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Preparation and Properties of Perarylated 3,4-Disila-1,5-hexadienes. A Fluorescent Disilane Accommodated in the Crystal Lattice

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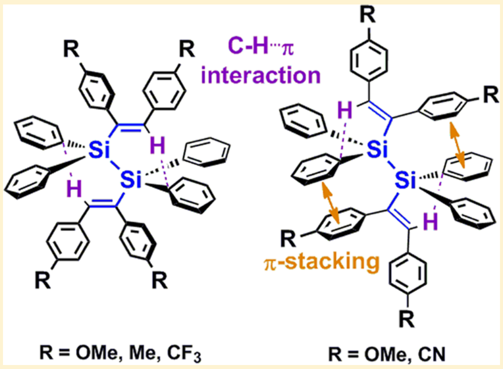
Supporting Information

ABSTRACT: A dinickel complex with bridging silyl ligands, $[\{Ni(PCy_3)\}_2(\mu\text{-}SiHPh_2)_2]$ (**1**), prepared from $[Ni(cod)_2]$, PCy_3, and H_2SiPh_2, underwent exchange of the PCy_3 ligands with 1,2-bis(dimethylphosphino)ethane (dmpe) to yield a complex coordinated by the two bidentate ligands, $[\{Ni(dmpe)\}_2(\mu\text{-}SiHPh_2)_2]$. Reactions of diarylacetylenes, ArC≡CAr (Ar = C_6H_5, C_6H_4OMe-4, C_6H_4Me-4, C_6H_4F-4, $C_6H_4CF_3$-4, C_6H_4CN-4), with **1** in a 4/1 ratio afforded 1,2-bis{(*E*)-1,2-diarylethenyl}-1,1,2,2-tetraphenyldisilanes via addition of the Si−H bond of the bridging silyl ligand to the alkynes and subsequent coupling of the resulted tertiary silyl ligand. X-ray crystallography of the dialkenyldisilanes resulted in three kinds of conformation of the C═C−Si−Si−C═C chain depending on the aryl group at the vinyl carbon. The disilane with phenyl substituents, **4a** (Ar = C_6H_5), contained a planar C═C−Si−Si−C═C alignment with small Si−Si−C═C torsion angles (1.7(5) and 6.9(5)°). The other dialkenyldisilanes, **4b,c,e,f**, had much larger torsion angles (30.9(3)−49.2(3)°), and the twisted conformation of the molecules was classified into two types. Compound **4a** exhibited a fluorescence maximum at 488 nm in the solid state, while **4b−f** showed peaks at 393−427 nm. The red shift in the emission of **4a** is ascribed to orthogonal intramolecular charge transfer (OICT) from the electron-donating Si−Si to accepting C═C bonds.



INTRODUCTION

Cyclic π-conjugated compounds having an Si atom in the ring system, such as silacyclopentadienes (siloles),[1] 9-silafluorenes,[2] and dithienosiloles,[3] have been investigated as the materials for organic light-emitting devices. The siloles have small HOMO−LUMO gaps suited for emissive organic materials, but their molecular aggregation in solution often causes concentration quenching. In the solid state, perarylated siloles exhibit high luminescent properties owing to restricted rotation of the aromatic rings.[4] The luminescent properties of the siloles were attributed to their low LUMO level caused by conjugation of σ*(Si) and π*(diene) orbitals.[1c,d] 1,2-Disilacyclohexadienes with a six-membered ring composed of two C═C bonds and an Si−Si bond were reported to possess nonplanar ring structures.[3b,5] Marder et al. compared the electronic state and luminescent behavior of the siloles and 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disila-3,5-cyclohexadiene.[6] Acyclic disilanes with π-conjugated substituents also show unique luminescent properties based on the intramolecular charge-transfer mechanism between the Si−Si σ bonds and π orbitals of C≡C bonds[7] or aromatic rings.[8−10] Similar intramolecular charge transfer from the disilanylene unit was also proposed for disilanylene-bridged silafluorene with a rigid planar structure, which emitted at a longer wavelength in the solid state.[11] Recently, we found a new method to prepare a dialkenyldisilane from alkyne and dinickel complexes with bridging silyl ligands and their emission in the solid state.[12] This paper presents the preparation of the related disilanes and details of the structures and properties in the solid state.

RESULTS AND DISCUSSION

The reaction of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene), H_2SiPh_2, and PCy_3 in a 1/1/1 ratio at room temperature produced a dinickel(I) complex with bridging diphenylsilyl ligands, $[\{Ni(PCy_3)\}_2(\mu\text{-}SiHPh_2)_2]$ (**1**), as an orange powder in 97% yield (Scheme 1). Complex **1** reacted with bidentate phosphines to undergo ligand exchange of the PCy_3 to yield $[(NiL)_2(\mu\text{-}SiHPh_2)_2]$ (**2**, L = 1,2-bis(dimethylphosphino)ethane (dmpe), **3**, L = 1,2-bis(diethylphosphino)ethane (depe)), in 90 and 42% yields, respectively. The direct preparation of **2** was achieved in 40% yield by starting from $[Ni(cod)_2]$, H_2SiPh_2, and dmpe. Complex **1** is extremely air-sensitive, while **2** and **3** with 18-electron Ni centers are stable toward air in the solid state.

Exchange of PCy_3 ligands of **1** with dmpe caused quantitative formation of **2** at room temperature, whereas addition of depe to the solution of **1** at the same temperature produced a mixture of **3** and a dinickel intermediate having PCy_3 and depe ligands, $[\{Ni(PCy_3)\}(\mu\text{-}SiHPh_2)_2\{Ni(depe)\}]$. The unsymmetrical complex in the reaction mixture exhibits two $^{31}P\{^1H\}$ NMR peaks: a pair of doublets at δ 32.6 and triplet

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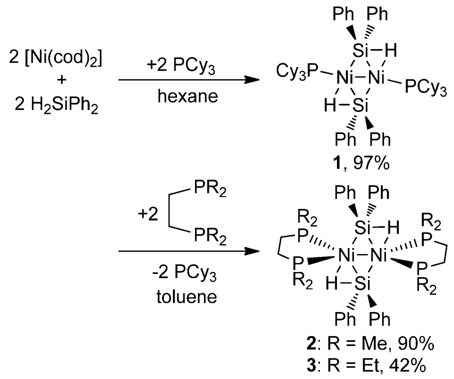
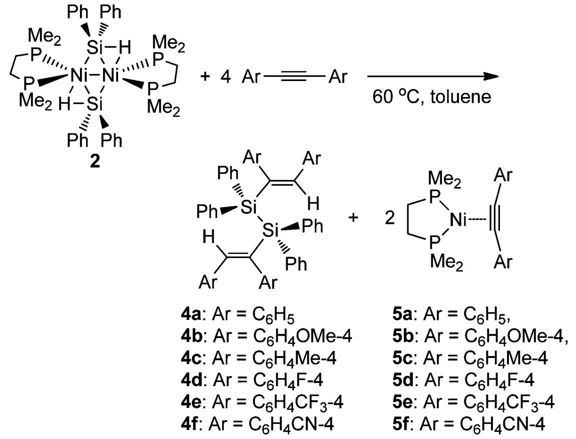
Scheme 1





(1)

signals at δ 44.4 with a $^3J_{P-P}$ value of 27 Hz. Heating of the reaction mixture for 3 h at 60 °C converted the intermediate to product **3**. Many dipalladium(I) and diplatinum(I) complexes with two bridging $SiHR_2$ ligands and two or three phosphine ligands have been reported,[13−15] while the dinuclear complexes of these metals with four phosphine ligands are not known. Similar ligand exchange of $[\{Pt(PCy_3)\}_2(\mu\text{-}SiHPh_2)_2]$ with dmpe afforded a stable Pt(II) complex with a bridging silylene ligand, $[\{Pt(dmpe)\}_2(\mu\text{-}SiPh_2)_2]$.[14e,16] Thus, dinickel(I) complexes with 18 electrons and bridging silyl ligands are obtained as the first examples of such complexes containing group 10 transition metals.

The X-ray crystallographic results of **1** and **2** have already been reported in a preliminary communication.[12] Dinuclear Ni complexes **1**−**3** were characterized by NMR spectroscopy in solution. The ^1H NMR signals of the bridging Si−H groups of **1**−**3** appear at δ −2.04, −4.02, and −6.04, which are at higher magnetic field than the corresponding peaks of the dipalladium and diplatinum analogues $[\{M(PCy_3)\}_2(\mu\text{-}SiHPh_2)_2]$ (M = Pd, δ 2.07; M = Pt, δ 2.47).[15a] The ^1H NMR peaks of the Ni−H−Si 3c-2e bond at high magnetic field positions were reported for the mononuclear Ni complexes $[(dtbpe)Ni(\mu\text{-}H)SiMePh_2]$ (δ −6.49)[17a] and $[(dtbpe)Ni(\mu\text{-}H)SiMes_2][B(C_6H_3(CF_3)_2\text{-}3,5)_4]$ (δ −8.64)[17b] (dtbpe = $P^tBu_2(CH_2)_2P^tBu_2$). Complexes **1** and **2** exhibit single $^{29}Si\{^1H\}$ NMR signals at δ 121.8 (J_{P-Si} = 25 Hz) and 113.6 (J_{P-Si} = 20 Hz), respectively. The $^{13}C\{^1H\}$ NMR spectrum of **2** displays two CH_3 carbon signals of the dmpe ligands at δ 20.0 and 17.0, indicating the presence of inequivalent CH_3 groups on different sides of the NiPP plane. Complex **3**, on the other hand, shows single ^{13}C NMR signals of CH_2 and CH_3 carbons at δ 21.7 and 8.45, respectively, probably because of fluxional behavior of the depe ligand such as those involving its partial dissociation.

