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Structural and Coordination Properties of 3,3-Diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-2-(trimethylsilyl)-1,3-diphosphapropene Derivatives Showing Interesting Conformational Features

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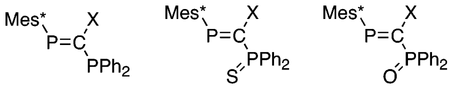
(*E*)-3,3-Diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-2-(trimethylsilyl)-1,3-diphosphapropene was prepared from (2-(2,4,6-tri-*tert*-butylphenyl)-1-(trimethylsilyl)-2-phosphaethenyl)lithium and chlorodiphenylphosphine, and the properties involving conformational aspects, coordination to metals, and sulfurization were investigated. The structure of 2-(trimethylsilyl)-1,3-diphosphapropene shows C_1 symmetry with the phosphino lone pair almost perpendicular to the P═C π-system, whereas the 2-chloro- and 2-methyl-1,3-diphosphapropene derivatives show nearly C_s symmetry with the phosphino lone pair almost coplanar with the P═C plane. A very small $^{2}J_{PP}$ coupling constant for the 2-(trimethylsilyl)-1,3-diphosphapropene was observed by ^{31}P NMR spectroscopy, indicating that the conformation of the C_1 symmetry was kept in solution. On coordination of the phosphorus atoms to the carbonyltungsten(0) moiety, the inherently predominant C_1 form of the 2-(trimethylsilyl)-1,3-diphosphapropene changed to C_s symmetry. On the other hand, sulfurization of the 2-(trimethylsilyl)-1,3-diphosphapropene afforded the corresponding 3-thioxo-2-(trimethylsilyl)-1,3-diphosphapropene, indicating C_1 symmetry with the P═S bond almost perpendicular to the P═C moiety. The 2-(trimethylsilyl)-1,3-diphosphapropene acts as a P2 chelate ligand of a dichloropalladium(II) complex, which showed moderate catalytic activity in the Sonogashira cross-coupling reaction. The structure of the dichloropalladium(II) complex bearing the ligated 2-(trimethylsilyl)-1,3-diphosphapropene was analyzed by X-ray crystallography, indicating structure effects on the properties.

Introduction

Phosphaalkenes (methylenephosphines) containing the P═C moiety have been synthesized since kinetic protection by using sterically encumbered substituents was established to isolate various multiply bonded heavier main group elements in the early 1980s.[1,2] As phosphines have been widely utilized as ligands of metal complexes, phosphaalkenes have attracted much attention from the point of view of coordination chemistry in the last two decades. We[3] and others[1] have reported a considerable number of metal complexes bearing ligated phosphaalkenes, and the coordination properties of the P═C moieties have been studied. Several phosphaalkenes such as 3,4-diphosphinidenecyclobutenes (DPCBs) are available to develop specific catalysts for organic synthesis.[4,5]

Chart 1



1 **2** **3**

X = Cl (**A**), Me (**B**), SiMe$_3$ (**C**) Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$

In the course of research on low-coordinated phosphorus compounds stabilized by the Mes* (2,4,6-tri-*tert*-butylphenyl) substituent, we have reported the preparation and coordination properties of several 1,3-diphosphapropenes **1**, which contain both a low-coordinated sp^2-type phosphorus and a normal sp^3-type phosphino phosphorus (Chart 1).[6] Such a combination of an sp^3-type phosphorus with an sp^2-type phosphorus provides peculiar ligand design to coordination chemistry. So far, we have revealed several structural properties of 1,3-diphosphapropenes **1** in relation to coordination chemistry as follows. (1) Basically, the phosphino group of **1** predominantly coordinates on metals because its basicity is greater than that of the sp^2-type phosphorus.[6] (2) As indicated by the molecular structure of **1**, the two lone pairs of phosphorus atoms are in the P═CP plane to show a suitable conformation to act as a P2-chelate ligand.[6c,7d] (3) The conformation of **1** remained unchanged upon coordination to the carbonyltungsten(0) moieties.[6a,b] Additionally, the conformation of 1,3-diphosphapropenes **1A** and **1B**[7d,8]

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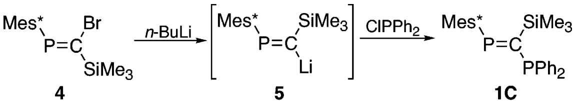
Scheme 1



was not affected by chalcogenation, affording the corresponding 3-chalcogeno-1,3-diphosphapropenes **2** and **3**: the P=CP=E (E = S, O) skeletons are almost coplanar.[7]

Indeed, 1,3-diphosphapropene derivatives contain rotational isomerism around the phosphino group, and the conformation of 1,3-diphosphapropene has been discussed theoretically. The theoretical calculation pointed out that the conformation experimentally observed in **1A** and **1B** is not an energetic minimum; another conformation was determined as the energetically minimum form.[9] In the course of our research on the P=CP molecular system to develop novel metal complexes of catalytic activity,[6,7] we found that the trimethylsilyl group at the 2-position of 1,3-diphosphapropene is effective to investigate the rotational isomerism of the P=CP< molecular system. In addition, the silyl groups are effective substituents to obtain several exotic organic compounds.[10] In this paper we describe the preparation, structure, and reactivity of 3,3-diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-2-(trimethylsilyl)-1,3-diphosphapropene (**1C**), which shows a conformation different from those of 1,3-diphosphapropenes **1A** and **1B**.[6c,8] The molecular structures of 2-silyl-1,3-diphosphapropenes are discussed on the basis of results obtained by X-ray crystallography and theoretical calculations. Additionally, the 2-(trimethylsilyl)-1,3-diphosphapropene **1C** was employed as a ligand of the dichloropalladium(II) complex to develop a novel catalyst for a cross-coupling reaction. The structure of the dichloropalladium(II) complex bearing **1C** was determined by X-ray crystallography, and the structure effects are discussed.

