Synthesis, Structure, and Properties of 9-Phospha-10-silatriptycenes and their Derivatives

Hayato Tsuji,*[,†,‡] Tomoyuki Inoue,[†] Yasuhiro Kaneta,[†] Shohei Sase,[†] Atsushi Kawachi,[†] and Kohei Tamao*[,†,§]

International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan

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A variety of 9-phospha-10-silatriptycenes (PSiT) and some derivatives, such as the phosphine selenides and *cis*-platinum complexes, have been prepared in order to study their structures and characteristics as a phosphine ligand. The ^1J(P−Se) NMR coupling constant of the phosphine selenides demonstrate the large s character of the lone pair orbital on the phosphorus atom, attributable to the small C−P−C bond angles of the PSiT framework, as confirmed by X-ray crystallography. The strong trans influence of PSiT has been determined from the ^1J(Pt−C) coupling constant measurements of the *cis*-[$PtMe_2$(psit)$_2$], which is due to the increase in the P−Pt−P angle in the complexes derived from the steric repulsion between the two bulky PSiT ligands. Both the substituent on the silicon and the bridging benzene rings affect the electronic character. Electron-withdrawing substituents on the silicon atom slightly increase the s character of the phosphorus lone pair orbital, and the isopropoxy groups on the bridging benzene rings increase the trans influence.

Introduction

Organophosphorus compounds with the phosphorus atom fixed at the bicyclic bridgehead positions constitute a unique class of ligands in organometallic chemistry. For example, phosphabarrelenes,[1] phosphatriptycenes,[2,3] the silicon-constrained monodentate alkylphosphine (SMAP),[4] and bicyclic phosphites[5] have been already reported. Some transition metal complex-catalyzed reactions are known to easily proceed using such a structurally fixed phosphorus ligand.[1,2c,6] Besides the catalytic activity, applications in functional materials science are also envisioned based on their structural features. That is, the phosphorus lone pair and the substituent on the other bridgehead position are directed opposite on the same straight line, which can be leveraged for molecular assembly, such as a one-dimensional metal-coordinating polymer[7] and a monolayer on a metal surface.

Among these constrained phosphorus compounds, a series of phosphatriptycenes with a group 14 or 15[2d,8−11] element on the other bridgehead position have been extensively studied (Figure 1a). Focused on the former series, the molecular structure and the electronic character of the phosphorus lone pair are expected to be modified by changing the other bridgehead atom and the substituent on it. While phosphatriptycene (E = C, Figure 1a)[2] and phosphagermatriptycene (E = Ge)[3a] have already been reported, phosphasilatriptycene (E = Si) is unprecedented, to the best of our knowledge. It would be important to prepare the "missing link" compound for the systematic study of the group 14 element-containing phosphatriptycenes as well as exploring the application of the phosphatriptycene family as a new series of coordinating ligands. We now report the synthesis of the 9-phospha-10-silatriptycenes (PSiT) (Figure 1b) and some derivatives, such as the phosphine selenides and *cis*-dimethylplatinum complexes, in order to study their structures and characteristics as a phosphine ligand.

Results and Discussion

1. Synthesis and Structure. 1.1 Preparation of PSiT Frameworks. Several synthetic routes to the unsymmetrical heteroatom-substituted triptycenes have been already reported. Bickelhaupt and co-workers employed *o*-phenylenemagnesium derived from *o*-phenylenemercury[12] to prepare symmetrical and unsymmetrical 9,10-dimetallatriptycenes, such as the 9-germa-10-phosphatriptycene derivative.[3a] Takahashi[13] and Kawashima[2b,d] prepared a 9,10-disilatriptycene derivative and a 9-phospha-

* To whom correspondence should be sent. E-mail: tsuji@chem.s.u-tokyo.ac.jp.

† Kyoto University.

‡ Present address: Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

§ Present address: RIKEN Frontier Research System, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan.

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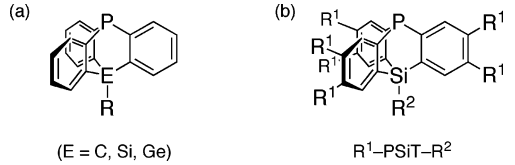
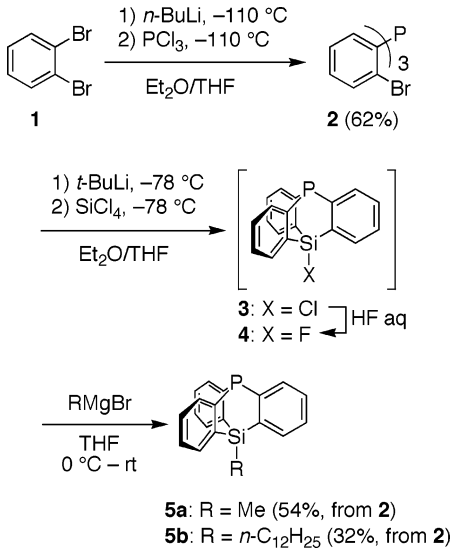


Figure 1. Structures of (a) phosphatriptycenes with a group 14 element on the other bridgehead and (b) 9-phospha-10-silatriptycenes with substituents R^1 and R^2.

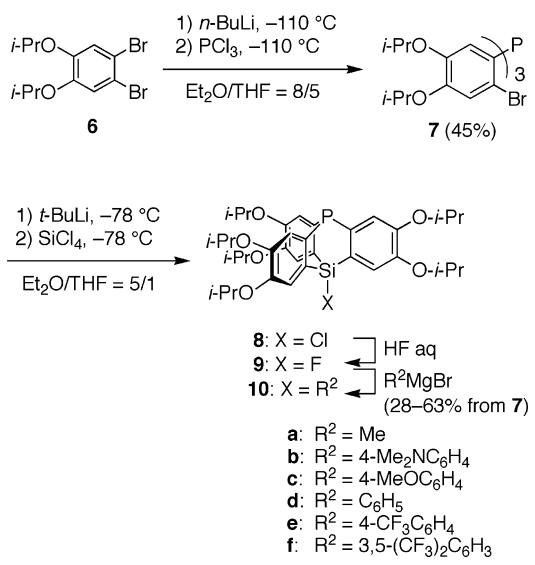
Scheme 1



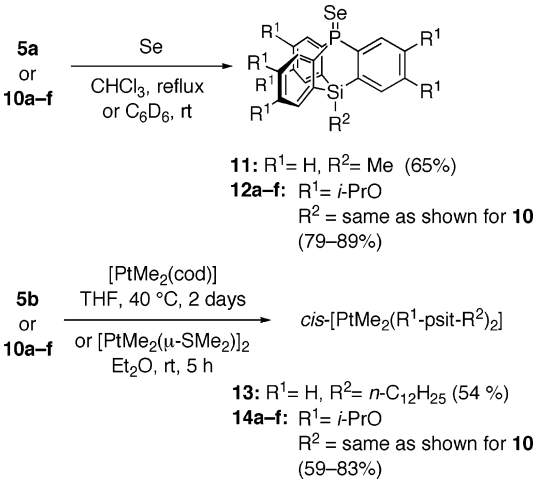
triptycene using tri(*o*-lithiophenyl)silane and tri(*o*-lithiophenyl)-phosphine derivatives as the key intermediate, respectively. We employed halogen−metal exchange reactions using *o*-dibromobenzene **1** as the starting material[14] for the preparation of PSiT.

