located in the same plane (mean deviation from plane 0.023 Å).

Crystals of **3** were grown from pentane solutions at -40 °C in several experiments. In one sample after 4 weeks of crystallization compound **3** decomposed to some extent. The ^{31}P NMR spectrum displayed a doublet at δ 194.68 ($^1J_{PP}$ = 94 Hz) and a doublet of quartets at δ 136.00 ($^1J_{PP}$ = 94, $^3J_{PF}$ = 26 Hz) in addition to the resonances of **3**. Both compounds were present in the ratio 3:4 = 3:1. The PP coupling constant is consistent with a PP single bond, whereas the size of the PF coupling suggests the presence of a $PC(CF_3)_2$ group. Both complexes could not be separated on a preparative scale.

A red crystal of **4** was picked out of the crop and submitted to an X-ray diffraction study (Figure 2 and Table II). The analysis shows the presence of an essentially planar 1-oxa-2,3-diphosphetane (mean deviation from plane 0.01 Å) which is linked to the (η^5-C_5Me_5)(CO)$_2$Fe fragment via an Fe–P single bond (2.327 (4) Å). Compound **4** is obviously the result of a formal [2 + 2] cycloaddition between **1** and hexafluoroacetone. The P–P bond of 2.249 (5) Å reveals a bond order of unity. In the four-membered ring the oxygen atom of the ketone is added to the arylated P atom (P(2)–O(3) = 1.722 (8) Å). In keeping with this, the (CF$_3$)$_2$C fragment in **4** is connected

to the metalated phosphorus via a long P–C single bond (P(1)–C(13) = 1.927 (13) Å), which is quite common for diphosphetane derivatives.[5,6]

Due to the longer distance P(1)–P(2) the bond angles at the phosphorus atoms are markedly more acute (C-(13)–P(1)–P(2) = 72.3 (4)°, P(1)–P(2)–O(3) = 81.3 (3)°) as compared to the angles at carbon and oxygen (102.2 (9) and 104.2 (7)°, respectively). The *E* configuration of **1** has been maintained throughout the cycloaddition.

At room temperature solutions of **3** and **4** in benzene decompose within 1 week to give **1** and unidentified species. We suggest that the formation of **3** and **4** is initiated by a [2 + 1] cycloaddition to the transient adduct **2**. Subsequent scission of the P–C linkage in **2** and attack of the carbanion at a positively polarized carbon atom of a terminal carbonyl ligand affords metallaheterocycle **3** (path a), whereas P–O bond rupture in **2** and attack of the oxygen at the arylated P atom yields **4**. The dissociation of **3** into **1** and free (CF$_3$)$_2$CO and a subsequent [2 + 2] cycloaddition to compound **4** cannot be excluded at the moment. The nature of the transformation of **3** into **4** is presently under investigation.

(16) Crystal data for complex **4**: space group $C2/c$, a = 46.97 (3) Å, b = 9.316 (5) Å, c = 16.611 (5) Å, β = 101.52 (3)°, V = 7121 (6) Å^3, Z = 8, ρ_{calcd} = 1.344 g cm^{-3}, Mo Kα (graphite monochromator, λ = 0.710 73 Å), ω-scan data collection at 179 K (3.0 ≤ 2θ ≤ 45.0°), 4661 unique reflections, 2143 unique observed reflections (F > 4.0σ(F)), Siemens P2$_1$ four-circle diffractometer, structure solved by direct methods and refinement by full-matrix least squares, with use of the Siemens SHELXTL PLUS software on a Micro VAXII computer. All non-hydrogen atoms were refined anisotropically with 254 parameters (hydrogen atoms in calculated positions, riding on the corresponding C atoms), U(H) = 0.08 Å^2, R = 0.080, R_w = 0.058, w^{-1} = σ^2(F), maximum rest electron density 0.50 e/Å^3.

