

Experimental procedure

1: A solution of **9** [25] (22 mmol) in Et₂O (40 mL) was added slowly over 15 min at 0 °C to a solution of phenylsilane (2.4 g, 22 mmol) in Et₂O (40 mL). The mixture was stirred at room temperature for 2 h and then hydrolyzed at 0 °C with 0.4 mL of H₂O. After filtration on celite, distillation gave 5.4 g (83%) of **1** as a colorless oil. B.p. 115–117 °C/0.02 Torr; ¹H NMR (250 MHz, CDCl₃, TMS): δ = 2.0 (s, 12 H, CH₃), 3.51 (s, 4 H, CH₂), 4.82 (s, 2 H, SiH₂); ²⁹Si NMR (200 MHz, CDCl₃, TMS): δ = –51.5 (t, ¹J(SiH) = 200 Hz); IR (CCl₄): ν̄[cm⁻¹] = 2111 (SiH₂). Correct elemental analyses (C,H,N,Si).

2a: A solution of iodine (0.43 g, 1.67 mmol) in ether (10 mL) was added dropwise to a solution of silane **1** (1 g, 3.35 mmol) in Et₂O (10 mL) at room temperature under argon. The resulting mixture was stirred until evolution of H₂ had ceased. It became progressively colorless as a precipitate appeared. The mixture was then filtered, and the residue washed twice with ether to give 1.4 g (100% yield) of a white microcrystalline powder. M.p. 135 °C (decomp); ¹H NMR (250 MHz, CD₂Cl₂, TMS): δ = 2.2 (s, 6 H, CH₃), 2.85 (s, 6 H, CH₃), 4.0 (d, ²J(H,H) = 16 Hz, 2 H, CH₂), 4.25 (d, ²J(H,H) = 16 Hz, 2 H, CH₂), 5.3 (s, 1 H, SiH); ¹³C NMR (200 MHz, CDCl₃, TMS): δ = 63.1 (CH₂N), 47.1, 47.6 (N(CH₃)₂), 123.2, 124.2, 127.3, 128.8, 131.2, 134.0, 143.0; ²⁹Si NMR (200 MHz, CDCl₃, TMS): δ = –29.7 (d, ¹J(Si,H) = 280 Hz); IR (KBr): ν̄[cm⁻¹] = 2202.

2c: A solution of **9** [25] (7.38 mmol) in Et₂O (50 mL) was added slowly to a solution of dichlorophenylsilane (1.1 mL, 7.38 mmol) in Et₂O (50 mL). The mixture was stirred at room temperature for 2 h. After filtration, the solid obtained was dissolved in CH₂Cl₂ to precipitate LiCl which was removed by filtration. After concentration, Et₂O was added to precipitate crude **2c** as a white solid (1.9 g, 90%) whose characteristics are the same as those of **2a**.

6: A solution of I₂ (0.4 g, 1.56 mmol) in Et₂O (15 mL) was added dropwise at –5 °C to a solution of silane **5** (b.p. = 45–50 °C/0.1 Torr) (0.7 g, 3.15 mmol) in Et₂O (15 mL). The mixture was stirred at room temperature for 4 h, filtered, and the solid obtained washed twice with Et₂O to give 1.1 g (100%) of crude **6**. M.p. 145 °C (decomp); ¹H NMR (80 MHz, CDCl₃, TMS): δ = 2.9 (s, 12 H, CH₃), 4.4 (s, 4 H, CH₂), 4.9 (s, 2 H, SiH₂); ²⁹Si NMR (250 MHz, CDCl₃, TMS): δ = –46.4 (t, ¹J(Si,H) = 265 Hz); IR (KBr): ν̄[cm⁻¹] = 2191 and 2209.

8: CF₃SO₃SiMe₃ (0.57 mL, 2.95 mmol) was added dropwise at 0 °C to a solution of **7** (b.p. = 120 °C/0.2 Torr) (0.7 g, 2.8 mmol) in Et₂O (15 mL). After stirring (30 min), the solvent was removed, and the solid obtained washed twice with Et₂O to give 1.1 g (100%) of crude **8**. M.p. = 118–121 °C; ¹H NMR (250 MHz, CDCl₃, TMS): δ = 0.4 (s, 6 H, Si(CH₃)₃), 2.4 (s, 12 H, N(CH₃)₂), 3.8 (s, 4 H, CH₂); ¹⁹F NMR (80 MHz, CDCl₃, C₆F₆), δ = 85 (s); ²⁹Si NMR (250 MHz, CDCl₃, TMS): δ = –4.1 (s); positive-ion FAB-MS: *m/z* 249 (*M*⁺, 100%).

