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Silica-supported Triptycene-type Phosphine. Synthesis, Characterization, and Application to Pd-Catalyzed Suzuki–Miyaura Cross-coupling of Chloroarenes

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KEYWORDS: silica-supported catalyst, phosphine, triptycene, palladium, chloroarene

ABSTRACT: A silica-supported triptycene-type phosphine, Silica-TRIP, comprising a 9-phospha-10-silatriptycene (TRIP) and silica gel as a P-coordination center and a solid support, respectively, was synthesized and structurally characterized by nitrogen absorption measurements and solid-state CP/MAS NMR spectroscopy. Silica-TRIP exhibited a mono-P-ligating feature toward a Pd(II) complex, resulting in selective formation of a 1:1 Pd-P species even with an excess amount of the ligand. As a result, Silica-TRIP enabled Pd-catalyzed Suzuki–Miyaura cross-coupling reactions of chloroarenes under mild conditions, regardless of the moderate electron-donating nature of the triarylphosphine-based ligand.

INTRODUCTION

Silica-supported ligands,[1] which are generally synthesized by silane coupling between silicon-functionalized organic molecules and a silanol-containing surface, have been widely studied to prepare heterogenized transition metal catalysts with practical merits such as easy separation and reusability.[2,3] However, steric hindrance of the solid surface toward the active site often causes a decrease in catalytic performance compared to the corresponding homogeneous molecular catalysts. Moreover, commonly used flexible linkers (e.g., alkyl chains) between ligands and silica gel impart significant mobility to the coordination centers, resulting in difficulty in ligand design based on the features of the solid surface. We envisaged to solve these problems by limiting the mobility of the ligand on the silica surface by introducing a rigid linker system between the metal-coordinating atom and the surface, for allowing the use of the solid surface as a tool for producing highly active catalyst species rather than merely for having the benefit of easy separation, reuse, and recycling of the catalyst.

To this end, we have recently designed and synthesized a silica-supported monophosphine, Silica-SMAP (Figure 1a), providing a novel example of increased catalytic activity by surface immobilization.[4,5] The rigidity of the caged trialkylphosphine (SMAP)[6] and the cage-to-surface immobilization made the P-coordination center stand upward on the surface and hence exist in isolation (Figure 1b).[7] Thus, Silica-SMAP could form 1:1 metal-phosphine complexes exclusively with a range of transition metal species regardless of its compactness. The transition metal complexes prepared in this manner performed as useful heterogeneous catalysts for various reactions.[4]

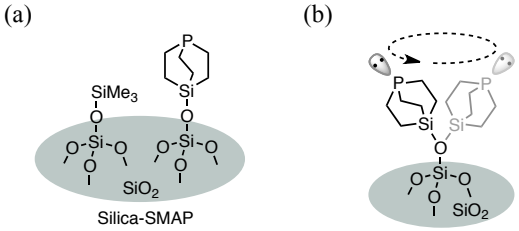


Figure 1. (a) Structure of Silica-SMAP and (b) restricted mobility of the SMAP moiety on silica surface.

On the basis of these considerations, we focused on 9-phospha-10-sila*trip*tycenes (TRIP), which were previously synthesized by Tsuji and Tamao et al.,[8] as a new motif for silica-supported ligands. We expected that silica-supported triptycene-type phosphine Silica-TRIP (Figure 2) would function as a supported ligand complementary to Silica-SMAP-based systems. SMAP and TRIP moieties are trialkyl- and triarylphosphines, respectively, thus having contrasting electronic natures; the former should be much more electron-donating. The two ligands also differ in steric demand; the latter is significantly bulkier. In fact, a Silica-TRIP-Rh catalyst system realized heteroatom-directed borylation of C(sp^3)–H bonds of amides, ureas, and 2-aminopyridines at the position α to the N atom, for which Silica-SMAP was not effective, affording the corresponding primary and secondary α-aminoalkylboronates (Scheme 1, top),[9] while both Silica-SMAP and Silica-TRIP were effective for the Ir-catalyzed N-directed C(sp^3)–H borylation of 2-alkylpyridines (Scheme 1, middle).[4j] This article describes details of our studies on the synthesis of Silica-TRIP, its coordination properties toward Pd(II) complexes, and its catalytic application to Pd-catalyzed

Suzuki–Miyaura cross-coupling of chloroarenes (Scheme 1, bottom).[10,11] The use of bulky and electron-rich monophosphine[12] or NHC[13] ligands is a common strategy for enabling the Pd-catalyzed cross-coupling of chloroarenes under mild conditions, and there are only a limited number of reports on effective catalyst systems with moderately electron-donating triarylphosphine-based ligands; chloroarenes are more desirable but less reactive than bromoarenes and iodoarenes.[14–17]

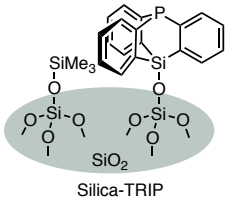
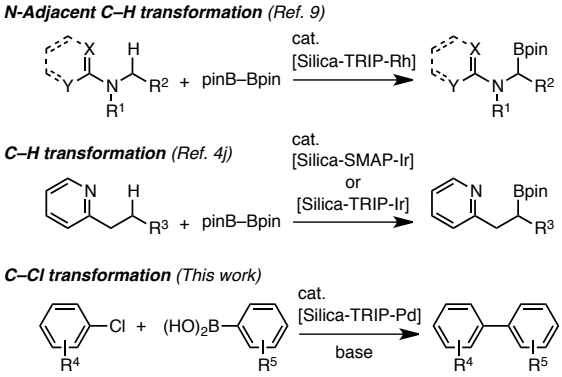


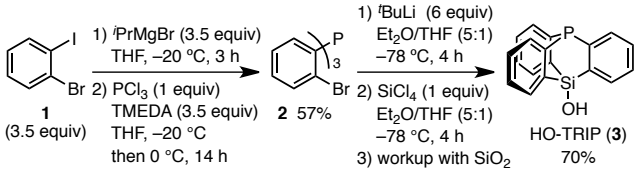
Figure 2. Structure of Silica-TRIP.



Scheme 1. Transformations of C(sp^3)–H and C(sp^2)–Cl bonds with Silica-TRIP-metal catalyst systems.

RESULTS AND DISCUSSION

Preparation of Silica-Supported Triptycene-Type Phosphine (Silica-TRIP). For the synthesis of the precursor for Silica-TRIP, a soluble triptycene-type phosphine **3** having a silanol group at the bridgehead, we followed Tsuji and Tamao's procedure for the synthesis of 9-phospha-10-silatriptycenes with a slight modification.[8] Thus, commercially available 1-bromo-2-iodobenzene (**1**) was converted to tris(*o*-bromophenyl)phosphine (**2**) by treatment with *i*PrMgBr for Mg-I exchange at –20 °C,[18] followed by the reaction with PCl_3 in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as an additive. This procedure avoids the extremely low temperature conditions (–110 °C) employed in Tsuji and Tamao's procedure.[8] The trilithiated species generated from **2** with 6 equivalents of *t*BuLi in Et_2O/THF was reacted with $SiCl_4$. Purification by silica gel chromatography gave the silanol HO-TRIP (**3**) in 70% yield as an air- and moisture-stable solid. Single-crystal X-ray diffraction analysis of **3** confirmed its three-dimensional molecular structure having a triptycene cage, the bridgehead of which was substituted with P and Si atoms (Figure 3). Interestingly, six molecules of **3** in the crystal structure adopted a chair form hydrogen-bonding network consisting of six silanol groups as shown in Figure 4 (average distance of $Ar_3SiO\cdots OSiAr_3$; 2.651 Å).[19,20] The existence of the silanol group was supported by the observation of a broad absorption band at 3347 cm^{-1} by IR spectroscopy, which was assignable to an (Si)O–H stretching vibration.



Scheme 2. Preparation of silanol HO-TRIP (**3**).

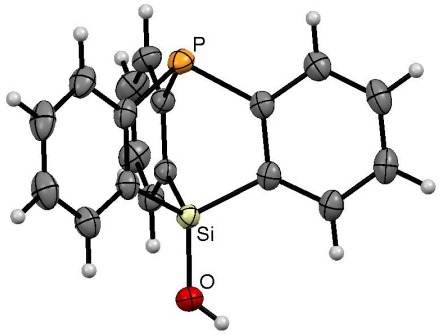


Figure 3. Molecular structure of **3** at 50% probability level; a solvent molecule ($CHCl_3$) and one of the disordered hydrogen atoms of the silanol moiety (SiO–*H*) are omitted for clarity.