Results and Discussion

Preparation and Structure of the 2-(Trimethylsilyl)-1,3-diphosphapropene 1C. (*Z*)-2-Bromo-1-(2,4,6-tri-*tert*-butylphenyl)-2-(trimethylsilyl)-1-phosphaethene (**4**) was allowed to react with butyllithium to generate the (phosphavinyl)lithium intermediate **5** in THF,[10c,11] and the solution containing **5** was mixed with chlorodiphenylphosphine to afford the 2-(trimethylsilyl)-1,3-diphosphapropene **1C** in 71% yield as pale yellow crystals (Scheme 1). In the ^{31}P NMR spectrum, the sp^2 phosphorus and the sp^3 phosphorus were observed at δ_P 382.7 and −1.6, respectively. In contrast to the case for 1,3-diphosphapropenes **1A** and **1B**,[6,7] the $^2J_{PP}$ constant of **1C** was extremely small (37.1 Hz). The small $^2J_{PP}$ constant is almost equal to that of the configurational stereoisomer of **1A** and **1B**, where the lone pair of the sp^2 phosphorus and the phosphino group are on the opposite side.[6] However, the geometrical configuration of **1C** was analyzed by X-ray crystallography to confirm the *E* form, where the lone pair of the sp^2 phosphorus and the phosphino group are on the same side (Figure 1, Table 1). These findings indicate that the magnitude of the $^2J_{PP}$ constant of 1,3-diphosphapropenes is not only dependent on the geometrical configuration around the P=C plane but also on other factors, such as the conformation of the 1,3-diphosphapropene skeleton. The lone pair of the phosphino group of **1C** is almost perpendicular to the P=C bond to show C_1 symmetry, whereas in the case of **1A**, the lone pair of the phosphino group is almost coplanar with the P=C plane to show C_s symmetry (Chart 2).[6c] As for the geometrical parameters of **1C**, the P(1)−C(1) distance and the C(1)−P(2)−C(2) angle demonstrate the basic features of a low-coordinated phosphaalkene.[1] The wider P(1)−C(1)−Si angle might indicate steric repulsion between the Mes* group and the trimethylsilyl group. The smaller P(1)−C(1)−P(2) and P(2)−C(1)−Si angles of **1C** as compared to the corresponding data for **1A**[6c] might indicate reduction of the steric congestion around the diphenylphosphino group, which is suggested by theoretical calculations (vide infra). The Si−C(1) distance is slightly longer than the corresponding Si−C distances for 1-(2,4,6-tri-*tert*-butylphenyl)-2,2-bis(trimethylsilyl)-1-phosphaethene (1.891(4), 1.887(4) Å),[12] indicating the influence of the phosphino group.

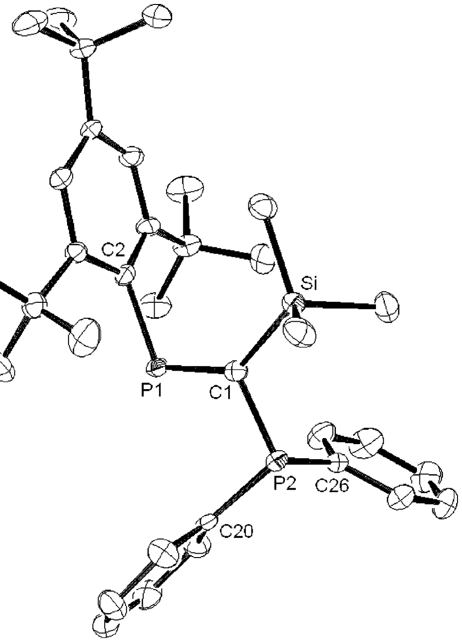
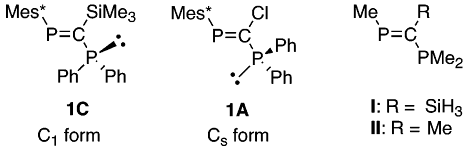


Figure 1. Thermal ellipsoid plot (50% probability surface) of the molecular structure of **1C**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−C(1) = 1.672(3), P(1)−C(2) = 1.860(3), P(2)−C(1) = 1.843(3), P(2)−C(20) = 1.843(3), P(2)−C(26) = 1.845(4), Si−C(1) = 1.908(3); C(1)−P(1)−C(2) = 107.6(1), C(1)−P(2)−C(20) = 105.7(1), C(1)−P(2)−C(26) = 104.2(2), C(20)−P(2)−C(26) = 102.4(2), P(1)−C(1)−P(2) = 116.2(2), P(1)−C(1)−Si = 134.2(2), P(2)−C(1)−Si = 109.1(2), θ[P(1)−C(1)−P(2)−C(20)] = −9.7(3), θ[P(1)−C(1)−P(2)−C(26)] = 97.8(2).

Chart 2



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(8) (*E*)-3,3-Bis(*p*-anisyl)-1-(2,4,6-tri-*tert*-butylphenyl)-2-methyl-1,3-diphosphapropene was analyzed by X-ray crystallography.[7d]

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Table 1. X-ray Data for Compounds 1C and 6−9

	1C	**6**	**7**	**8**	**9**·2CH₂Cl₂
formula	$C_{34}H_{48}P_2Si$	$C_{39}H_{48}O_5P_2SiW$	$C_{38}H_{48}O_4P_2SiW$	$C_{34}H_{48}P_2SSi$	$C_{34}H_{48}P_2SiPd\cdot 2CH_2Cl_2$
fw	546.79	870.69	842.68	578.85	893.97
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P2_1/a$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)
a/Å	10.2492(7)	17.595(1)	11.203(5)	17.706(2)	17.961(4)
b/Å	29.368(1)	10.7937(7)	19.351(5)	27.180(2)	14.094(3)
c/Å	11.0728(8)	21.0617(8)	9.385(4)	13.821(2)	19.103(5)
α/deg	90	90	98.04(2)	90	90
β/deg	99.791(1)	95.979(3)	102.946(6)	90	110.279(4)
γ/deg	90	90	95.85(2)	90	90
V/Å^3	3284.3(3)	3978.1(4)	1944(1)	6651(1)	4536(1)
Z	4	4	2	8	4
T/K	150	223	223	133	223
ρ_{calcd}/mg cm^{-3}	1.106	1.454	1.439	1.156	1.306
μ/mm^{-1}	0.189	3.06	3.12	0.250	0.882
$2\theta_{max}$/deg	55	51	55	55	55
no. of obsd rflns	26 757	23 377	15 297	48 169	22 145
no. of unique rflns	7249	6602	8128	7629	4653
R_{int}	0.086	0.063	0.065	0.156	0.076
R1 ($I > 2\sigma(I)$)	0.046	0.051	0.073	0.060	0.136
wR2 (all data)	0.103	0.106	0.089	0.149	0.355
no of params	334	431	415	686	433
GOF	1.005	1.079	1.464	1.193	1.831

Table 2. Calculated ^{31}P NMR Data ($^2J_{PP}$ (Hz), δ_P (ppm)) for I and II[a]

	$^2J_{PP}$	δ_P(P=C)	δ_P(PMe$_2$)
I-C_1	62.8	427.4	38.2
I-C_s	411.4	505.0	19.7
II-C_1	56.1	310.2	32.1
II-C_s	399.0	364.7	4.3

[a] B3LYP/6-311+G(2df,p) level.