The dinickel complex **1** reacted with ArC≡CAr (Ar = C_6H_5, C_6H_4OMe-4, C_6H_4Me-4, C_6H_4F-4, $C_6H_4CF_3$-4, C_6H_4CN-4) in a 1/4 molar ratio at 60 °C to produce 1,2-bis{(*E*)-1,2-diarylethenyl}-1,1,2,2-tetraphenyldisilane (**4a**−**f**) in 10−45% isolated yields, together with alkyne-coordinated Ni complexes $[Ni(\eta^2\text{-}ArC{\equiv}CAr)(dmpe)]$[18] (**5a**−**f**) in 70−96% NMR yields, as shown in eq 1. The isolated yields, melting points, and selected NMR data of **4a**−**f** are summarized in Table 1. Compound **4f** was obtained in an extremely low yield due to loss during purification. The NMR spectroscopic data of the reaction mixtures indicated no formation of the geometrical isomers of **4a**−**f**. The addition of an excess amount of PhC≡CPh to the solution of **2** did not change the reaction products. Although Ni complexes with PCy_3 ligands such as **1** catalyzed the cyclotrimerization of PhC≡CPh at 60 °C to give hexaphenylbenzene in 96% yield,[19] the above reactions do not form hexaarylbenzene derivatives at all. Heating of H_2SiPh_2 and PhC≡CPh in the presence of a catalytic amount of **2** at 60 °C formed a hydrosilylation product as a mixture of two stereoisomers, (*E*)- and (*Z*)-1-diphenylsilyl-1,2-diphenylethene, in 43% yields (*E*/*Z* = 49/51). Heating of the isolated *E* compound[20,21] in the presence of **2** or $[Ni(dmpe)_2]$ at 60 °C for 35 h did not afford any disilanes, due to the low reactivity of the tertiary Si−H bond. These results suggested that formation of **4a**−**f** in eq 1 involved addition of the Si−H bonds of the bridging silyl ligands to the C≡C bond and successive intramolecular Si−Si coupling of the formed silyl ligands. Similar Si−Si bond-forming reactions of the bridging silylene and silyl ligands in the dinuclear nickel(III) complexes were proposed.[22]

Figure 1a−e summarizes the molecular structures of **4a**−**c**,**e**,**f**, which were determined by X-ray crystallography, and selected bond distances and angles of **4a**−**c**,**e**,**f** are given in Table 2.

Table 1. Yields, Melting Points, and Selected NMR Spectroscopic Data of 4a−f

			^1H NMR[b]	$^{13}C\{^1H\}$ NMR[c]		$^{29}Si\{^1H\}$ NMR[d]
compd	yield[a]/%	mp/°C	=C*H*	=CH	=CSi	
4a[e]	24	171−173	7.17[f]	145.2	142.0	−20.3
4b	34	240−242	7.06	144.7	138.7	−19.0
4c	28	245−247	7.08	144.5	140.8	−20.0
4d	42	234−236	7.08	144.3	140.8	−20.9
4e	45	278−280	7.18	144.2	140.9	−20.5
4f	10	281−283	7.11	144.2	141.4	−18.8

[a] Isolated yields before recrystallization. [b] In ppm, 400 MHz in THF-d_8. [c] In ppm, 101 MHz in THF-d_8. [d] In ppm, 79 or 99 MHz in THF-d_8. [e] Taken from ref 12. [f] The =C*H* hydrogen signal is overlapped with the SiC_6H_5 signals.

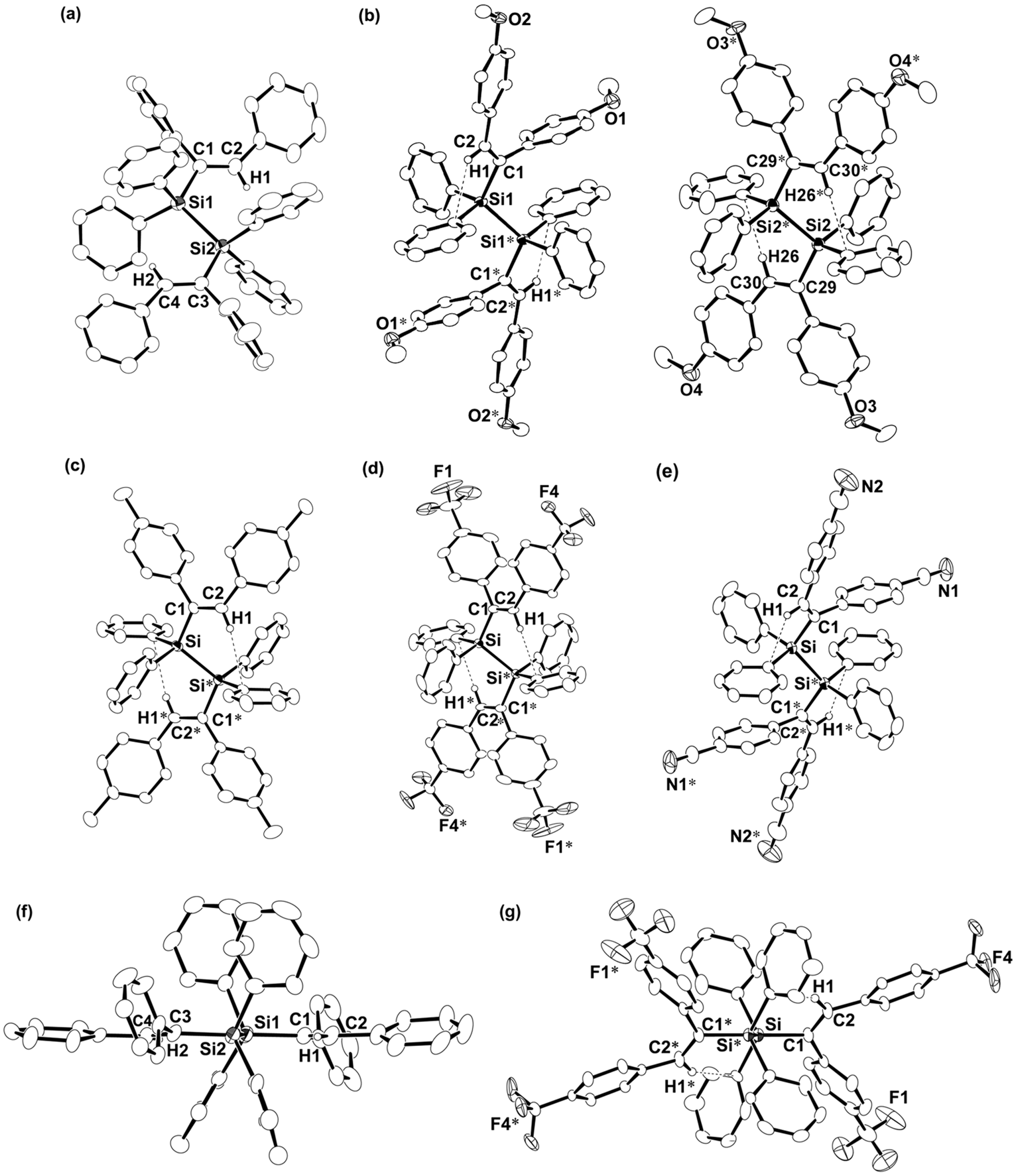


Figure 1. Thermal ellipsoid diagrams of (a) **4a** (probability 30%) taken from ref 12, (b) **4b** (50%), (c) **4c** (50%), (d) **4e** (50%), (e) **4f** (50%), (f) the Si−Si plane of **4a** (torsion angles 1.7(5) and 6.9(5)°), and (g) the Si−Si plane of **4e** (torsion angle 49.2(3)°). The dotted lines show close contacts between a =CH hydrogen and an aromatic carbon due to C−H/π interaction.