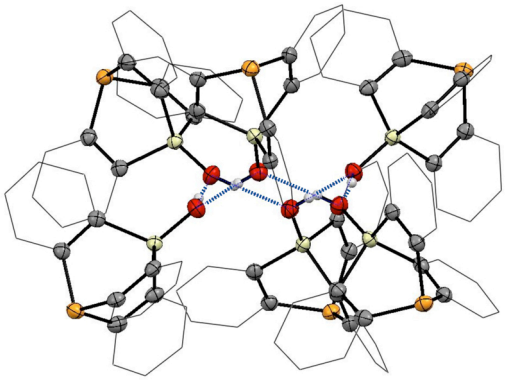
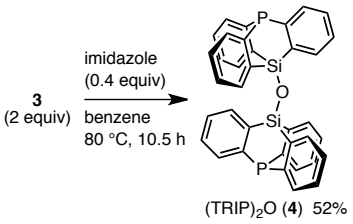
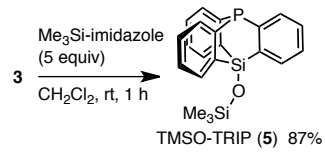


Figure 4. Chair form hydrogen-bonding network (blue-dotted lines) of **3** in the crystal structure.

Interestingly, the triarylsilanol **3** did not react with silica gel during the chromatography, while the purified **3** underwent slow self-condensation to form the corresponding disiloxane $(TRIP)_2O$ (**4**). The self-condensation was more rapid in the presence of a base. In fact, heating of **3** with imidazole in benzene at 80 °C caused its complete consumption, forming white precipitates (Scheme 3).[21] Filtration of the precipitates followed by washing with benzene gave the disiloxane **4** in 52% isolated yield. Treatment of the silanol **3** with *N*-trimethylsilylimidazole provided the 1,1,1-trimethyl-substituted disiloxane TMSO-TRIP (**5**) in 87% yield (Scheme 4).

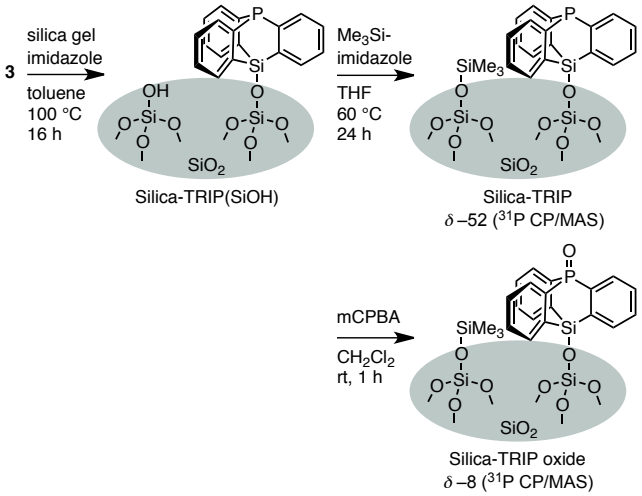


Scheme 3. Preparation of disiloxane $(TRIP)_2O$ (**4**).



Scheme 4. Preparation of disiloxane TMSO-TRIP (**5**).

The preparation of silica-supported triptycene-type phosphine (Silica-TRIP) with a direct disiloxane linkage is shown in Scheme 5. We made slight modifications to the procedure described in our original report[4h] for more expeditious operation in large-scale synthesis. Specifically, the silanol phosphine **3** was grafted to a silica gel surface (CARiACT Q10, 75–150 μm) in the presence of imidazole and toluene under gentle stirring at 100 °C over 16 h. The resulting colorless solids were collected by filtration, washed successively with degassed toluene, toluene-MeOH (1:1), and MeOH, and then dried under vacuum to afford phosphine-functionalized silica-gel Silica-TRIP(SiOH). Unreacted surface silanols were Me_3Si-endcapped through treatment with excess *N*-trimethylsilylimidazole in THF at 60 °C for 24 h, to furnish Silica-TRIP. The P loading to silica gel was calculated to be 0.078 mmol/g based on the ability of the gel to bind a Pd(II) complex in a 1:1 Pd/P coordination mode (*vide infra*). The phosphine moiety of Silica-TRIP underwent oxidation by *m*-chloroperoxybenzoic acid in CH_2Cl_2 at room temperature, to give the immobilized phosphine Silica-TRIP oxide.[22]



Scheme 5. Preparation of Silica-TRIP and Silica-TRIP oxide.

Figure 5 shows nitrogen adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) plots for Silica-TRIP. The structural parameters (specific surface area, pore diameter and pore volume) are summarized in Table 1. Silica-TRIP exhibited a hysteresis loop, indicating the existence of mesopores with a broad pore-diameter distribution at an average of 17.2 nm. The surface modification of CARiACT Q10 silica gel (75–150 μm) for the preparation of Silica-TRIP as well as Silica-SMAP reasonably reduced their structural parameters such as surface area and pore volume.[4c] A surface P density of Silica-TRIP on the basis of the surface area (244 m^2/g) and the estimated TRIP loading (0.078 mmol/g) was calculated to be 0.19 nm^{-2}. This value was comparable to that of Silica-SMAP (0.19 nm^{-2}).

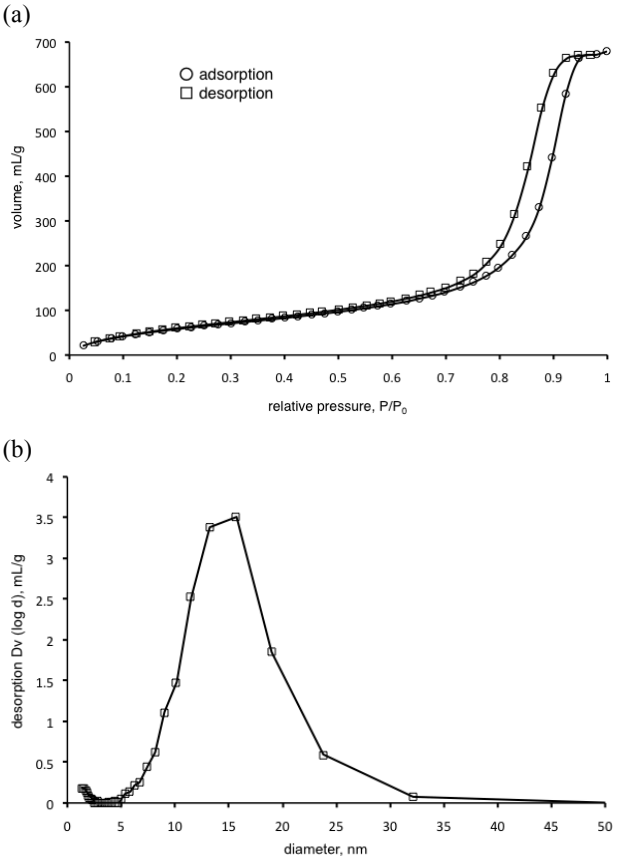


Figure 5. (a) Nitrogen adsorption–desorption isotherms and (b) BJH pore-diameter distribution plots of Silica-TRIP.

Table 1. Structural parameters.

materials	surface area (BET, m^2/g)	pore diameter (nm)	pore volume (mL/g)
Silica-TRIP	244	17.2	1.05
Silica-SMAP[a]	220	17.3	1.08
CARiACT Q10[a]	284	17.8	1.32

[a] Data were taken from ref 4c.

Solid-State NMR Spectra of Silica-TRIP. The silica-supported phosphine Silica-TRIP was characterized by solid-state ^{31}P, ^{13}C, and ^{29}Si NMR spectroscopies with comparison to the solution NMR spectra of the soluble disiloxane phosphine **5** in $CDCl_3$.[3] The ^{31}P CP/MAS NMR spectrum of Silica-TRIP showed a singlet signal at δ –52 (ppm) assignable to the P atom of the TRIP moiety (Figure 6a) (^{31}P NMR for **5**; δ –54.9). The ^{13}C CP/MAS spectrum showed a sharp signal at δ 2 ppm for the Me carbons of the trimethylsilyl endcaps and multiple broad signals around δ 130 for the aromatic carbons of the TRIP moiety (Figure 6b). In the ^{29}Si CP/MAS NMR spectrum (Figure 6c), a weak signal at δ –36 was assigned to the bridgehead Si atom of the TRIP moiety (^{29}Si NMR for **5**; δ –38.9).