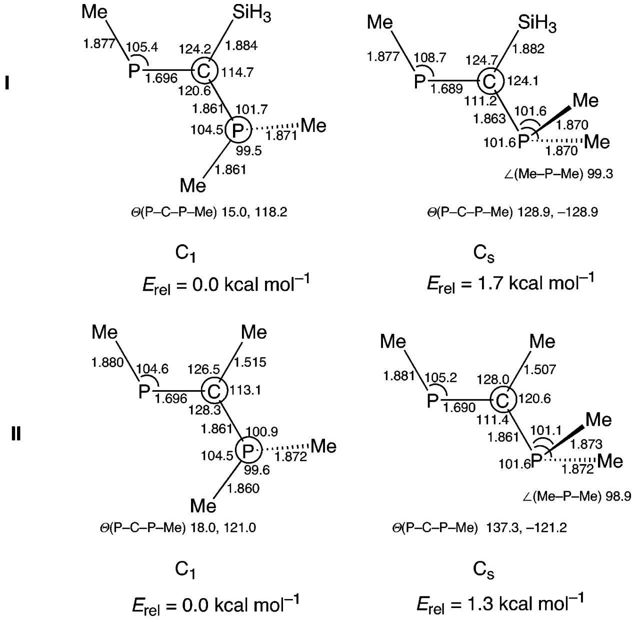

Figure 2. Calculated structures and relative energies for **I** and **II**.

Theoretical calculations for the model compounds 1,3,3-trimethyl-2-silyl-1,3-diphosphapropene (**I**) and 1,2,3,3-tetramethyl-1,3-diphosphapropene (**II**) showed that the C_1 form, which is observed in **1C**, is slightly stable than the C_s form by 1.7 kcal/mol (for **I**) or 1.3 kcal/mol (for **II**) at the B3LYP/6-31G(d) level (Figure 2).[13] Therefore, the estimated K_{eq} ($=[C_1]/[C_s]$) constants at 300 K for **I** and **II** were 17.4 and 8.9, respectively. These results are consistent with the calculations for 1,3-diphosphapropene ($HP{=}CHPH_2$)[9] and are in contrast to the results for vinylphosphine ($CH_2{=}CHPH_2$).[14] Furthermore, the calculated ^{31}P NMR data at the B3LYP/6-311+G(2df,p) level supported an exceptionally small $^2J_{PP}$ constant in the C_1 conformer, whereas the C_s isomers indicate larger $^2J_{PP}$ constants (Table 2). Therefore, the C_1 conformation of **1C** remains even in solution. Moreover, the C_1 conformation of **1C** was still maintained upon heating, while the $^2J_{PP}$ constant of 43.0 Hz was observed at 378 K in toluene. The dependence of the coupling constant between the two nonequivalent phosphorus atoms on the conformations might be comparable to the Karplus rule that the coupling constant depends on the dihedral angle between the vicinal hydrogens.[15] The calculated ^{31}P NMR chemical shifts indicated that the sp^2 phosphorus atoms in the C_1-symmetric forms afford shifts higher than those in the C_s-symmetric forms, whereas the sp^3 phosphorus atoms in the C_1 forms exhibit lower shifts (Table 2). In comparison with the C_s-symmetric form, the higher shift of the sp^2 phosphorus in the C_1-symmetric form is due to π-donation to the P=C group by the lone-pair electrons on the sp^3 phosphorus, which accordingly shows a lower shift. In the case of the C_s-symmetric form, the P−Me σ^* orbital interacts with the P=C π orbital, which demonstrates the lower shift of the sp^2 phosphorus and the higher shift of the sp^3 phosphorus, respectively.

Although 1,3-diphosphapropenes **1A** and **1B** showed the C_s conformation in the crystalline state,[6c,8] the theoretical investigation concluded that the C_1 form would be the predominant conformation of the 1,3-diphosphapropene skeleton. In the case

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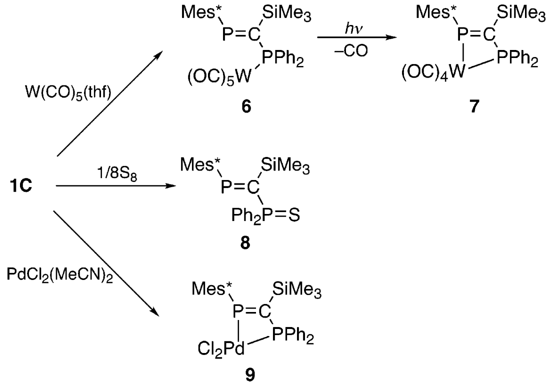
Scheme 2



of vinylphosphine ($H_2C{=}CHPH_2$), the stable conformation has been determined as the C_s conformation by theoretical and experimental studies,[14] suggesting hyperconjugation between the C=C π orbital and the P−H σ^* orbital. On the other hand, the P=C bond in 1,3-diphosphapropene has a considerably low lying LUMO[1,4,5] and the lone pair of the phosphino group might interact with the π orbital of the P=C bond. Furthermore, in the case of **1C**, the silyl group functions as a π-electron accepting group to enhance the stability of the C_1 conformation of the 1,3-diphosphapropene system, which might cause elongation of the Si−C(1) distance, as observed in the molecular structure (vide supra). On the other hand, in the cases of 1,3-diphosphapropenes **1A** and **1B**,[6c,8] steric hindrance might be effective in raising the stability of the C_s conformation.

Even if the ^{31}P NMR data correspond to the conformation of the 1,3-diphosphapropenes, the thermodynamic predominance of the C_1 form over the C_s form is small, suggesting that interchange between the C_1 and C_s forms might occur easily. Furthermore, the two Ph groups in **1C** were equivalently observed, indicating a rocking motion or a full rotation. We are currently investigating the molecular dynamics in more detail.