The synthetic procedure of H−PSiT−R^2 **5** is shown in Scheme 1. The halogen−lithium exchange reaction of one of the two bromine atoms of the *o*-dibromobenzene **1** was performed in an Et_2O/THF mixed solvent at −110 °C, followed by the reaction with phosphorus trichloride to give tris(2-bromophenyl)phosphine **2**. The trilithio species, generated from **2** and *tert*-butyllithium, was treated with silicon tetrachloride to give the desired phosphasilatriptycene derivative H−PSiT−Cl **3**. After the exchange of the chlorine atom on the silicon center of **3** to a fluorine atom using aqueous hydrofluoric acid, the resulting fluorosilane **4** was treated with methylmagnesium bromide and *n*-dodecylmagnesium bromide to afford the corresponding H−PSiT−Me **5a** and H−PSiT-*n*-$C_{12}H_{25}$ **5b** in 54% and 32% yields from **2**, respectively, as moisture- and air-stable solids. The ^{31}P and ^{29}Si NMR chemical shifts of the phosphorus and the silicon nuclei of **5** (in THF-d_8) were significantly upfield shifted (δ_P −44.4, δ_{Si} −27.9 for **5a**; δ_P −42.5, δ_{Si} −29.9 for **5b**) as compared with those of the triphenylphosphine (δ_P −3.1 in C_6D_6) and methyltriphenylsilane (δ_{Si} −10.4 in C_6D_6), similar to the other phospha- and silatriptycenes.[10−13] These observations are reasonably understood by the narrowed C−P−C and C−Si−C angles of the PSiT framework, as observed in the palladium complex *trans*-[$PdCl_2$(psit-Me)$_2$], which we recently reported.[15]

Scheme 2



Scheme 3



Similarly, a series of *i*-PrO−PSiT−R^2 **10a**−**f** and their derivatives with various substituents on the bridgehead silicon atom and two isopropoxy groups on the benzene rings have been synthesized using 1,2-dibromo-4,5-diisopropoxybenzene **6** as the starting material (Scheme 2) to investigate the substituent effect on the phosphorus lone pair orbital of PSiT. The isopropoxy groups were introduced to enhance the solubility of the PSiT derivatives.

1.2. Preparation of PSiT Derivatives. To clarify the structures and properties of the PSiT framework, some derivatives were synthesized (Scheme 3). The phosphine selenides **11** and **12** were prepared by the reaction of **5a** and **10** with selenium powder, respectively.[16] The ligand exchange reaction of *cis*-[$PtMe_2$(cod)][17] or [$PtMe_2(\mu$-$SMe_2)]_2$[18] with PSiT derivatives **5b** and **10** afforded the soluble transition metal complexes *cis*-[$PtMe_2$(psit)$_2$] **13** and **14**, respectively.

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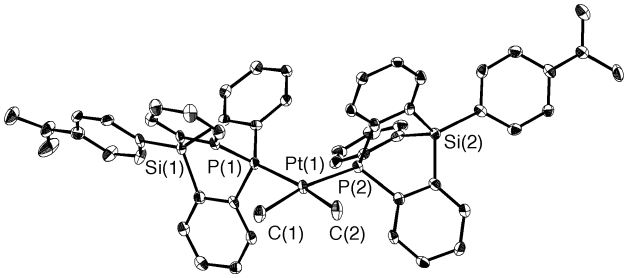

Figure 2. ORTEP drawing of the platinum complex **14b** with thermal ellipsoid plot (50% probability). Hydrogen atoms and isopropoxy groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−C(1) 2.110(5), Pt(1)−C(2) 2.141(5), Pt(1)−P(1) 2.2865(13), Pt(1)−P(2) 2.2964(13), P(1)···Si(1) 3.1012(19), C(1)−Pt(1)−C(2) 81.31(19), P(1)−Pt(1)−P(2) 106.32(5).

Table 1. Crystal Data and Details of the Structure Determination for 14b

	14b·AcOEt
empirical formula	$C_{94}H_{130}N_2O_{14}P_2PtSi_2$
fw	1825.21
temperature	173(2) K
wavelength	0.71070 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 15.139(4)$ Å, $\alpha = 80.194(11)°$ $b = 16.748(4)$ Å, $\beta = 69.414(10)°$ $c = 20.323(5)$ Å, $\gamma = 78.327(11)°$
volume	4696.4(19) Å^3
Z	2
density (calcd)	1.291 Mg/m^3
absorp coeff	1.614 mm^{-1}
$F(000)$	1912
cryst size	0.20 × 0.15 × 0.15 mm^3
θ range for data collection	3.22° to 25.50°
index ranges	$-18 \le h \le 18$, $-20 \le k \le 17$, $-23 \le l \le 24$
no. of reflns collected	33 086
no. of indep reflns	17 045
completeness	97.5%
max. and min. transmn	0.7938 and 0.7385
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	17 045/0/1067
goodness-of-fit on F^2	1.064
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0516$, $wR_2 = 0.1079$
R indices (all data)	$R_1 = 0.0673$, $wR_2 = 0.1161$
largest diff peak and hole	1.086 and −0.811 e·Å^{-3}

1.3. Structure of the *cis*-Dimethylplatinum Complex. The structure of the platinum complex **14b** determined by X-ray crystallography is shown in Figure 2, and the details are summarized in Table 1. The platinum complex **14b** possesses a distorted square-planar geometry about the platinum center with a large P−Pt−P angle (106.32(5)°) and a small C−Pt−C angle (81.31(19)°), which is due to the steric congestion of the bulky PSiT ligands located at the cis positions. Such a severe steric hindrance distorts even the PSiT structure as compared to the *trans*-[$PdCl_2$(psit)$_2$].[15] Thus, one of the three C−P−C bond angles of PSiT in **14b** is exceptionally smaller (94.9(2)° for P(1); 94.4(2)° for P(2)) than the others (102.2(2)° and 103.1(2)° for P(1); 102.6(2)° and 103.1(2)° for P(2)). The P···Si distances (3.1012(19) and 3.0983(18) Å) are smaller than the sum (3.90 Å) of the van der Waals radii of each atom and are almost the same as that in the palladium complex.[15]

2. Properties of PSiT as a Ligand. 2.1. The s Character of the Phosphorus Lone Pair Orbital. To estimate the s character of the lone pair orbital of PSiT, the NMR coupling constant ^1J(P−Se) of the phosphine selenides **11** and **12** was measured.[16] Table 2 lists the data together with those of some other phosphine selenides, including **15** derived from a 9-phosphatriptycene derivative[2b] for comparison. The ^1J(P−Se) value of **11** (795 Hz) is comparable to that of the tri(2-furyl)phosphine selenide (793 Hz)[16] and between those of Ph_3P═Se (732 Hz) and the selenide of phosphatriptycene **15** (828 Hz). This trend in the ^1J(P−Se) values (Ph_3P═Se < **11** < **15**) agrees with the descending order of the C−P−C angles: Ph_3P > PSiT[15] > 9-phosphatriptycene.[2,19] These results demonstrate that the PSiT derivatives possess a larger s character and thus work as weaker σ-donating ligands, as compared to the ordinary triarylphosphines such as Ph_3P.

