

The palladium catalyzed synthesis of substituted phenylethynylpentamethyldisilanes and phenylethynylheptamethyltrisilanes

Keith A. Horn, Robert B. Grossman and Anne A. Whitenack

Engineered Materials Sector, Allied-Signal Corporation, Morristown, NJ 07960 (U.S.A.)

(Received February 27th, 1987)

Abstract

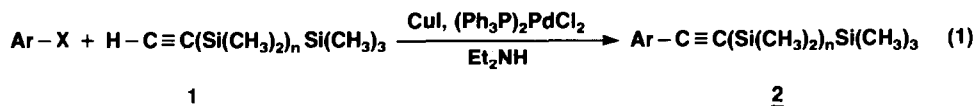
Bis(triphenylphosphine)palladium(II) chloride-cuprous iodide or tetrakis(triphenylphosphine)palladium(0)-cuprous iodide catalyze the formation of phenylethynylpentamethyldisilanes from substituted bromo- or iodo-benzenes and ethynylpentamethyldisilane. Concurrent silicon-silicon bond cleavage is not observed. The synthesis of 4-cyanophenylethynylheptamethyltrisilane from 4-bromobenzonitrile and ethynylheptamethyltrisilane was also demonstrated.

Introduction

The phenylethynylpermethylpolysilanes are valuable precursors for the preparation of silacyclopropenes and silapropadienes [1-7]. Additional interest in the availability of the phenylethynylpolysilanes has arisen since detailed photochemical investigations have shown that phenylethynylpentamethyldisilane possesses unique charge-transfer emission characteristics [8]. However, methodology for the synthesis of phenylethynylpolysilanes has been limited to the reaction of lithium and magnesium acetylides with polysilanyl-mono- or -di-chlorides [9-15]. Thus severe restrictions are placed on the functional groups which may be incorporated and, in particular, nitrile, carbomethoxy, nitro, and keto functionalized phenylethynylpolysilanes cannot be synthesized by this route. We now report that good to excellent yields of substituted phenylethynylpentamethyldisilanes can be obtained by the reaction of iodo- or bromo-benzenes with ethynylpentamethyldisilane in the presence of catalytic amounts of bis(triphenylphosphine)palladium(II) chloride-cuprous iodide. Similar systems have been used by Cassar [16], Heck [17], and Hagihara [18,19] to prepare a variety of substituted arylacetylenes.

Results and discussion

As illustrated in eq. 1, a typical procedure for the synthesis of a substituted phenylethynylpentamethyldisilane involves the addition of 1–2 mol% bis(triphenylphosphine)palladium(II) chloride and 0.5–1.0 mol% of cuprous iodide to a solution of the starting aryl halide and ethynylpentamethyldisilane in diethylamine. The reaction is stirred at 23° C for 18 h under nitrogen, concentrated in vacuo and the product purified by chromatography on silica gel. Generally a slight excess of

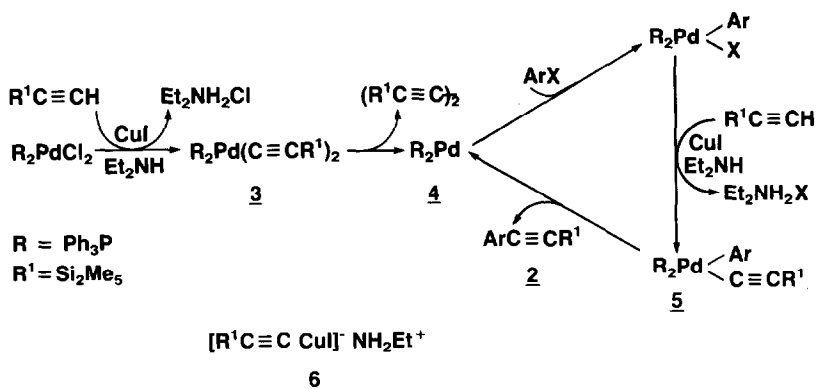


X = I, Br

ethynylpentamethyldisilane is used since 1,4-bis(pentamethyldisilanyl)-1,3-butadiene is formed as a by-product through reductive elimination from a palladium-acetylide complex (vide infra). Si–Si bond cleavage was not observed in either the ethynylpentamethyldisilane or the product phenylethynylpentamethyldisilanes even though both bis(triphenylphosphine)palladium(II) chloride and tetrakis(triphenylphosphine)palladium(0) have been shown to effect the facile cleavage of polysilanes [20–22]. Thus, the mild reaction conditions and the ease of work-up allow the routine preparation of multi-gram quantities of highly substituted phenylethynylpentamethyldisilanes.