Complexation and Sulfurization of the 2-(Trimethylsilyl)-1,3-diphosphapropene 1C. 1,3-Diphosphapropene **1C** was allowed to react with W(CO)$_5$(thf) at room temperature to afford the monocoordinated complex **6** (Scheme 2). The coordination of the phosphino group was determined by observation of J_{PW} satellite peaks, which appeared only at the higher field signal in ^{31}P NMR. Similar to the case for the complex of **1A**,[6a] extremely different magnitudes of $^1J_{PC}$ constants of P=*C*P in **6** were observed in the ^{13}C NMR spectrum (one of the $^1J_{PC}$ constants is almost 0 Hz). The molecular structure was unambiguously determined by X-ray crystallography, as displayed in Figure 3. In contrast to the conformation of **1C**, the P=CP< skeleton of **6** shows a C_s symmetry, which is similar to that for the monotungsten(0) complex bearing the ligated 1,3-diphosphapropene **1A**.[6a] Indeed, the C_s P=CP< conformation of **6** might correspond to a $^2J_{PP}$ constant of 349.6 Hz. Steric congestion around the P=CP skeleton, especially due to repulsion between the trimethylsilyl group and the W(CO)$_5$ moiety, putatively causes this P=CP< conformational isomerization from C_1 (**1C**) to C_s (**6**). The P−W distance is longer than the corresponding bond of [**1A**][W(CO)$_5$] (2.540(1) Å),[6a] probably due to the steric bulkiness increasing the P−W distance.

Irradiation of the monocoordinated tungsten(0) complex **6** caused release of one of the CO ligands and afforded the corresponding chelate complex **7** as a deep red solid (Scheme 2). Upon formation of a four-membered chelate ring, the $^2J_{PP}$ constant was reduced. In ^{13}C NMR, the $^1J_{PC}$ constants of the P=C moiety are extremely small, probably indicating the effects of the silyl group. The structure of **7** was unambiguously determined by X-ray crystallography (Figure 4), revealing the four-membered chelate ring. Thus, the conformation of the P=CP< skeleton of **1C** is flexible in coordinating to the carbonyltungsten moieties. The structure of **7** is comparable to those of [**1A**][W(CO)$_4$][6a] and [**1B**][W(CO)$_4$].[6b]

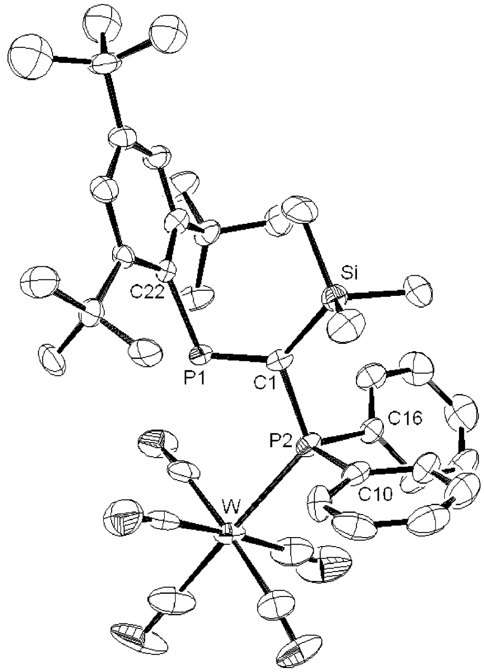


Figure 3. Thermal ellipsoid plot (50% probability surface) of the molecular structure of **6**. Hydrogen atoms are omitted for clarity. The *p-tert*-butyl group is disordered, and the atoms with predominant occupancy factors (0.54) are displayed. Selected bond distances (Å) and angles (deg): W−P(2) = 2.598(2), P(1)−C(1) = 1.688(8), P(1)−C(22) = 1.856(7), P(2)−C(1) = 1.854(7), P(2)−C(10) = 1.850(9), P(2)−C(16) = 1.835(8), Si−C(1) = 1.922(8); C(1)−P(1)−C(22) = 111.6(4), C(1)−P(2)−C(10) = 104.0(4), C(1)−P(2)−C(16) = 104.3(3), C(10)−P(2)−C(16) = 102.4(2), P(1)−C(1)−P(2) = 107.3(4), P(1)−C(1)−Si = 131.2(2), P(2)−C(1)−Si = 121.2(4), θ[P(1)−C(1)−P(2)−C(10)] = −136.2(4), θ[P(1)−C(1)−P(2)−C(16)] = 115.0(4), θ[W−P(2)−C(1)−P(1)] = −9.3(5).

Sulfurization showed other properties of 2-(trimethylsilyl)-1,3-diphosphapropene **1C** (Scheme 2). Compound **1C** was allowed to react with sulfur, and the monosulfurized product **8** was obtained. The structure of **8** was confirmed by X-ray crystallography, as shown in Figure 5. The structure of **8** shows a C_1 conformation in which the sulfur atom replaces the lone pair of **1C**. Therefore, the sulfur atom might not affect the conformation of the 1,3-diphosphapropene skeleton, probably due to the smaller spherical size of sulfur compared with that of the W(CO)$_5$ moiety. The $^2J_{PP}$ constant is close to those of **2A** and **2B**,[7] indicating that rotational isomerism of 3-thioxo-1,3-diphosphapropene had almost no effect on the $^2J_{PP}$ constant in ^{31}P NMR.

Preparation and Catalytic Activity of a Palladium(II) Complex Bearing the Ligated 2-(Trimethylsilyl)-1,3-diphosphapropene 1C. One of the purposes of the preparation of **1C** was to develop novel synthetic catalysts bearing 1,3-diphosphapropene ligands, and here we demonstrate a novel dichloropalladium(II) complex with **1C** to utilize for a cross-coupling reaction. Compound **1C** was allowed to react with bis(acetonitrile)dichloropalladium(II) to afford the corresponding