10: A solution of **9** [25] (11.1 mmol) in Et₂O (30 mL) were added slowly to a solution of HSiCl₃ (1.2 g, 11.1 mmol) in Et₂O (30 mL). After 1 h at room temperature, the solvent was removed under vacuum, and CH₂Cl₂ (50 mL) was added. After filtration and evaporation of the solvent the oil obtained was solidified by addition of Et₂O. After washing twice with Et₂O, 2.5 g (78%) of crude **10** was obtained as a light yellow-green solid. M.p. 140 °C (decomp); ¹H NMR (250 MHz, CDCl₃, TMS): δ = 2.9 (s, 12 H, CH₃), 4.4 (s, 4 H, CH₂), 5.2 (s, 1 H, SiH); ²⁹Si-NMR (250 MHz, CDCl₃, TMS): δ = –40.3 (d, ¹J(Si,H) = 334 Hz). IR (KBr): ν̄[cm⁻¹] = 2204.

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[23] A suspension of *N*-chlorosuccinimide (0.56 g, 4.15 mmol) in CCl₄ (15 mL) was added slowly at 0 °C to a solution of the silane **3** (b.p. 104–110 °C/0.06 Torr) (1 g, 4.15 mmol) in CCl₄ (15 mL). The mixture was then stirred for 5 h at room temperature. After the succinimide had been filtered off and the solvent removed, **4** was obtained in 85% yield; ¹H NMR (80 MHz, CDCl₃, TMS): δ = 1.85 (s, 6 H, CH₃), 3.4 (q, ²J(H,H) = 6 Hz, 2 H, CH₂), 5.5 (s, 1 H, SiH); ²⁹Si NMR (250 MHz, CDCl₃, TMS): δ = –53.6 (d, ¹J(Si,H) = 279 Hz).
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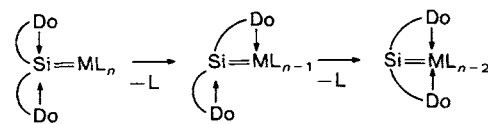
Photochemical 1,2 Shift of the Phosphane Ligands in the Silanediyl Complex [(2-Ph₂PCH₂C₆H₄)₂Si=Cr(CO)₅]*

By Hermann Handwerker, Martin Paul, Janet Blümel, and Christian Zybilla*

Dedicated to Professor Robert West on the occasion of his 65th birthday

The successive 1,2 shifts of two intramolecular donor groups from an atom A to an atom B in a molecule can be considered as a tandem reaction;^[1] in the case discussed here A=Si and B=M=Cr.

Tandem reactions of this kind permit the abstraction of weakly bonded donor groups from silicon atoms in silanediyl complexes, by migration to the metal (Scheme 1).



Scheme 1.

Thus, the 1,2 shift of phosphane or amine donor groups opens up a thermodynamically favored route to silanediyl complexes containing a three-coordinate silicon atom.^[2]

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The key silanediyl complex **1** is prepared by the reaction of the corresponding dichlorosilane with $\text{Na}_2[\text{Cr}(\text{CO})_5]$; ¹³ complex **1** is remarkable in many ways:

The single-crystal X-ray analysis of **1** (Fig. 1) shows a Cr–Si double bond length of 2.414(1) Å.^[4] The P1–Si distance (2.380(1) Å) is longer than that of the covalent P–Si bond in H_3SiPH_2 (2.25 Å), and the P2–Si distance of 3.725(1) Å is considered as nonbonding.^[5] The phosphorus atom P2 of the diphenylphosphino unit is orientated towards the silicon atom in the crystal; this configuration also corresponds to the sterically most favored arrangement of the phenyl substituents. The sum of the bond angles of the three substituents covalently bonded to the silicon atom is 352.1°.^[6]