Table 2. ^1J(P−Se) Values for Phosphine Selenides Derived from PSiT, Ph_3P, (2-furyl)$_3$P, and Phosphatriptycene

entry	Ar_3P═Se	^1J(P−Se)/Hz
1	**11**	795
2	**12a**	786
3	**12b**	786
4	**12c**	786
5	**12d**	786
6	**12e**	794
7	**12f**	794
8	Ph_3P═Se	732[a]
9	(2-furyl)$_3$P═Se	793[a]
10	**15**[b]	828

[a] Ref 16. [b] Structure is shown below. See ref 2.

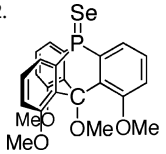

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Table 3. ^1J(Pt−C) Values for *cis*-[$PtMe_2L_2$]

entry	*cis*-[$PtMe_2L_2$]	^1J(Pt−C)/Hz
1	**13**	607
2	**14a**	601
3	**14b**	602
4	**14c**	602
5	**14d**	602
6	**14e**	602
7	**14f**	603
8	[$PtMe_2(PPh_3)_2$]	616
9	[$PtMe_2(PPhMe_2)_2$]	594

The data for **12a**−**f** in Table 2 represent the influence of the silicon substituents. Although the substituent effect on the ^1J(P−Se) values is not as drastic as the structural effect, the following trends have been observed. The electron-donating groups on the silicon atom, such as 4-Me_2N−C_6H_4 and 4-MeO−C_6H_4, do not cause any change in the ^1J(P−Se) values as compared to the parent C_6H_5 group (entries 3−5). In contrast, the electron-withdrawing groups, such as 4-CF_3−C_6H_4 and 3,5-$(CF_3)_2$−C_6H_3, slightly increase the ^1J(P−Se) value (entries 5−7). Not only the substituents on the silicon atom but also the isopropoxy groups on the bridging benzene rings affect the ^1J(P−Se) values; the ^1J(P−Se) of **12a** is smaller than that of **11** (entries 1 and 2) by 9 Hz.

2.2. Trans Influence of PSiT as a Ligand. The trans influence[20] of the PSiT ligand in *cis*-[$PtMe_2$(psit)$_2$] was evaluated on the basis of the coupling constant ^1J(Pt−C) measurements as listed in Table 3. The ^1J(Pt−C) values of **13** and **14a**−**f** are between those of *cis*-[$PtMe_2(PPh_3)_2$] and *cis*-[$PtMe_2$(PMe$_2$-

(19) The estimated C−P−C angles of the optimized structure at the B3LYP/6-311G* level are as follows: Ph_3P (102.4°) > 9-phospha-10-silatriptycene (98.7°) > 9-phosphatriptycene (94.1°).

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$Ph)_2$],[21] demonstrating that the trans influence of PSiT is greater than that of PPh_3 and smaller than that of PMe_2Ph. Although the aryl groups on the silicon atom exhibit a negligible effect, the substituents on the bridging benzene rings affect the electronic nature of the PSiT. Thus, the ^1J(Pt−C) value of *cis*-[$PtMe_2$(*i*PrO−PSiT−Me)$_2$] **14a** is smaller than that of *cis*-[$PtMe_2$(H−PSiT-*n*-$C_{12}H_{25})_2$] **13**. The enhancement of the trans influence in **14a** as compared to **13** is attributable to the greater electron-donating ability of the isopropoxy groups on the bridging benzene rings.

The greater trans influence of PSiT than that of PPh_3 seems to contradict the fact that the lone pair orbital of PSiT has a high degree of s character as estimated using the phosphine selenides. This discrepancy can be understood to be due to steric effects. In general, the greater trans influence is observed for complexes having a larger bite angle (P−M−P),[22] which is also the case with these *cis*-[$PtMe_2$(psit)$_2$] complexes, as observed by the X-ray structure of **14b** (Figure 2).

Conclusion

In summary, we have synthesized phosphasilatriptycenes (PSiT) and their derivatives, such as phosphine selenide and the *cis*-[$PtMe_2$(psit)$_2$] complexes, in order to study the ability of PSiT as a ligand. The NMR coupling constant measurements of the phosphine selenides demonstrate the large s character of the lone pair orbital due to the small C−P−C bond angles, and the strong trans influence as a ligand in *cis*-[$PtMe_2$(psit)$_2$] compared to PPh_3 due to the steric bulkiness. Regarding the substituent effect, the isopropoxy groups on the bridging benzene rings intensify the trans influence of PSiT. However, at least in the cis bis(phosphine) complexes, the trans influence is dominated by the steric bulkiness rather than the electronic effect.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. ^{1}H NMR spectra were measured with a Varian Mercury-300 (300 MHz) spectrometer. ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR were measured with a JEOL EX-270 (67.8 MHz for ^{13}C, 254 MHz for ^{19}F, 53.5 MHz for ^{29}Si, and 109 MHz for ^{31}P). Chemical shifts are reported in δ (ppm), referenced to ^{1}H of residual protons and ^{13}C signals of deuterated solvents as internal standards or to ^{19}F, ^{29}Si, and ^{31}P of $CFCl_3$, Me_4-Si, and 85% H_3PO_4 as external standards, respectively. Melting points were determined with a Yanaco MP-S3 instrument. Mass spectra and elemental analysis were performed at the Mass Spectrum and Microanalysis Division of Institute for Chemical Research, Kyoto University. [$PtMe_2$(cod)][23] and [$PtMe_2$(μ-SMe_2)]$_2$[24] were prepared according to the reported procedures. Benzene was distilled over sodium. Other chemicals and solvents (Wako Pure Chemical Industries, anhydrous products) were used without further purification.

Preparation of Tris(2-bromophenyl)phosphine (2). A solution of *n*-BuLi in hexane (1.60 M, 80.0 mL, 128 mmol) was added dropwise to a solution of 1,2-dibromobenzene **1** (30.2 g, 128 mmol) in Et_2O (256 mL) and THF (200 mL) at −110 °C. After the addition was completed, the mixture was stirred for an additional 2 h, and a solution of phosphorus trichloride (4.88 g, 35.5 mmol) in Et_2O (20 mL) was added dropwise to the mixture at −110 °C. After the mixture was stirred for an additional 2 h, the mixture was allowed to warm gradually to room temperature. The solvents were evaporated, and the residue was dissolved in toluene and passed through a pad of silica gel. The filtrate was concentrated to give the crude product. The crude product was recrystallized from toluene/EtOH to give **2** (10.9 g, 21.8 mmol, 62%) as colorless crystals. ^{1}H NMR (C_6D_6): δ 6.69−6.82 (m, 6H), 6.90−6.94 (m, 3H), 7.36−7.40 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 127.7, 130.2, (d, J(C−P) = 34 Hz), 130.6, 133.1, 134.6, 136.6 (d, J(C−P) = 11 Hz). ^{31}P NMR ($CDCl_3$): δ −3.00.