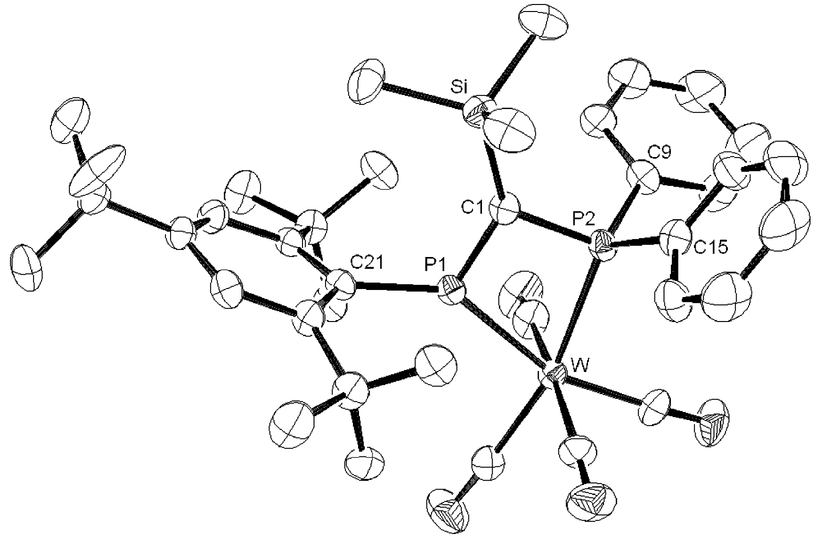


Figure 4. Thermal ellipsoid plot (50% probability surface) of the molecular structure of **7**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): W−P(1) = 2.459(2), W−P(2) = 2.533(2), P(1)−C(1) = 1.681(8), P(1)−C(21) = 1.842(8), P(2)−C(1) = 1.803(7), P(2)−C(9) = 1.838(8), P(2)−C(15) = 1.823(8), Si−C(1) = 1.907(8); P(1)−W−P(2) = 62.68(6), W−P(1)−C(1) = 103.6(3), W−P(1)−C(21) = 142.5(2), W−P(2)−C(1) = 97.3(2), W−P(2)−C(9) = 124.5(3), W−P(2)−C(15) = 114.0(3), C(1)−P(1)−C(21) = 113.8(3), C(1)−P(2)−C(9) = 105.9(4), C(1)−P(2)−C(15) = 110.1(4), C(9)−P(2)−C(15) = 104.3(4), P(1)−C(1)−P(2) = 96.3(4), P(1)−C(1)−Si = 134.1(4), P(2)−C(1)−Si = 128.5(4), θ[P(1)−C(1)−P(2)−C(9)] = −126.6(4), θ[P(1)−C(1)−P(2)−C(15)] = 121.3(4).

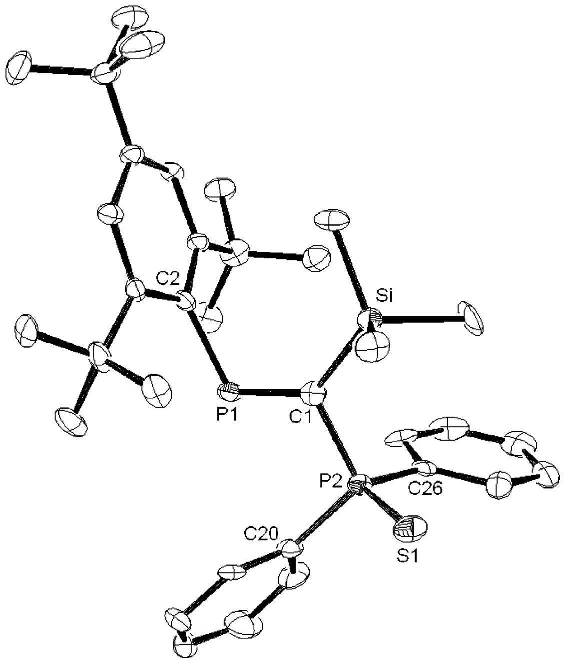
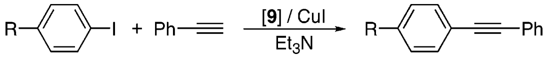


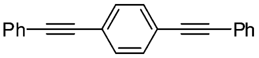
Figure 5. Thermal ellipsoid plot (50% probability surface) of the molecular structure of **8**. One of the two independent molecules is displayed. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): S(1)−P(2) = 1.959(3), P(1)−C(1) = 1.689(8), P(1)−C(2) = 1.853(7), P(2)−C(1) = 1.842(7), P(2)−C(20) = 1.828(8), P(2)−C(26) = 1.832(7), Si(1)−C(1) = 1.906(7); C(1)−P(1)−C(2) = 108.5(3), S(1)−P(2)−C(1) = 113.8(2), S(1)−P(2)−C(20) = 110.1(3), S(1)−P(2)−C(26) = 112.8(3), C(1)−P(2)−C(20) = 107.4(3), C(1)−P(2)−C(26) = 105.6(3), C(20)−P(2)−C(26) = 106.7(3), P(1)−C(1)−P(2) = 111.1(4), P(1)−C(1)−Si(1) = 133.8(4), θ[P(1)−C(1)−P(2)−S(1)] = −136.6(3), θ[P(1)−C(1)−P(2)−C(20)] = −14.4(5), θ[P(1)−C(1)−P(2)−C(26)] = 99.1(4).

Table 3. The Sonogashira Reaction Catalyzed by Dichloropalladium(II) Complex 9



entry	R	yield/%
1	H	96
2	Br	85
3	Me	60
4	OMe	57[a]
5[b]	I	65[c,d]

[a] Diphenylbutadiyne was obtained in 5% yield. [b] Two molar equivalents of phenylacetylene was used. [c] Product:



[d] *p*-$IC_6H_4C\equiv CPh$ was also obtained in 15% yield.

dichloropalladium(II) complex **9** in 95% yield (Scheme 2). When the spectroscopic data are taken into account, the structure of **9** corresponds to a dichloropalladium(II) complex bearing the ligated **1B**.[6b] In the presence of **9**, the Sonogashira cross-coupling reaction of aryl iodides with phenylacetylene afforded the corresponding acetylene derivatives (Table 3). Iodobenzene gave the cross-coupling product almost quantitatively (entry 1), and the cross-coupling with *p*-bromoiodobenzene indicated the predominant reactivity toward iodide over bromide, affording 4-bromodiphenylacetylene (entry 2). On the other hand, electron-donating substituents at the para position of aryl iodides showed relatively low reactivity (entries 3 and 4). In the reaction with *p*-iodoanisole, diphenybutadiyne was obtained as a side product (see the footnote for Table 3). *p*-Diiodobenzene and 2 molar equiv of phenylacetylene gave 1,4-bis(phenylethynyl)benzene in moderate yield together with a mono cross-coupling product, 4-iododiphenylacetylene (entry 5). As shown in Table 3, the air-stable **9** displayed considerable catalytic activity in the Sonogashira cross-coupling reaction, although some limitations were also recognized.