Table 2. Selected Bond Distances (Å) and Angles (deg) of 4a−c,e,f

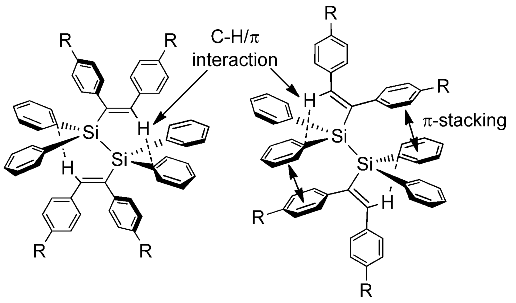
compd	Si−Si bond	Si−C bond	C=C bond	CH···Ph distance[a]	Si−Si−C= angle	Si−Si−C=C torsion angle
4a[b]	2.402(3)	1.903(6)	1.336(8)		109.2(3)	1.7(5)
		1.910(6)	1.365(8)		110.1(2)	6.9(5)
4b[c,d]	2.375(1)	1.903(4)	1.353(5)	2.670	112.0(1)	36.8(2)
	2.369(2)	1.888(5)	1.361(7)	2.635	108.5(1)	47.8(3)
4c[d]	2.374(2)	1.895(3)	1.352(3)	2.709	109.76(8)	30.9(3)
4e[c,d]	2.362(2)	1.903(4)	1.345(7)	2.642	108.2(2)	48.0(4)
	2.365(2)	1.888(4)	1.353(5)	2.659	108.7(1)	49.2(3)
4f[d]	2.395(1)	1.899(3)	1.351(5)	2.640	111.53(9)	34.8(2)

[a] Distances between the vinyl hydrogens and the ipso carbon atoms of the Ph ring. [b] Taken from ref 12. [c] There are two independent molecules in the unit cell. [d] The molecules have a crystallographic symmetry center at the midpoint between Si and Si*.

Compound **4a** has remarkably small Si−Si−C=C torsion angles (1.7(5) and 6.9(5)°), and its C=C−Si−Si−C=C chain is included in the same plane (Figure 1a,f). On the other hand, the Si−Si and C=C bonds of **4b**,**c**,**e**,**f** are twisted with larger torsion angles (30.9(3)−49.2(3)°), as shown in Figure 1g. The crystal structures of diaryldisilanes prefer a perpendicular conformation of the Si−Si bond to the attached aromatic rings, which favors overlap of the Si−Si σ orbitals and C=C π orbitals (σ−π conjugation).[23] The Si−Si bond distance of **4a** (2.402(3) Å) is longer than those of **4b**,**c**,**e**,**f** (2.362(2)−2.395(1) Å) regardless of the electronic effects of the substituents and is longer than normal Si−Si bond distances (2.33−2.37 Å).[24] The elongated Si−Si bond distance and small Si−Si−C=C dihedral angle of **4a** induce facile intramolecular charge transfer from the Si−Si to the C=C bonds. Such a conformation leads to the significant bathochromic shift of **4a**.

The molecular conformations of **4b**,**c**,**e**,**f** in the crystalline state are classified into two types, as illustrated in Chart 1. Compounds **4c**,**e** are included in type **A**, while **4f** has a conformation of type **B**. Crystals of **4b** contain both structures as the crystallographically independent molecules in the unit cell (Figure 1b). Molecules of type **A** have a C−H/π interaction between the vinylic C−H groups and the aryl group attached to the different Si atom.[25] The conformation of type **B** has a C−H/π interaction between the vinylic C−H bond and the aryl group attached to the same Si atom and an intramolecular π−π stacking interaction between one aryl group of the C=C bond and the Ph ring bonded to Si atoms.[26] Less bulky and electron-withdrawing CN substituents of the aryl groups are suggested to favor π stacking interactions between two aromatic rings.

Chart 1



type **A**

type **B**

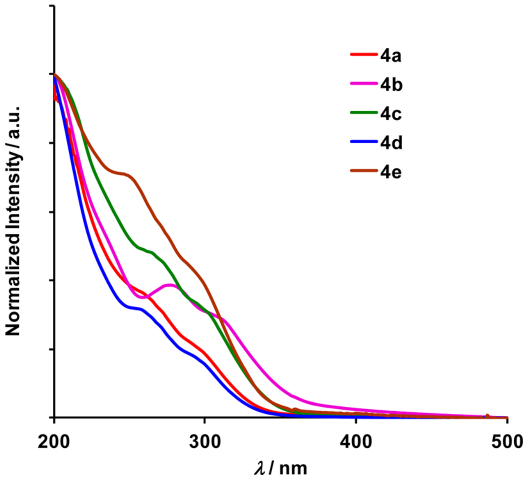


Figure 2. UV−vis absorption spectra of **4a**−**e** in the solid state.

Table 3. Photophysical Data of 4a−f in the Solid State and in Solution

compd	solid state[a] absorption (λ_{abs}/nm)	solid state[a] fluorescence[b] (λ_{em}/nm)	solution absorption (λ_{abs}/nm)	solution fluorescence[b] (λ_{em}/nm)
4a	258, 270, 294	488	257, 295	323
4b	277, 310	427	271, 309	338
4c	264, 296	417	265, 300	329
4d	257, 270, 291	404	254, 295	323
4e	249, 272, 291	393	246, 299	328
4f	257, 314	419	254, 306	332

[a] Casted film prepared from a toluene solution. [b] Excited at the longest absorption wavelengths.

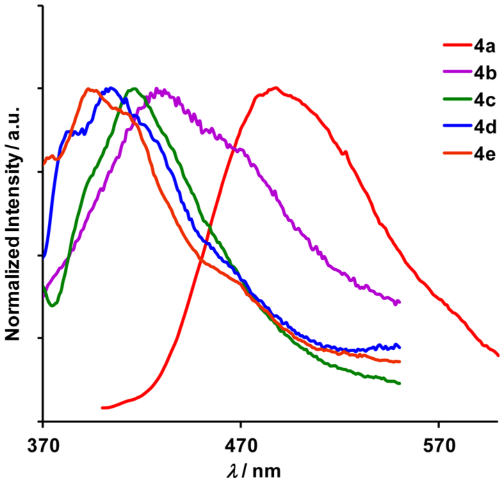


Figure 3. Fluorescence spectra of **4a**−**e** in the solid state.

Figure 2 shows the absorption spectra of **4a**−**e** in the solid state, and the photophysical properties in the solid state are summarized in Table 3. The absorption spectra of **4a**−**e** are similar in shape and exhibit two or three shoulders in the range between 249 and 310 nm, which are at significantly longer wavelengths in comparison to that of divinyldislane ($(CH_2{=}CHSiMe_2)_2$ (λ_{max} 227 nm).[27] The bathochromic shifts of **4a**−**e** are attributed to the extension of σ−π conjugation between the Si−Si bond and the aromatic rings. Solid disilanes **4a**−**e** show blue or blue-green emission upon irradiation. The emission of **4a** is observed as a widely broadening peak at a maximum (λ_{em}) of 488 nm, which is significantly red-shifted relative to those of **4b**−**e** (λ_{em} 393−427 nm), as shown in Figure 3. Emission at longer wavelength of **4a** and the conformation of the molecule in the solid state are consistent with emission via orthogonal intramolecular charge transfer (OICT) from electron-donating σ(Si−Si) bonds to electron-accepting π^*(C=C) bonds. Kira, Sakurai, and Ishikawa[9,10] reported luminescent properties of aryldisilanes and attributed them to the OICT mechanism. The molecule prefers a conformation having the Si−Si bond in a plane at the photoexcited state by rotation of the Si−C(aryl) bonds, giving low-lying charge-transfer states in comparison to the normal excited state. The conformation with a planar orientation between the Si−Si and the C=C bonds of **4a** (Si−Si−C=C torsion angles 1.7(5) and 6.9(5)°) is suited for the OICT, whereas **4b**−**e** with twisted geometries (30.9(3)−49.2(3)°) show luminescence due to σ−π conjugation. An electron-withdrawing cyano substituent at the aryl groups appears to induce the OICT.[10] The absorption spectrum of **4f** in the solid state, however, is similar in shape to those of **4a–e**, while the emission peak of **4f** (419 nm) appears within the range of 393–427 nm of **4b–e** (Figure 4). The electronic effect of the cyano group does not influence the absorption and emission peaks. Thus, the fluorescent properties of the dialkenyldisilanes **4** and their steric effect, the planarity of the C═C–Si–Si–C═C skeletons in particular, have significant relevance.

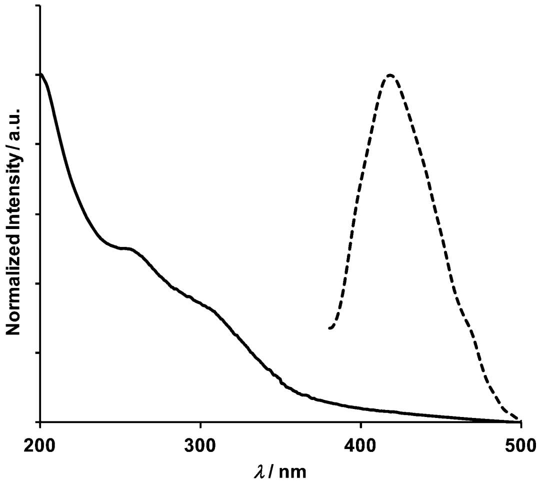


Figure 4. UV–vis absorption spectrum (solid line) and fluorescence spectrum (hashed line) of **4f** in the solid state.