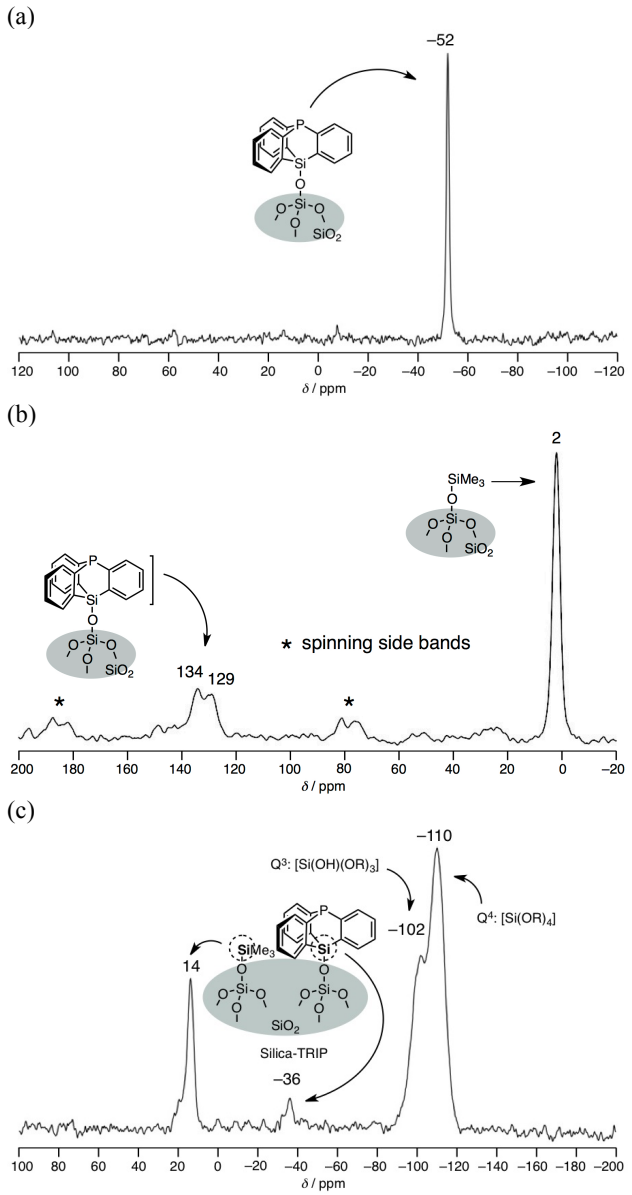


Figure 6. CP/MAS NMR spectra of Silica-TRIP for (a) ^{31}P (b) ^{13}C and (c) ^{29}Si nuclei.

Coordination toward a Pd(II) Complex. The coordination property of Silica-TRIP in the reaction with $PdCl_2(py)_2$ (py = pyridine) was investigated. Specifically, the reaction of Silica-TRIP with an excess amount of $PdCl_2(py)_2$ (Pd/P 2:1) in CH_2Cl_2 at room temperature for 0.5 h produced pale yellow silica gel, indicating that Pd atoms were bound to the gel. Unreacted $PdCl_2(py)_2$ was recovered from the filtrate, and its weight was measured. This procedure allowed us to estimate the amount of P loading on the silica gel, which was calculated to be 0.078 mmol/g under the assumption of selective formation of $PdCl_2(py)$(Silica-TRIP) with a Pd/P stoichiometry of 1:1 (*vide infra* for the structure assignment). On the other hand, the inductively coupled plasma-atomic emission spectroscopic (ICP-AES) analysis of $PdCl_2(py)$(Silica-TRIP) gave P and Pd loading values of 0.063 and 0.072 mmol/g, respectively. For convenience, the value of 0.07 mmol/g was used for P loading in metal complexations and catalytic applications (*vide infra*). The ^{31}P CP/MAS NMR spectrum of the silica-supported Pd complex obtained in this manner showed a singlet peak at –5 ppm (Figure 7a). The comparison of this chemical shift value with those of homogeneous Pd complexes prepared from TMSO-TRIP (**5**) (Pd/P 0:1, 1:1, 1:2 in Figure 8) is consisted with the formation of mono-P-ligated Pd complex $PdCl_2(py)$(Silica-TRIP) without forming a bis-P-ligated Pd complex $PdCl_2$(Silica-TRIP)$_2$ [^{31}P NMR in $CDCl_3$ for $PdCl_2(py)$(**5**) δ –6.5; for $PdCl_2$(**5**)$_2$ δ –19.5]. Notably, the mono-P-ligated Pd complex was formed selectively even when excess P was present (Pd/P 1:2, in CH_2Cl_2 at room temperature for 0.5 h) (Figure 7b).

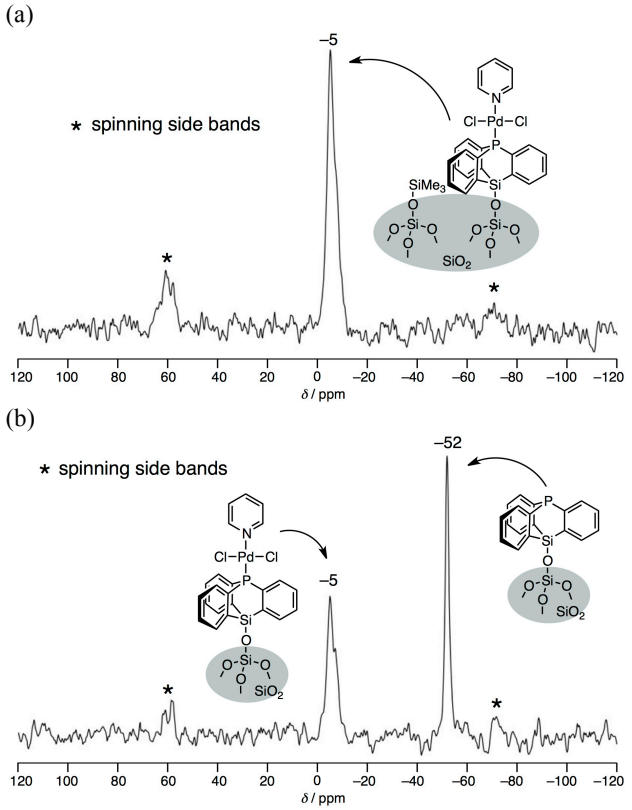


Figure 7. ^{31}P CP/MAS NMR spectra obtained from (a) $PdCl_2(py)_2$/Silica-TRIP (Pd/P 2:1) and (b) $PdCl_2(py)_2$/Silica-TRIP (Pd/P 1:2).

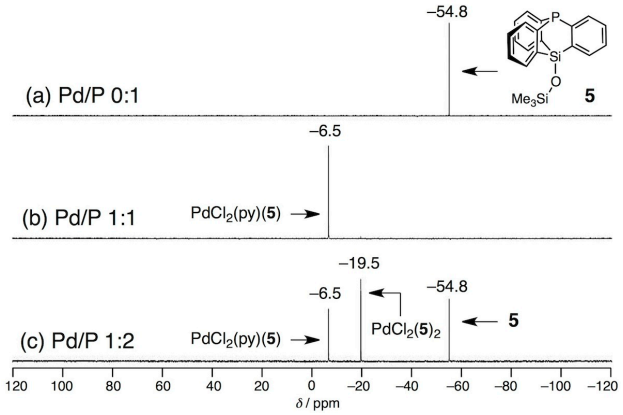


Figure 8. ^{31}P NMR spectra obtained from $PdCl_2(py)_2$ and TMSO-TRIP (**5**) [in $CDCl_3$, Pd/P (a) 0:1; (b) 1:1; (c) 1:2].

In contrast, the reaction of $PdCl_2(py)_2$ with silica-supported non-cage-type triarylphosphine Silica-1p-TPP[4h,17b] (Pd/P 1:2, in CH_2Cl_2 at room temperature for 1 h) gave well-separated two ^{31}P signals at δ 29 and δ 23 (Figure 9), which were assignable to a 1:1 Pd/P complex $PdCl_2(py)$(Silica-1p-TPP) and a 1:2 Pd/P complex $PdCl_2$(Silica-1p-TPP)$_2$, respectively, on the basis of the ^{31}P NMR studies using the corresponding soluble phosphine PPh_2[4-Me$_2$(*i*PrO)Si-C_6H_4] (**6**)[17b] (Pd/P 0:1, 1:1 or 1:2; in $CDCl_3$, Figure 10), along with a signal for the free phosphine at δ –4.[23] Comparison of the Pd coordination properties of Silica-TRIP and Silica-1p-TPP indicated that the cage-to-surface direct immobilization was an effective means for site isolation of the P centers to allow selective mono-P-ligation.

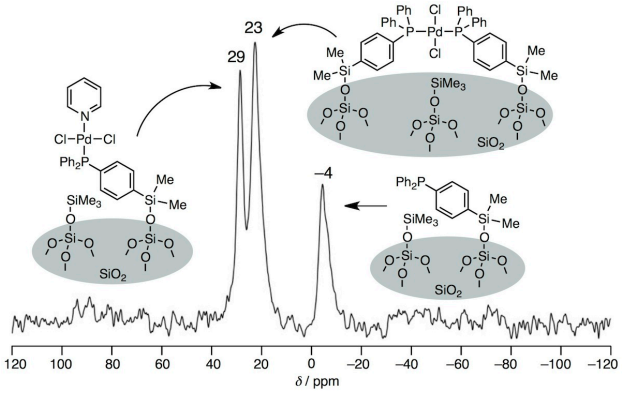


Figure 9. ^{31}P CP/MAS NMR spectrum obtained from $PdCl_2(py)_2$/Silica-1p-TPP (Pd/P 1:2).