The molecular structure of **9** was unambiguously determined by X-ray crystallography, as shown in Figure 6. Although the quality of the data for **9**·2CH_2Cl_2 is insufficient to discuss the metric parameters in detail, the four-membered-ring structure with the P═CP skeleton is obvious. The P(1)−Pd distance is shorter than the P(2)−Pd bond, which is comparable to the case for **7**. The acute P−Pd−P angle of **9**, which is close to the corresponding value for $[Ph_2PCH_2PPh_2][PdCl_2]$ (72.68(3)°),[16]

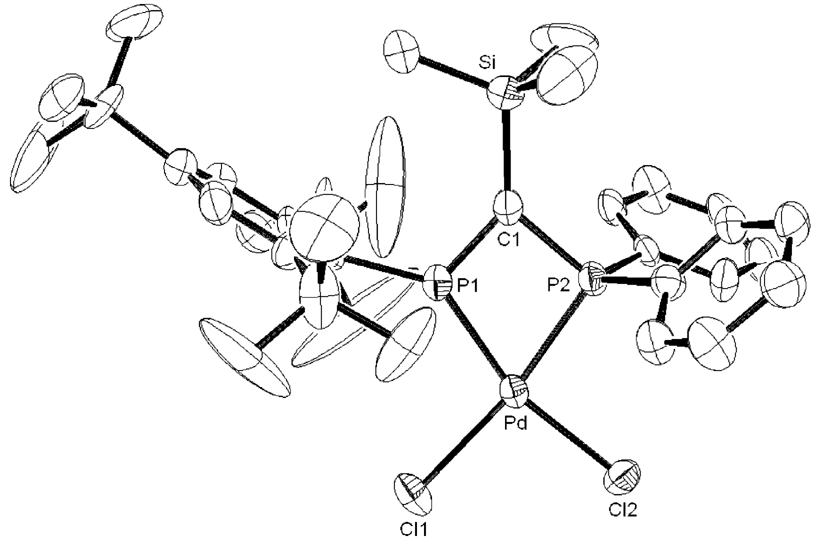


Figure 6. Thermal ellipsoid plot (30% probability surface) of the molecular structure of **9**$\cdot$2CH$_2$Cl$_2$. Hydrogen atoms and the solvent molecules (CH$_2$Cl$_2$) are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd−Cl(1) = 2.358(4), Pd−Cl(2) = 2.339(4), Pd−P(1) = 2.207(4), Pd−P(2) = 2.255(4), P(1)−C(1) = 1.68(1), P(1)−C(2) = 1.82(1), P(2)−C(1) = 1.83(1), Si−C(1) = 1.89(2); Cl(1)−Pd−Cl(2) = 95.7(2), Cl(1)−Pd−P(1) = 100.4(1), Cl(1)−Pd−P(2) = 168.9(1), Cl(2)−Pd−P(1) = 163.9(1), Cl(2)−Pd−P(2) = 94.7(1), P(1)−Pd−P(2) = 69.3(1), C(1)−P(1)−C(2) = 117.4(6), P(1)−C(1)−P(2) = 92.3(7), P(1)−C(1)−Si = 134.8(8), P(2)−C(1)−Si = 132.2(8), θ[Pd−P(1)−C(1)−P(2)] = −0.7(7).

might determine the catalytic activity together with the presence of the P═C double bond.[4,5]

Conclusion

We have demonstrated that the 2-(trimethylsilyl)-1,3-diphosphapropene **1C**, prepared from the corresponding (phosphaethenyl)lithium **5**, shows a conformation around the phosphino group with C_1 symmetry, in contrast to the C_s symmetry displayed by 1,3-diphosphapropenes **1A** and **1B**. Theoretical calculations suggested that the C_1 conformation of the P═CP< system is predominant, and the C_s conformation of 1,3-diphosphapropenes **1A** and **1B** might be affected by the steric effects of the substituents. These results suggest that the conformation of 1,3-diphosphapropene depends on the substituent at the 2-position. The C_1 conformation of **1C** was transformed into the C_s conformation upon coordination of the carbonyltungsten(0) moiety, as shown in the structures of **6** and **7**, whereas heating as well as sulfurization, affording **8**, had almost no influence on the conformation of **1C**. The structure of the palladium(II) complex **9** was analyzed by X-ray crystallography, and some catalytic activity of **9** for the Sonogashira reaction was confirmed. Investigations concerning the molecular dynamics of the 1,3-diphosphapropenes and the catalytic activity of metal complexes to understand the novel effects of the silyl group are in progress.

Experimental Section

General Methods. All manipulations were carried out under an argon atmosphere by means of the standard Schlenk techniques or in a glovebox. All solvents employed were dried by appropriate methods. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance 400 spectrometer in CDCl$_3$ with Me$_4$Si (^{1}H, ^{13}C) and H$_3$PO$_4$ (^{31}P), respectively, as internal or external standard. IR spectra were measured on a Horiba FT-300 spectrometer as KBr pellets. Mass spectra were recorded on a Bruker APEX3 spectrometer. Elemental analyses were performed in the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. Compound **4** was prepared by the procedures described in the literature.[10c,11]

Preparation of 1C. To a solution of **4** (1.00 g, 2.27 mmol) in THF (20 mL) was added butyllithium (2.3 mmol, 1.6 M solution in hexane, 1 M = 1 mol dm^{-3}) at −78 °C. After 10 min, to the reaction mixture containing **5** was added chlorodiphenylphosphine (2.3 mmol), and this mixture was warmed to room temperature. After 2 h, the volatiles were removed and the residual materials were purified by silica gel column chromatography (hexane/AcOEt = 19:1) to afford **1C** as pale yellow crystals (0.88 g, 71%). Mp: 124−125 °C. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 382.7 (d, $^2J_{\mathrm{PP}}$ = 37.1 Hz), −1.6 (d, $^2J_{\mathrm{PP}}$ = 37.1 Hz). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.87−7.85 (m, 4H, arom), 7.58−7.51 (m, 8H, arom), 1.70 (s, 18H, *o-t*-Bu), 1.51 (s, 9H, *p-t*-Bu), 0.53 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 184.0 (dd, $^1J_{\mathrm{P=C}}$ = 88.1 Hz, $^1J_{\mathrm{P-C}}$ = 62.0 Hz, P═C), 153.7 (s, *o*-C of Mes*), 151.0 (s, *p*-C of Mes*), 142.8 (dd, $^1J_{\mathrm{PC}}$ = 79.4 Hz, $^3J_{\mathrm{PC}}$ = 6.4 Hz, *ipso*-C of Mes*), 133.8 (pt, ($^1J_{\mathrm{PC}}$+$^3J_{\mathrm{PC}}$)/2 = 15.0 Hz, *ipso*-Ph), 135.1 (d, $^2J_{\mathrm{PC}}$ = 20.4 Hz, *o*-Ph), 129.1 (s, *p*-Ph), 128.6 (d, $^3J_{\mathrm{PC}}$ = 7.1 Hz, *m*-Ph), 122.4 (s, *m*-C of Mes*), 38.8 (s, *o*-*C*Me$_3$), 35.5 (s, *p*-*C*Me$_3$), 34.1 (d, $^4J_{\mathrm{PC}}$ = 7.3 Hz, *o*-C*Me*$_3$), 32.0 (s, *p*-C*Me*$_3$), 0.4 (d, $^3J_{\mathrm{PC}}$ = 8.2 Hz, SiMe$_3$). Anal. Calcd for C$_{34}$H$_{48}$P$_2$Si: C, 74.69; H, 8.85. Found: C, 73.94; H, 8.86. ESI-MS: calcd for M$^+$ (C$_{34}$H$_{48}$P$_2$Si + H) 547.3073, found 547.3074.