Preparation of H−PSiT−Cl (3). A solution of *t*-BuLi in pentane (1.56 M, 55 mL, 86 mmol) was added dropwise to a solution of **2** (7.00 g, 14.0 mmol) in Et_2O (140 mL) and THF (30 mL) at −78 °C. After the addition was completed, the mixture was stirred for an additional 2 h and a solution of silicon tetrachloride (1.52 g, 14.0 mmol) in Et_2O (30 mL) was added dropwise to the mixture at −78 °C. After the mixture was stirred for an additional 2 h, chlorotrimethylsilane (9.77 g, 90.0 mmol) was added and the mixture was allowed to warm to room temperature. The solvents were evaporated, and the residue was dissolved in toluene and filtered. The filtrate was concentrated to give the crude product **3**. The crude product was used in the preparation of **4** without further purification. ^{1}H NMR (C_6D_6): δ 6.88−6.99 (m, 6H), 7.81−7.92 (m, 6H). ^{13}C NMR (THF-d_8): δ 128.1, 129.2, (d, J(C−P) = 27 Hz), 132.2, 135.2 (d, J(C−P) = 46 Hz), 140.1, 146.3. ^{29}Si NMR (THF-d_8): δ −18.4 (d, J(Si−P) = 9.5 Hz). ^{31}P NMR (THF-d_8): δ −55.4.

Preparation of H−PSiT−F (4). A 47% aqueous solution of hydrofluoric acid (50 mL) was added to a solution of **3** (7.78 g, 24.1 mmol) in toluene (300 mL) at room temperature. The mixture was stirred for 2 h. After removal of the aqueous layer, the organic layer was washed with water, dried over $MgSO_4$, and filtered. The filtrate was concentrated to give the crude product **4**. The crude product was used in the next step without further purification. ^{1}H NMR (C_6D_6): δ 6.90−6.95 (m, 6H), 7.75−7.78 (m, 3H), 7.84−7.90 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 128.2 (d, J = 27 Hz), 128.6, 131.7, 134.7 (dd, J = 46 and 2.2 Hz), 138.6 (d, J = 15 Hz), 145.6 (dd, J = 10 and 6.7 Hz). ^{19}F NMR (C_6D_6): δ −195.7. ^{29}Si NMR ($CDCl_3$): δ −22.6 (dd, J = 308 and 9.4 Hz). ^{31}P NMR (C_6D_6): δ −54.8. HRMS (EI): calcd for $C_{18}H_{12}FPSi$ 306.0430, found 306.0443.

Preparation of H−PSiT−R (5a,b). A typical procedure is reported for **5b**. A solution of *n*-$C_{12}H_{25}MgBr$ in THF (0.736 M, 2.70 mL, 3.67 mmol) was added dropwise to a solution of the crude product **4** (3.00 g, 9.80 mmol) in THF at 0 °C. The mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was quenched with 5% aqueous NH_4Cl. The aqueous layer was extracted with Et_2O, and the combined organic layer was washed with water, dried over $MgSO_4$, and filtered. The filtrate was concentrated to give the crude product **5b**. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 100/1) to give **5b** (46.4 mg, 0.102 mmol, 32% yield based on **2**) as colorless crystals.

5a: colorless crystals. Mp: 278−279 °C. ^{1}H NMR (C_6D_6): δ 0.83 (s, 3H), 6.96−7.06 (m, 6H), 7.51−7.54 (m, 3H), 8.00−8.06 (m, 3H). ^{13}C NMR (THF-d_8): δ −14.0, 128.2 (d, J(C−P) = 16 Hz), 132.3, 134.5, 135.2, 143.4, 147.5 (d, J(C−P) = 9.0 Hz). ^{29}Si NMR (THF-d_8): δ −27.9 (d, J(Si−P) = 6.8 Hz). ^{31}P NMR (THF-d_8): δ −44.4. Anal. Calcd for $C_{19}H_{15}PSi$: C, 75.47; H, 5.00. Found: C, 75.37; H, 5.14.

5b: colorless crystals. Mp: 89−90 °C. ^{1}H NMR (C_6D_6): δ 0.98 (m, 3H), 1.37−1.44 (m, 16H), 1.60−1.68 (m, 4H), 2.02−2.07 (m, 2H), 6.97−7.10 (m, 6H), 7.71−7.73 (m, 3H), 8.04−8.09 (m, 3H). ^{13}C NMR (C_6D_6): δ 6.45, 14.5, 23.3, 24.3, 29.8, 30.0, 30.26, 30.31, 30.34, 30.4, 32.5, 34.7, 128.0 (d, J = 30 Hz), 132.7, 134.9, 135.6, 143.2 (d, J = 2.2 Hz), 147.7 (d, J = 8.9 Hz). ^{29}Si NMR (C_6D_6):

(21) *^{13}C NMR data for Organometallic Compounds*; Mann, B. E., Taylor, B. F., Eds.; Academic Press: London, 1981.

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δ −29.9 (d, J = 6.7 Hz). ^{31}P NMR (C_6D_6): δ −42.5. HRMS (EI): calcd for $C_{30}H_{37}PSi$ 456.2402, found 456.2422.

Preparation of Tris(2-bromo-4,5-diisopropoxyphenyl)phosphine (7). The preparative procedure is the same as that of **2**. Yield: 45%, colorless solid. Mp: 149−150 °C. ^{1}H NMR ($CDCl_3$): δ 1.13 (d, J = 6.0 Hz, 18H), 1.34 (d, J = 6.0 Hz, 18H), 4.05 (sept, J = 6.0 Hz, 3H), 4.49 (sept, J = 6.0 Hz, 3H), 6.28 (d, J = 2.4 Hz,3H), 7.13 (d, J = 3.6 Hz,3H). ^{13}C NMR ($CDCl_3$): δ 22.1, 22.3, 72.4, 72.5, 121.3 (d, J(C−P) = 3.3 Hz), 121.4 (d, J(C−P) = 35 Hz), 123.7, 128.8 (d, J(C−P) = 11 Hz), 148.3, 150.7. ^{31}P NMR ($CDCl_3$): δ −1.31. MS(EI): 848 (M^+). Anal. Calcd for $C_{36}H_{48}Br_3O_6P$: C, 51.02; H, 5.71. Found: C, 51.13; H, 5.59.

Preparation of *i*-PrO−PSiT−Cl (8). A solution of *t*-BuLi (1.56 M, 46.0 mL, 71.8 mmol) in pentane was added dropwise to a solution of **7** (10.0 g, 11.8 mmol) in Et_2O (120 mL) and THF (24 mL) at −78 °C. After the addition was completed, the mixture was stirred for an additional 1 h and a solution of silicon tetrachloride (2.00 g, 11.8 mmol) in Et_2O (25 mL) was added dropwise to the mixture at −78 °C. After the mixture was stirred for an additional 2 h, the mixture was allowed to warm to room temperature. The solvents were evaporated, and the residue was dissolved in hexane and filtered. The filtrate was concentrated to give the crude product **8**. The crude product was used in the next reaction without further purification. ^{1}H NMR (C_6D_6): δ 1.12 (d, J = 6.3 Hz, 18H), 1.16 (d, J = 6.6 Hz), 4.24 (sept, J = 6.0 Hz, 3H), 4.34 (sept, J = 6.0 Hz, 3H), 7.76 (s, 3H), 7.81 (d, J = 11.7 Hz, 3H). ^{31}P NMR (C_6D_6): δ −52.6. HRMS (EI): calcd for $C_{36}H_{48}O_6{}^{35}ClPSi$ 670.2646, found 670.2637.

