PtP}$ value are similar to those observed in the *trans*-$H_{3-n}X_nSiPtX(PEt_3)_2$ (X = Cl, Br) species.[44]

(c) *trans*-$R_2MeSiPtI(PEt_3)_2$. The ^{1}H chemical shifts of the MeSiPt moieties follow the sequence $R_2 = Me_2 < Me(Me_3Si) < MePh < PhH$, which, with the exception of $Me(Me_3Si)$ species, may reflect the electronegativity of the R_2 substituents. On the other hand, the relevant coupling constants increase in the orders $R_2 = Me_2 < MePh < PhH < Me(Me_3Si)$ for $^3J_{PtH}$, $Me(Me_3Si) < PhH < MePh < Me_2$ for $^2J_{PtC}$, $Me(SiMe_3) < Me_2 < MePh < PhH$ for $^1J_{PtSi}$, and $Me_2 < MePh < Me(SiMe_3) < PhH$ for $^2J_{PSi}$. Although the inconsistency between them has not been rationalized yet, the trend for $^3J_{PtH}$, $^1J_{PtSi}$, and $^2J_{PSi}$, except for those of the $Me(SiMe_3)$ species, seems to be consistent with the favorable effect of the electronegative substituents on stabilizing the silicon−metal bonds. Meanwhile, the $^1J_{PtP}$ value follows the order $R_2 = PhH < MePh < Me(SiMe_3) < Me_2$, suggesting that the cis influence[45] of the R_2MeSi ligand decreases in the reverse order.

The disilanylplatinum species **2h** displays two ^{29}Si resonances at similar positions (−20.8 and −17.9 ppm). However, the values of $^1J_{PtSi}$ and $^2J_{PSi}$ for the silicon atom (Si$^{\alpha}$) bound to the platinum (1198 and 9.2 Hz, respectively) are much larger than those for the silicon atom (Si$^{\beta}$) remote from the platinum (119 and ~0 Hz, respectively).

(d) *trans*-$Me_3SiPtIL_2$. The Me_3Si ^{1}H and ^{13}C NMR and ^{195}Pt NMR resonances tend to shift downfield by increasing the basicity of L ($PMe_2Ph < PMe_3 < PEt_3$). The same order is observed for the value of $^1J_{PtSi}$, suggesting that the order of the cis influence is $PMe_2Ph > PMe_3 > PEt_3$; less basic cis ligands are likely to weaken the Si−Pt bond. The tendency for $^1J_{PtP}$ is similar to that observed for other bis(phosphine)platinum(II) complexes.[46]

Conclusion

We have demonstrated that oxidative addition of silicon−halogen bonds to platinum(0) complexes proceeds, depending on the nature of the silicon−halogen bonds and the phosphine ligands, to provide various *trans*-halogeno(silyl)bis(phosphine)platinum(II) complexes. The silyplatinum species undergo cleavage of the Si−Pt bonds in the reactions with phosphines, group 12 organometals, hydrosilanes, and an olefin. In addition, measurements of the ^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{195}Pt NMR spectra of the resulting silylplatinum species have revealed some relationships between ligated groups, and chemical shifts and coupling constants.

Development of new catalyses that involve oxidative addition of the silicon−halogen bonds and clarification of the reactivities of other organosilanes and/or silylmetal complexes are subjects for further investigations.