Platinum-Complex-Catalyzed 1,4-Disilylation of 1,3-Dienes Using Organodisilanes: Remarkable Effect of a Phenyl Functionality on a Silicon Atom

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Summary: Organodisilanes having a phenyl functionality on the silicon atom smoothly react with 1,3-dienes at 130 °C to afford the corresponding 1,4-disilylation adducts in high yields in the presence of platinum catalyst. However, other substituents such as Me, *n*-Bu, *t*-Bu, CH$_2$C$_6$H$_5$, CH$_2$CH=CH$_2$, and CH=CH$_2$ on the silicon atom are totally ineffective.

Activation of a silicon–silicon bond by a transition-metal catalyst[1] and subsequent insertions of 1,3-dienes,[2] acetylenes,[3] and olefins[4a,b] into silicon–silicon linkages are of current interest. 1,4-Disilylation of 1,3-dienes is especially important, since it affords adducts[5] having two versatile allylic silane[6] moieties. Transition-metal-catalyzed 1,4-

(1) (a) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974. (b) Rich, J. D. *Organometallics* **1989**, *8*, 2609. (c) Rich, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5886. (d) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692. (e) Kraft, T. E.; Rich, J. D.; McDermott, P. J. *J. Org. Chem.* **1990**, *55*, 5430.

(2) (a) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87. (b) Matsumoto, H.; Shono, K.; Wada, A.; Matsubara, I.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 185. (c) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (d) Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1801. (e) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett.* **1975**, 887. (f) Sakurai, H.; Eriyama, Y.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1984**, *264*, 229.

(3) (a) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948. (b) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241. (c) Watanabe, H.; Kobayahsi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51. (d) Matsumoto, H.; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 43. (e) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149. (f) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. (g) Sakurai, H.; Kamiyama, Y.; Nakadaira Y. *J. Am. Chem. Soc.* **1975**, *97*, 931.
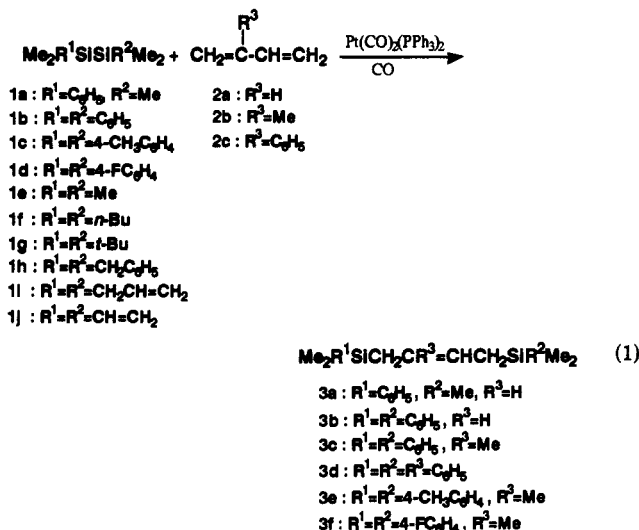
(4) (a) Murakami, M.; Anderson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987. (b) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280. (c) Hayashi, T.; Kawamoto, A. M.; Kobayashi, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1990**, 563.

(5) (a) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912. (b) Richter, W. J.; Neugebauer, B. *Synthesis* **1985**, 1059. (c) Dunogues, J.; Arreguy, B.; Biran, C.; Calas, R.; Pisciotti, F. *J. Organomet. Chem.* **1973**, *63*, 119.

(6) (a) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 2, Chapter 14, pp 893–963. (b) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic: London, 1988; pp 25–37.

disilylation of 1,3-dienes using organodisilanes has been studied, and electronegative substituents (F,[2a] Cl,[2b,f] OMe[2b,f]) on the silicon atom were found indispensable to realize high reactivity. Similar effects of electronegative substituents were also evident in disilylation of acetylenes[3c-f] and olefins[4b] using organodisilanes. However, it has been exceedingly difficult to utilize disilanes having only hydrocarbon substituents in transition-metal-catalyzed 1,4-disilylation of 1,3-dienes.[7] Strained disilacycloalkanes[2e] and hexamethyldisilane (1e)[2f] only afforded α,ω-disilylated products with concomitant dimerization of 1,3-dienes in the presence of palladium catalyst.