Preparation of *i*-PrO−PSiT−F (9). The procedure is the same as that of **4**. The obtained crude product **9** was used in the next reaction without further purification. ^{1}H NMR (C_6D_6): δ 1.12 (d, J = 4.2 Hz, 18H), 1.16 (d, J = 9.9 Hz), 4.20−4.30 (m, 6H), 7.69 (s, 3H), 7.80 (dd, J = 1.5, 11.9 Hz, 3H). ^{13}C NMR (C_6D_6): δ 22.4, 71.6, 71.7, 120.6, 124.1 (d, J = 47 Hz), 129.3, 132.4, 141.0 (dd, J = 6.6, 6.6 Hz), 149.4 (d, J = 15 Hz). ^{19}F NMR (C_6D_6): δ −193.2 (d, J = 5.1 Hz). ^{31}P NMR (C_6D_6): δ −55.9. HRMS (EI): calcd for $C_{36}H_{48}O_6FPSi$ 654.2942, found 654.2954.

Preparation of *i*-PrO−PSiT−R (10a−f). PSiT **10a**−**f** were prepared similarly to **5a** in 28, 63, 45, 42, 55, and 37% yields based on **7**, respectively.

10a: colorless crystals. Mp: 175−176 °C. ^{1}H NMR (C_6D_6): δ 0.99 (s, 3H), 1.13 (d, J = 6.3 Hz, 18H), 1.22 (d, J = 6.3 Hz, 18H), 4.26 (sept, J = 6.0 Hz, 3H), 4.45 (sept, J = 6.0 Hz, 3H), 7.50 (s, 3H), 7.88 (d, J(H−P) = 12.0 Hz, 3H). ^{13}C NMR (C_6D_6): δ −14.3, 21.2, 21.4, 70.1, 71.1, 121.5 (d, J(C−P) = 2.2 Hz), 122.7 (d, J(C−P) = 50 Hz), 135.2 (d, J(C−P) = 2.2 Hz), 140.8 (d, J(C−P) = 6.7 Hz), 147.4, 148.0 (d, J(C−P) = 18 Hz). ^{29}Si NMR (C_6D_6): δ −27.0 (d, J(Si−P) = 5.4 Hz). ^{31}P NMR (C_6D_6): δ −48.6. HRMS (EI): calcd for $C_{37}H_{51}O_6PSi$ 650.3193, found 650.3195.

10b: colorless crystals. Mp: >300 °C. ^{1}H NMR (C_6D_6): δ 1.14 (s, 18H), 1.16 (s, 18H), 2.54 (s, 6H), 4.31 (sept, J = 6.0 Hz, 3H), 4.40 (sept, J = 6.0 Hz, 3H), 6.77 (d, J = 8.7 Hz, 2H), 7.83 (s, 3H), 7.98 (d, J(H−P) = 12.6 Hz, 3H), 8.35 (d, 8.7 Hz, 2H). ^{13}C NMR (C_6D_6): δ 22.5, 22.6, 39.6, 71.4, 72.1, 113.0, 123.9, 124.6, 136.9 (d, J(C−P) = 2.2 Hz), 137.7, 142.4 (d, J(C−P) = 5.6 Hz), 148.7, 148.9, 149.2, 152.1. ^{29}Si NMR (C_6D_6): δ −36.3 (d, J(Si−P) = 5.4 Hz). ^{31}P NMR (C_6D_6): δ −43.0. MS(EI): 755 (M^+). Anal. Calcd for $C_{42}H_{53}O_6PSi$: C, 69.90; H, 7.73. Found: C, 69.74; H, 7.84.

10c: colorless crystals. Mp: 168−169 °C. ^{1}H NMR (C_6D_6): δ 1.14 (d, J = 6.0 Hz, 18H), 1.15 (d, J = 6.0 Hz, 18H), 3.35 (s, 3H), 4.30 (sept, J = 6.0 Hz, 3H), 4.38 (sept, J = 6.0 Hz, 3H), 7.00 (d, J = 8.7 Hz, 2H), 7.74 (s, 3H), 7.97 (d, J(H−P) = 12.3 Hz,3H), 8.32 (d, 8.7 Hz, 2H). ^{13}C NMR (C_6D_6): δ 22.5, 22.6, 54.8, 71.4, 72.2, 115.2, 123.8, 124.5, 136.2 (d, J(C−P) = 2.2 Hz), 138.1, 142.3 (d, J(C−P) = 5.6 Hz), 148.7, 149.1, 149.3, 162.2. ^{29}Si NMR (C_6D_6): δ −36.3 (d, J(Si−P) = 5.4 Hz). ^{31}P NMR (C_6D_6): δ −42.9. MS(EI): 742 (M^+). Anal. Calcd for $C_{43}H_{55}O_7PSi$: C, 69.51; H, 7.46. Found: C, 69.21; H, 7.53.

10d: colorless crystals. Mp: 195−197 °C. ^{1}H NMR (C_6D_6): δ 1.13 (d, J = 6.0 Hz, 18H), 1.14 (d, J = 6.0 Hz, 18H), 4.29 (sept, J = 6.0 Hz, 3H), 4.34 (sept, J = 6.0 Hz, 3H), 7.37 (m, 2H), 7.69 (s, 3H), 7.96 (d, J(H−P) = 12.3 Hz,3H), 8.38 (m, 2H). ^{13}C NMR (C_6D_6): δ 22.5, 22.5, 71.4, 72.1, 123.6 (d, J(C−P) = 2.2 Hz), 124.1 (d, J(C−P) = 53.2 Hz), 129.1, 131.0, 135.7, 136.6, 142.2 (d, J(C−P) = 5.6 Hz), 148.7, 149.1, 149.3. ^{29}Si NMR (C_6D_6): δ −36.3 (d, J(Si−P) = 5.4 Hz). ^{31}P NMR (C_6D_6): δ −42.8. MS(EI): 712 (M^+). Anal. Calcd for $C_{42}H_{53}O_6PSi$: C, 70.76; H, 7.49. Found: C, 70.49; H, 7.61.

