

## Carbon-Hydrogen Bond Activation by a Nickel Complex for the Catalytic Formation of Diene Systems

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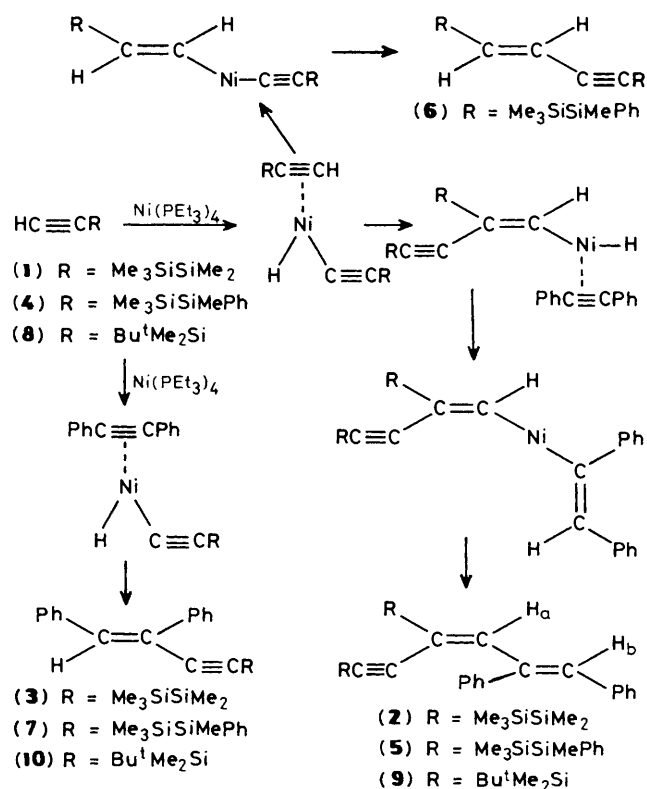
The reaction of ethynyl-substituted mono- and di-silanes with tolan in the presence of a catalytic amount of Ni(PEt<sub>3</sub>)<sub>4</sub> affords dienyne.

During the course of our studies on the transition-metal catalysed formation of unsaturated silicon compounds,<sup>1-3</sup> we found that the nickel-catalysed reactions of ethynyl-substituted disilanes in the presence of tolan afforded a diene system. Thus, heating a benzene solution of a 1:1 mixture of ethynylpentamethyldisilane (**1**) and tolan in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) at 100 °C for 20 h gave a diene whose spectral data identified it as (*E,E*)-bis(pentamethyldisilanyl)-5,6-diphenylhexa-3,5-dien-1-yne (**2**)<sup>†</sup> in 60% yield, in addition to a small amount of

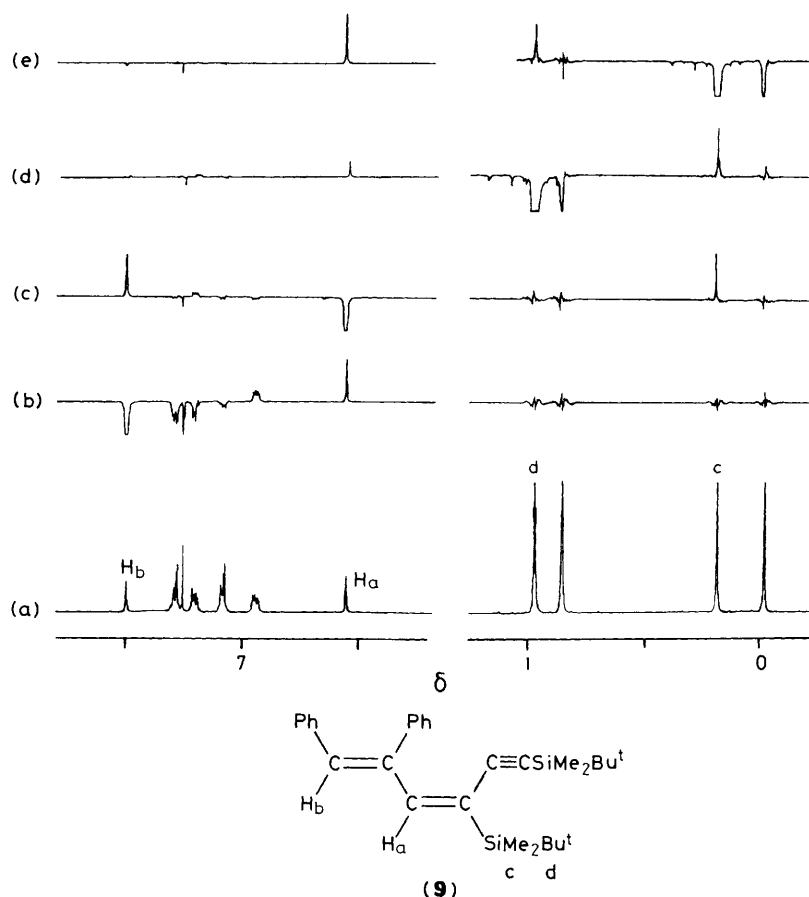
<sup>†</sup> All new compounds gave satisfactory analytical and spectroscopic data. Selected data for compound (**2**): 400 MHz <sup>1</sup>H n.m.r., δ (CDCl<sub>3</sub>) 0.05 (9H, s, Me<sub>3</sub>Si), 0.07 (6H, s, Me<sub>2</sub>Si), 0.14 (9H, s, Me<sub>3</sub>Si), 0.25 (6H, s, Me<sub>2</sub>Si), 6.50 (1H, d, *J* 0.73 Hz, H<sub>a</sub>), 6.93–7.32 (10H, m, ring protons), 7.37 (1H, br. s, H<sub>b</sub>); <sup>13</sup>C n.m.r., δ (CDCl<sub>3</sub>) -4.2, -2.6, -2.4, -1.8 (C-Si), 107.5, 107.9 (C≡C), 127.0, 127.3, 127.8, 128.5, 129.6, 129.7, 130.7, 132.3, 136.9, 140.1, 140.3, 147.1 (ring carbons and olefinic carbons); m.s., *m/z* 490 (*M*<sup>+</sup>); i.r., ν<sub>C≡C</sub> 2100 cm<sup>-1</sup>.