In this communication, we wish to report the remarkable effect of a phenyl functionality on a silicon atom. Organodisilanes having a phenyl functionality on the silicon atom smoothly react with 1,3-dienes to afford the corresponding 1,4-disilylation adducts in high yields in the presence of platinum catalyst (eq 1). Quite recently,

$$Me_2R^1SISIR^2Me_2 + CH_2=\overset{R^3}{\underset{|}{C}}\!-\!CH=CH_2 \xrightarrow[CO]{Pt(CO)_x(PPh_3)_z}$$

1a : R^1=C_6H_5, R^2=Me   2a : R^3=H
1b : R^1=R^2=C_6H_5 2b : R^3=Me
1c : R^1=R^2=4-CH$_3$C$_6$H$_4$ 2c : R^3=C$_6$H$_5$
1d : R^1=R^2=4-FC$_6$H$_4$
1e : R^1=R^2=Me
1f : R^1=R^2=n-Bu
1g : R^1=R^2=t-Bu
1h : R^1=R^2=CH$_2$C$_6$H$_5$
1i : R^1=R^2=CH$_2$CH=CH$_2$
1j : R^1=R^2=CH=CH$_2$

$$Me_2R^1SICH_2CR^3\!=\!CHCH_2SIR^2Me_2 \qquad (1)$$

3a : R^1=C_6H_5, R^2=Me, R^3=H
3b : R^1=R^2=C_6H_5, R^3=H
3c : R^1=R^2=C_6H_5, R^3=Me
3d : R^1=R^2=R^3=C_6H_5
3e : R^1=R^2=4-CH$_3$C$_6$H$_4$, R^3=Me
3f : R^1=R^2=4-FC$_6$H$_4$, R^3=Me

Ishikawa and co-workers reported 1,4-disilylation of 1,3-dienes using 1,2,2,2-tetramethylphenylvinyldisilane in the presence of a catalytic amount of nickel(0) complex at 150 °C.[8] They claimed that the vinyl, not the phenyl, substituent on the silicon atom was important, since pentamethylphenyldisilane (1a) did not react at all. This report prompts us to publish our independent observations that the phenyl substituent has a distinct effect. The prominent effect of the phenyl functionality is also observed in disilylation of an alkyne under similar reaction conditions (eqs 4 and 5).

Reaction of 1a with 1,3-butadiene (2a) in the presence of a catalytic amount (5 mol %) of Pt(CO)$_2$(PPh$_3$)$_2$ at 130 °C gave the 1,4-disilylation product 3a in excellent yield (Table I, entry 1).[9] The platinum complex is highly active as the catalyst precursor, whereas palladium complexes such as Pd(PPh$_3$)$_4$,[2a,b] PdCl$_2$(PPh$_3$)$_2$,[2a,b,d,e] and Pd(CO)-(PPh$_3$)$_3$ do not show any catalytic activity (entry 2).

Table I. Platinum-Complex-Catalyzed 1,4-Disilylation of 1,3-Dienes Using Disilanes[a]

entry no.	disilane	diene	product	yield, %[b]	E/Z[c]
1	1a	2a	3a	99 (91)	4.6
2[d]	1a	2a		0	
3	1b	2a	3b	98	3.0
4	1b	2b	3c	91	2.1
5[e]	1b	2c	3d	(51)	0.5
6	1c	2b	3e	(91)	1.7
7	1d	2b	3f	(70)	2.0

[a]Conditions: 1 (0.5 mmol), 2 (1.8 mmol), Pt(CO)$_2$(PPh$_3$)$_2$ (0.025 mmol), THF (1.5 mL), carbon monoxide (initial 10 kg cm^{-2}), 18 h at 130 °C. [b]By GLC; numbers in parentheses show isolated yields. [c]By NMR and/or GLC. [d]Catalyst: Pd(PPh$_3$)$_4$, PdCl$_2$(PPh$_3$)$_2$, or Pd(CO)(PPh$_3$)$_3$; under carbon monoxide pressure (initial 10 kg cm^{-2}) or an argon atmosphere. [e]2c (0.5 mmol).