10e: colorless crystals. Mp: 220−221 °C. ^{1}H NMR (C_6D_6): δ 1.13 (d, J = 6.0 Hz, 18H), 1.16 (d, J = 6.0 Hz, 18H), 4.28 (sept, J = 6.0 Hz, 3H), 4.38 (sept, J = 6.0 Hz, 3H), 7.47 (d, J = 8.1 Hz, 2H), 7.58 (s, 3H), 7.95 (d, J(H−P) = 12.3 Hz,3H), 8.23 (d, 7.5 Hz, 2H). ^{13}C NMR (C_6D_6): δ 22.4, 22.6, 71.4, 72.5, 123.7, 123.9, 124.4, 125.6 (d, J = 3.3 Hz), 134.8, 136.8, 142.28 (d, J = 5.6 Hz), 148.7, 149.4, 149.7. ^{19}F NMR (C_6D_6): δ −62.6. ^{29}Si NMR (C_6D_6): δ −36.7 (d, J(Si−P) = 6.7 Hz). ^{31}P NMR (C_6D_6): δ −42.7. MS(EI): 780 (M^+). Anal. Calcd for $C_{43}H_{52}F_3O_6PSi$: C, 66.13; H, 6.71. Found: C, 66.34; H, 6.84.

10f: colorless crystals. Mp: 208−209 °C. ^{1}H NMR (C_6D_6): δ 1.13 (d, J = 6.0 Hz, 18H), 1.17 (d, J = 6.0 Hz, 18H), 4.29 (sept, J = 6.0 Hz, 3H), 4.34 (sept, J = 6.0 Hz, 3H), 7.45 (s, 3H), 7.94 (d, J(H−P) = 12.0 Hz,3H), 8.02 (m, 1H), 8.83 (m, 2H). ^{13}C NMR (C_6D_6): δ 22.42, 71.62, 72.12, 122.1, 124.0, 124.7, 132.0, 132.5, 133.7, 133.8 (d, J = 2.2 Hz), 136.2, 141.7 (d, J = 5.6 Hz), 149.0, 149.2, 149.5. ^{19}F NMR (C_6D_6): δ −62.5. ^{29}Si NMR (C_6D_6): δ −36.7 (d, J(Si−P) = 5.4 Hz). ^{31}P NMR (C_6D_6): δ −43.2. MS-(EI): 848 (M^+). Anal. Calcd for $C_{43}H_{52}F_3O_6PSi$: C, 62.25; H, 6.06. Found: C, 62.08; H, 6.21.

Preparation of Phosphine Selenide of H−PSiT−Me (11). A mixture of **5a** (31.5 mg, 0.0417 mmol) and selenium (27.6 mg, 0.349 mmol) in $CHCl_3$ (2.5 mL) was stirred for 3.5 h under reflux. The excess of selenium in the reaction mixture was removed by filtration, and the filtrate was evaporated to give the crude product, which was recrystallized from toluene/EtOH to give pure **11** (246 mg, 0.645 mmol, 65% yield) as colorless crystals. Mp: >300 °C. ^{1}H NMR (CD_2Cl_2): δ 1.30 (s, 3H), 7.36−7.46 (m, 6H), 7.74−7.79 (m, 3H), 8.36−8.45 (m, 3H). ^{13}C NMR ($CDCl_3$): δ −14.3, 128.2 (d, J(C−P) = 13 Hz), 128.8 (d, J(C−P) = 2.2 Hz), 130.8 (d, J(C−P) = 10 Hz), 131.2 (d, J(C−P) = 13 Hz), 138.3 (d, J(C−P) = 71 Hz), 140.3 (d, J(C−P) = 7.8 Hz). ^{29}Si NMR ($CDCl_3$): δ −30.9 (d, J(Si−P) = 29.6 Hz). ^{31}P NMR ($CDCl_3$): δ 11.9 (satellite, J(P−Se) = 795 Hz). Anal. Calcd for $C_{19}H_{15}PSiSe$: C, 59.84; H, 3.96. Found: C, 59.61; H, 4.12.

Preparation of Phosphine Selenide of *i*-PrO−PSiT−R (12a−f) and Their Spectral Data. Phosphine selenides PSiT **12a**−**f** were prepared similarly to **11** in 87, 86, 85, 89, 83, and 79% yields, respectively.

12a: colorless crystals. Mp: >300 °C. ^{1}H NMR (C_6D_6): δ 0.86 (s, 3H), 1.13 (d, J = 6.3 Hz, 18H), 1.19 (d, J = 6.0 Hz), 4.39−4.55 (m, 6H), 7.37 (d, J(H−P) = 4.2 Hz, 3H), 8.65 (d, J(H−P) = 15.9 Hz, 3H). ^{13}C NMR (C_6D_6): δ −14.1, 22.2, 22.6, 71.3, 72.6, 120.0 (d, J(C−P) = 17 Hz), 121.7 (d, J(C−P) = 12 Hz), 134.0 (d, J(C−P) = 5.6 Hz), 134.5 (d, J(C−P) = 92 Hz), 149.2 (d, J(C−P) = 2.2 Hz), 149.8 (d, J(C−P) = 17 Hz). ^{29}Si NMR (C_6D_6): δ −30.6 (d, J(Si−P) = 29.5 Hz). ^{31}P NMR (C_6D_6): δ 15.9 (satellite, J(P−Se) = 786 Hz). HRMS (EI): calcd for $C_{37}H_{51}O_6PSeSi$ 730.2358, found 730.2319.

12b: colorless crystals. Mp: >300 °C. ^{1}H NMR (C_6D_6): δ 1.11 (d, J = 6.3 Hz, 18H), 1.13 (d, J = 6.3 Hz), 2.52 (s, 6H), 4.34 (m, 6H), 6.72 (d, J = 8.4 Hz, 2H), 7.75 (d, J(H−P) = 4.2 Hz, 3H), 8.23 (d, J = 8.7 Hz, 2H), 8.37 (d, J(H−P) = 12.6 Hz, 3H). ^{29}Si NMR (C_6D_6): δ −40.5 (d, J(Si−P) = 29.5 Hz). ^{31}P NMR (C_6D_6):

δ 16.2 (satellite, J(P−Se) = 786 Hz). HRMS (FAB): calcd for $C_{44}H_{59}NO_6PSeSi$ $[M + H]^+$ 836.3014, found 836.3022.

12c: colorless crystals. Mp: 263−264 °C. ^{1}H NMR (C_6D_6): δ 1.12 (d, J = 6.0 Hz, 18H), 1.15 (d, J = 6.0 Hz), 3.33 (s, 3H), 4.36 (sept, J = 6.0 Hz, 3H), 4.56 (sept, J = 6.0 Hz, 3H), 6.96 (d, J = 8.7 Hz, 2H), 7.63 (d, J(H−P) = 4.2 Hz, 3H), 8.19 (d, J = 8.7 Hz, 2H), 8.76 (d, J(H−P) = 15.9 Hz, 3H). ^{31}P NMR (C_6D_6): δ 16.4 (satellite, J(P−Se) = 786 Hz). EI-MS: 823 ($[M + H]^+$). Anal. Calcd for $C_{43}H_{55}O_7PSeSi$: C, 62.84; H, 6.74. Found: C, 62.72; H, 7.02.