Experimental Section

^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{195}Pt NMR spectra were recorded on Hitachi R-40, JEOL FX-90A, Bruker AC-200, and/or Bruker ARX-300 instruments (90, 200, or 300 MHz for ^{1}H; 50.3 or 75.5 MHz for ^{13}C; 59.6 MHz for ^{29}Si; 36.2 or 121.5 MHz for ^{31}P; 64.5 MHz for ^{195}Pt). An INEPT technique was used for ^{29}Si NMR measurements ($\tau = 37$ ms, $\Delta = 12$ ms).[47] The chemical shifts referenced to are as follows: Me_4Si (0 ppm), C_6D_5H (7.16 ppm), or $C_6D_5CD_2H$ (2.09 ppm) for ^{1}H NMR; C_6D_6 (128.0 ppm) or $C_6D_5CD_3$ (20.44 ppm) for ^{13}C NMR; H_3PO_4 (85% solution in D_2O, 0 ppm) for ^{31}P NMR; Me_4Si (0 ppm) for ^{29}Si NMR; Na_2PtCl_6 (saturated solution in D_2O, 0 ppm) for ^{195}Pt NMR. IR spectra were obtained using Jasco A-302 and/or Jasco FT/IR-5000 spectrometers. GC−MS analyses were performed with a Shimadzu QP-1000 GC-MS spectrometer (EI, 70 eV).

Benzene and benzene-*d*$_6$ were dried with sodium or molecular sieves 4A and were distilled under nitrogen. The platinum complexes $Pt(PPh_3)_4$[48] (**1a**), $Pt[Ph_2P(CH_2)_2PPh_2]_2$[49] (**1b**), $Pt(PEt_3)_4$[50a] (**1c**), $Pt(PEt_3)_3$[50b] (**1d**), $Pt(PMe_3)_4$[51] (**1e**), $Pt(PMe_2Ph)_4$[52] (**1f**), and *trans*-$Me_3SiPtCl(PEt_3)_2$[15a] were prepared according to procedures in the literature. The halosilanes Me_3SiBr, Me_3SiCl, Me_2SiCl_2, $MeSiCl_3$, and $MePh_2SiCl$ were purchased and were distilled before use. The iodosilanes Me_3SiI[53] and $Me_3SiSiMe_2I$[54] were synthesized by the reported methods. Hydrosilanes (Me_2PhSiH, $MePhSiH_2$) and olefins (isoprene, styrene) were dried with molecular sieves 4A and were distilled in vacuo or under nitrogen. Et_2Zn (1 M hexane solution), Ph_2Hg, and Ph_4Sn were used as purchased. All manipulations for the reactions and the isolation procedures were carried out under nitrogen unless otherwise noted.

The identification of the products, such as Me_3SiH, Me_3SiEt, Me_3SiPh, $(Me_3Si)_2O$, and $PhCH{=}CHSiMe_3$,[55] was made by comparison with the authentic samples and/or by NMR and MS spectra.

Reactions of Platinum(0) Complexes with Halosilanes. The general procedure for NMR monitoring was as follows. To a benzene-*d*$_6$ or benzene (0.20−0.60 mL) solution of a platinum(0) complex (0.075−0.30 mmol) placed in a thick-walled NMR tube (ca. 5 mm o.d.) was added a halosilane (~3 equiv), and the tube was sealed under nitrogen or in vacuo. The tube was then heated at the temperature specified in Table 1. Occasionally the heating was discontinued and ^{1}H and/or ^{31}P NMR spectra were measured to evaluate the progress of the reaction.

When oxidative addition of the silicon-halogen bonds to Pt(0) complexes took place, new MeSi proton signals with ^{195}Pt satellites appeared in the region of 0−1 ppm. These chemical shifts and the coupling constants of $^3J_{PtH}$ were similar to those of the purified samples (Table 2). In ^{31}P NMR the reactions of **1c**,**d** showed new signals with ^{195}Pt satellites having coupling constants similar to those of the isolated samples (Table 4). However, the reaction mixtures of **1e**,**f** showed only broad singlets without detectable ^{195}Pt satellites, probably due to rapid phosphine exchange reactions. The NMR yields of

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[44] Anderson, D. W. W.; Ebsworth, E. A. V.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1973**, 2370.

[45] For instance, see: (a) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2117 and references cited therein. (b) Reference 2, p 253.

[46] For instance: (a) MacDougall, J. J.; Nelson, J. H.; Mathey, F. *Inorg. Chem.* **1982**, *21*, 2145. In the series of bis(trialkylphosphine)platinum(II) species, replacement of the alkyl groups by phenyl groups seems to enlarge the $^1J_{PtP}$ value. See also: (b) Reference 42. (c) Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133.