Tetramethyl-1,2-diphenyldisilane (1b) also gave the 1,4-disilylation products with 2a and isoprene (2b) in excellent yields (entries 3 and 4), and with 2-phenyl-1,3-butadiene (2c) in good isolated yield (entry 5). Furthermore, 4-methylphenyl and 4-fluorophenyl derivatives (1c and 1d) reacted with 2b to give the corresponding 1,4-disilylation products 3e and 3f in high yields (entries 6 and 7). In these transformations, carbon monoxide pressure (10 kg cm^{-2}) is required to maintain the active catalyst species. Under an argon atmosphere, essentially no reactions occur.[10]

The distinct effect of the phenyl substituent on the silicon is demonstrated by the following observations. Peralkylated disilanes such as 1e, 1,2-dibutyltetramethyldisilane (1f), and 1,2-di-*tert*-butyltetramethyldisilane (1g) afforded only a trace of 1,4-disilylation products under the same reaction conditions as in Table I. Modification of the catalyst system for these peralkylated disilanes by use of other selected catalyst precursors (Pd(PPh$_3$)$_4$,[2a,b] PdCl$_2$(PPh$_3$)$_2$[2b-e] PdCl$_2$(PhCN)$_2$,[2f] Pd(dba)$_2$ + 3P(OCH$_2$)$_3$CEt,[3b] PtCl$_2$(cod), PtCl$_2$(PhCN)$_2$) under carbon monoxide pressure or an argon atmosphere were totally unsuccessful. Furthermore, 1,2-dibenzyltetramethyldisilane (1h) remains intact under the various reaction conditions, whereas 1,2-diallyltetramethyldisilane (1i) reacted with 2b to afford 1:1 and 1:2 (1i:2b) adducts in quite low yields (each <10% by GC/MS) in the presence of Pd(dba)$_2$ or Pt(dba)$_2$ as catalyst precursor (5 mol %) under an argon atmosphere. On the other hand, tetramethyl-1,2-divinyldisilane (1j) showed very high reactivity and was converted completely to give an intractable mixture of products. No 1,3-diene was incorporated in those products, and apparently homodimers and cyclic homodimers of 1j

(7) Quite recently, the first successful example has been reported[8] (vide infra).

(8) Ishikawa, M.; Nishimura, Y.; Sakamoto, H.; Ono, T.; Ohshita, J. *Organometallics* 1992, 11, 483.

(9) A typical procedure is as follows: A 30-mL stainless steel autoclave was charged with 1a (104 mg, 0.5 mmol), 2a (1.8 mmol, 1.1 mL of a 1.6 M stock solution in toluene), Pt(CO)$_2$(PPh$_3$)$_2$ (19 mg, 0.025 mmol), and THF (1.5 mL) under an argon flow. After the aparatus was sealed, an air purge was confirmed by pressurization (10 kg cm^{-2})–depressurization sequences with carbon monoxide; then the autoclave was pressurized to 10 kg cm^{-2} at room temperature. The reactor was heated to 130 °C and thermostated at this temperature for 18 h with stirring. GLC analysis (OV-17) with biphenyl as an internal standard showed that 3a was formed in 99% yield. The product was isolated by Kugelrohr distillation in 91% yield (120 mg).