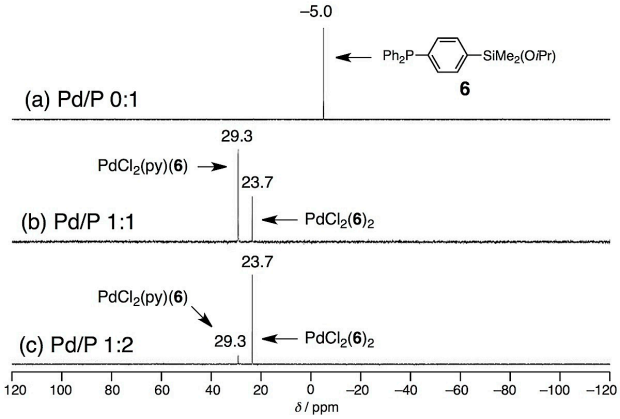
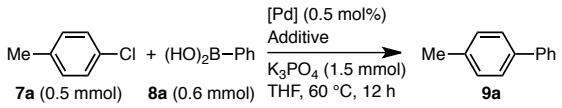


Figure 10. ^{31}P NMR spectra obtained from $PdCl_2(py)_2$ and PPh_2[4-Me$_2$(*i*PrO)Si-C_6H_4] (**6**) [in $CDCl_3$, Pd/P (a) 0:1; (b) 1:1; (c) 1:2].

Pd-Catalyzed Suzuki–Miyaura Cross-Coupling of Chloroarenes. To demonstrate ligand characteristics of Silica-TRIP for catalytic applications, we examined Pd-catalyzed Suzuki–Miyaura coupling of chloroarenes, in which mono-ligation of two-electron donor ligands is important for high catalytic activity.[12–14] Specifically, the reaction of 4-chlorotoluene (**7a**, 0.5 mmol) and phenylboronic acid (**8a**, 0.6 mmol) was conducted at 60 °C for 12 h in the presence of K_3PO_4 as a base and a palladium source (0.5 mol%). The results are summarized in Table 2.

The pre-formed immobilized mono-P-ligated Pd complex $PdCl_2(py)$(Silica-TRIP) initiated the coupling reaction to give the desired product **9a** in 56% yield, regardless of the moderate electron-donor power of Silica-TRIP as a triarylphosphine (Table 2, entry 1). However, the heterogeneous catalyst prepared *in-situ* from $PdCl_2(py)_2$ and Silica-TRIP were less efficient (5%, entry 2). In both cases, their solution phases changed from colorless to dark brown during the reactions probably due to leaching of Pd. More active catalyst was produced by a combination of Silica-TRIP and commercially available $Pd(OAc)_2$ (93%, entry 3).[24] The supernatant of the mixture after the coupling reaction was colorless; however, 3% Pd leaching into solution was observed by the ICP-AES analysis. Using unmodified silica gel CARiACT Q10 or TMS-endcapped CARiACT Q10 in place of Silica-TRIP under the conditions of entry 3 caused no reaction, indicating that $Pd(OAc)_2$ directly bound to silica gel was not effective (entries 4 and 5).

Table 2. Pd-catalyzed Suzuki–Miyaura cross-coupling between **7a** and **8a**.[a]



7a (0.5 mmol) **8a** (0.6 mmol) **9a**

entry	Pd source [Pd]	additive	yield (%)[b]
1	$PdCl_2$(py)(Silica-TRIP)	none	56
2[c]	$PdCl_2(py)_2$	Silica-TRIP	5
3[c]	$Pd(OAc)_2$	Silica-TRIP	93 (88)
4[d]	$Pd(OAc)_2$	CARiACT Q10 (unmodified)	0
5[d]	$Pd(OAc)_2$	CARiACT Q10 (TMS-endcapped)	0

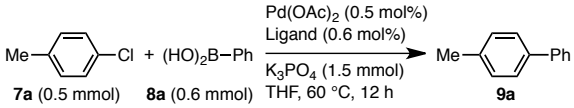
[a] Conditions: **7a** (0.5 mmol), **8a** (0.6 mmol), [Pd] (0.0025 mmol, 0.5 mol%), K_3PO_4 (1.5 mmol), THF (1.5 mL), 60 °C, 12 h. [b] Yields of **9a** were determined by ^{1}H NMR. Isolated yield is given in parentheses. [c] Silica-TRIP (0.030 mmol, 0.6 mol%). [d] CARiACT Q10 (42.9 mg).

Effects of phosphine ligands shown in Figure 11 were investigated in the presence of a catalytic amount of $Pd(OAc)_2$ (0.5 mol%, Table 3). Cage-type trialkylphosphine Silica-SMAP[4] and tripodally immobilized triarylphosphine Silica-3p-TPP,[17b] which possess mono-P-ligating features toward transition metals, promoted the coupling reaction, but their reaction efficacies were slightly less than that of Silica-TRIP (Table 2, entry 3 *vs*. Table 3, entries 1 and 2). The conventional monopodally silica-immobilized ligand Silica-1p-TPP, in which site-isolation of the P center was not enough as shown in Figure 9, was much less effective (9% yield, entry 3). In contrast to the silica-supported catalyst systems, their homogeneous counterparts TMSO-TRIP (**5**), Ph-TRIP,[4h] Ph-SMAP,[6] or PPh_3 induced no or trace of coupling reactions (entries 4–7). These results indicated that immobilization of ligands for obtaining a mono-P-ligating feature (e.g., cage-to-surface or tripod), which was supported by NMR studies of Pd-P coordination (Figure 7), is crucial for the high catalytic activities obtained with Silica-TRIP. Under the present reaction conditions, sterically demanding homogeneous trialkylphosphines such as PCy_3 and P*t*Bu$_3$ were not as effective as Silica-TRIP (entries 8 and 9), while a (dicyclohexylphosphino)biphenyl-type ligand XPhos,[12a] which is one of the most efficient ligands reported to date in the cross-coupling reactions, gave **9a** quantitatively (entry 10)

The heterogeneous Silica-TRIP-Pd catalyst has the advantage of catalyst-product separation over homogeneous molecular catalyst systems. Thus, after the reaction between **7a** and **8a** in the presence of the Silica-TRIP/$Pd(OAc)_2$ catalyst system (Table 2, entry 3), the reaction mixture was filtered through Celite®. The ICP-AES analysis indicated that Pd residues in the filtrate were 3% of the loaded Pd. This value was much less than the corresponding value (58% of the loaded Pd) in the experiment for the homogeneous system with the XPhos ligand (Table 3, entry 10). The hot filtration test with the Silica-TRIP/$Pd(OAc)_2$ catalyst showed no catalytic activity in the solution phase (Figure S6).[25]

The utility of Silica-TRIP for the Pd-catalyzed Suzuki–Miyaura coupling of various chloroarenes **7** and arylboronic acids **8** is summarized in Table 4. In the presence of 0.5–1 mol% of the Pd catalyst, chloroarenes with electron-donating (**7b–7c**) and electron-withdrawing (**7d–7g**) substituents at the *para* position of the aromatic ring smoothly reacted with **8a**, yielding the corresponding biaryls in good to high yields (entries 1–6). The reaction between 3-chloropyridine (**7h**) and 4-*t*-butylphenylboronic acid (**8b**) afforded the 3-arylpyridine **9h** in 88% yield (entry 7). Sterically hindered chloroarenes such as 2-chlorotoluene (**7i**) and 2,6-dimethylchlorobenzene (**7j**) were also suitable substrates (entries 8 and 9). The use of preformed catalyst $PdCl_2$(py)(Silica-TRIP) was more efficient than that of *in situ* prepared complex $Pd(OAc)_2$/Silica-TRIP in the reaction of 2,4,6-trimethoxychlorobenzene (**7k**) (entry 10). *ortho*-Substituted arylboronic acids such as 1-naphthylboronic acid (**8c**) and 2-tolylboronic acid (**8d**) were applicable to the coupling reactions, providing the corresponding biaryls in high yields (entries 11 and 12). Sterically congested 2,2',6-trimethylbiphenyl was obtained through the coupling reaction between **7j** and **8d** (entry 13).

Table 3. Ligand effects in Pd-catalyzed Suzuki–Miyaura cross-coupling between **7a** and **8a**.[a]



7a (0.5 mmol) **8a** (0.6 mmol) **9a**

entry	ligand	yield (%)[b]
1[c]	Silica-SMAP	82[d]
2	Silica-3p-TPP	83
3	Silica-1p-TPP	9
4	TMSO-TRIP (**5**)	1
5	Ph-TRIP	0
6	Ph-SMAP	0
7	PPh_3	<1
8	PCy_3	51
9	P*t*Bu$_3$	14
10	XPhos	>99

[a] Conditions: **7a** (0.5 mmol), **8a** (0.6 mmol), $Pd(OAc)_2$ (0.0025 mmol, 0.5 mol%), ligand (0.003 mmol, 0.6 mol%), K_3PO_4 (1.5 mmol), THF (1.5 mL), 60 °C, 12 h. [b] Yields of **9a** were determined by ^{1}H NMR. [c] 0.5 mol% of ligand, for 10 h. [d] Data were taken from ref. 4g.