As shown in Table 1, a wide range of substituted halobenzenes is acceptable, and high yields are realized with either electron-donating substituents or electron-withdrawing substituents (compare 4-iodoanisole and 4-iodomethylbenzoate, entries 1 and 5 of Table 1) or with substitution patterns involving both types of substituents (2,6-diodo-4-nitroanisole, entry 9). Polynuclear aromatics can also be used as is demonstrated by the synthesis of 2-naphthylethynylpentamethyldisilane (entry 10). In addition, *ortho*, *meta* and *para* halogen substitution all result in facile reaction and excellent yields. The reactivity and selectivity order for the halogens is I > Br >> Cl. Thus the aryl iodides are markedly superior to the aryl bromides both in rate of product formation and product yield, and the extent of selectivity evidenced between aryl iodides and aryl chlorides is sufficient so that 4-iodochlorobenzene reacts exclusively at the site of iodine substitution (entry 4). Tetrakis(triphenylphosphine)palladium(0) can be used in lieu of bis(triphenylphosphine)palladium(II) chloride with little or no effect on product yield (entry 6). We have found it to be somewhat more convenient to use the palladium(II) catalyst because of its greater stability. Ethynylheptamethyltrisilane can also be used to prepare substituted phenylethynylheptamethyltrisilanes as demonstrated by the synthesis of 4-cyanophenylethynylheptamethyltrisilane (entry 11) in 60% yield from 4-bromobenzonitrile and ethynylheptamethyltrisilane.

A plausible mechanism for the reaction is shown in Scheme 1. Initial formation of bis(ethynylpentamethyldisilanyl)bis(triphenylphosphine)palladium (**3**) followed by reductive elimination of 1,4-bis(pentamethyldisilanyl)-1,3-butadiene generates a bis(triphenylphosphine)palladium(0) complex (**4**) as the active catalytic species. An alkynyl copper ate complex (**6**) may be involved in the formation of the initial alkyne-palladium complex since the reaction does not proceed in the absence of



Scheme 1

cuprous iodide and since similar ate complexes have been previously observed in the presence of Bu_4NI and palladium complexes [23,24]. Oxidative addition of the aryl halide to the palladium(0) complex (4) and alkynylation of the resulting adduct would then give the arylethynylpalladium(II) adduct (5). The bis(triphenylphosphine)palladium(0) complex is then regenerated by reductive elimination of the product arylethynylpentamethyldisilane. This mechanism is consistent with the observations that no substitution or coupling takes place in the absence of cuprous iodide, that 1,4-bis(pentamethyldisilanyl)-1,3-butadiyne is isolated as a by-product and that tetrakis(triphenylphosphine)palladium(0)-cuprous iodide efficiently catalyzes the substitution reaction. The yield of 1,4-bis(pentamethyldisilanyl)-1,3-butadiyne isolated in each case (ca. 10% based on the amount of ethynylpentamethyldisilane used) represents ca. 2.5 times the molar quantity of the catalyst, bis(triphenylphosphine)palladium(II) chloride, used. In the absence of aryl halide, higher molar ratios are obtained (ca. 4 times the molar quantity of catalyst). An additional oxidative coupling route not shown in Scheme 1 is therefore operative. Formation of a dialkyne-palladium complex as a competing reaction in the catalytic cycle may be involved since tetrakis(triphenylphosphine)palladium(0)-cuprous iodide also catalyzes the formation of 1,4-bis(pentamethyldisilanyl)-1,3-butadiyne.

We are currently examining the photophysical properties of these functionalized phenylethynylpermethylpolysilanes.