UV irradiation of **4a–f** in organic solvents led to the formation of complicated compound mixtures, probably due to photochemical Si–Si bond cleavage of the vinyldisilanes.[28] The photochemical decomposition of **4a–f** is observed even within the time of the fluorescent measurements. Therefore, Figures 5 and 6 display absorption and emission spectra which are obtained with the first scanning of each sample. The UV–vis absorption spectra of **4a–f** are similar to those in the solid state and exhibit two shoulder peaks in the range 246–309 nm. The fluorescent spectra of **4a–f** in solution display the peaks in the range 323–338 nm in comparison to those of **4b–f** in the solid state (393–427 nm). Blue-shifted emission in solution can be attributed to free rotation of the Si–Si or Si–C bonds and lack of $\sigma-\pi$ conjugation of the Si–Si–C═C chain. The fluorescence spectrum of **4f** displays a regular emission at 332 nm and a shoulder peak at 354 nm. The latter red-shifted emission is ascribed to the OICT induced by the strongly electron accepting cyano group.[10]

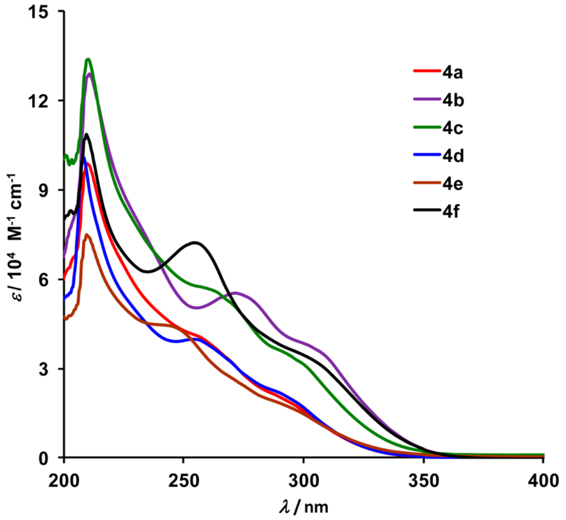


Figure 5. UV–vis absorption spectra of **4a–f** in THF solution (0.01 mM).

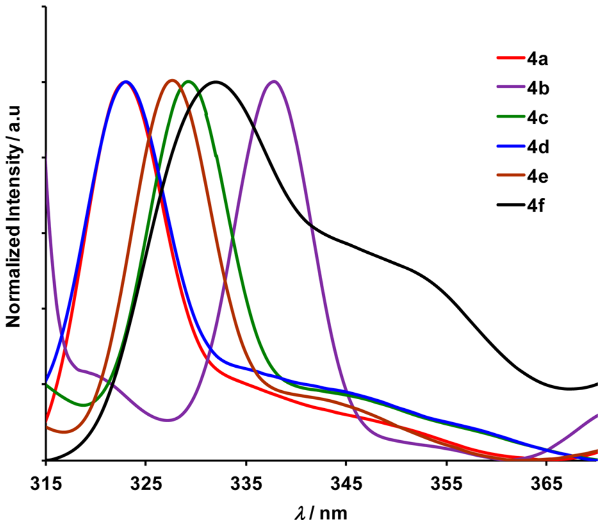


Figure 6. Fluorescence spectra of **4a–f** in THF solution (0.001 mM).

CONCLUSIONS

We prepared dinickel complexes with bridging secondary silyl ligands and found a new route to synthesize dialkenyldisilanes from their reactions with alkynes. The reactions of the dinuclear complexes with bridging silyl ligands toward alkynes are much rarer than those using mononuclear transition-metal complexes with the silyl ligands.[29] The reactions of alkynes with **2** produce dialkenyldisilanes **4**, which are suggested to involve consecutive Si–C and Si–Si bond-making processes on the dinickel structure. It should be noted that the C_6H_5-substituted disilane **4a** possesses a planar C═C–Si–Si–C═C chain with a small dihedral angle and shows strong blue-green emission in the solid state because of the conformation.

EXPERIMENTAL SECTION

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere or in a nitrogen-filled glovebox (Miwa MFG). Hexane, toluene, and THF were purified by using a Grubbs-type solvent purification system (Glass Contour).[30] Dehydrated CH_2Cl_2 (Kanto Chemical) for purification was used as received. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on JEOL JNM-500 MHz and Bruker Biospin Avance III 400 MHz NMR spectrometers. Chemical shifts in ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual peaks of the solvents used.[31] The peak positions of the ^{19}F{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} NMR spectra were referenced to external CF_3COOH (δ −76.5), $SiMe_4$ (δ 0), and 85% H_3PO_4 (δ 0), respectively, in C_6D_6 or THF-d_8. All signals of **4a–f** in the ^{1}H and ^{13}C{^{1}H} NMR spectra were assigned by 2D NMR experiments. IR spectra were recorded on a JASCO FTIR-4100 spectrometer. High-resolution FAB (matrix nitrobenzyl alcohol, NBA) mass spectra were performed using a JEOL JMS-700 mass spectrometer. UV–vis spectra of **4a–e** in the solid state were recorded using an Agilent 8453 spectrometer. Fluorescence spectra of **4a–e** in the solid state were recorded using a Hitachi F 4500 spectrometer. UV−vis spectra of **4f** in the solid state and **4a**−**f** in solution were recorded using a JASCO V-530 spectrometer. Fluorescence spectra of **4f** in the solid state and **4a**−**f** in solution were recorded using a JASCO FP-3600 spectrometer. Melting points were measured using a Yanaco MP-J3 apparatus and were uncorrected. Elemental analyses were performed using a LECO CHNS-932 or Yanaco MT-5 CHN autorecorder at the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology. [Ni(cod)$_2$], tricyclohexylphosphine, 1,2-bis(dimethylphosphino)ethane (dmpe), and bis(diethylphosphino)ethane (depe) (Sigma-Aldrich) and H_2SiPh_2 and PhC≡CPh (Tokyo Chemical Industry) were purchased and used as received. 4-Me-, 4-MeO-, 4-F-, 4-F_3C-, and 4-NC-substituted diarylacetylenes were prepared according to the reported procedure.[32]

Preparation of [{Ni(PCy$_3$)}$_2$(μ-SiHPh$_2$)$_2$] (1). To a hexane solution (30 mL) of [Ni(cod)$_2$] (1.74 g, 6.33 mmol) and PCy$_3$ (2.53 g, 9.02 mmol) was added H_2SiPh_2 (1.60 mL, 8.62 mmol). The reaction mixture was stirred at room temperature for 20 h, giving an orange precipitate from the red solution. The precipitate was collected by filtration, washed with hexane (20 mL × 2), and dried under vacuum to give **1** (3.20 g, 97%) as an orange solid. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 8.11 (d, 8H, C_6H_5 *ortho*, $^3J_{H-H}$ = 7.4 Hz), 7.34 (t, 8H, C_6H_5 *meta*, $^3J_{H-H}$ = 7.4 Hz), 7.22 (t, 4H, C_6H_5 *para*, $^3J_{H-H}$ = 7.4 Hz), 1.86−1.76 (m, 18H, PC_6H_{11}), 1.51 (br, 18H, PC_6H_{11}), 1.30 (m, 12H, PC_6H_{11}), 0.99 (m, 18H, PC_6H_{11}), −2.04 (m, 2H, Ni*H*Si, J_{P-H} = 15 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, room temperature): δ 144.7 (C_6H_5 *ipso*), 136.8 (C_6H_5 *ortho*), 128.3 (C_6H_5 *meta*), 127.6 (C_6H_5 *para*), 36.8 (apparent triplet, PCH, $|^1J_{P-C} + {}^4J_{P-C}|$ = 8.3 Hz), 30.7 ($PCHCH_2$), 27.8 (apparent triplet, $PCHCH_2CH_2$, J_{P-C} = 5.1 Hz), 26.6 ($PCHCH_2CH_2CH_2$). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, room temperature): δ 121.8 (m, $^2J_{P-Si}$ = 25 Hz). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, room temperature): δ 45.9. IR (KBr): 1590 (ν_{Si-H}) cm^{-1}. Anal. Calcd for $C_{60}H_{88}Ni_2P_2Si_2$: C, 68.97; H, 8.49. Found: C, 66.86; H, 8.68. It was difficult to obtain satisfactory data for the elemental analysis and HRMS due to the severe air sensitivity of **1**.