[47] For a review of ^{29}Si NMR, see: Blinka, T. A.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 193.

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the silylplatinum species were estimated on the basis of the proton integral ratios of the phosphines and/or the unreacted halosilanes to the produced MeSi−Pt moieties.

Each silylplatinum was isolated in a separate reaction as described below. NMR spectral data on the purified samples of ^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{195}Pt are shown in Tables 2−4.[56]

(a) *trans*-$Me_3SiPtBr(PEt_3)_2$ (2a). Me_3SiBr (1.29 mmol) was added to a benzene (0.50 mL) solution of **1d** (0.517 mmol) in a glass tube (8 mm o.d.), which was then sealed and heated at 120 °C for 7 h. The reaction mixture was concentrated in vacuo, and pentane (∼1 mL) was added to the residue. Filtration of the pentane solution followed by cooling of the filtrate to −80 °C gave a yellow solid of crude **2a**. Recrystallization from pentane (∼0.5 mL) gave pure **2a** (0.303 mmol, 59% yield) in the form of pale yellow needles. **2a**: mp 58−60 °C (under N_2); IR (Nujol) 1236 (w), 1038 (s), 840 (s), 768 (m), 742 (m), 618 (w) cm^{-1}. Anal. Calcd for $C_{15}H_{39}BrP_2PtSi$: C, 30.82; H, 6.73. Found: C, 30.80; H, 6.80.

(b) *trans*-$Me_3SiPtI(PEt_3)_2$ (2b). A mixture of Me_3SiI (5.32 mmol), **1d** (2.13 mmol), and benzene (1.7 mL) was heated in a closed Schlenk tube at 80 °C for 50 min. Through a purification procedure similar to that for **2a**, **2b** (1.74 mmol, 82% yield) was obtained in the form of pale yellow needles. **2b**: mp 79−80 °C (under N_2); IR (Nujol) 1253 (w), 1234 (w), 1036 (m), 835 (s), 756 (m), 735 (m), 719 (m), 669 (w), 617 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{39}IP_2PtSi$: C, 28.53; H, 6.22. Found: C, 28.75; H, 6.12.

(c) *trans*-$Me_2ClSiPtCl(PEt_3)_2$ (2c). A mixture of Me_2SiCl_2 (0.837 mmol), **1d** (0.335 mmol), and benzene (0.40 mL) was heated in a sealed glass tube at 120 °C for 2 h. Concentration of the mixture in vacuo gave nearly pure **2c** (∼0.3 mmol, ≥95% purity, ≥95% yield) as a colorless viscous oil. **2c**: IR (neat) 1456 (s), 1421 (m), 1379 (m), 1243 (s), 1035 (s), 835 (s), 801 (s), 768 (s), 723 (s), 679 (m), 652 (m), 443 (s), 429 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{36}Cl_2P_2PtSi$: C, 30.00; H, 6.47. Found: C, 31.65; H, 6.82. A satisfactory elemental analysis of **2c** was not obtained because of its high susceptivity to moisture.

(d) *trans*-$MeCl_2SiPtCl(PEt_3)_2$ (2d). A mixture of $MeSiCl_3$ (0.770 mmol), **1d** (0.308 mmol), and benzene (0.40 mL) was heated in a sealed glass tube at 90 °C for 30 min. Concentration of the mixture in vacuo gave nearly pure **2d** (∼0.3 mmol, ≥95% purity, ≥95% yield) as a colorless waxy solid. **2d**: IR (neat) 1458 (s), 1421 (s), 1381 (s), 1247 (s), 1036 (s), 790 (s), 772 (s), 729 (s), 704 (s), 632 (s), 458 (m), 420 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{33}Cl_3P_2PtSi$: C, 26.88; H, 5.73. Found: C, 27.08; H, 5.61.