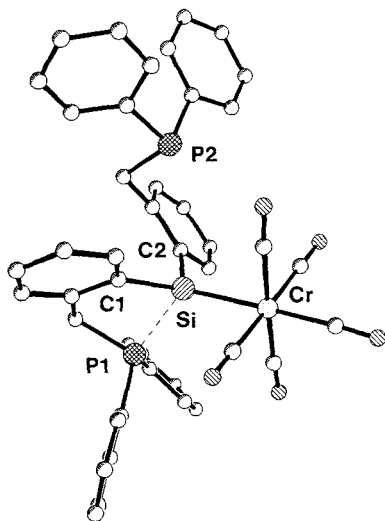


Fig. 1. Crystal structure of **1**. Selected distances [Å] and angles [°]: Cr–Si 2.414(1), P1–Si 2.380(1), P2–Si 3.725(1); C1–Si–Cr 121.8(1), C2–Si–Cr 121.0(1), C2–Si–C1 109.3(1).

A solid-state ³¹P CP-MAS NMR spectrum (CP = cross polarization, MAS = magic angle spinning) of **1** as a powder shows two distinct signals for the two phosphane ligands at $\delta = -5.3$ and 19.6 (Fig. 2).

A dynamic “flip-flop” coordination of each phosphorus atom to the silicon is observed in solution.^[7] The C_2 -sym-

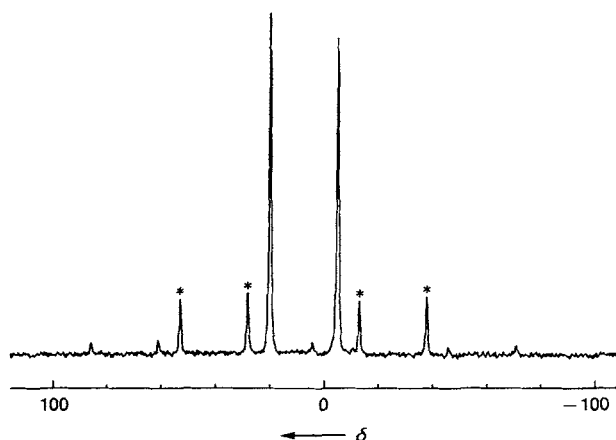
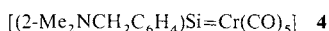


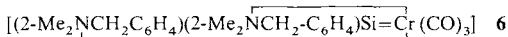
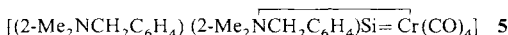
Fig. 2. Solid-state ³¹P CP-MAS NMR (121.5 MHz) spectrum of **1**, spin frequency 4 kHz, ext. standard $\delta[(\text{NH}_4)_2\text{H}_2\text{PO}_4] = 0$, contact pulse = 1 ms, 90° pulse = 4 μs. Asterisks denote spinning bands.

metrical transition state of this rapid exchange process can be detected by NMR spectroscopy (³¹P NMR: $\delta = 1.78$ (s); ²⁹Si NMR: $\delta = 73.2$ (t, $^1J(^{31}\text{P}^{29}\text{Si}) = 17.5$ Hz); ¹H NMR: $\delta = 3.20, 3.47$ (ABX system, CH_2). In the ¹³C NMR spectrum two sets of signals are found for the diphenylphosphino units. The C_6H_5 rings are diastereotopic due to the rigid tetrahedral geometry at the P atom. Therefore, in contrast to complexes with N donor groups such as **4**, the flip-flop coord-

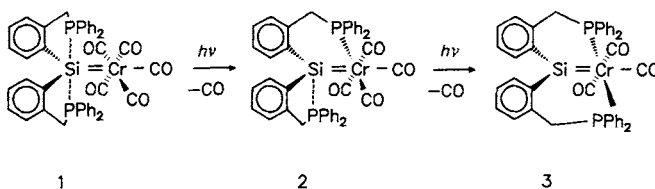


dination in **1** occurs without simultaneous inversion at the P atom. A related example with similar molecular dynamics is the stannanediyl complex $[(2\text{-Ph}_2\text{PCH}_2\text{C}_6\text{H}_4)_2\text{Sn}=\text{W}(\text{CO})_5]$ reported by Abicht and Issleib.^[3, 8] An asymmetric coordination of both phosphane or amine ligands to the silicon atom in the silanediyl complexes **1** and **4** in the ground state can be proven by the consistent results of the crystal structure analyses and variable temperature NMR studies. The two energetically degenerate ground states are interconverted via a C_2 -symmetric transition state, with the retention of configuration at the silicon atom. The C_2 -symmetric transition state is “seen” NMR spectroscopically in solution at 22 °C; the determination of the activation barrier for this exchange process has been described.^[5a, c]