Preparation of [{Ni(dmpe)}$_2$(μ-SiHPh$_2$)$_2$] (2). To a toluene solution (20 mL) of **1** (1.21 g, 1.16 mmol) was added dmpe (390 μL, 2.34 mmol), and then the mixture was stirred at room temperature for 16 h. The solution was evaporated under reduced pressure to give an orange residue, which was washed with hexane (9 mL × 3) and dried under vacuum to give **2** (815 mg, 90%) as a red solid. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 7.84 (d, 8H, C_6H_5 *ortho*, $^3J_{H-H}$ = 6.0 Hz), 7.27−7.21 (m, 12H, C_6H_5 *meta* and *para*), 1.23 (br, 8H, PCH_2), 0.83−0.88 (br, 24H, PCH_3), −4.02 (br m, 2H, Ni*H*Si). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8, room temperature): δ 148.7 (apparent quintet, C_6H_5 *ipso*, $^3J_{P-C}$ = 4.0 Hz), 134.3 (C_6H_5 *ortho*), 126.2 (C_6H_5 *para*), 126.0 (C_6H_5 *meta*), 32.2 (m, PCH_2), 20.0 (br, PCH_3), 17.0 (br, PCH_3). ^{29}Si{^{1}H} NMR (99 MHz, THF-d_8, room temperature): δ 113.6 (apparent quintet, $^2J_{P-Si}$ = 20 Hz). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, room temperature): δ 8.31. IR (KBr): 1579 (ν_{Si-H}) cm^{-1}. Anal. Calcd for $C_{36}H_{54}Ni_2P_4Si_2$: C, 55.13; H, 6.94. Found: C, 54.55; H, 6.82. HRMS (FAB): calcd for $C_{36}H_{54}Ni_2P_4Si_2$ [M]$^+$ 782.1422, found *m*/*z* 782.1440. The direct preparation of **2** was performed from the reaction of [Ni(cod)$_2$] (172 mg, 0.63 mmol), dmpe (120 μL, 0.72 mmol), and H_2SiPh_2 (130 μL, 0.70 mmol) in toluene (15 mL). The reaction mixture was stirred for 45 h at room temperature, resulting in the formation of an orange slurry. The precipitate was collected by filtration, washed with hexane (5 mL × 3), and dried under vacuum to give **2** (97 mg, 40%).

Preparation of [{Ni(depe)}$_2$(μ-SiHPh$_2$)$_2$] (3). To a toluene solution (10 mL) of **1** (213 mg, 0.20 mmol) was added depe (100 μL, 0.43 mmol), and then the mixture was stirred at 60 °C for 6 h. The solution was evaporated under reduced pressure to give an orange residue, which was washed with hexane (3 mL × 2) and dried under vacuum to give **3** (77 mg, 42%) as a brown solid. The product **3** in solution was partially decomposed during the ^{13}C{^{1}H} NMR measurement. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 7.93 (d, 8H, C_6H_5 *ortho*, $^3J_{H-H}$ = 6.6 Hz), 7.28 (t, 8H, C_6H_5 *meta*, $^3J_{H-H}$ = 7.2 Hz), 7.22 (t, 4H, C_6H_5 *para*, $^3J_{H-H}$ = 7.0 Hz), 1.39−1.26 (m, 24H, $P(CH_2)_2$ + PCH_2CH_3), 0.75 (m, 24H, PCH_2CH_3), −6.04 (m, 2H, Ni*H*Si, J_{P-H} = 6.0 Hz). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8, room temperature): δ 150.6 (C_6H_5 *ipso*), 136.9 (C_6H_5 *ortho*), 127.1 (C_6H_5 *para*), 126.7 (C_6H_5 *meta*), 21.7 (PCH_2CH_3), 8.45 (PCH_2CH_3). The $P(CH_2)_2$ carbon signal is overlapped with solvent signals. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, room temperature): δ 21.6. IR (KBr): 1538 (ν_{Si-H}) cm^{-1}. A suitable ^{29}Si NMR signal was not observed due to decomposition during the measurement. HRMS (FAB): calcd for $C_{44}H_{70}Ni_2P_4Si_2$ [M]$^+$ 894.2673, found *m*/*z* 894.2585. The ^{31}P{^{1}H} NMR spectra of the reaction mixture at room temperature in C_6D_6 displayed two signals at δ 32.6 and 44.4 with the same $^3J_{P-P}$ values (27 Hz), which were assigned to the dinickel intermediate [{Ni(depe)}(μ-SiHPh$_2$)$_2${Ni(PCy$_3$)}]. After heating at 60 °C for 3 h, these signals became negligible and the signal of product **3** (δ 21.6) increased.

Preparation of 1,2-Bis{(*E*)-1,2-diphenylethenyl}-1,1,2,2-tetraphenyldisilane (4a). The experimental procedure was modified simply from that of the previous report.[12] To a toluene solution (10 mL) of **2** (198 mg, 0.25 mmol) was added PhC≡CPh (196 mg, 1.10 mmol), followed by stirring at 60 °C for 15 h. The reaction solution was diluted in CH_2Cl_2 (30 mL) and filtered through Florisil to remove the Ni complex. The solvent was evaporated under reduced pressure to give a yellow oil. The crude product was washed with hexane (3 mL × 2) and dried in vacuo to give **4a** (43 mg, 24%) as a white solid. Recrystallization with toluene/hexane (1/7) afforded colorless crystals of **4a** suitable for X-ray crystallography. The ^{1}H NMR spectrum of the reaction mixture before purification displayed the complete conversion of **2** into **4a** and [Ni(η^2-PhC≡CPh)(dmpe)][18] (**5a**; 94% NMR yield). Data for **4a** are as follows. ^{1}H NMR (400 MHz, THF-d_8, room temperature): δ 7.44 (d, 8H, SiC_6H_5 *ortho*, $^3J_{H-H}$ = 7.0 Hz), 7.29 (t, 4H, SiC_6H_5 *para*, $^3J_{H-H}$ = 7.1 Hz), 7.17 (apparent triplet, 10H, C_6H_5 *meta* and =C*H*, $^3J_{H-H}$ = 6.9 Hz), 7.01 (m, 6H, =CC_6H_5 *para* and *meta*), 6.91 (br, 6H, =CC_6H_5 *para* and *meta*), 6.78 (m, 8H, =CC_6H_5 *ortho*). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8, room temperature): δ 145.2 (=CH), 142.5 (=CC_6H_5 *ipso*), 142.0 (=CSi), 138.0 (=CC_6H_5 *ipso*), 137.5 (SiC_6H_5 *ortho*), 135.6 (SiC_6H_5 *ipso*), 130.2 (=CC_6H_5 *ortho*), 129.7 (SiC_6H_5 *para*), 129.1 (=CC_6H_5 *ortho*), 128.7 (=CC_6H_5 *meta*), 128.4 (=CC_6H_5 *meta*), 128.2 (SiC_6H_5 *meta*), 127.9 (=CC_6H_5 *para*), 126.3 (=CC_6H_5 *para*). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, room temperature): δ −20.3. Anal. Calcd for $C_{52}H_{42}Si_2$: C, 86.38; H, 5.85. Found: C, 86.34; H, 5.79. To isolate the Ni complex from the mixture, the solvent was removed under reduced pressure. The crude product was washed with hexane (2 mL × 2) and purified repeatedly with toluene/hexane (10/3) to give **5a** as a pale yellow solid (2.9 mg, 6%). Data for **5a** are as follows. ^{1}H NMR (400 MHz, THF-d_8, room temperature): δ 7.48 (d, 4H, C_6H_5 *ortho*, $^3J_{H-H}$ = 6.8 Hz), 7.21 (t, 4H, C_6H_5 *meta*, $^3J_{H-H}$ = 7.6 Hz), 7.04 (t, 2H, C_6H_5 *para*, $^3J_{H-H}$ = 7.4 Hz), 1.64 (m, 4H, PCH_2, J_{P-H} = 13 Hz), 1.42 (apparent triplet, 12H, PCH_3, $|^2J_{P-C} + {}^4J_{P-C}|$ = 3.2 Hz). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8, room temperature): δ 138.2 (apparent triplet, C_6H_5 *ipso*, $^3J_{P-C}$ = 8.9 Hz), 137.6 (d, ≡CC_6H_5, $^2J_{P-C}$ = 13 Hz), 129.3 (C_6H_5 *ortho*), 128.3 (C_6H_5 *mata*), 125.2 (C_6H_5 *para*), 30.3 (apparent triplet, PCH_2, $|^1J_{P-C} + {}^2J_{P-C}|$ = 22 Hz), 15.6 (apparent triplet, PCH_3, $|^1J_{P-C} + {}^3J_{P-C}|$ = 11 Hz). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8, room temperature): δ 22.5.