(e) *trans*-$Me_3SiPtBr(PMe_3)_2$ (2e). A mixture of Me_3SiBr (0.644 mmol), **1e** (0.160 mmol), and benzene (0.40 mL) was heated in a sealed glass tube at 120 °C for 20 h. Concentration of the reaction mixture followed by extraction with benzene (0.5 mL × 2) gave relatively pure **2e** (∼50 mg) as a pale yellow solid. Its ^{1}H and ^{31}P NMR spectra in benzene-d_6 displayed PMe signals arising from mainly two species, **2e** (^{1}H NMR δ 1.34 (br s); ^{31}P NMR δ −12.2 (br s)) and unreacted **1e** (^{1}H NMR δ 1.41 (br s, $^3J_{PtH} \approx 20$ Hz); ^{31}P NMR δ 53.4 (s, $^1J_{PtP} = 3835$ Hz)) (**2e**:**1e** ≈ 5:2). The attempt to improve the purity of **2e** by recrystallization from pentane was not successful. Although the phosphine ligand of the relatively pure **2e** showed rather broad NMR resonances without detectable ^{195}Pt satellites at room temperature, well-resolved signals could be observed in toluene-d_8 at −30 °C.

(f) *trans*-$Me_3SiPtI(PMe_3)_2$ (2f). A mixture of Me_3SiI (0.527 mmol), **1e** (0.151 mmol), and benzene (0.30 mL) was heated in a closed Schlenk tube at 80 °C for 1 h. Through a purification procedure similar to that for **2a** (recrystallization from benzene−pentane), reasonably pure **2f** (∼40 mg) was obtained as a yellow solid. Although its elemental analysis was almost satisfactory, the NMR signals for the phosphine ligand were rather broad singlets at room temperature, indicating occurrence of rapid phosphine exchange between **2f** and PMe_3-containing impurities such as $[PMe_3(SiMe_3)]^+I^-$; the integral ratio of the PMe protons of **2f**:impurities was estimated at ≥9:1. The broad NMR signals were well-resolved in toluene-d_8 at −20 °C. **2f**: IR (Nujol) 1305 (m), 1282 (m), 1234 (m), 948 (s), 830 (s), 737 (m), 727 (m), 673 (m), 656 (m), 619 (m) cm^{-1}. Anal. Calcd for $C_9H_{27}IP_2PtSi$: C, 19.75; H, 4.97. Found: C, 19.97; H, 4.57.

(g) *trans*-$Me_3SiPtI(PMe_2Ph)_2$ (2g). A mixture of Me_3SiI (0.583 mmol), **1f** (0.168 mmol), and benzene (0.50 mL) was heated in a sealed glass tube at 120 °C for 21 h. Concentration of the mixture in vacuo gave relatively pure **2g** (∼110 mg) as a yellow solid. Its ^{1}H and ^{31}P NMR in toluene-d_8 showed the existence of mainly two PMe species, **2g** (^{1}H NMR δ ∼1.8 (br s); ^{31}P NMR δ −5.8 (br s)) and unreacted **1f** (^{1}H NMR δ 1.45 (br s, $^3J_{PtH} \approx 20$ Hz); ^{31}P NMR δ −34.4 (s, $^1J_{PtP} = 3808$ Hz)) (**2g**:**1f** ≈ 9:1). Attempts to improve the purity of **2g** by recrystallization with benzene or column chromatography with alumina or Florisil were unsuccessful. Although the ligated PMe_2Ph of the relatively pure **2g** showed rather broad NMR resonances without detectable ^{195}Pt satellites at room temperature, relatively well-resolved signals could be observed at −60 °C.