(10) After the reaction, the cooled reaction mixtures were analyzed by FT-IR spectroscopy at ambient pressure. Although carbon monoxide pressure has a dramatic effect in the present reaction (vide supra), the resultant reaction mixtures obtained under carbon monoxide (10 kg cm^{-2}) and argon atmospheres gave nearly identical IR spectra, showing a strong characteristic absorption at 1805 cm^{-1}. A strong absorption at 1982 cm^{-1} (lit.[11] 1983 cm^{-1}) due to Pt(CO)$_2$(PPh$_3$)$_2$ almost disappeared. It is well-known that platinum complexes exhibit a high aptitude for formation of homopolynuclear carbonyls, especially with phosphine ligands. Chatt et al. reported cluster formation from Pt(CO)$_2$(PPh$_3$)$_2$ involving the equilibria[12]

$$5Pt(CO)_2(PPh_3)_2 \rightleftharpoons Pt_3(CO)_3(PPh_3)_4 + 2Pt(PPh_3)_3 + 7CO \quad (i)$$

$$2Pt_3(CO)_3(PPh_3)_4 + 3CO \rightleftharpoons Pt_4(CO)_5(PPh_3)_4 + 2Pt(CO)_2(PPh_3)_2 \quad (ii)$$
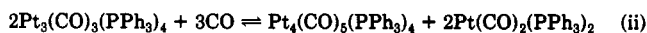
The Pt$_3$ cluster shows a strong absorption at 1803 cm^{-1} due to μ-CO,[12] which is close to the absorption observed with our reaction mixtures. Accordingly, it is conceivable that an active catalyst species in the present reaction is mononuclear and carbon monoxide pressure maintains the catalytically active mononuclear species (cf. eq ii). Even when the reaction is carried out under carbon monoxide pressure, workup procedures involving discharge of the carbon monoxide pressure moves the equilibria toward the catalytically inactive clusters, which are major species in the reaction under an argon atmosphere.

(11) Chini, P.; Longoni, G. *J. Chem. Soc. A* 1970, 1542.

(12) Chatt, J.; Chini, P. *J. Chem. Soc. A* 1970, 1538.

were formed via insertion of the vinyl functionality into the silicon–silicon bond (GC/MS and DEPT; supplementary material).

The present effect of the phenyl substituents cannot be attributed to their electronegativities.[13] Actually, 1a–d remained almost unchanged in the presence of Pd-(PPh₃)₄[2a,b] and PdCl₂(PPh₃)₂,[2a,b,d,e] which were reported[2] to be highly active toward disilanes having electronegative substituents. In an effort to elucidate the function of the phenyl substituents, kinetic measurements were carried out. The rate shows first-order dependence on disilane concentration and also on diene concentration (eq 2).

$$\text{rate} = k_{obs}[1][2] \tag{2}$$

Observed second-order rate constants (k_{obs}) for 1b, 1c, and 1d with 2b are 2.52×10^{-3}, 3.07×10^{-3}, and 6.26×10^{-4} min⁻¹ M⁻¹ (at 110 ± 1 °C), respectively, indicating that lower electron density on the phenyl rings decelerates the 1,4-disilylation reaction. It is well-known that essentially all the transition metals form π-arene complexes.[14] Various kinds of π-arene complexes (η^2, η^4, η^6) have been isolated and structurally characterized. In the case of (η^6-C₆H₅X)Cr(CO)₃, electronegative substituents (F and Cl) as X weakened the π-complexation.[15] Hence, it is conceivable that a π-arene complex intermediate would be responsible for the present distinct effect of the phenyl substituents.[16] Coordination via a π-arene complex as shown in eq 3 can facilitate the succeeding oxidative-addition reaction, which seems to be the most crucial step in the catalytic cyclic.