Preparation of 1,2-Bis{(*E*)-1,2-bis(4-methoxyphenyl)-ethenyl}-1,1,2,2-tetraphenyldisilane (4b). The procedure was similar to the preparation of **4a**. To a toluene solution (10 mL) of **2** (193 mg, 0.25 mmol) was added ArC≡CAr (Ar = C_6H_4OMe-4; 252 mg, 1.06 mmol), followed by stirring at 60 °C for 44 h to produce **4b** (71.7 mg, 34%) as a white solid. Vapor diffusion crystallization with CH_2Cl_2/toluene afforded colorless crystals of **4b** suitable for X-ray crystallography. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixture displayed signals of [Ni(η^2-ArC≡CAr)(dmpe)] (**5b**; 86% NMR yield, δ_P 23.2 in C_6D_6). ^{1}H NMR (400 MHz, THF-d_8, room temperature): δ 7.42 (d, 8H, SiC_6H_5 *ortho*, $^3J_{H-H}$ = 6.8 Hz), 7.27 (t, 4H, SiC_6H_5 *para*, $^3J_{H-H}$ = 7.2 Hz), 7.16 (t, 8H, SiC_6H_5 *meta*, $^3J_{H-H}$ = 7.4 Hz), 7.06 (s, 2H, =C*H*), 6.74 (d, 4H, =CC_6H_4 *ortho*, $^3J_{H-H}$ = 8.8 Hz), 6.71 (d, 4H, =CC_6H_4 *ortho*, $^3J_{H-H}$ = 8.8 Hz), 6.58 (d, 4H, =CC_6H_4 *meta*, $^3J_{H-H}$ = 8.8 Hz), 6.47 (d, 4H, =CC_6H_4 *meta*, $^3J_{H-H}$ = 8.8 Hz), 3.66 (s, 6H, OCH_3), 3.59 (s, 6H, OCH_3). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8, room temperature): δ 159.9 (=CC_6H_4 *para*), 158.8 ($=CC_6H_4$ *para*), 144.7 ($=CH$), 138.7 ($=CSi$), 137.5 (SiC_6H_5 *ortho*), 136.3 (SiC_6H_5 *ipso*), 134.7 ($=CC_6H_4$ *ipso*), 131.6 ($=CC_6H_4$ *ortho*), 130.8 ($=CC_6H_4$ *ipso*), 130.3 ($=CC_6H_4$ *ortho*), 129.4 (SiC_6H_5 *para*), 128.1 (SiC_6H_5 *meta*), 114.2 ($=CC_6H_4$ *meta*), 113.8 ($=CC_6H_4$ *meta*), 55.1 (OCH_3), 54.9 (OCH_3). $^{29}Si\{^1H\}$ NMR (99 MHz, THF-d_8, room temperature): δ −19.0. Anal. Calcd for $C_{56}H_{50}O_4Si_2{\cdot}C_7H_8{\cdot}CH_2Cl_2$: C, 75.34; H, 5.93. Found: C, 75.31; H, 5.68.

Preparation of 1,2-Bis{(*E*)-1,2-bis(4-tolyl)ethenyl}-1,1,2,2-tetraphenyldisilane (4c). The procedure was similar to the preparation of **4a**. To a toluene solution (10 mL) of **2** (85.3 mg, 0.11 mmol) was added ArC≡CAr (Ar = C_6H_4Me-4; 96.3 mg, 0.47 mmol), followed by stirring at 60 °C for 10 h to produce **4c** (23.8 mg, 28%) as a white solid. Vapor diffusion crystallization with CH_2Cl_2/toluene afforded colorless crystals of **4c** suitable for X-ray crystallography. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture displayed signals of [Ni(η^2-ArC≡CAr)(dmpe)] (**5c**; 88% NMR yield, δ_p 23.3 in C_6D_6). ^1H NMR (400 MHz, THF-d_8, room temperature): δ 7.41 (d, 8H, SiC_6H_5 *ortho*, $^3J_{H-H}$ = 6.8 Hz), 7.27 (t, 4H, SiC_6H_5 *para*, $^3J_{H-H}$ = 7.4 Hz), 7.15 (t, 8H, SiC_6H_5 *meta*, $^3J_{H-H}$ = 7.4 Hz), 7.08 (s, 2H, $=CH$), 6.82 (d, 4H, $=CC_6H_4$ *ortho*, $^3J_{H-H}$ = 7.2 Hz), 6.69 (m, 12H, $=CC_6H_4$ *ortho* and *meta*), 2.18 (s, 6H, $C_6H_4CH_3$), 2.11 (s, 6H, $C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8, room temperature): δ 144.5 ($=CH$), 140.8 ($=CSi$), 139.6 ($=CC_6H_4$ *ipso*), 137.6 ($=CC_6H_4$ *ipso*), 137.5 (SiC_6H_5 *ortho*), 136.0 (SiC_6H_5 *ipso*), 135.6 ($=CC_6H_4$ *para*), 135.4 ($=CC_6H_4$ *para*), 130.2 ($=CC_6H_4$ *ortho*), 129.5 (SiC_6H_5 *para*), 129.3 ($=CC_6H_4$ *ortho*), 129.1 ($=CC_6H_4$ *meta*), 129.0 ($=CC_6H_4$ *meta*), 128.1 (SiC_6H_5 *meta*), 21.0 (CH_3), 20.9 (CH_3). $^{29}Si\{^1H\}$ NMR (79 MHz, THF-d_8, room temperature): δ −20.0. Anal. Calcd for $C_{56}H_{50}Si_2$: C, 86.32; H, 6.47. Found: C, 86.15; H, 6.33.

Preparation of 1,2-Bis{(*E*)-1,2-bis(4-fluorophenyl)ethenyl}-1,1,2,2-tetraphenyldisilane (4d). The procedure was similar to the preparation of **4a**. To a toluene solution (15 mL) of **2** (258 mg, 0.33 mmol) was added ArC≡CAr (Ar = C_6H_4F-4; 304 mg, 1.42 mmol), followed by stirring at 60 °C for 18 h to give **4d** (110 mg, 42%) as a pale yellow solid. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture displayed signals of [Ni(η^2-ArC≡CAr)(dmpe)] (**5d**; 96% NMR yield, δ_p 23.5 in C_6D_6). ^1H NMR (400 MHz, THF-d_8, room temperature): δ 7.43 (d, 8H, SiC_6H_5 *ortho*, $^3J_{H-H}$ = 7.6 Hz), 7.33 (t, 4H, SiC_6H_5 *para*, $^3J_{H-H}$ = 7.4 Hz), 7.22 (t, 8H, SiC_6H_5 *meta*, $^3J_{H-H}$ = 7.4 Hz), 7.08 (s, 2H, $=CH$), 6.72−6.82 (m, 12H, $=CC_6H_4$ *ortho* and *meta*), 6.65 (apparent triplet, 4H, $=CC_6H_4$ *meta*, $|^3J_{F-H} + {}^3J_{H-H}|$ = 8.8 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8, room temperature): δ 162.8 (d, $=CC_6H_4$ *para*, J_{F-C} = 249 Hz), 162.1 (d, $=CC_6H_4$ *para*, J_{F-C} = 245 Hz), 144.3 ($=CH$), 140.8 ($=CSi$), 138.0 (d, $=CC_6H_4$ *ipso*, $^4J_{F-C}$ = 3 Hz), 137.4 (SiC_6H_5 *ortho*), 135.2 (SiC_6H_5 *ipso*), 134.0 (d, $=CC_6H_4$ *ipso*, $^4J_{F-C}$ = 3 Hz), 132.0 (d, $=CC_6H_4$ *ortho*, $^3J_{F-C}$ = 8 Hz), 130.8 (d, $=CC_6H_4$ *ortho*, $^3J_{F-C}$ = 8 Hz), 130.0 (SiC_6H_5 *para*), 128.5 (SiC_6H_5 *meta*), 115.7 (d, $=CC_6H_4$ *meta*, $^2J_{F-C}$ = 21 Hz), 115.5 (d, $=CC_6H_4$ *meta*, $^2J_{F-C}$ = 21 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, THF-d_8, room temperature): δ −121.4, −124.4. $^{29}Si\{^1H\}$ NMR (79 MHz, THF-d_8, room temperature): δ −20.9. Anal. Calcd for $C_{52}H_{38}F_4Si_2$ + C_4H_8O: C, 77.57; H, 5.35; F, 8.76. Found: C, 77.77; H, 5.06; F, 8.48.

Preparation of 1,2-Bis{(*E*)-1,2-bis(*p*-trifluoromethylphenyl)ethenyl}-1,1,2,2-tetraphenyldisilane (4e). The procedure was similar to the preparation of **4a**. To a toluene solution (10 mL) of **2** (293 mg, 0.37 mmol) was added ArC≡CAr (Ar = $C_6H_4CF_3$-4; 494 mg, 1.57 mmol), followed by stirring at 60 °C for 17 h to give **4e** (167 mg, 45%) as a white solid. Vapor diffusion crystallization with CH_2Cl_2/toluene afforded colorless crystals of **4e** suitable for X-ray crystallography. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture displayed signals of [Ni(η^2-ArC≡CAr)(dmpe)] (**5e**; 80% NMR yield, δ_p 24.2 in C_6D_6). ^1H NMR (400 MHz, THF-d_8, room temperature): δ 7.46 (d, 8H, SiC_6H_5 *ortho*, $^3J_{H-H}$ = 8.0 Hz), 7.41 (d, 4H, $=CC_6H_4$ *meta*, $^3J_{H-H}$ = 8.4 Hz), 7.38 (t, 4H, SiC_6H_5 *para*, $^3J_{H-H}$ = 7.2 Hz), 7.26 (t, 8H, SiC_6H_5 *meta*, $^3J_{H-H}$ = 7.6 Hz), 7.23 (d, 4H, $=CC_6H_4$ *meta*, partly overlapped), 7.18 (s, 2H, $=CH$), 6.92 (d, 4H, $=CC_6H_5$ *ortho*, $^3J_{H-H}$ = 8.4 Hz), 6.91 (d, 4H, $=CC_6H_5$ *ortho*, $^3J_{H-H}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8, room temperature): δ 145.9 ($=CC_6H_4$ *ipso*), 144.2 ($=CH$), 144.1 ($=CC_6H_4$ *ipso*), 140.9 ($=CSi$), 137.4 (SiC_6H_5 *ortho*), 134.3 (SiC_6H_5 *ipso*), 130.4 ($=CC_6H_4$ *ortho* and SiC_6H_5 *para*), 130.0 (q, $=CC_6H_4$ *para*, $^2J_{F-C}$ = 32 Hz), 129.5 ($=CC_6H_4$ *ortho*), 129.2 (q, $=CC_6H_4$ *para*, $^2J_{F-C}$ = 32 Hz), 128.7 (SiC_6H_5 *meta*), 125.8 (q, $=CC_6H_4$ *meta*, $^3J_{F-C}$ = 4 Hz), 125.7 (q, $=CC_6H_4$ *meta*, $^3J_{F-C}$ = 4 Hz), 125.0 (q, CF_3, J_{F-C} = 272 Hz), 124.9 (q, CF_3, J_{F-C} = 272 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, THF-d_8, room temperature): δ −70.1, −70.4. $^{29}Si\{^1H\}$ NMR (99 MHz, THF-d_8, room temperature): δ −20.5. Anal. Calcd for $C_{52}H_{38}F_4Si_2$: C, 67.59; H, 3.85; F, 22.91. Found: C, 67.38; H, 3.71; F, 22.80.