Experimental

General

NMR spectral data were obtained with a Varian Associates XL200 200 MHz spectrometer. ^1H and ^{29}Si chemical shifts are reported relative to internal TMS in deuteriochloroform and all ^{13}C chemical shifts are referenced to deuteriochloroform. The electron impact mass spectral data (70 eV) were obtained with a Finnigan Model 3300 instrument using direct probe sample introduction. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tennessee.

Chloropentamethyldisilane was prepared by the procedure of Kumada et al. [25] (**Caution!** Several violent exotherms occurred during the distillation of samples of

chloropentamethyldisilane. These resulted in rapid temperature increases to greater than 220 °C in the distillation head.) Ethynylpentamethyldisilane [26] was prepared by the reaction of ethynylmagnesium bromide and chloropentamethyldisilane according to the procedure reported for ethynyltrimethyldisilane [27]. Bis(triphenylphosphine)palladium(II) chloride and tetrakis(triphenylphosphine)palladium(0) were purchased from the Aldrich Chemical Company, Inc., and used without further purification. 4-Iodomethylbenzoate was prepared either by the esterification of 4-iodobenzoic acid or by the reaction of methanol with 4-iodobenzoyl chloride. 2,6-Diiodo-4-nitroaniline was obtained from Lancaster Synthesis Ltd. All other starting aryl halides were purchased from the Aldrich Chemical Company, Inc., and used as received.

General synthetic procedure for arylolethynylpentamethyldisilanes: 4-carbomethoxyphenylethynylpentamethyldisilane

Bis(triphenylphosphine)palladium(II) chloride (74 mg, 0.11 mmol) and cuprous iodide (9 mg, 0.05 mmol) were added to a solution of 4-iodomethylbenzoate (1.13 g, 4.3 mmol) and ethynylpentamethyldisilane (0.81 g, 5.2 mmol) in 25 ml of diethylamine. The reaction was stirred for 18 h under nitrogen at 23 °C. Concentration in vacuo and chromatography (silica gel, 5% ether/hexanes) gave 4-carbomethoxyphenylpentamethyldisilane (1.16 g, 4.0 mmol, 92%). Recrystallization from ethanol gave white needles of m.p. 64.5–66.0 °C.

Phenylethynylpentamethyldisilane [8]

Yield: 68%, colorless oil after chromatography (silica gel, hexanes). All spectral properties were identical with the reported values.

4-Methoxyphenylethynylpentamethyldisilane

Yield: 96%, oil after chromatography (silica gel, 10% ether in hexanes). ¹H NMR δ (ppm): 7.36, 6.8 (AA'BB'q, 4H), 3.77 (s, 3H), 0.23 (s, 6H), 0.13 (s, 9H). ¹³C NMR δ (ppm): 159.60, 133.38, 115.68, 113.79, 107.32, 91.33, 55.23, -2.49, -2.89. ²⁹Si NMR δ (ppm): -18.70, -37.03. IR (cm⁻¹) neat film: 2978m, 2080m, 1615m, 1520s, 1250s, 1040m, 855s, 835s, 800s. MS (*m/e*): *M*⁺ = 262, 189 (*M*⁺ - Si(CH₃)₃), 174, 73. The oxidative instability of 4-methoxyphenylethynylpentamethyldisilane as a neat oil precluded elemental analysis.

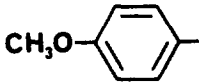
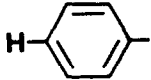
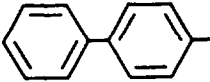
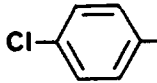
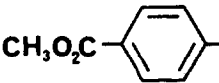
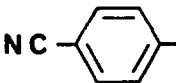
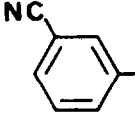
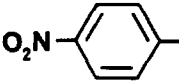
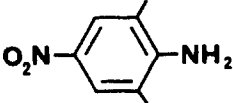
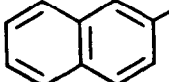
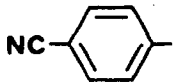
Biphenylethynylpentamethyldisilane