The similar prominent effect of the phenyl subsituent is observed in the disilylation of alkyne. It is a quite recent finding that an even less reactive peralkylated disilane, i.e. 1e, could be utilized in the disilylation of acetylene by selecting a suitable ligand (1,1,3,3-tetramethylbutyl iso-

(3)
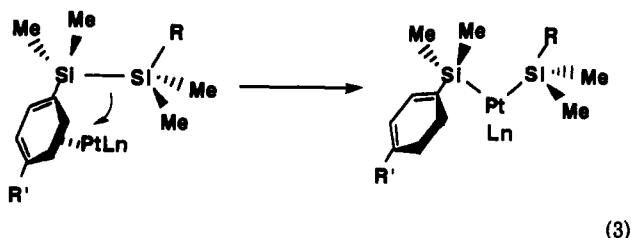
cyanide[3a] or P(OCH₂)₃CEt[3b]) with palladium catalyst. The platinum complex Pt(dba)₂ under carbon monoxide pressure is highly active for the disilylation of phenylacetylene using 1a and 1b (eqs 4 and 5).[17] Again, other disilanes such as 1e, 1f, 1g, 1h, and 1i remained unchanged, while 1j was converted completely to afford the homodimers.

(4)

(5)
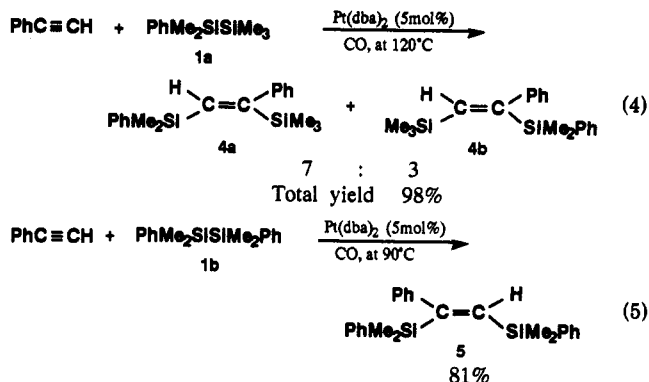
Acknowledgment. We are grateful to Professor Takashi Kawamura of Gifu University for his useful discussion and encouragement. R.M.L. thanks the Ministry of Education, Science, and Culture of Japan for supporting the student exchange program between the Universidade Estadual de Campinas, Brazil, and Gifu University.

Supplementary Material Available: Text giving experimental details (reaction of 1j and kinetic measurement) and ¹H NMR, ¹³C NMR, and MS (including some HRMS) spectral data for 3a–f, 4, and 5 (4 pages). Ordering information is given on any current masthead page.

OM920155I

(13) Group electronegativities: F, 3.93; OMe, 3.54; Cl, 3.19; CH=CH₂, 2.79; C₆H₅, 2.72; CH₂C₆H₅, 2.51; CH 2.47. (a) March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1985; p 14. (b) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1003. (c) Reference 4b.

(14) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987, pp 158–165, 921–940. (b) McGlinchey, M. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, U.K., 1982; Vol. 1, pp 558–566.

(15) (a) Adedeji, F. A.; Brown, D. L.; Connor, J. A.; Leung, M. L.; P.-Andrade, I. M.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221. (b) Mahaffy, C. A. L.; Pauson, P. *J. Chem.Res., Synop.* **1979**, 126.

(16) For π-arene complexes of group 10 metals, see: (a) Browning, J.; Green, M.; Penfold, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31. (b) Allegra, G.; Casagrande, T.; Immizi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289. (c) Bauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884. (d) Jonas, K. *J. Organomet. Chem.* **1974**, *78*, 273.

(17) The same procedures as in eq 1 were used: phenylacetylene (0.5 mmol), 1 (0.25 mmol), Pd(dba)₂ (0.0125 mmol), 30 kg cm⁻² of initial carbon monoxide pressure, 120 °C (with 1a) or 90 °C (with 1b), 15 h. The regio- and stereochemistry of 4 have been established unambiguously by NOE difference spectra with irradiation at the methyl protons of the SiMe₃ and SiMe₂Ph moieties. The stereochemistry of 5 was determined via phenylation (with PhLi) of authentic (Z)-FMe₂SiPhC=CHSiMe₂F.[9]