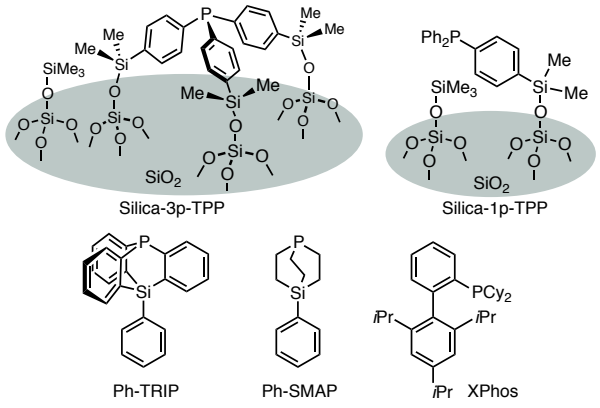
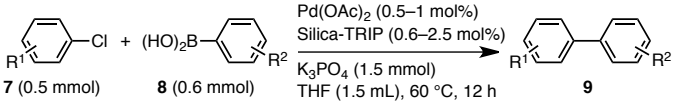
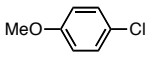
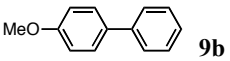
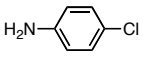
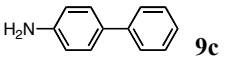
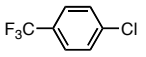
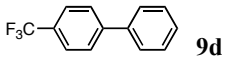
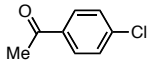
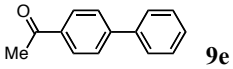
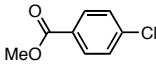
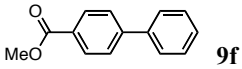
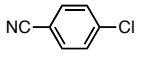
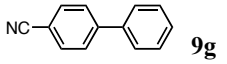
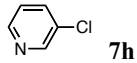
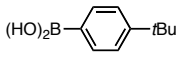
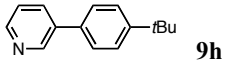
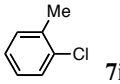
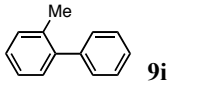
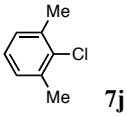
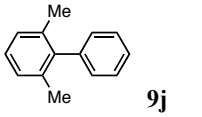
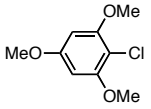
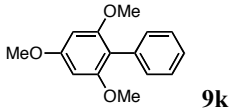
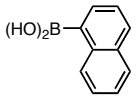
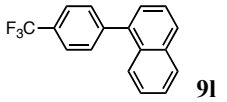
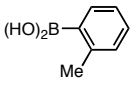
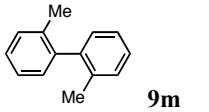
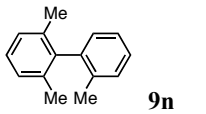


Figure 11. Heterogeneous and homogeneous phosphine ligands employed in Table 3.

Table 4. Silica-TRIP-Pd catalyzed Suzuki–Miyaura cross-coupling of **7** and **8**.[a]



entry	chloroarenes **7**	arylboronic acids **8**	[Pd] loading (mol%)	[P] loading (mol%)	product **9**	yield (%)[b]
1	 **7b**	**8a**	1	1.2	 **9b**	94
2	 **7c**	**8a**	1	2.5	 **9c**	83
3	 **7d**	**8a**	0.5	1	 **9d**	92
4	 **7e**	**8a**	0.5	1	 **9e**	78
5	 **7f**	**8a**	0.5	0.6	 **9f**	74
6	 **7g**	**8a**	0.5	1	 **9g**	88
7	 **7h**	 **8b**	1	1.2	 **9h**	88
8	 **7i**	**8a**	1	2.5	 **9i**	94
9	 **7j**	**8a**	1	2.5	 **9j**	91
10[c,d]	 **7k**	**8a**	1	1	 **9k**	80
11[c,d]	**7d**	 **8c**	0.7	0.7	 **9l**	86
12[d]	**7i**	 **8d**	0.5	0.7	 **9m**	80
13[d]	**7j**	**8d**	0.5	0.8	 **9n**	88[e]

[a] Conditions: **7** (0.5 mmol), **8** (0.6 mmol), $Pd(OAc)_2$ (0.0025–0.005 mmol, 0.5–1 mol%), Silica-TRIP (0.003–0.0125 mmol, 0.6–2.5 mol%), K_3PO_4 (1.5 mmol), THF (1.5 mL), 60 °C, 12 h. [b] Yields of isolated products. [c] $PdCl_2$(py)(Silica-TRIP) was used instead of Silica-TRIP/$Pd(OAc)_2$. [d] **8** (1 mmol) was used. [e] Isolated product was contaminated with **9m** (4%).

Unfortunately, reusability of the Silica-TRIP/$Pd(OAc)_2$ catalyst system was unsatisfactory under the present conditions. Specifically, the reaction of **7a** (0.5 mmol) and **8a** (0.75 mmol) with K_3PO_4 (1.5 mmol) in THF (1 mL) at 60 °C for 1 h in the presence of a heterogeneous catalyst prepared from $Pd(OAc)_2$ (1 mol%) and Silica-TRIP (1.5 mol%) gave **9a** in 97% yield (^{1}H NMR). Insoluble solids were recovered by filtration through a cotton plug followed by washing successively with H_2O, THF, and Et_2O. The catalysts recovered in this way gave decreased product yields with the increasing of the reuse (2nd run, 28%; 3rd run, 3%). Black color of the solid phase was supportive of the formation of inactive Pd species in the solid phase. The gradual Pd leaching was also observed during the catalyst reuse experiment; during the second run, color of the solution phase turned to dark brown. This Pd leaching may be due to the moderate coordination ability of the triarylphosphine center of Silica-TRIP.[26]

CONCLUSION

Silica-supported triptycene-type phosphine Silica-TRIP, comprising a 9-phospha-10-silatriptycene (TRIP) and silica gel as a coordinating moiety and a solid support, respectively, was synthesized in an efficient way. This material was characterized by nitrogen adsorption measurements and ^{13}C, ^{29}Si and ^{31}P CP/MAS NMR spectroscopies. Because of the cage-to-surface direct immobilization, Silica-TRIP exhibited a mono-P-ligating feature toward a Pd(II) complex, resulting in selective formation of a 1:1 Pd-P species even with the P-ligand in excess. This coordination behavior was confirmed by ^{31}P CP/MAS NMR spectroscopy. Usefulness of Silica-TRIP was previously demonstrated in the application to the Rh-catalyzed heteroatom-directed borylation of $C(sp^3)$–H bonds of amides, ureas, and 2-aminopyridines at the position α to the N atom. In the present work, Silica-TRIP was used as a ligand for the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction with chloroarenes. This catalytic reaction occurred under mild conditions, regardless of the moderate electron-donating nature of the triarylphosphine-based ligand. The facile catalyst-product separation by filtration was demonstrated as the merit of the heterogeneous Pd catalyst system over homogeneous systems. However, catalyst deactivation in the Suzuki–Miyaura coupling hampered the efficient reuse of the Pd catalyst.

EXPERIMENTAL SECTION

General. All reactions were carried out under nitrogen or argon atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Although Silica-SMAP[4a,c] and Silica-TRIP[4h] are commercially available,[5] the silica-supported ligands for this work were prepared according to the reported procedure or the modified procedure described below, respectively. CARiACT Q-10 silica gel (Catalyst grade, 75–150 μm, Fuji Silysia Chemical, Ltd.) was dehydrated by heating at 120 °C under vacuum for 10 h and stored in a glove box before use. Silica-3p-TPP,[17b] Silica-1p-TPP,[17b] Ph-SMAP,[6] and Ph-TRIP[4h] were prepared according to the reported procedure. $Pd(OAc)_2$ was purchased from Aldrich Co., Ltd., and $PdCl_2(py)_2$ was prepared according to the literature.[27] Phenylboronic acid (**8a**) was purchased from TCI Co., Ltd., and was recrystallized from hot water before use. K_3PO_4 was purchased from Junsei Chemicals Co., Ltd., and dried at 150 °C for 10 h under vacuum. All solvents for catalytic reactions were degassed via three freeze–pump–thaw cycles.