Preparation of 6. To a solution of **1C** (350 mg, 0.641 mmol) in THF (10 mL) was added W(CO)$_5$(thf) (ca. 1.00 mmol, prepared from W(CO)$_6$ by irradiation for 12 h with a medium-pressure 100 W Hg lamp at 0 °C in THF), and the mixture was stirred at room temperature for 12 h. The volatiles were removed, and the residual materials were purified by silica gel column chromatography (10/1 hexane/chloroform) and recrystallization from hexane to afford **6** as yellow crystals (167 mg, 30%). Mp: 240−242 °C dec. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 437.3 (d, $^2J_{\mathrm{PP}}$ = 349.6 Hz), −29.3 (d, $^2J_{\mathrm{PP}}$ = 349.6 Hz, satellite $^1J_{\mathrm{PW}}$ = 245.4 Hz). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.78−7.76 (m, 4H, arom), 7.48−7.46 (m, 6H, arom), 7.39 (s, 2H, arom), 1.61 (s, 18H, *o-t*-Bu), 1.35 (s, 9H, *p-t*-Bu), −0.81 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 201.6 (d, $^2J_{\mathrm{PC}}$ = 21.3 Hz, CO$_{\mathrm{ax}}$), 198.9 (dd, $^2J_{\mathrm{PC}}$ = 9.8 Hz, $^4J_{\mathrm{PC}}$ = 6.4 Hz CO$_{\mathrm{eq}}$), 175.0 (d, $^1J_{\mathrm{P=C}}$ = 76.5 Hz, P═C), 154.5 (s, *o*-C of Mes*), 151.8 (s, *p*-C of Mes*), 139.7 (dd, $^1J_{\mathrm{PC}}$ = 79.6 Hz, $^3J_{\mathrm{PC}}$ = 44.7 Hz, *ipso*-C of Mes*), 138.3 (dd, $^1J_{\mathrm{PC}}$ = 35.6 Hz, $^3J_{\mathrm{PC}}$ = 13.7

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(16) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.

Hz, *ipso*-Ph), 132.5 (d, $^{2}J_{\mathrm{PC}} = 11.3$ Hz, *o*-Ph), 130.0 (d, $^{4}J_{\mathrm{PC}} = 1.3$ Hz, *p*-Ph), 128.6 (d, $^{3}J_{\mathrm{PC}} = 9.2$ Hz, *m*-Ph), 122.5 (d, $^{3}J_{\mathrm{PC}} = 1.2$ Hz, *m*-C of Mes*), 38.9 (s, *o*-*C*Me$_3$), 35.3 (s, *p*-*C*Me$_3$), 34.8 (d, $^{4}J_{\mathrm{PC}} = 7.2$ Hz, *o*-C*Me*$_3$), 31.6 (s, *p*-C*Me*$_3$), 2.5 (s, SiMe$_3$). IR (KBr): ν(CO) 2065, 1981, 1932, 1907 cm^{-1}. Anal. Calcd for $C_{39}H_{48}O_5P_2SiW$: C, 53.80; H, 5.56. Found: C, 53.98; H, 5.58.

Preparation of 7. A solution of **6** (110 mg, 0.126 mmol) in THF (5 mL) was irradiated with a medium-pressure 100 W Hg lamp at 0 °C for 12 h. The volatiles were removed, and the residual materials were purified by silica gel column chromatography (10/1 hexane/AcOEt) to afford **7** as red crystals (62 mg, 58%). Mp: 240−242 °C dec. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 320.0 (d, $^{2}J_{\mathrm{PP}} = 57.2$ Hz, satellite $^{1}J_{\mathrm{PW}} = 211.0$ Hz), −8.4 (d, $^{2}J_{\mathrm{PP}} = 57.2$ Hz, satellite $^{1}J_{\mathrm{PW}} = 186.3$ Hz). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.67−7.62 (m, 4H, arom), 7.47−7.45 (m, 6H, arom), 7.43 (d, $^{4}J_{\mathrm{PH}} = 1.2$ Hz, 2H, arom), 1.78 (s, 18H, *o*-*t*-Bu), 1.34 (s, 9H, *p*-*t*-Bu), −0.60 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 212.7 (dd, $^{2}J_{\mathrm{PC}} = 32.5$ Hz, $^{2}J_{\mathrm{PC}} = 8.2$ Hz, CO$_{\mathrm{eq}}$), 210.8 (dd, $^{2}J_{\mathrm{PC}} = 21.8$ Hz, $^{2}J_{\mathrm{PC}} = 9.3$ Hz, CO$_{\mathrm{eq}}$), 206.4 (dd, $^{2}J_{\mathrm{PC}} = 9.8$ Hz, $^{2}J_{\mathrm{PC}} = 6.4$ Hz CO$_{\mathrm{ax}}$), 191.0 (d, $^{1}J_{\mathrm{P=C}} = 3.2$ Hz, P=C), 155.8 (s, *o*-C of Mes*), 153.6 (s, *p*-C of Mes*), 134.8 (dd, $^{1}J_{\mathrm{PC}} = 34.1$ Hz, $^{3}J_{\mathrm{PC}} = 18.5$ Hz, *ipso*-Ph), 132.5 (d, $^{2}J_{\mathrm{PC}} = 13.1$ Hz, *o*-Ph), 130.6 (d, $^{4}J_{\mathrm{PC}} = 1.7$ Hz, *p*-Ph), 128.9 (d, $^{3}J_{\mathrm{PC}} = 10.1$ Hz, *m*-Ph), 122.8 (d, $^{3}J_{\mathrm{PC}} = 4.3$ Hz, *m*-C of Mes*), 39.4 (s, *o*-*C*Me$_3$), 35.6 (s, *p*-*C*Me$_3$), 35.1 (s, *o*-C*Me*$_3$), 31.5 (s, *p*-C*Me*$_3$), 0.9 (s, SiMe$_3$) (*ipso*-C of Mes* could not be determined). IR (KBr): ν(CO) 2015, 1915, 1905, 1888 cm^{-1}. Anal. Calcd for $C_{38}H_{48}O_4P_2SiW$: C, 54.16; H, 5.74. Found: C, 54.04; H, 5.71.