12d: colorless crystals. Mp: 271−272 °C. ^{1}H NMR (C_6D_6): δ 1.10 (d, J = 6.3 Hz, 18H), 1.15 (d, J = 6.0 Hz), 4.32 (sept, J = 6.3 Hz, 3H), 4.55 (sept, J = 6.0 Hz, 3H), 7.33 (m, 3H), 7.58 (d, J(H−P) = 4.2 Hz, 3H), 8.24 (m, 2H), 8.75 (d, J(H−P) = 16.5 Hz, 3H). ^{31}P NMR (C_6D_6): δ 16.5 (satellite, J(P−Se) = 786 Hz). HRMS (EI): calcd for $C_{42}H_{53}O_6PSeSi$ 792.2514, found 792.2514.

12e: colorless crystals. Mp: 284−286 °C. ^{1}H NMR (C_6D_6): δ 1.13 (d, J = 6.0 Hz, 18H), 1.14 (d, J = 6.3 Hz), 4.37 (sept, J = 6.0 Hz, 6H), 4.54 (sept, J = 6.3 Hz, 3H), 7.46 (s, 3H), 7.47 (s, 3H), 8.10 (d, J(H−P) = 7.8 Hz, 2H), 8.74 (d, J(H−P) = 16.2 Hz, 3H). ^{31}P NMR (C_6D_6): δ 16.6 (satellite, J(P−Se) = 794 Hz). HRMS (FAB): calcd for $C_{43}H_{52}F_3O_6PSeSi$ 860.2388, found 860.2421.

12f: colorless crystals. Mp: 283−285 °C. ^{1}H NMR (C_6D_6): δ 1.10 (d, J = 6.0 Hz, 18H), 1.16 (d, J = 6.0 Hz), 4.31 (m, 3H), 7.37 (d, J(H−P) = 4.2 Hz, 3H), 8.00 (s, 1H), 8.35 (d, J(H−P) = 12.3 Hz, 3H), 8.72 (s, 2H). ^{31}P NMR (C_6D_6): δ 16.2 (satellite, J(P−Se) = 794 Hz). HRMS (FAB): calcd for $C_{44}H_{52}F_6O_6PSeSi$ $[M + H]^+$ 929.2340, found 929.2327.

Preparation of *cis*-[PtMe$_2$(H−PSiT−*n*-C$_{12}$H$_{25}$)$_2$] (13). A solution of [PtMe$_2$(cod)] (14.6 mg, 0.0438 mmol) and **5b** (40.0 mg, 0.0876 mmol) in THF (3.0 mL) was stirred for 38 h at 40 °C. The solvents were evaporated, and the residue was washed with hexane to remove COD. The crude product was recrystallized from CH_2Cl_2/hexane to give **7** as colorless crystals (27.0 mg, 54% yield). Mp: 157−158 °C (dec). ^{1}H NMR (C_6D_6): δ 0.90−1.05 (m, 6H), 1.21−1.54 (m, 36H), 1.54−1.70 (m, 4H), 1.88 ($A_3A_3'XX'$ satellite, J(H−Pt) = 70.2 Hz, 6H), 1.96−2.12 (m, 4H), 6.74−6.98 (m, 12H), 7.61−7.70 (m, 6H), 8.67−8.79 (m, 6H). ^{13}C NMR (THF-d_8): δ 1.09, 5.98, 8.76 (dd satellite, J = 99, 10, and 607 Hz), 14.1, 23.3, 24.4, 29.9, 30.0, 30.3, 30.36, 30.41, 32.6, 34.9, 127.1 (virtual quintet, J = 5.6 Hz), 127.7, 131.9, 136.5 (virtual quintet, J = 15 Hz), 143.2 (virtual triplet, J = 7.8 Hz), 143.7 (virtual dt, J = 41 and 10 Hz). ^{31}P NMR (C_6D_6): δ 9.85 (satellite, J = 1972 Hz). HRMS (FAB): calcd for $C_{62}H_{80}P_2{}^{195}PtSi_2$ 1137.4922, found 1137.4956.

Preparation of *cis*-PtMe$_2$(psit)$_2$ (14a−f). *cis*-PtMe$_2$(psit)$_2$ **14a** and **14c**−**e** were prepared in a manner similar to **13** in 72, 59, 74, and 62% yields, respectively.

14a: colorless crystals. Mp: 226−227 °C (dec). ^{1}H NMR (C_6D_6): δ 0.90 (s, 6H), 1.16 (d, J = 6.2 Hz, 36H), 1.23 (d, J = 5.9 Hz, 36H), 1.71 ($A_3A_3'XX'$ satellite, J(H−Pt) = 69.9 Hz, 6H), 4.17 (sept, J = 6.2 Hz, 6H), 4.40 (sept, J = 5.9 Hz, 6H), 7.37 (s, 6H), 8.32 (d, J = 12.4 Hz, 6H). ^{13}C NMR (acetone-d_6): δ −13.4, 10.1 (dd satellite, J = 98, 10, and 602 Hz), 22.6, 22.8, 71.2, 72.7, 121.8, 125.1 (virtual quintet, J = 15 Hz), 137.1 (virtual triplet, J = 7.8 Hz), 137.9 (virtual dt, J = 46 and 7.8 Hz), 148.3 (virtual triplet, J = 7.9 Hz), 148.9. ^{31}P NMR (C_6D_6): δ 9.55 (satellite, J = 1993 Hz). HRMS (FAB): calcd for $C_{76}H_{108}O_{12}P_2{}^{195}PtSi_2$ 1525.6502, found 1525.6527.

14c: colorless crystals. Mp: 258−259 °C (dec). ^{1}H NMR (C_6D_6): δ 1.17 (d, J = 6.0 Hz, 36H), 1.22 (d, J = 6.0 Hz, 36H), 1.82 ($A_3A_3'XX'$ satellite, J(H−Pt) = 69.9 Hz, 6H), 3.35 (s, 6H), 4.24−4.41 (m, 12H), 7.00 (d, J = 8.4 Hz, 4H), 7.66 (s, 6H), 8.32 (d, J = 8.4 Hz, 4H), 8.48 (d, J = 12.9 Hz, 6H). ^{13}C NMR (acetone-d_6): δ 10.4 (dd satellite, J = 98, 8.9, and 602 Hz), 22.6, 22.8, 55.8, 1.3, 72.8, 116.0, 117.4, 122.8, 125.3 (virtual quintet, J = 13 Hz), 136.3 (virtual triplet, J = 6.7 Hz), 138.1 (virtual dt, J = 46 and 8.9 Hz), 138.7, 148.4 (virtual triplet, J = 7.8 Hz), 148.8, 163.2. ^{31}P NMR (109 MHz, C_6D_6): δ 10.3 (satellite, J = 2005 Hz). MS (FAB): 1711 ($[M + H]^+$). Anal. Calcd for $C_{76}H_{106}O_{14}P_2PtSi_2$: C, 61.77; H, 6.83. Found: C, 61.76; H, 6.89.