Compound (**5**): 100 MHz <sup>1</sup>H n.m.r. δ (CCl<sub>4</sub>) -0.04 (9H, s, Me<sub>3</sub>Si), 0.18 (9H, s, Me<sub>3</sub>Si), 0.28 (3H, s, MeSi), 0.53 (3H, s, MeSi), 6.55 (1H, br. s, H<sub>a</sub>), 6.71–7.71 (21H, m, ring protons and H<sub>b</sub>); <sup>13</sup>C n.m.r., δ (CDCl<sub>3</sub>) -5.2, -3.9, -2.3, -1.3 (C-Si), 105.3, 108.7 (C≡C), 127.0–129.9 (*o*-, *m*-, and *p*-carbons for four phenyl rings), 134.2, 134.8, 137.4, 140.7, 141.7, 147.3 (*ipso* carbons and olefinic carbons); m.s., *m/z* 614 (*M*<sup>+</sup>); i.r., ν<sub>C≡C</sub> 2100 cm<sup>-1</sup>.

Compound (**9**): 400 MHz <sup>1</sup>H n.m.r., δ (CDCl<sub>3</sub>) -0.02 (6H, s, Me<sub>2</sub>Si), 0.18 (6H, s, Me<sub>2</sub>Si), 0.85 (9H, s, Bu<sup>t</sup>), 0.97 (9H, s, Bu<sup>t</sup>), 6.55 (1H, d, *J* 0.87 Hz, H<sub>a</sub>), 6.93–7.31 (10H, m, ring protons), 7.50 (1H, br. s, H<sub>b</sub>); <sup>13</sup>C n.m.r., δ (CDCl<sub>3</sub>) -6.1, -4.3 (C-Si), 16.7, 17.9 (C-Me), 26.3, 26.9 (Me<sub>3</sub>C), 106.9, 107.1 (C≡C), 127.1, 127.4, 127.8, 128.5, 129.5, 129.8, 130.7, 132.7, 136.9, 138.5, 139.9, 149.6 (phenyl and olefinic carbons); m.s., *m/z* 458 (*M*<sup>+</sup>); i.r. ν<sub>C≡C</sub> 2100 cm<sup>-1</sup>.



Scheme 1



**Figure 1.** N.O.e.-f.i.d. difference spectra of compound (9): (a) 400 MHz  $^1\text{H}$  n.m.r. spectrum of (9) in  $\text{CDCl}_3$ ; (b) irradiation of  $\text{H}_b$  proton; (c) irradiation of  $\text{H}_a$  proton; (d) irradiation of t-butyl protons; (e) irradiation of dimethylsilyl protons.

an enyne,<sup>4-8</sup> (*E*)-(pentamethyldisilanyl)-3,4-diphenylbut-3-en-1-yne (**3**) (9%).

Similar nickel-catalysed reaction of 1-ethynyl-1-phenyl-tetramethyldisilane (**4**) with tolan under the same conditions afforded (*E,E*)-1,3-bis(tetramethylphenyldisilanyl)-5,6-diphenyl-3,5-dien-1-yne (**5**) in 60% yield, in addition to the homo-coupling product (**6**) (10%) and the cross-coupling product (**7**) (8%).

Ethynyl-substituted monosilanes also react with tolan to give the dienyne system, analogous to the reaction of the ethynyldisilanes. When a 1:1 mixture of ethynyl-t-butyl-dimethylsilane (**8**) and tolan was heated in the presence of the nickel(0) catalyst at 100°C, (*E,E*)-1,3-bis(t-butyl-dimethylsilyl)-5,6-diphenylhexa-3,5-dien-1-yne (**9**) was obtained in 49% yield, in addition to (*E*)-1-t-butyl-dimethylsilyl-3,4-diphenyl-3-en-1-yne (**10**) (15%). All products were isolated by l.p.c. In all cases, only a single regio- and stereo-isomer is observed for the dienyne system. The (*E,E*)-geometry of products (**2**), (**5**), and (**9**) was easily established from their nuclear Overhauser effect-free induction decay (n.o.e.-f.i.d.) difference spectra. Figure 1 shows the results of n.o.e. experiments for product (**9**) as a typical example.

Scheme 1 illustrates a possible mechanistic interpretation. The formation of the dienyne system requires activation of a carbon-hydrogen bond, followed by successive formation of two carbon-carbon bonds. In fact, the reaction of 1,3-bis(pentamethyldisilanyl)but-3-en-1-yne (**11**) prepared by an

independent route with tolan in the presence of  $\text{Ni}(\text{PEt}_3)_4$  under the same conditions gave no dienyne system, but the starting (**11**) was recovered unchanged.

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