Yield: 54% after chromatography (silica gel, hexanes), clear platelets from ethanol, m.p. 64–66 °C. ¹H NMR δ (ppm): 7.65–7.28 (m, 9H), 0.27 (s, 6H), 0.16 (s, 9H). ¹³C δ (ppm): 140.99, 140.34, 132.3, 128.8, 127.58, 127.0, 126.8, 122.38, 107.14, 93.94, -2.50, -2.99. ²⁹Si NMR δ (ppm): -18.58, -36.64. IR (cm⁻¹), KBr: 2975m, 2080m, 1480m, 1405w, 1245s, 845s, 800s, 765s, 720m, 690s. MS (*m/e*): *M*⁺ = 308, 293 (*M*⁺ - CH₃), 235 (*M*⁺ - Si(CH₃)₃), 217, 211, 205, 181, 165, 73. Anal. Found: C, 73.80. H, 7.93. C₁₉H₂₄Si₂ calcd.: C, 73.96. H, 7.84%.

4-Chlorophenylethynylpentamethyldisilane

Yield: 100%, oil, white needles from the oil, m.p. 28–28.5 °C. ¹H NMR δ (ppm): 7.35, 7.24 (AA'BB', q, 4H), 0.24 (s, 6H), 0.13 (s, 9H). ¹³C NMR δ (ppm): 134.28, 133.10, 128.52, 121.97, 105.98, 94.50, -2.50, -3.08. ²⁹Si NMR δ (ppm): -18.55,

Table 1
Synthesis of arylethynylpermethylpolysilanes 2

| Entry | ArX ^a 1 | X | n | Catalyst ^b | Yield of 2 ^c (%) |
|-------|---|----|---|-----------------------|--------------------------------|
| 1 |  | I | 1 | A | 96 |
| | | Br | 1 | A | 38 |
| 2 |  | I | 1 | A | 68 |
| 3 |  | Br | 1 | A | 54 |
| 4 |  | I | 1 | A | 100 ^d |
| 5 |  | I | 1 | A | 92 |
| 6 |  | Br | 1 | A | 48 |
| | | Br | 1 | B | 86 |
| 7 |  | Br | 1 | A | 50 |
| 8 |  | Br | 1 | A | 51 |
| 9 |  | I | 1 | A | 56 |
| 10 |  | Br | 1 | A | 55 |
| 11 |  | Br | 2 | A | 60 |

^a All reactions run at 23°C on a scale of ≥ 4 mmol of starting aryl halide. ^b A = bis(triphenylphosphine)palladium dichloride/CuI; B = tetrakis(triphenylphosphine)palladium/CuI. ^c Yields represent unoptimized yields of isolated pure compounds. ^d Yield based on the limiting reagent 4-chloroiodobenzene and determined by integration of the ¹H NMR of the product after removal of the catalyst by filtration. 1,4-Bis(pentamethyldisilanyl)-1,3-butadiyne from coupling of the excess ethynylpentamethyldisilane was also present ($\leq 13\%$)

– 36.49. IR (cm^{-1}) neat film: 2975m, 2080m, 1485s, 1245s, 1095s, 1020m, 830s, 800s, 780m, 695s, MS (m/e): $M^+ = 266, 268, 251, 253$ ($M^+ - \text{CH}_3$), 193 ($M^+ - \text{Si}(\text{CH}_3)_3$), 158, 73. Anal. Found: C, 58.47. H, 7.17. $\text{C}_{13}\text{H}_{19}\text{ClSi}_2$ calcd.: C, 58.49, H, 7.18%.

4-Carbomethoxyphenylethynylpentamethyldisilane

Yield: 92% after chromatography (silica gel, 5% ether in hexanes), needles from ethanol, m.p. 64.5–66°C. ^1H NMR δ (ppm): 7.95, 7.48 (AA'BB', q, 4H), 3.90 (s, 3H), 0.26 (s, 6H) 0.15 (s, 9H). ^{13}C NMR δ (ppm): 166.48, 131.74, 129.45, 129.34, 128.10, 106.23, 97.00, –2.56, –3.19. ^{29}Si NMR δ (ppm): –18.50, –36.26. IR (cm^{-1}) neat film: 2975m, 2075w, 1715s, 1600m, 1435m, 1280s, 1245s, 855s, 835s, 810s. MS (m/e): $M^+ = 290, 289$ ($M^+ - \text{H}$), 275 ($M^+ - \text{CH}_3$), 217 ($M^+ - \text{Si}(\text{CH}_3)_3$) 158, 73. Anal. Found: C, 61.93. H, 7.89. $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Si}_2$ calcd.: C, 62.02. H, 7.63%.