14d: colorless crystals. Mp: 171−172 °C (dec). ^{1}H NMR (C_6D_6): δ 1.14 (d, J = 6.0 Hz, 36H), 1.21 (d, J = 6.0 Hz, 36H), 1.80 ($A_3A_3'XX'$ satellite, J(H−Pt) = 70.8 Hz, 6H), 4.22−4.35 (m, 12H), 7.35−7.39 (m, 6H), 7.60 (d, J = 1.2 Hz, 6H), 8.36−8.39 (m, 4H), 8.46 (d, J = 12.6 Hz, 6H). ^{13}C NMR (acetone-d_6): δ 10.4 (dd satellite, J = 98, 10, and 604 Hz), 22.6, 22.7, 71.3, 72.9, 122.8 (virtual triplet, J = 3.3 Hz), 125.3 (virtual quintet, J = 15 Hz), 127.4, 130.0, 132.4, 136.0 (virtual triplet, J = 7.8 Hz), 137.1, 138.1 (virtual dt, J = 45 and 8.9 Hz), 148.5 (virtual quintet, J = 7.8 Hz), 148.9. ^{31}P NMR (C_6D_6): δ 10.0 (satellite, J = 2005 Hz). HRMS (FAB): calcd for $C_{86}H_{112}O_{12}P_2{}^{195}PtSi_2$ 1649.6815, found 1649.6833.

14e: colorless crystals. Mp: 278−279 °C (dec). ^{1}H NMR (C_6D_6): δ 1.17 (d, J = 5.7 Hz, 36H), 1.20 (d, J = 5.9 Hz, 36H), 1.80 ($A_3A_3'XX'$ satellite, J(H−Pt) = 69.9 Hz, 6H), 4.23−4.38 (m, 12H), 7.47 (d, J = 7.8 Hz, 4H), 7.50 (s, 6H), 8.25 (d, J = 7.8 Hz, 4H), 8.45 (d, J = 12.4 Hz, 6H). ^{13}C NMR (acetone-d_6): δ 10.5 (dd satellite, J = 98, 10, and 604 Hz), 22.6, 22.7, 71.4, 72.9, 122.7, 125.2 (q, J = 270 Hz), 125.3 (virtual quintet, J = 13 Hz), 126.5 (q, J = 3.4 Hz), 133.1, 133.3 (q, J = 32 Hz), 135.1 (virtual triplet, J = 6.6 Hz), 137.9, 138.0 (virtual dt, J = 45 and 8.9 Hz), 148.6 (virtual quintet, J = 8.9 Hz), 149.0. ^{19}F NMR (acetone-d_6): δ −62.5. ^{31}P NMR (C_6D_6): δ 10.5 (satellite, J = 2005 Hz). MS (FAB): 1787 ($[M + H]^+$). Anal. Calcd for $C_{88}H_{110}F_6O_{12}P_2PtSi_2$: C, 59.15; H, 6.20. Found: C, 58.97; H, 6.18.

cis-PtMe$_2$(psit)$_2$ **14b** and **14f** were prepared according to the following procedure: A solution of [PtMe$_2$(μ-SMe$_2$)]$_2$ (28.4 mg, 0.0495mmol) and **10b** (150 mg, 0.198 mmol) in Et$_2$O (3.0 mL) was stirred for 5 h. The solvents were removed, and the residue was recrystallized from CH_2Cl_2/hexane to give **14b** (133 mg, 83% yield) as colorless crystals. *cis*-PtMe$_2$(psit)$_2$ **14f** was similarly prepared in 60% yield.

14b: colorless crystals. Mp: >300 °C (dec). ^{1}H NMR (C_6D_6): δ 1.17 (d, J = 6.2 Hz, 36H), 1.24 (d, J = 5.9 Hz, 36H), 1.83 ($A_3A_3'XX'$ satellite, J(H−Pt) = 69.9 Hz, 6H), 2.53 (s, 12H), 4.26−4.42 (m, 12H), 6.76 (d, J = 8.6 Hz, 4H), 7.76 (s, 6H), 8.35 (d, J = 8.6 Hz, 4H), 8.51 (d, J = 12.4 Hz, 6H). ^{13}C NMR (acetone-d_6): δ 10.9 (dd satellite, J = 99, 8.9, and 603 Hz), 22.6, 22.8, 40.2, 71.2, 72.8, 110.1, 113.4, 123.0, 125.2 (virtual quintet, J = 16 Hz), 137.0 (virtual triplet, J = 6.7 Hz), 138.0, 138.2 (virtual dt, J = 45 and 8.9 Hz), 148.3 (virtual triplet, J = 7.8 Hz), 148.7, 153.3. ^{31}P NMR (C_6D_6): δ 10.5 (satellite, J = 2005 Hz). HRMS (FAB): calcd for $C_{90}H_{122}N_2O_{12}P_2{}^{195}PtSi_2$ 1735.7659, found 1735.7683.

14f: colorless crystals. Mp: 240−241 °C (dec). ^{1}H NMR (C_6D_6): δ 1.18 (d, J = 6.5 Hz, 36H), 1.21 (d, J = 6.2 Hz, 36H), 1.82 ($A_3A_3'XX'$ satellite, J(H−Pt) = 70.8 Hz, 6H), 4.21−4.36 (m, 12H), 7.39 (s, 6H), 8.00 (s, 2H), 8.43 (d, J(H−P) = 12.4 Hz, 6H), 8.86 (s, 4H). ^{13}C NMR (acetone-d_6): δ 10.4 (dd satellite, J = 98, 10, and 605 Hz), 22.56, 22.60, 71.4, 72.8, 122.0 (virtual triplet, J = 3.3 Hz), 124.5 (q, J = 271 Hz), 125.4 (virtual quintet, J = 15 Hz), 126.1 (virtual triplet, J = 3.3 Hz), 132.0, 132.5 (q, J = 33 Hz), 134.4 (virtual triplet, J = 7.8 Hz), 137.2, 137.8 (virtual dt, J = 45 and 8.9 Hz), 148.6 (virtual quintet, J = 8.9 Hz), 149.1. ^{19}F NMR (acetone-d_6): δ −62.3. ^{31}P NMR (C_6D_6): δ 10.1 (satellite, J = 1993 Hz). MS (FAB): 1923 ($[M + H]^+$). Anal. Calcd for $C_{90}H_{108}F_{12}O_{12}P_2PtSi_2$: C, 56.21; H, 5.66. Found: C, 56.05; H, 5.70.

X-ray Crystallographic Analysis of 14b. A colorless crystal (0.20 × 0.15 × 0.15 mm) was mounted using a cryoloop. The intensity data were collected using a Rigaku single-crystal CCD X-ray diffractometer (Saturn 70) with Mo Kα radiation (λ = 0.71070 Å) and a graphite monochromator. The structure was solved by direct methods (SIR-97) and refined by full-matrix least-squares

on F^2 (SHELXL-97). All the non-hydrogen atoms were anisotropically refined, and all the hydrogen atoms were placed using the AFIX instructions and refined isotopically. The crystal data and analytical conditions are summarized in Table 1.

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Supporting Information Available: CIF files of **14b**. NMR chart of **3**, **4**, **5b**, **8**, **9**, **10a**, **12a**,**b**, **12d**−**f**, **13**, **14a**,**b**, and **14d**. Cartesian coordinates of PPh_3, PSiT, and 9-phosphatriptycene optimized at the B3LYP/6-311G* level. This material is available free of charge via the Internet at http://pubs.acs.org.

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