Preparation of 8. A solution of **1C** (0.50 g, 0.99 mol) and sulfur (0.99 mmol as S) in toluene (10 mL) was refluxed for 2 h. After the mixture was cooled to room temperature, the volatiles were removed and the residual materials were purified by silica gel column chromatography (19/1 hexane/AcOEt) to afford **8** as pale yellow crystals (0.52 g, 91%). Mp: 97−98 °C. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 409.6 (d, $^{2}J_{\mathrm{PP}} = 140.5$ Hz), 50.7 (d, $^{2}J_{\mathrm{PP}} = 140.5$ Hz). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06−8.01 (m, 4H, arom), 7.50−7.48 (m, 6H, arom), 7.40 (s, 2H, arom), 1.52 (s, 18H, *o*-*t*-Bu), 1.36 (s, 9H, *p*-*t*-Bu), 0.23 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 176.7 (dd, $^{1}J_{\mathrm{P=C}} = 85.3$ Hz, $^{1}J_{\mathrm{P-C}} = 26.0$ Hz, P=C), 153.9 (s, *o*-C of Mes*), 151.8 (s, *p*-C of Mes*), 138.7 (dd, $^{1}J_{\mathrm{PC}} = 77.5$ Hz, $^{3}J_{\mathrm{PC}} = 29.8$ Hz, *ipso*-C of Mes*), 135.3 (dd, $^{1}J_{\mathrm{PC}} = 81.9$ Hz, $^{3}J_{\mathrm{PC}} = 6.5$ Hz, *ipso*-Ph), 133.2 (d, $^{3}J_{\mathrm{PC}} = 9.8$ Hz, *m*-Ph), 131.4 (d, $^{4}J_{\mathrm{PC}} = 2.7$ Hz, *p*-Ph), 128.4 (d, $^{3}J_{\mathrm{PC}} = 12.2$ Hz, *o*-Ph), 122.6 (s, *m*-C of Mes*), 38.9 (s, *o*-*C*Me$_3$), 35.4 (s, *p*-*C*Me$_3$), 34.5 (d, $^{4}J_{\mathrm{PC}} = 7.0$ Hz, *o*-C*Me*$_3$), 31.8 (s, *p*-C*Me*$_3$), 3.0 (s, SiMe$_3$). IR (KBr): ν(P=S) 706, 652 cm^{-1}. Anal. Calcd for $C_{34}H_{48}P_2SSi$: C, 70.55; H, 8.36; S, 5.54. Found: C, 70.40; H, 8.10; S, 5.20.

Preparation of 9. A solution of **1C** (290 mg, 0.53 mmol) and Cl$_2$Pd(MeCN)$_2$ (0.53 mmol) in dichloromethane (30 mL) was stirred for 12 h. The reaction mixture was diluted with 10 mL of hexane to give yellow precipitates of **9**. The precipitates were filtered and washed with hexane (365 mg, 95%). Mp: 216−219 °C dec. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 260.6 (d, $^{2}J_{\mathrm{PP}} = 110.0$ Hz), −27.3 (d, $^{2}J_{\mathrm{PP}} = 110.0$ Hz). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.05−7.99 (m, 4H, arom), 7.76−7.72 (m, 2H, arom), 7.65−7.60 (m, 6H, arom), 1.85 (s, 18H, *o*-*t*-Bu), 1.39 (s, 9H, *p*-*t*-Bu), −0.45 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 185.1 (d, $^{1}J_{\mathrm{P=C}} = 6.6$ Hz, P=C), 157.1 (s, *o*-C of Mes*), 157.0 (s, *p*-C of Mes*), 134.3 (d, $J_{\mathrm{PC}} = 11.7$ Hz, *o*- or *m*-Ph), 129.1 (d, $^{4}J_{\mathrm{PC}} = 2.9$ Hz, *p*-Ph), 129.7 (d, $J_{\mathrm{PC}} = 12.5$ Hz, *o*- or *m*-Ph), 126.8 (dd, $^{1}J_{\mathrm{PC}} = 55.8$ Hz, $^{3}J_{\mathrm{PC}} = 4.7$ Hz, *ipso*-Ph), 125.0 (d, $^{3}J_{\mathrm{PC}} = 7.9$ Hz, *m*-C of Mes*), 122.9 (dd, $^{1}J_{\mathrm{PC}} = 33.7$ Hz, $^{3}J_{\mathrm{PC}} = 10.3$ Hz, *ipso*-C of Mes*), 39.6 (s, *o*-*C*Me$_3$), 35.8 (s, *p*-*C*Me$_3$), 35.4 (s, *o*-C*Me*$_3$), 31.1 (s, *p*-C*Me*$_3$), −0.4 (s, SiMe$_3$). Anal. Calcd for $C_{34}H_{48}Cl_2P_2PdSi$: C, 56.40; H, 6.68. Found: C, 56.10; H, 6.93.

The Sonogashira Reaction with 9: Typical Procedure. A solution of iodobenzene (2.0 mmol), phenylacetylene (2.0 mmol), **9** (0.050 mmol), and copper(I) iodide (0.050 mmol) in triethylamine (8 mL) was stirred for 4 h at room temperature. The volatiles were removed, and the residue was extracted with hexane. Silica gel column chromatography (hexane) of the hexane extracts afforded diphenylacetylene (96% yield).

X-ray Crystallography. A Rigaku RAXIS-IV imaging-plate detector with graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å) was used. The structure was solved by direct methods (SIR92)[17] and expanded using Fourier techniques (DIRDIF94).[18] A symmetry-related absorption correction using the program ABSCOR[19] was applied for **7** and **9**·2CH$_2$Cl$_2$. Attempts to solve the structure of **6** from the diffraction data, including the absorption correction, failed. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms (calculated) were refined isotropically. The data were corrected for Lorentz−polarization effects. Structure solution, refinement, and graphical representation were carried out using the teXsan package.[20] The X-ray crystallographic data for **1C** (CCDC-288846), **6** (CCDC-288848), **7** (CCDC-2888499), **8** (CCDC-288850), and **9** (CCDC-288847) can be obtained via www.ccdc.cam.ac.uk/data request/cif.

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Supporting Information Available: X-ray crystallographic data (as CIF files) for **1C** and **6**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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