The photolysis of **1** results in the direct formation of **3** in a tandem reaction (Scheme 2). In the reaction of **4** with (2-dimethylaminomethyl)phenyl ligands, the intermediate **5** of one 1,2 amine shift was isolated and characterized by a single-crystal X-ray analysis.^[5a] The product **6** of the tandem



reaction **4** → **5** → **6** is thermally labile, but can be detected by trapping reactions with MeOH or HCl.^[9a]



Scheme 2.

The rearrangement **1** → **2** → **3** (Scheme 2) proceeds more quickly by an order of magnitude, however, **2** can be observed by IR spectroscopy (2021, 1901, 1875 cm^{-1}). Finally, the (phosphino)silanediylchromium complex **3** is obtained as an extremely air-sensitive, deep red powder, and is spectroscopically fully characterized. (²⁹Si NMR: $\delta = 159.7$, see also Experimental Procedure).^[10] According to this the two phosphane ligands in **3** are arranged in a *trans* and the CO ligands in a meridional configuration. The silicon atom in **3** is three-coordinate. Photochemical 1,2 shifts of the donor ligands from silicon to the metal thus allow general access to complexes with low-coordinate silicon.

Experimental Procedure

1: A solution of bis(2-diphenylphosphinomethyl)phenyldichlorosilane (3.57 g, 5.5 mol) in THF (50 mL) was added slowly to a solution of $\text{Na}_2[\text{Cr}(\text{CO})_5]$ (1.37

g, 5.8 mmol) in THF (150 mL) at -40°C . The mixture was stirred for a further 5 h at room temperature after which the precipitated NaCl was filtered off. Compound **1** was isolated as a pale yellow powder in 34% yield. The compound was recrystallized from THF/pentane.

^1H NMR (400 MHz, CD_2Cl_2 , 25°C , TMS): $\delta = 3.20$ (dd), 3.47 (d, ABX system, $^2J(\text{HH}) = 14.0$, $^2J(\text{H}^{31}\text{P}) = 8.5$ Hz, 4H, CH_2), 6.75 (t, $^3J(\text{HH}) = 7.3$, 2H), 6.86 (d, $^3J(\text{HH}) = 7.3$, 2H), 6.97 (t, $^3J(\text{HH}) = 7.9$, 2H), 7.20–7.28 (br, 12H), 7.30–7.38 (br, 6H), 7.43 (t, $^3J(\text{HH}) = 7.0$, 2H), 7.64 (d, $^3J(\text{HH}) = 7.9$, 2H, $\text{C}_6\text{H}_5\text{P}$); ^{13}C NMR (CD_2Cl_2 , 25°C): $\delta = 33.9$ (tdd, $^1J(\text{H}^{13}\text{C}) = 126$, $^1J(\text{H}^{31}\text{P}) = 9.2$, $^1J(\text{H}^{13}\text{C}) = 3.9$, $\text{P}-\text{CH}_2$), 128.9 (dd, $^1J(\text{H}^{13}\text{C}) = 160$, $^3J(\text{H}^{31}\text{P}^{13}\text{C}) = 8.7$), 130.4 (dd, $^1J(\text{H}^{13}\text{C}) = 160$, $^2J(\text{H}^{13}\text{C}) = 8.3$, $m-\text{C}_6\text{H}_5$), 130.5 (d, $^1J(\text{H}^{13}\text{C}) = 155$), 130.8 (d, $^1J(\text{H}^{13}\text{C}) = 156$, $p-\text{C}_6\text{H}_5$), 133.3 (dd, $^1J(\text{H}^{13}\text{C}) = 161$, $^2J(\text{H}^{31}\text{P}^{13}\text{C}) = 13.5$, 133.6 (dd, $^1J(\text{H}^{13}\text{C}) = 161$, $^2J(\text{H}^{31}\text{P}^{13}\text{C}) = 14.3$, $o-\text{C}_6\text{H}_5$), 126.5 (d, $^1J(\text{H}^{13}\text{C}) = 158$), 129.3 (d, $^1J(\text{H}^{13}\text{C}) = 160$, $i-\text{C}_6\text{H}_5$), 130.8 (d, $^1J(\text{H}^{13}\text{C}) = 160$), 131.8 (dm, $^1J(\text{H}^{13}\text{C}) = 156$), 138.3 (dm, $^1J(\text{H}^{13}\text{C}) = 157$, 139.4 (dm, $^1J(\text{H}^{13}\text{C}) = 159$), 140.9 (m), 141.2 (m), 222.3 (s, CO_{ar}), 226.1 (t, $^3J(\text{H}^{31}\text{P}^{13}\text{C}) = 1.8$, CO_{al}); ^{31}P NMR (CD_2Cl_2): 1.78 (s); ^{29}Si NMR (CD_2Cl_2 , 25°C , TMS): 73.2 (t, $^1J(\text{H}^{31}\text{P}^{29}\text{Si}) = 17.5$). IR (CH_2Cl_2): $\tilde{\nu}[\text{cm}^{-1}] = 2038$ (s), 1981 (w), 1912 (ss, br). Correct elemental analysis (C, H, P). M.p. 156°C .