Solution NMR spectra were recorded on a JEOL ECX-II (400 MHz for ^1H NMR, 100.5 MHz for ^{13}C NMR, 79.4 MHz for ^{29}Si NMR and 161.8 MHz for ^{31}P NMR). Chemical shift values are referenced to Me_4Si (^1H and ^{29}Si), the residual solvent (^{13}C), and H_3PO_4 (^{31}P). Magic angle spinning (MAS) NMR spectra were recorded on a Bruker MSL-300 spectrometer, operating at 75.5 MHz for ^{13}C NMR, 59.6 MHz for ^{29}Si NMR, and 121.5 MHz for ^{31}P NMR. Combustion elemental analyses (J-SCIENCE Micro Corder JM10 or Yanako MT-6) and high-resolution mass spectra (Thermo Scientific Exactive or JEOL JMS-T100LC for ESI-MS, and JEOL JMS-T100GCv for EI-MS) were recorded at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University. N_2 adsorption (Quantachrome Autosorb-6) and ICP-AES analysis (Shimadzu ICPE-9000) were performed at Hokkaido University Sousei Hall. A microwave digestion system (Milestone, ETHOS One) was used to prepare samples for ICP-AES analysis. IR spectra were measured with a Perkin-Elmer Spectrum One. GLC analyses were conducted on a Shimadzu GC-14B equipped with a flame ionization detector. Melting points were determined on a micro melting point apparatus (Yanaco MP-500D).

Preparation of Tris(2-bromophenyl)phosphine (2).[8a] A solution of *i*PrMgBr in THF (0.92 M, 38 mL, 35 mmol), which was freshly prepared from *i*PrBr and Mg, was added over 25 min to a solution of 1-bromo-2-iodobenzene (**1**, 9.90 g, 35 mmol) in THF (35 mL) at –20 °C. The reaction mixture turned into a gray slurry after stirring at –20 °C for an additional 3 h. After complete consumption of **1**, which was confirmed by GC analysis of a small aliquot of the reaction mixture, TMEDA (5.25 mL, 35 mmol) and PCl_3 (872 μL, 10 mmol) were added in a dropwise manner in that order at –20 °C. The resulting mixture was allowed to warm to 0 °C and stirred at this temperature for an additional 14 h to give a clear pale-yellow solution. After quenching with NH_4Cl aq. at 0 °C, the reaction mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was passed through a short silica gel column with toluene as an eluting solvent, and the eluent was evaporated under vacuum. The residual solids were recrystallized from benzene/MeOH to give tris(2-bromophenyl)phosphine as a while solid (2.86 g, 57% yield).

^1H NMR ($CDCl_3$): δ 6.74–6.77 (m, 3H), 7.22–7.28 (m, 6H), 7.63–7.66 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 127.78, 130.37 (d, $J_{C–P}$ = 34.4 Hz), 130.73, 133.19 (d, $J_{C–P}$ = 1.9 Hz), 134.69, 136.72 (d, $J_{C–P}$ = 11.5 Hz). ^{31}P NMR ($CDCl_3$): δ –2.8.

Preparation of Silanol 3. For the preparation of **3**, Tsuji and Tamao's procedure for the synthesis of 10-chloro-9-phospha-10-silatriptycene[8a] was modified as follows. A solution of *t*BuLi in pentane (1.77 M, 5.1 mL, 9.0 mmol) was added over 15 min to a solution of **2** (748 mg, 1.5 mmol) in THF (4.5 mL) and Et_2O (23 mL) at –78 °C. After stirring for 4 h, $SiCl_4$ (172 μL, 1.5 mmol) was added in a dropwise manner at –78 °C, and the resulting mixture was stirred at this temperature for an additional 4 h. After quenching the excess organolithium species with Me_3SiCl (1.1 mL, 9 mmol) at –78 °C, the mixture was allowed to warm to room temperature and stirred for an additional 13 h. After evaporation of the volatiles, the residue was dissolved in toluene and filtered through a Celite® pad. The filtrate was concentrated, and the crude product was purified by silica gel column chromatography (hexane/EtOAc 100:0–80:20) followed by reprecipitation from CH_2Cl_2/hexane to give silanol **3** as a white solid (321 mg, 70% yield). Single crystals of **3** suitable for X-ray diffraction studies were obtained by recrystallization from a $CHCl_3$/hexane solution (CCDC: 1060983).

M.p.: 120 °C (decomp.). ^1H NMR ($CDCl_3$): δ 3.32 (s, 1H), 7.21–7.28 (m, 6H), 7.81 (d, J = 6.4 Hz, 3H), 7.87 (dd, J = 10.8, 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 127.86, 128.10 (d, $J_{C–P}$ = 15.2 Hz), 131.56, 134.69 (d, $J_{C–P}$ = 45.8 Hz), 141.13, 146.12 (d, $J_{C–P}$ = 8.6 Hz). ^{29}Si NMR ($CDCl_3$): δ –30.6 (d, $J_{Si–P}$ = 8.5 Hz). ^{31}P NMR ($CDCl_3$): δ –54.0. IR (ATR): 3347 (br), 3052, 2964, 1688, 1572, 1430, 1260, 896, 755, 666 cm^{-1}. HRMS–ESI (*m/z*): $[M–H]^-$ calcd for $C_{18}H_{12}OPSi$, 303.04005; found, 303.04086.

Preparation of Disiloxane 4. Silanol **3** (30.0 mg, 0.1 mmol) and imidazole (1.4 mg, 0.02 mmol) were dissolved in benzene (0.5 mL), and the mixture was stirred at 80 °C for

10.5 h. After cooling to room temperature, the insoluble solids were filtered and washed with benzene to give the disiloxane **4** as a white solid (15.0 mg, 52% yield). Due to the low solubility of **4** into organic solvents, clear NMR data were not obtained.

White solid. M.p. 430 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.22–7.26 (m, 6H), 7.31 (t, J = 7.2 Hz, 6H), 7.91 (d, J = 6.4 Hz, 6H), 7.98 (dd, J = 11.2, 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 128.27, 128.47 (d, J_{C-P} = 15.3 Hz), 131.77, 134.98 (d, J_{C-P} = 45.8 Hz), 140.77, 146.31 (d, J_{C-P} = 9.6 Hz). ^{31}P NMR ($CDCl_3$): δ –55.1. HRMS-EI (*m/z*) Calcd for $[M]^+$ $C_{36}H_{24}OP_2Si_2$, 590.08409; found, 590.08389.

Preparation of TMSO-TRIP 5. A solution of silanol **3** (45.7 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of *N*-trimethylsilylimidazole (105 mg, 0.75 mmol) in CH_2Cl_2 (2 mL). After stirring at room temperature for 1 h, MeOH (2 mL) was added to quench the excess *N*-trimethylsilylimidazole, and then the mixture was stirred for additional 10 min. The volatiles were removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluting with CH_2Cl_2) to give 10-{(trimethylsilyl)oxy}-9-phospha-10-silatriptycene (**5**) as a white solid (49.0 mg, 87% yield).

M.p.: 225–228 ºC. ^{1}H NMR ($CDCl_3$): δ 0.52 (s, 9H), 7.19–7.28 (m, 6H), 7.76 (dd, J = 6.8, 0.8 Hz, 3H), 7.85 (dd, J = 11.6, 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 2.48, 127.79–127.94 (m), 131.58, 134.61 (d, J_{C-P} = 45.8 Hz), 142.09, 146.12 (d, J_{C-P} = 7.6 Hz). ^{31}P NMR ($CDCl_3$): δ –54.9. ^{29}Si NMR ($CDCl_3$): δ –38.9 (d, J_{Si-P} = 9.1 Hz), 14.4. HRMS-EI (*m/z*) Calcd for $[M]^+$ $C_{21}H_{21}OPSi_2$, 376.08685; found, 376.08541.

Preparation of Silica-TRIP. Silanol **3** (365 mg, 1.2 mmol), CARiACT Q-10 silica gel (10.6 g), imidazole (408 mg, 6.0 mmol), and anhydrous, degassed toluene (42 mL) were placed in a 200-mL three-necked flask equipped with a mechanical stirrer under argon atmosphere. The suspension was gently stirred at 100 °C for 16 h. After cooling to room temperature, the mixture was filtered, washed successively with degassed toluene, toluene-MeOH (1:1), and MeOH, and dried under vacuum at 120 °C overnight. Next, a solution of *N*-trimethylsilylimidazole (5.3 mL) in THF (30 mL) was added to the flask with the functionalized silica gel Silica-TRIP(SiOH). The suspension was stirred at 60 °C for 24 h under argon atmosphere. After cooling to room temperature, solids were collected by filtration through a glass filter, washed with MeOH, and dried under vacuum at 120 °C overnight to give 9.4 g of Silica-TRIP.

^{13}C CP/MAS NMR: δ 2, 123–150 (br m). ^{29}Si CP/MAS NMR: δ –110, −102, –36, 14. ^{31}P CP/MAS NMR: δ –52. Elemental Anal. found: C 5.33; H 1.19.

Preparation of Silica-TRIP oxide. Silica-TRIP (200 mg, 0.014 mmol, 0.07 mmol/g) and *m*-chloroperbenzoic acid (≤77%, 9.4 mg, 0.042 mmol) were placed in a vial containing a magnetic stirring bar. CH_2Cl_2 (1 mL) was added, and the tube was sealed with a screw cap. The mixture was stirred at room temperature for 1 h. The suspension was filtered, washed with CH_2Cl_2, and dried under vacuum to give Silica-TRIP oxide (183.4 mg). The sample for analysis was prepared after drying under vacuum at 120 °C overnight.