(h) *trans*-$Me_3SiMe_2SiPtI(PEt_3)_2$ (2h). A mixture of $Me_3SiSiMe_2I$ (1.80 mmol), **1d** (1.02 mmol), and benzene (1.0 mL) was heated in a sealed glass tube at 60 °C for 1 h. The mixture was concentrated in vacuo, and pentane (∼5 mL) was added to the residue. Filtration of the pentane solution followed by cooling of the filtrate to −20 °C gave nearly pure **2h** (0.063 mmol, 68% yield) in the form of yellow cubic crystals. Recrystallization from pentane gave analytically pure **2h**. **2h**: mp 76−80 °C (under N_2); IR (Nujol) 1252 (w), 1236 (m), 1036 (s), 860 (w), 836 (m), 790 (s), 764 (m), 718 (m), 684 (w), 646 (w), 620 (w) cm^{-1}. Anal. Calcd for $C_{17}H_{45}IP_2PtSi_2$: C, 29.61; H, 6.58. Found: C, 29.78; H, 6.29.

A benzene-d_6 solution of **2h** was left in a sealed NMR tube at room temperature for 2.5 years. ^{1}H and ^{31}P NMR of the resulting solution showed consumption of **2h** (≥95% conversion) and formation of **2b** (≥80% NMR yield). In ^{1}H NMR, several unknown SiMe signals were also observed at 0−0.4 ppm with their integral ratio to **2b** being ∼2:3 (two major resonances of almost equal intensity at 0.268 and 0.270 ppm with a combined ratio to total unknown SiMe signals being ∼2:5). GC−MS of the reaction mixture showed a major peak, the parent ion of which corresponded to $(SiMe_2)_5O$. GC−MS: *m/z* (relative intensity) 306 (0.8, M$^+$), 291 (3), 232 (96), 217 (26), 173 (15), 159 (21), 158 (35), 157 (18), 144 (27), 143 (16), 73 (100), 59 (17), 45 (30).

Reactions of 2a with PEt_3 or PPh_3. A mixture of **2a** (0.030 mmol), PEt_3 (0.060 mmol), and benzene-d_6 (0.20 mL) was sealed in an NMR tube. No substantial change was shown by ^{1}H NMR after the mixture was heated to 90 °C for 30 min. When the mixture was heated to 120 °C, ^{1}H NMR showed new signals of Me_3SiBr (0.30 ppm) and $(Me_3Si)_2O$ (0.11 ppm) with concomitant consumption of **2a**. The yields of Me_3SiBr and $(Me_3Si)_2O$ and the conversion of **2a** were respectively estimated by NMR at ∼15, ∼5, and ∼20% after 40 min of heating, ∼50, ∼10, and ∼60% after 3 h, and ∼50, ∼10, and ∼60% after 5 h. ^{31}P NMR spectra of the reaction mixture displayed the signal of **1d** at ∼40 (br, $^1J_{PtP} \approx 4070$ Hz) ppm with the signals of free PEt_3 at −18 (br) ppm and unreacted **2a**.

Similarly, in the reaction using **2a** (0.030 mmol), PPh_3 (0.060 mmol), and benzene-d_6 (0.20 mL), the yields of Me_3SiBr and $(Me_3Si)_2O$ and the conversion of **2a** were respectively estimated at ∼25, ∼10, and ∼35% after 40 min of heating, ∼70, ∼10, and ∼80% after 3 h, and ∼80, ∼10, and ∼90% after 5 h. ^{31}P NMR indicated formation of **1d** (small) and several unidentified (phosphine)platinum species (6.9 ($^1J_{PtP} \approx 2730$ Hz), 12.4 ($^1J_{PtP} \approx 2770$ Hz) ppm, etc.) along with free PPh_3 at −2 (br) ppm and unreacted **2a**. In the reaction without extra phosphines, the yields of Me_3SiBr and $(Me_3Si)_2O$ and the conversion of **2a** were respectively estimated at ∼5, ∼10, and ∼15% after

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[56] The reported chemical shifts[8] for **2** slightly deviated.

40 min, ~10, ~15, and ~25% after 3 h, and ~10, ~15, and ~25% after 5 h.