4-Cyanophenylethynylpentamethyldisilane

Yield: 86% after chromatography (silica gel, 5% ether in hexanes), white needles, m.p. 47.5–49.5°C. ^1H NMR δ (ppm): 7.58, 7.47 (AA'BB', q, 4H), 0.26 (s, 6H), 0.15 (s, 9H). ^{13}C NMR δ (ppm): 132.3, 131.9, 128.27, 118.47, 111.51, 105.14, 99.04, –2.55, –3.29. ^{29}Si NMR δ (ppm): –18.4, –35.9. IR (cm^{-1}) neat film from CHCl_3 : 2970m, 2110m, 2070w, 1600m, 1495m, 1250s, 840s, 800m. MS (m/e): $M^+ = 257, 242$ ($M^+ - \text{CH}_3$) 184 ($M^+ - \text{Si}(\text{CH}_3)_3$), 154, 130, 73. Anal. Found: C, 64.76. H, 7.18. N, 5.52. $\text{C}_{14}\text{H}_{19}\text{NSi}_2$ calcd.: C, 65.31. H, 7.44. N, 5.44%.

3-Cyanophenylethynylpentamethyldisilane

Yield: 62%, oil after chromatography (silica gel, 5% ether in hexanes). ^1H NMR δ (ppm): 7.72–7.67 (m, 1H), 7.66–7.52 (m, 3H), 7.44–7.33 (m, 1H), 0.25 (s, 6H), 0.14 (s, 9H). ^{13}C NMR δ (ppm): 135.77, 135.09, 131.30, 129.05, 124.98, 117.96, 112.67, 104.33, 96.72, –2.50, –3.19. ^{29}Si NMR δ (ppm): –18.49, –36.00. IR (cm^{-1}) neat film: 2990s, 2120s, 2075w, 1590m, 1570m, 1475s, 1410m, 1245s, 920s, 835s, 800s. MS (m/e) CI (methane): $M\text{H}^+ = 258, 286, 298$ (addition ions), 184 ($M\text{H}^+ - \text{Si}(\text{CH}_3)_3$), 155, 73. Anal. Found: C, 65.74. H, 7.36. N, 5.44. $\text{C}_{14}\text{H}_{19}\text{NSi}_2$ calcd.: C, 65.31. H, 7.44. N, 5.44%.

4-Nitrophenylethynylpentamethyldisilane

Yield: 51% after chromatography (silica gel, elution with hexanes followed by 10% ether in hexanes) light yellow crystals, m.p. 72.5–75.5°C. ^1H NMR δ (ppm): 8.14, 7.55 (AA'BB', q, 4H), 0.27 (s, 6H), 0.15 (s, 9H). ^{13}C NMR δ (ppm): 146.97, 132.55, 130.27, 123.45, 104.89, 100.20, –2.58, –3.33. ^{29}Si NMR δ (ppm): –18.33, –35.77. IR (cm^{-1}) KBr: 2960m, 1590s, 1518s, 1345s, 1250s, 1110m, 860s, 850s, 840s, 820s. MS (m/e): $M^+ = 277, 262$ ($M^+ - \text{CH}_3$), 232, 204 ($M^+ - \text{Si}(\text{CH}_3)_3$), 203, 188, 173, 158, 143, 73. Anal. Found: C, 56.07. H, 7.13. N, 5.14. $\text{C}_{13}\text{H}_{19}\text{NO}_2\text{Si}_2$ calcd.: C, 56.27. H, 6.90. N, 5.05%.