^{13}C CP/MAS NMR: δ 2, 130 (br), 143 (br). ^{29}Si CP/MAS NMR: δ –110, –101, –38, 14. ^{31}P CP/MAS NMR: δ –8. Elemental Anal. found: C 5.42; H 0.99.

Reaction of $PdCl_2(py)_2$ and Silica-TRIP (Pd/P 2:1). Silica-TRIP (401.5 mg, 0.028 mmol, 0.07 mmol/g) and $PdCl_2(py)_2$ (18.8 mg, 0.056 mmol) were placed in a vial containing a magnetic stirring bar. Anhydrous, degassed CH_2Cl_2 (2 mL) was added, and the tube was sealed with a screw cap. The mixture was stirred at room temperature for 0.5 h. The suspension was filtered and washed with CH_2Cl_2. The filtrate was evaporated to recover unreacted $PdCl_2(py)_2$ (8.3 mg, 0.025 mmol). The pale yellow silica gel was dried under vacuum to give $PdCl_2$(py)(Silica-TRIP) (375.1 mg). Thus, P loading on Silica-TRIP was calculated to be 0.078 mmol/g based on a Pd to P stoichiometry of 1:1 [{(18.8–8.3)/335.53}/0.4015 = 0.078]. For convenience, the value of 0.07 mmol/g was used for P loading in metal complexations and catalytic applications.

^{13}C CP/MAS NMR: δ 3, 120–158 (br m). ^{31}P CP/MAS NMR: δ –5.

Reaction of $PdCl_2(py)_2$ and Silica-TRIP (Pd/P 1:2). Silica-TRIP (399.2 mg, 0.028 mmol, 0.07 mmol/g) and $PdCl_2(py)_2$ (4.8 mg, 0.014 mmol) were placed in a vial containing a magnetic stirring bar. Anhydrous, degassed CH_2Cl_2 (2 mL) was added, and the tube was sealed with a screw cap. The mixture was stirred at room temperature for 0.5 h. The suspension was filtered and washed with CH_2Cl_2. The pale yellow silica was dried under vacuum to give a mixture of $PdCl_2$(py)(Silica-TRIP) and unreacted Silica-TRIP (363.5 mg).

^{31}P CP/MAS NMR: δ –52, –5.

Reaction of $PdCl_2(py)_2$ and TMSO-TRIP (Pd/P 1:1, 1:2). TMSO-TRIP (**5**) (0.02 mmol) and $PdCl_2(py)_2$ (0.02 mmol for Pd/P 1:1; 0.01 mmol for Pd/P 1:2) were placed in a 5-mL glass tube containing a magnetic stirring bar. $CDCl_3$ (0.7 mL) was added and stirred at room temperature for 5 min. The mixture was analyzed with ^{31}P NMR spectroscopy.

Preparation of $PdCl_2$(py)(5). A solution of **5** (18.8 mg, 0.05 mmol) in $CHCl_3$ (1.5 mL) was added dropwise to a solution of $PdCl_2(py)_2$ (17.8 mg, 0.05 mmol) in $CHCl_3$ (1.5 mL). The mixture was stirred at room temperature for 0.5 h. The volatiles were evaporated. The residue was extracted with benzene. After filtration, the solution was evaporated. The residue was recrystallized from $CHCl_3$/hexane to give $PdCl_2$(py)(**5**) as a yellow solid (22.8 mg, contaminated with 3% of $PdCl_2(py)_2$, 71% yield)

M.p.: 190 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 0.53 (s, 9H), 7.30–7.39 (m, 6H), 7.50 (t, J = 7.2 Hz, 2H), 7.71 (d, J = 6.8 Hz, 3H), 7.88 (t, J = 7.2 Hz, 1H), 9.12 (dd, J = 13.6, 7.3 Hz, 3H), 9.16–9.19 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 2.37, 124.89 (d, J_{C-P} = 3.8 Hz), 127.96 (d, J_{C-P} = 13.4 Hz), 128.73, 130.49 (d, J_{C-P} = 7.6 Hz), 136.74 (d, J_{C-P} = 19.2 Hz), 138.57, 140.04 (d, J_{C-P} = 49.8 Hz), 140.99, 151.47. ^{31}P NMR ($CDCl_3$): δ –6.5. Attempts to obtain MS spectra (ESI or FAB) of $PdCl_2$(py)(**5**) were unsuccessful.

Preparation of $PdCl_2(5)_2$. The mixture of **5** (37.6 mg, 0.10 mmol), $PdCl_2(py)_2$ (17.8 mg, 0.05 mmol) and $CHCl_3$ (2 mL) was stirred at room temperature for 1 h. The volatiles were evaporated. The residue was washed with $CHCl_3$ to give $PdCl_2(\mathbf{5})_2$ as a yellow solid (39.6 mg, 43% yield).

M.p.: 310 ºC (decomp.). ^{1}H NMR ($CDCl_3$): δ 0.55 (s, 18H), 7.30–7.43 (m, 12 H), 7.78 (d, J = 7.6 Hz, 6H), 9.18–9.24 (m, 6H). ^{31}P NMR ($CDCl_3$): δ –19.5. HRMS-ESI (*m/z*) Calcd for $[M+Na]^+$ $C_{42}H_{42}Cl_2O_2P_2PdSi_4Na$, 953.00508; found 953.00236. ^{13}C NMR data are not available due to the low solubility of $PdCl_2(\mathbf{5})_2$ in organic solvents.

Reaction of $PdCl_2(py)_2$ and Silica-1p-TPP (Pd/P 1:2). Silica-1p-TPP (200 mg, 0.018 mmol, 0.09 mmol/g) and $PdCl_2(py)_2$ (3.0 mg, 0.0089 mmol) were placed in a vial con-

taining a magnetic stirring bar. Anhydrous, degassed CH_2Cl_2 (2 mL) was added, and the tube was sealed with a screw cap. The mixture was stirred at room temperature for 1 h. The suspension was filtered and washed with CH_2Cl_2. The pale yellow silica was dried under vacuum to give a mixture of $PdCl_2$(py)(Silica-1p-TPP), $PdCl_2$(Silica-1p-TPP)$_2$ and unreacted Silica-TRIP (200 mg).

^{31}P CP/MAS NMR: δ –4, 23, 29.

Reaction of $PdCl_2(py)_2$ and PPh_2[4-Me_2(*i*PrO)Si-C_6H_4] (Pd/P 1:1, 1:2). PPh_2[4-Me_2(*i*PrO)Si-C_6H_4] (**6**) (0.02 mmol) and $PdCl_2(py)_2$ (0.02 mmol for Pd/P 1:1; 0.01 mmol for Pd/P 1:2) were placed in a 5-mL glass tube containing a magnetic stirring bar. $CDCl_3$ (0.7 mL) was added and stirred at room temperature for 5 min. The mixture was analyzed with ^{31}P NMR spectroscopy.

Preparation of $PdCl_2$(py)(6). A solution of **6** (18.9 mg, 0.05 mmol) in $CHCl_3$ (1.5 mL) was added dropwise to a solution of $PdCl_2(py)_2$ (17.8 mg, 0.05 mmol) in $CHCl_3$ (1.5 mL). The mixture was stirred at room temperature for 0.5 h. The volatiles were evaporated. The residue was extracted with benzene. After filtration, the solution was evaporated. The residue was recrystallized from benzene/hexane to give $PdCl_2$(py)(**6**) as a yellow solid (16.8 mg, contaminated with 6% of $PdCl_2(py)_2$, 51% yield)

M.p.: 210 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 0.37 (s, 6H), 1.15 (d, J = 6.4 Hz, 6H), 4.02 (sept, J = 6.4 Hz, 1H), 7.35–7.51 (m, 8H) 7.64 (dd, J = 8.4, 2.8 Hz, 2H), 7.76–7.84 (m, 7H), 8.99–9.01 (m, 2H). ^{13}C NMR ($CDCl_3$): δ –1.16, 25.68, 65.51, 124.59 (d, J_{C-P} = 2.8 Hz), 128.09 (d, J_{C-P} = 11.5 Hz), 129.21 (d, J_{C-P} = 58.4 Hz), 130.16 (d, J_{C-P} = 56.5 Hz), 131.02 (d, J_{C-P} = 2.8 Hz), 133.02 (d, J_{C-P} = 10.6 Hz), 133.90 (d, J_{C-P} = 9.5 Hz), 134.82 (d, J_{C-P} = 9.5 Hz), 138.20, 142.33 (d, J_{C-P} = 1.9 Hz), 151.60. ^{31}P NMR ($CDCl_3$): δ 29.3. Attempts to obtain MS spectra (ESI or FAB) of $PdCl_2$(py)(**6**) were unsuccessful.