Reactions of 2a with Et_2Zn or Ph_2Hg. A hexane solution of Et_2Zn (~1.0 M, 0.050 mL) was added to a benzene-d_6 (~0.15 mL) solution of **2a** (0.050 mmol) placed in an NMR tube. ^1H and ^{31}P NMR and GC−MS after ~10 min at room temperature showed ≥95% conversion of **2a** and formation of Me_3SiEt (^1H NMR δ −0.08 (s, $SiCH_3$) ppm, ≥90% yield) along with several unidentified (phosphine)platinum species (mainly three, A1:A2:A3 = ~2:~2:1). ^{31}P NMR: A1, δ 12.7 (s, $^1J_{PtP} = 2979$ Hz); A2, δ 18.1 (s, $^1J_{PtP} = 2878$ Hz); A3, δ 28.3 (s, $^1J_{PtP} = 3247$ Hz).

Similarly, in the reaction of **2a** (0.050 mmol) with Ph_2Hg (0.050 mmol) in benzene-d_6 (0.2 mL) at 60 °C for 40 min, ^1H and ^{31}P NMR and GC−MS showed almost complete consumption of **2a** and formation of Me_3SiPh (0.18 (s, $SiCH_3$) ppm, ~90% yield) along with several unidentified (phosphine)platinum species (mainly four, B1:B2:B3:B4 = 6:8:7:4). ^{31}P NMR: B1, δ 3.0 (s, $^1J_{PtP} = 4146$ Hz); B2, δ 6.7 (s, $^1J_{PtP} = 2395$ Hz); B3, δ 11.3 (s, $^1J_{PtP} = 2778$ Hz); B4, δ 20.9 (s, $^1J_{PtP} = 2690$ Hz).

Reactions of 2a,b with Me_2PhSiH or $MePhSiH_2$. A mixture of **2a** (0.030 mmol), Me_2PhSiH (0.060 mmol), and benzene-d_6 (0.20 mL) was heated in a sealed NMR tube at 60 °C for 10 min. ^1H NMR showed formation of the new SiMe species *trans*-$(Me_2PhSi)PtBr(PEt_3)_2$ (**2i**; 0.60 (s, $^3J_{PtH} = 27.0$ Hz) ppm, ~10% yield) and Me_3SiH (−0.02 (d, $^3J_{HH} = 3.6$ Hz) ppm) with concomitant consumption of **2a** (~10% conversion of **2a**). The resulting mixture was further heated at the elevated temperature of 90 °C. The yields of **2i** (approximately equal to the conversions of **2a**) were estimated by ^1H NMR at ~85% after 10 min of heating and ~95% after 30 min. ^{31}P NMR spectra of the reaction mixture displayed a new signal for **2i** at 17.1 ($^1J_{PtP} = 2781$ Hz) ppm. In a separate reaction of **2a** (0.045 mmol) with Me_2PhSiH (0.090 mmol) in benzene-d_6 (0.30 mL) at 90 °C for 1 h, the reaction mixture was concentrated in vacuo. Recrystallization from pentane gave **2i** (0.0309 mmol, 69% yield) as a white solid.

Similarly, when a mixture of **2b** (0.030 mmol), Me_2PhSiH (0.060 mmol), and benzene-d_6 (0.20 mL) was left for 1 h at room temperature, ^1H and ^{31}P NMR showed formation of *trans*-$(Me_2PhSi)PtI(PEt_3)_2$ (**2j**, ~5% yield; ^1H NMR δ 0.60 ($^3J_{PtH} = 26.4$ Hz, $SiCH_3$); ^{31}P NMR δ 14.2 ($^1J_{PtP} = 2797$ Hz)) and Me_3SiH with ~5% conversion of **2b**. The resulting mixture was heated at 60 °C. The yields of **2j** (approximately equal to the conversions of **2b**) were estimated at ~90% after 10 min and ~95% after 30 min. Concentration of the reaction mixture followed by recrystallization from pentane gave **2j** (0.026 mmol, 86% yield) as a pale yellow solid.