3: **1** (0.26 g, 0.3 mmol) was suspended in methylcyclohexane (100 mL) in a quartz Schlenk tube at -30°C and photolyzed at 254 nm (Hg low-pressure lamp) for 30 h. The color of the suspension changed from pale yellow to dark red. After removal of the solvent, **3** was obtained (171 mg) as a red powder in 80% yield.

^1H NMR (400 MHz, CD_2Cl_2 , 25°C , TMS): $\delta = 2.3$ (s, 2H, CH_2), 7.6–7.1 (m, 14H, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C , TMS): $\delta = 36.2$ (d, $^1J(\text{H}^{31}\text{P}^{13}\text{C}) = 8.7$, CH_2), 129.3 (d, $^3J(\text{H}^{31}\text{P}^{13}\text{C}) = 8.5$), 132.5 (s), 134.1 (d, $^2J(\text{H}^{31}\text{P}^{13}\text{C}) = 12.1$), 142.1 (d, $^1J(\text{H}^{31}\text{P}^{13}\text{C}) = 5.1$, C_6H_5), 220.1 (t, $^2J(\text{H}^{31}\text{P}^{13}\text{C}) = 5.2$, CO), 227.1 (t, $^2J(\text{H}^{31}\text{P}^{13}\text{C}) = 9.2$, CO); ^{31}P NMR (CD_2Cl_2 , 49.2 (s); ^{29}Si NMR (CD_2Cl_2 , 159.7 (t, $^2J(\text{H}^{31}\text{P}^{29}\text{Si}) = 12$ Hz). IR (methylcyclohexane): $\tilde{\nu}[\text{cm}^{-1}] = 2038$ (s), 1988 (s) (νCO), MS (70 eV): $m/z = 714$ (M^+ for $\text{C}_{44}\text{H}_{32}\text{CrO}_5\text{P}_2\text{Si}$ with correct isotope distribution, 5%), 686 ($M^+ - \text{CO}$, 1.5%), 658 ($M^+ - 2\text{CO}$, 0.9%), 630 ($M^+ - 3\text{CO}$, 0.8%). M.p. 148°C . Correct elemental analysis (C, H, P).