Preparation of 1,2-Bis{(*E*)-1,2-bis(4-cyanophenyl)ethenyl}-1,1,2,2-tetraphenyldisilane (4f). The procedure was similar to the preparation of **4a**. To a toluene solution (10 mL) of **2** (115 mg, 0.15 mmol) was added ArC≡CAr (Ar = C_6H_4CN-4; 132 mg, 0.58 mmol), followed by stirring at 60 °C for 24 h to give **4f** (11.6 mg, 10%) as a white solid. Vapor diffusion crystallization with CH_2Cl_2/toluene afforded colorless crystals of **4f** suitable for X-ray crystallography. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture displayed signals of [Ni(η^2-ArC≡CAr)(dmpe)] (**5f**, 70% NMR yield, δ_p 25.5 in THF-d_8). ^1H NMR (400 MHz, THF-d_8, room temperature): δ 7.46−7.42 (m, 12H, SiC_6H_5 *ortho* + $=CC_6H_4$ *meta*), 7.41 (t, 4H, SiC_6H_5 *para*, $^3J_{H-H}$ = 7.6 Hz), 7.28 (t, 8H, SiC_6H_5 *meta*, $^3J_{H-H}$ = 7.6 Hz), 7.24 (d, 4H, $=CC_6H_4$ *ortho*, $^3J_{H-H}$ = 8.4 Hz), 7.11 (s, 2H, $=CH$), 6.87 (d, 4H, $=CC_6H_5$ *ortho*, $^3J_{H-H}$ = 7.6 Hz), 6.85 (d, 4H, $=CC_6H_5$ *ortho*, $^3J_{H-H}$ = 8.4 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8, room temperature): δ 146.4 ($=CC_6H_4$ *ipso*), 144.8 ($=CC_6H_4$ *ipso*), 144.2 ($=CH$), 141.4 ($=CSi$), 137.3 (SiC_6H_5 *ortho*), 133.9 (SiC_6H_5 *ipso*), 132.7 ($=CC_6H_4$ *meta*), 132.6 ($=CC_6H_4$ *meta*), 130.6 (SiC_6H_5 *para* + $=CC_6H_4$ *ortho*), 129.8 ($=CC_6H_4$ *ortho*), 128.9 (SiC_6H_5 *meta*), 118.7 (CN), 118.5 (CN), 112.4 ($=CC_6H_5$ *para*), 111.3 ($=CC_6H_5$ *para*). $^{29}Si\{^1H\}$ NMR (79 MHz, THF-d_8, room temperature): δ −18.8. It was difficult to obtain the satisfactory data for the elemental analysis.

Cyclotrimerization of PhC≡CPh Catalyzed by 1. To a toluene solution (5 mL) of PhC≡CPh (56.3 mg, 0.32 mmol) was added a catalytic amount of **1** (16.5 mg, 16 μmol). The reaction mixture was then stirred at 60 °C for 16 h. The reaction solution was diluted in CH_2Cl_2 (20 mL) and filtered through Florisil to remove decomposition products. The solvent was removed under vacuum to give pure hexaphenylbenzene (54.2 mg, 96%). The NMR spectra of the product were identified on the basis of literature data.[19]

Hydrosilylation of PhC≡CPh with H_2SiPh_2 Catalyzed by 1. To a mixture of PhC≡CPh (130 mg, 0.73 mmol) and H_2SiPh_2 (168 μL, 0.91 mmol) in THF (5 mL) was added complex **1** (37.6 mg, 36 μmol), followed by stirring at 60 °C for 9 h. The reaction solution was diluted in CH_2Cl_2 (20 mL) and filtered through Florisil to remove decomposition products. The solvent was evaporated under reduced pressure to give a colorless oil. The crude product was purified by column chromatography on silica gel (eluent CH_2Cl_2/hexane 1/10, R_f = 0.54) and dried under vacuum to give (*E*)-1-diphenylsilyl-1,2-diphenylethene as a white solid (198 mg, 75% based on PhC≡CPh). The NMR spectra of the product were identified on the basis of literature data.[20]

Hydrosilylation of PhC≡CPh with H_2SiPh_2 Catalyzed by 2. The procedure was similar to the above reaction. To a mixture of PhC≡CPh (183 mg, 1.03 mmol) and H_2SiPh_2 (184 μL, 0.99 mmol) in toluene (5 mL) was added complex **2** (38.4 mg, 49 μmol), followed by stirring at 60 °C for 24 h. After purification by column chromatography, the product contained a mixture of (*E*)- and (*Z*)-1-diphenylsilyl-1,2-diphenylethene as a colorless oil (159 mg, 43% based on PhC≡CPh, *E*/*Z* = 49/51). The *Z* isomer of the mixtures was identified by comparison to the data of the *E* isomer. Data for the *Z* isomer are as follows. ^1H NMR (400 MHz, $CDCl_3$, room temperature): δ 7.62 (s, 1H, $=CH$), 7.48 (d, 4H, SiC_6H_5 *ortho*, $^3J_{H-H}$ = 6.8 Hz), 6.98−7.39 ($=CC_6H_5$ *ortho*, *meta*, *para*, and SiC_6H_5 *meta*, *para*, overlapped with the signals of *E* isomer), 5.34 (s, 1H, Si*H*, J_{Si-H} = 204 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, room temperature): δ 148.5 ($=CH$), 145.5 ($=CC_6H_5$ *ipso*), 139.7 ($=CSi$), 138.5 ($=CC_6H_5$ *ipso*), 136.1 (SiC_6H_5 *ortho*), 133.7 (SiC_6H_5 *ipso*), 129.7, 129.1, 128.0 (SiC_6H_5 *meta*), 127.7 ($=CC_6H_5$ *para*), 126.5 ($=CC_6H_5$ *para*). Three signals were overlapped with those of the *E* isomer. The *ortho* and *meta* carbons of the $=CC_6H_5$ groups and the *para* carbons of the SiC_6H_5 group were not assigned. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, room temperature): δ −25.1.

X-ray Crystal Structure Analyses. Single crystals of **4b**,**c**,**e**,**f** suitable for X-ray diffraction study were mounted on MicroMounts (MiTeGen). The crystallographic data of **4b**,**c**,**e**,**f** were collected on a Rigaku Saturn CCD area detector equipped with monochromated Mo Kα radiation (λ = 0.710 73 Å) at 113 K. Calculations were carried out using the Crystal Structure program package, version 4.0, for Windows. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares methods using SHELXL-97.[33] Hydrogen atoms were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms. The overall quality of the reflection data of **4b**,**e** was poor. The toluene molecule of **4b** as crystallization solvent was refined without hydrogen atoms. The data of **4e** resulted in a maximum residual electron density larger than that normally expected (Alert A by checkcif). Selected bond distances and angles of **4a**−**c**,**e**,**f** are given in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, a table, and CIF files giving crystallographic data for **4b**,**c**,**e**,**f** and NMR spectroscopic data for **1**−**3**, **4f**, **5a**, and the hydrosilylated products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Braye, E. H.; Hübel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961**, 83, 4406−4413. (b) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974−11975. (c) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327−2334. For reviews, see: (d) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693−3702.

(2) (a) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1955**, *77*, 6380−6381. (b) Lee, S. H.; Jang, B.-B.; Kafafi, Z. H. *J. Am. Chem. Soc.* **2005**, *127*, 9071−9078. (c) Sanchez, J. C.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Chem. Mater.* **2007**, *19*, 6459−6470. (d) Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Org. Lett.* **2007**, *9*, 133−136. (e) Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 9760−9764. (f) Tobisu, M.; Onoe, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2009**, *131*, 7506−7507. (g) Furukawa, S.; Kobayashi, J.; Kawashima, T. *J. Am. Chem. Soc.* **2009**, *131*, 14192−14193. (h) Ureshino, T.; Yoshida, T.; Kuninobu, Y.; Takai, K. *J. Am. Chem. Soc.* **2010**, *132*, 14324−14326. (i) Yabusaki, Y.; Ohshima, N.; Kondo, H.; Kusamoto, T.; Yamanoi, Y.; Nishihara, H. *Chem. Eur. J.* **2010**, *16*, 5581−5585.