Preparation of $PdCl_2(6)_2$. The mixture of **6** (22.7 mg, 0.06 mmol), $PdCl_2(py)_2$ (10.1 mg, 0.03 mmol) and $CHCl_3$ (1 mL) was stirred at room temperature for 1 h. The volatiles were evaporated. The resulting residue was recrystallized from CH_2Cl_2/hexane to give $PdCl_2$(**6**)$_2$ as a yellow solid (26.5 mg, contaminated with traces of impurities, 47% yield).

M.p.: 192–195 °C. ^{1}H NMR ($CDCl_3$): δ 0.36 (s, 12H), 1.14 (d, J = 6.4 Hz, 12H), 4.01 (sept, J = 6.4 Hz, 2H), 7.35–7.45 (m, 12H), 7.59 (d, J = 7.6 Hz, 4H), 7.68–7.73 (m, 12H). ^{13}C NMR ($CDCl_3$): δ –1.15, 25.68, 65.44, 128.03 (vt, J_{C-P} = 4.8 Hz), 129.51 (vt, J_{C-P} = 24.9 Hz), 130.48, 130.59 (vt, J_{C-P} = 23.9 Hz), 132.97 (vt, J_{C-P} = 4.8 Hz), 134.15 (vt, J_{C-P} = 5.7 Hz), 135.00 (vt, J_{C-P} = 6.7 Hz), 141.48. ^{31}P NMR ($CDCl_3$): δ 23.7. HRMS-ESI (m/z) Calcd for $[M+Na]^+$ $C_{46}H_{54}Cl_2O_2P_2PdSi_2Na$, 957.14513; found 957.14797.

Typical Procedure for the Suzuki–Miyaura Coupling Reaction. In a nitrogen-filled glove box, Silica-TRIP (0.07 mmol/g, 42.9 mg, 0.003 mmol) and a solution of $Pd(OAc)_2$ (0.56 mg, 0.0025 mmol) in anhydrous, degassed THF (0.5 mL) were placed in a 10-mL glass tube containing a magnetic stirring bar. After stirring at room temperature for 5 min, phenylboronic acid (**8a**, 73.1 mg, 0.6 mmol), K_3PO_4 (318 mg, 1.5 mmol), *p*-chlorotoluene (**7a**, 63.3 mg, 0.5 mmol), and THF (1 mL) were added successively. The tube was sealed with a screw cap and removed from the glove box. The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the mixture was diluted with Et_2O and filtered through a Celite® pad (eluting with Et_2O). The volatiles were evaporated, and an internal standard (1,1,2,2-tetrachloroethane) was added to determine the yield of 4-methylbiphenyl (**9a**, 93% yield). The crude product was purified by silica gel chromatography (eluting with hexane) to give **9a** (74.3 mg, 0.44 mmol, 88% yield).

ICP-AES Measurements for Pd Residue. After the reaction of **7a** (0.5 mmol) and **8a** (0.6 mmol) in the presence of 0.5 mol% the Silica-TRIP-Pd catalyst (Table 2, entry 3), the reaction mixture was diluted with Et_2O, and filtered through a Celite® pad (eluting with Et_2O). The volatiles were evaporated. A small aliquot of the residue (ca. 5 mg) was taken for a microwave-assisted acid digestion with aqua regia (1000 W, 220 °C) followed by a mixture of nitric acid and perchloric acid (1000 W, 220 °C). The resulting mixture was diluted in H_2O (20 mL). This solution was subjected to ICP-AES analysis.

Hot Filtration Test. In a nitrogen-filled glove box, Silica-TRIP (0.07 mmol/g, 42.9 mg, 0.003 mmol) and a solution of $Pd(OAc)_2$ (0.56 mg, 0.0025 mmol) in anhydrous, degassed THF (0.5 mL), and THF (1 mL) were placed in a 10-mL glass tube containing a magnetic stirring bar. After stirring at room temperature for 5 min, phenylboronic acid (**8a**, 73.2 mg, 0.6 mmol), K_3PO_4 (318 mg, 1.5 mmol), *p*-chlorotoluene (**7a**, 63.3 mg, 0.5 mmol), and 1,2-diphenylethane (91.1 mg, 0.5 mmol, internal standard) were added successively. The tube was sealed with a screw cap, and the mixture was stirred at 60 °C. A small aliquot was taken out from the reaction mixture at suitable interval, and the samples were diluted with Et_2O and analyzed by GC. After 15 min, the hot mixture was filtered through a Celite® pad. The filtrate was placed in a new 10-mL glass tube containing **8a** (0.5 mmol), K_3PO_4 (1.5 mmol), and a magnetic stirring bar. Again, the mixture was stirred at 60 °C. The yields of the product **9a** were determined by GC analysis.

Reuse of Silica-TRIP-Pd System. In a nitrogen-filled glove box, Silica-TRIP (0.07 mmol/g, 107 mg, 0.0075 mmol) and a solution of $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol) in anhydrous, degassed THF (1 mL) were placed in a 10-mL glass tube containing a magnetic stirring bar. After stirring at room temperature for 5 min, K_3PO_4 (318 mg, 1.5 mmol), phenylboronic acid (**8a**, 91.4 mg, 0.75 mmol) and *p*-chlorotoluene (**7a**, 63.3 mg, 0.5 mmol) were added successively. The tube was sealed with a screw cap and removed from the glove box. The mixture was stirred at 60 °C for 1 h. After cooling to room temperature, the mixture was diluted with Et_2O and filtered through a glass pipette equipped with a cotton plug (eluting with Et_2O). The inorganic salts were removed by washing H_2O, and then solvent displacement was performed with THF followed by Et_2O. After drying under vacuum, the recovered gel was placed in the vial tube that was used for second run. Anhydrous, degassed THF (1 mL), K_3PO_4 (318 mg, 1.5 mmol), **7a** (63.3 mg, 0.5 mmol) and **8a** (91.4 mg, 0.75 mmol) were added, and the mixture was stirred at 60 °C for 1 h. Yields of the products were determined by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. This recycling procedure was repeated two times (1st run, 97%; 2nd run, 28%; 3rd run, 3%).

X-ray Crystallographic Analysis of 3. Crystal data for 3{**3**·1/3($CHCl_3$)} (CCDC 1060983; recrystallization from $CHCl_3$/hexane). $C_{55}H_{40}Cl_3O_3P_3Si_3$, M = 1032.46, trigonal, space group $P\bar{3}c1$ (#165), a = 15.5297(5) Å, c = 24.1564(11) Å, V = 5045.3(4) Å^3, Z = 4, density (calc.) = 1.359, total reflections collected = 39823, unique reflections = 3860 (R_{int} = 0.0542), GOF = 1.139, $R1$ (I>2σ(I)) = 0.0461, $wR2$ = 0.1077.

Data were collected on a Rigaku Mercury 70 CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71075 Å) at 150 K, and processed using the CrystalClear software.[28] Structures were solved by a direct method using SIR-2004,[29] and refined by full-matrix least-square method using SHELXL-97.[30] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for the silanol protons were located on the calculated positions and refined using a riding model. The silanol protons (H1 and H2; disordered, 1:1) were located in the difference Fourier map and refined isotropically. All calculations were performed using the CrystalStructure software package.[31]

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and characterization of the products. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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(21) Without imidazole as an additive, a significant amount of silanol **3** remained in the crude product (ca. 20% conversion of **3** after 12 h).

(22) The oxidation of TMSO-TRIP (**5**) with mCPBA afforded the phosphine oxide TMSO-TRIP oxide (**S1**). See the Supporting Information for details.

(23) The coordination behavior of Silica-1p-TPP toward a Pd(II) center using $PdCl_2(PhCN)_2$ was studied previously. See, ref 17b.

(24) Reactions of $Pd(OAc)_2$ with Silica-TRIP (Pd/P 2:1 or 1:1), or TMSO-TRIP (Pd/P 2:1 or 1:1) were conducted to investigate their coordination properties toward the Pd center (Figures S3–S5).

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(26) The ^{31}P CP/MAS NMR spectrum of the silica gel Pd-Silica-TRIP recovered after the coupling reaction in a larger scale (**7a**, 2.5 mmol) showed a distinct major signal at δ 4 together with minor signals at δ –52 (Silica-TRIP) and –8 (overlapped with Silica-TRIP oxide) (Figure S7a). On the other hand, a sample obtained from the solution phase of the reaction mixture showed no signal in ^{31}P NMR spectroscopy (in $CDCl_3$, Figure S8). These results indicate that at least most of the phosphine moiety remained bound to the solid surface. However, partial degradation of the Silica-TRIP structure during the catalytic reaction cannot be ruled out due to poor signals of the aromatic carbons and the bridgehead Si atom of the TRIP moiety in the ^{13}C and ^{29}Si CP/MAS NMR spectra, respectively (Figures S7b and S7c).

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