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[3] The synthesis of lithiated phosphane precursors was first described by Issleib et al.: H. P. Abicht, K. Issleib, *Z. Anorg. Allg. Chem.* **1976**, *422*, 237.
[4] **1**: Crystallographic data: $\text{C}_{43}\text{H}_{32}\text{CrO}_5\text{P}_2\text{Si}$ ($0.4 \times 0.45 \times 0.4$ mm) $M_r = 770.76$, triclinic $P\bar{1}$ (no. 2), $a = 11.795(1)$, $b = 12.225(1)$, $c = 15.051(1)$ Å, $V = 1890.0$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.35$ g cm⁻³, $\mu(\text{MoK}\alpha) = 4.52$ cm⁻¹, $F(000) = 800$ e. Measurement parameters: Enraf-Nonius CAD4-Turbo, $T = 23^{\circ}\text{C}$. 5928 measured reflections ($13 \pm 13 \pm 17$ hkl), of which three reflections were discarded and 4623 unique reflections with $F_0 > 3\sigma(F_0)$ were used for the refinement. Decomposition (56 h, -1.8%), no decomposition, extinction, or absorption corrections were carried out. Structure solution: direct methods (SHELX86), 597 parameters, Refinement: full matrix least squares ($R = [\sum |F_0| - |\sum F_c|] / \sum |F_0|$, $R_w = [\sum (|F_0| - |F_c|)^2] / [\sum w(F_0 - F_c)^2]$, $w = 1/[\sigma^2(F_0) + kF_c^2]$, $k = 0.00$, $l = 2.5090$, $R = 0.038$, $R_w = 0.027$, all heavy atoms were refined with anisotropic and all hydrogen atoms with isotropic displacement parameters; residual electron density $+0.22/-0.20$ e Å⁻³. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-57430, the names of the authors, and the journal citation.
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Metal-Initiated Coupling of C_2 Units to Enynes and Butatrienes: Two Different Routes for the Dimerization of 1-Alkynes**

By Martin Schäfer, Norbert Mahr, Justin Wolf, and Helmut Werner*

Dedicated to Professor Reinhard W. Hoffmann on the occasion of his 60th birthday

It has recently been shown that the dimerization of 1-alkynes to enynes with electron-rich transition-metal compounds as catalysts can occur either by alkynyl–vinyl or alkynyl–vinylidene coupling.^[1] The enyne is liberated, sometimes stereoselectively, from the enynyl metal complexes formed as intermediates, on treatment with an additional molecule of the 1-alkyne $\text{RC}\equiv\text{CH}$. Furthermore, Wakatsuki et al. observed^[2] that the dimerization of $t\text{BuC}\equiv\text{CH}$ with $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ as catalyst does not lead to the enyne $t\text{BuC}\equiv\text{CCH}=\text{CH}t\text{Bu}$ but, surprisingly, to the isomeric butatriene (Z)- $t\text{BuCH}=\text{C}=\text{CH}t\text{Bu}$. The authors postulated that in this case an enynyl complex is also formed as intermediate which is in equilibrium with the σ -butatrienyl metal species that affords the butatriene. Using alkynyl(vinylidene)rhodium compounds as starting materials, we have now succeeded in preparing not only enyne but also enynyl metal complexes which react with acids HX to give, predominantly either enynes or butatrienes, depending on the strength of HX .

The key to success is the η^3 -benzylrhodium(I) compound **2**. It is formed in the same way as the derivative **3**^[3] on treatment of **1** with the appropriate Grignard reagent; the yield in both cases is about 80%. In solution, **2** and **3** show fluxional behavior. At low temperatures, a suprafacial rearrangement takes place,^[4,5] which is shown by the equivalence of the benzylic protons and of the ring protons in *ortho* and *meta* position; at higher temperatures a σ -to- π conversion^[6] occurs in addition to the suprafacial rearrangement, which is confirmed by the equivalence of the phosphane ligands. During this process, the coordinatively unsaturated intermediate $[\text{Rh}(\eta^1-\text{CH}_2\text{C}_6\text{H}_4\text{R})(\text{PiPr}_3)_2]$ is generated. Its formation explains why compound **2**, in contrast to the related allyl complex $[\text{Rh}(\eta^3-\text{C}_3\text{H}_5)(\text{PiPr}_3)_2]$,^[7] smoothly reacts with $\text{PhC}\equiv\text{CH}$ and $t\text{BuC}\equiv\text{CH}$ to give **4** and **5**, respectively. The addition of NEt_3 to the reaction mixture facilitates the formation of the alkynyl(vinylidene) species. If the reaction of **2** is carried out with phenylacetylene in pentane at -40°C , the alkyne(alkynyl)rhodium(I) intermediate **6** can be isolat-

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