(3) (a) Ohshita, J.; Nodono, M.; Watanabe, T.; Ueno, Y.; Kunai, A.; Harima, Y.; Yamashita, K.; Ishikawa, M. *J. Organomet. Chem.* **1998**, *553*, 487−491. (b) Ohshita, J.; Nodono, M.; Kai, H.; Watanabe, T.; Kuanai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Okita, K.; Harima, Y.; Yamashita, K.; Ishikawa, M. *Organometallics* **1999**, *18*, 1453−1459. (c) Ohshita, J.; Kai, H.; Takata, A.; Iida, T.; Kunai, A.; Ohta, N.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Sakamaki, K.; Okita, K. *Organometallics* **2001**, *20*, 4800−4805. For reviews, see: (d) Ohshita, J. *Macromol. Chem. Phys.* **2009**, *210*, 1360−1370.

(4) (a) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740−1741. For reviews, see: (b) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *J. Inorg. Organomet. Polym.* **2009**, *19*, 249−285. (c) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Commun.* **2009**, 4332−4353.

(5) (a) Hseu, T.-H.; Chi, Y.; Liu, C.-S. *J. Am. Chem. Soc.* **1982**, *104*, 1594−1598. (b) Hoshi, T.; Nakamura, T.; Suzuki, T.; Ando, M.; Hagiwara, H. *Organometallics* **2000**, *19*, 3170−3178.

(6) (a) Zhan, X.; Risko, C.; Korlyukov, A.; Sena, F.; Timofeeva, T. V.; Antipin, M. Y.; Barlow, S.; Brédas, J.-L.; Marder, S. R. *J. Mater. Chem.* **2006**, *16*, 3814−3822. For reviews, see: (b) Zhan, X.; Barlow, S.; Marder, S. R. *Chem. Commun.* **2009**, 1948−1955.

(7) (a) Ishikawa, M.; Sugisawa, H.; Fuchikami, T.; Kumada, M.; Yamabe, T.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* **1982**, *104*, 2872−2878. (b) Shizuka, H.; Okazaki, K.; Tanaka, H.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *J. Phys. Chem.* **1987**, *91*, 2057−2062. (c) Horn, K. A.; Grossman, R. B.; Thorne, J. R. C.; Whitenack., A. A. *J. Am. Chem. Soc.* **1989**, *111*, 4809−4821.

(8) (a) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1981**, 405−406. (b) Shizuka, H.; Sato, Y.; Ueki, Y.; Ishikawa, M.; Kumada, K. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 341−357. (c) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 383−401. (d) Yamamoto, M.; Kudo, T.; Ishikawa., M.; Tobita, S.; Shizuka, H. *J. Phys. Chem. A* **1999**, *103*, 3144−3154. For reviews, see: (e) Shizuka, H.; Hiratsuka, H. *Res. Chem. Intermed.* **1992**, *18*, 131−182. (f) Steinmetz, M. G. *Chem. Rev.* **1995**, *95*, 1527−1588.

(9) (a) Sakurai, H.; Sugiyma, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837−1843. (b) Kira, M.; Miyazawa, T.; Mikami, N.; Sakurai, H. *Organometallics* **1991**, *10*, 3793−3795. (c) Kira, M.; Miyazawa, T.; Sugiyama, H.; Yamaguchi, M.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 3116−3124.

(10) (a) Tajima, Y.; Ishikawa, H.; Miyazawa, T.; Kira, M.; Mikami, N. *J. Am. Chem. Soc.* **1997**, *119*, 7400−7401. (b) Ishikawa, H.; Shimanuki, Y.; Sugiyama, M.; Tajima, Y.; Kira, M.; Mikami, N. *J. Am. Chem. Soc.* **2002**, *124*, 6220−6230. (c) Ishikawa, H.; Sugiyama, M.; Shimanuki, Y.; Tajima, Y.; Setaka, W.; Kira, M.; Mikami, N. *J. Phys. Chem. A* **2003**, *107*, 10781−10786. (d) Ishikawa, H.; Sugiyama, M.; Baba, I.; Setaka, W.; Kira, M.; Mikami, N. *J. Phys. Chem. A* **2005**, *109*, 8959−8961.

(11) Shimizu, M.; Tatsumi, H.; Mochida, K.; Oda, K.; Hiyama, T. *Chem. Asian J.* **2008**, *3*, 1238−1247.

(12) Tanabe, M.; Yumoto, R.; Osakada, K. *Chem. Commun.* **2012**, *48*, 2125−2127.

(13) Pd_2 complexes: (a) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *Organometallics* **1998**, *17*, 4929−4931. (b) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *J. Chem. Soc., Dalton Trans.* **2000**, 417−421.

(14) Pt_2 complexes: (a) Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murray, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 659−666. (b) Sanow, L. M.; Chai, M.; McConnville, D. B.; Galat, K. J.; Simons, R. S.; Rinaldi, P. L.; Youngs, W. J.; Tessier, C. A. *Organometallics* **2000**, *19*, 192−205. (c) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Organometallics* **2000**, *19*, 5500−5510. (d) Arii, H.; Takahashi, M.; Noda, A.; Nanjo, M.; Mochida, K. *Organometallics* **2008**, *27*, 1929−1935. (e) Tanabe, M.; Ito, D.; Osakada, K. *Organometallics* **2008**, *27*, 2258−2267.

(15) Pd−Pt heterometallic complexes: (a) Tanabe, M.; Yamada, T.; Osakada, K. *Organometallics* **2003**, *22*, 2190−2192. (b) Yamada, T.; Tanabe, M.; Osakada, K.; Kim, Y.-J. *Organometallics* **2004**, *23*, 4771−4777.

(16) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Inorg. Chim. Acta* **2002**, *330*, 82−88.

(17) (a) Iluc, V. M.; Hillhouse, G. L. *Tetrahedron* **2006**, *62*, 7577−7582. (b) Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2010**, *132*, 11890−11892.

(18) Pörschke, K. R.; Mynott, R.; Angermund, K.; Krüger, C. *Z. Naturforsch.* **1985**, *40b*, 199−209.

(19) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1975−1981.

(20) Tillack, A.; Pulst, S.; Baumann, W.; Baudisch, H.; Kortus, K.; Rosenthal, U. *J. Oraganomet. Chem.* **1997**, *532*, 117−123.

(21) (*E*)-1-Diphenylsilyl-1,2-diphenylethene in 75% yield was synthesized from hydrosilylation of PhC≡CPh with H_2SiPh_2 catalyzed by complex **1**.

(22) Shimada, S.; Rao, M. L. N.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 213−216.

(23) (a) Ohshita, J.; Iida, T.; Ohta, N.; Komaguchi, K.; Shiotani, M.; Kunai, A. *Org. Lett.* **2002**, *4*, 403−406. (b) Sanji, T.; Yoshiwara, A.; Kibe, T.; Sakurai, H. *Silicon Chem.* **2003**, *2*, 151−155. (c) Iida, T.; Ohshita, J.; Ohta, N.; Komaguchi, K.; Itagaki, Y.; Shiotani, M.; Kunai, A. *J. Organomet. Chem.* **2003**, *688*, 192−199.

(24) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, Chapter 3.

(25) (a) Umezawa, Y.; Tsuboyama, S.; Honda, K.; Uzawa, J.; Nishio, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1207−1213. (b) Suezawa, H.; Yoshida, T.; Umezawa, Y.; Tsuboyama, S.; Nishio, M. *Eur. J. Inorg. Chem.* **2002**, 3148−3155.

(26) The distances (3.445(4), 3.378(3) Å) between the SiC_6H_5 and Ar groups of **4b**,**f** are shorter than the limit of distances of aromatic $\pi-\pi$ stacking (<3.5 Å). See also: Magistrato, A.; Pregosin, P. S.; Albinati, A.; Rothlisberger, U. *Organometallics* **2001**, *20*, 4178−4184.

(27) Sakurai, H.; Tominaga, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1279−1282.

(28) (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424−7425. (b) Ishiakwa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *149*, 37−48. (c) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W.; Venneri, P.; Conlin, R. T.; Dhurjati, M. S. K.; Ezhova, M. B. *J. Organomet. Chem.* **1998**, *561*, 19−27.

(29) (a) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., Chem. Commun.* **1980**, 278−279. (b) Takao, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1994**, *13*, 2554−2556. (c) Tanabe, M.; Jiang, J.; Yamazawa, H.; Osakada, K.; Ohmura, T.; Suginome, M. *Organometallics* **2011**, *30*, 3981−3991.

(30) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

(31) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176−2179.

(32) (a) Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199−3202. (b) Nishihara, Y.; Inoue, E.; Ogawa, D.; Okada, Y.; Noyori, S.; Takagi, K. *Tetrahedron Lett.* **2009**, *50*, 4643−4646.

(33) Sheldrick, G. M. *SHELXL-97: Program for Crystal Structures*; University of Gottingen, Gottingen, Germany, 1997.