In the reaction of **2b** (0.030 mmol) with $MePhSiH_2$ (0.060 mmol) in benzene-d_6 (0.20 mL) at room temperature, ^1H and ^{31}P NMR showed formation of *trans*-$(MePhHSi)PtI(PEt_3)_2$ (**2k**; ^1H NMR δ 0.80 (d, $^3J_{HH} = 4.0$ Hz, $^3J_{PtH} = 33.2$ Hz, $SiCH_3$); ^{31}P NMR δ 12.8 ($^1J_{PtP} = 2615$ Hz)) and Me_3SiH. The yields of **2k** (approximately equal to the conversions of **2b**) after standing for 30 min, 1 h, and 4 h were estimated at ~55, ~90, and ~100%, respectively. By recrystallization from pentane, **2k** (0.028 mmol, 93% yield) was isolated as a white solid.

NMR spectral data of **2i**−**k** are shown in Tables 2−4. Physical, IR, and analytical data of **2i**−**k** are as follows.

2i: mp 80−82 °C (under N_2); IR (Nujol) 1249 (m), 1102 (m), 1036 (m), 828 (m), 803 (s), 766 (s), 735 (s), 642 (m), 484 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{41}BrP_2PtSi$: C, 37.15; H, 6.39. Found: C, 36.56; H, 6.31.

2j: mp 77−78 °C (under N_2); IR (Nujol) 1259 (m), 1245 (m), 1098 (m), 1035 (s), 835 (m), 799 (s), 770 (s), 735 (s), 712 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{41}IP_2PtSi$: C, 34.64; H, 5.96. Found: C, 34.69; H, 5.87.

2k: mp 105−107 °C (under N_2); IR (Nujol) 2076 (s, SiH), 1311 (m), 1243 (m), 1100 (m), 1031 (s), 1004 (m), 886 (s), 866 (s), 764 (s), 745 (m), 717 (s), 683 (m), 632 (m), 468 (m), 418 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{39}IP_2PtSi$: C, 33.58; H, 5.78. Found: C, 33.93; H, 5.64.

Reaction of 2a with Styrene. A mixture of **2a** (0.05 mmol), styrene (0.10 mmol), and benzene-d_6 (0.20 mL) was sealed in an NMR tube. ^1H NMR after the mixture was heated to 90 °C for 15 min showed almost no change. When the mixture was further heated at 120 °C, new proton signals of Me_3SiBr (0.30 ppm) and $(Me_3Si)_2O$ (0.11 ppm) emerged with consumption of **2a**. The yields of Me_3SiBr and $(Me_3Si)_2O$ and the conversion of **2a** were respectively estimated by ^1H NMR at ~30, ~30, and ~65% after 1 h of heating and ~50, ~35, and ~90% after 4 h. ^{31}P NMR spectra of the resulting mixture displayed new signals at 18.2 ($^1J_{PtP} \approx 3550$ Hz) and 21.8 ($^1J_{PtP} \approx 2710$ Hz) ppm (about 1:1 ratio), which were similar to those of $Pt(PhCH{=}CH_2)(PEt_3)_2$[57] and *trans*-$PtHBr(PEt_3)_2$,[58] respectively. GC and GC−MS analysis of the reaction mixture showed formation of $PhCH{=}CHSiMe_3$ (~5%, $E/Z \approx 8/1$) and a small amount of its isomer (**A**, ≤0.3%). GC−MS: **A**, m/z (relative intensity) 176 (38, M$^+$), 161 (68), 135 (65), 73 (100).[59]

Similarly, when a mixture of **2a** (0.050 mmol), styrene (0.25 mmol), Et_3N (0.25 mmol), and benzene-d_6 (0.20 mL) was heated to 120 °C for 5.5 h, NMR, GC, and GC−MS analyses showed ≥95% conversion of **2a** with formation of $PhCH{=}CHSiMe_3$ (~2%, $E/Z \approx 4/1$), **A** (≤0.2%), Me_3SiBr (~75%), and $(Me_3Si)_2O$ (~15%).

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