Bis-2,6-(pentamethyldisilanylethynyl)-4-nitroaniline

Yield: 56% after chromatography (silica gel, 25% methylene chloride in hexanes), tan needles from ethanol, m.p. 74.5–76.5°C. ^1H NMR δ (ppm): 8.12 (s, 2H), 5.5 (broad, 2H), 0.30 (s, 6H), 0.16 (s, 9H). ^{13}C NMR δ (ppm): 153.76, 137.49, 128.11, 107.04, 102.04, 100.53, –2.56, –3.11. ^{29}Si NMR δ (ppm): –18.70, –35.84. IR

(cm^{-1}) KBr: 3250w, 3195w, 2980w, 2075w, 1510m, 1605m, 1340s, 1245m, 840s, 800s. MS (m/e): $M^+ = 446$ (less than 1% relative abundance), 431 ($M^+ - \text{CH}_3$), 254, 73. CI/MS $MH^+ = 447$, $M^+ = 446$, 431 ($MH^+ - \text{CH}_4$), 316 ($MH^+ - \text{Si}_2(\text{CH}_3)_5$), 73. Anal Found: C, 53.42. H, 7.80. N, 6.31. $\text{C}_{20}\text{H}_{34}\text{N}_2\text{O}_2\text{Si}_4$ calcd.: C, 53.76. H, 7.67. N, 6.27%.

2-Naphthylethynylpentamethyldisilane

Yield: 55% after chromatography (silica gel, hexanes), oil. ^1H NMR δ (ppm): 7.96 (s, 1H), 7.82–7.70 (m, 3H), 7.52–7.41 (m, 3H), 0.29 (s, 6H), 0.17 (s, 9H). ^{13}C NMR δ (ppm): 132.96, 132.86, 128.68, 127.86, 127.79, 126.67, 126.54 (2 carbons), 120.84, 107.67, 93.68, –2.41, –2.90. ^{29}Si NMR δ (ppm): –18.55, –36.61. IR (cm^{-1}) neat film: 3030w, 2980m, 2075m, 1600w, 1505w, 1250s, 960m, 900m, 840s, 800s, 770m, 745s. MS (m/e): $M^+ = 282$, 267 ($M^+ - \text{CH}_3$), 209 ($M^+ - \text{Si}(\text{CH}_3)_3$), 179, 73. Anal Found: C, 71.97. H, 8.04. $\text{C}_{17}\text{H}_{22}\text{Si}_2$ calcd.: C, 72.27. H, 7.85%.

4-Cyanophenylethynylheptamethyltrisilane

4-Bromobenzonitrile (0.87 g, 4.8 mmol) and ethynylheptamethyltrisilane [28] (0.85 g, 4.0 mmol) was dissolved in 20 ml of diethylamine. To this solution was added bis(triphenylphosphine)palladium(II) chloride (109 mg, 0.16 mmol) and cuprous iodide (8 mg, 0.04 mmol). The reaction was stirred under nitrogen at room temperature overnight. Concentration in vacuo followed by chromatography on silica gel (eluant, 10% ether in hexanes, $R_f = 0.50$) gave 0.74 g (2.3 mmol, 59%) of a colorless liquid. ^1H NMR δ (ppm): 7.48, 7.56 (AA'BB', q, 4H), 0.29 (s, 6H), 0.16 (s, 6H), 0.12 (s, 9H), ^{13}C NMR δ (ppm): 132.16, 131.84, 128.20, 118.37, 111.47, 105.29, 99.45, –1.46, –2.32, –7.02. ^{29}Si NMR δ (ppm): –15.75, –33.32, –47.15. MS (m/e): $M^+ = 315$, 300 ($M^+ - \text{CH}_3$), 242 ($M^+ - \text{Si}(\text{CH}_3)_3$), 184, 116, 73. IR (cm^{-1}) neat film: 2975m, 2120m, 2080w, 1605m, 1500m, 1250s, 840s, 785s. The instability of 4-cyanophenylethynylheptamethyltrisilane as a neat oil precluded elemental analysis.

Coupling of ethynylpentamethyldisilane with bis(triphenylphosphine)palladium(II) chloride

Ethynylpentamethyldisilane (320 mg, 2.04 mmol) bis(triphenylphosphine)palladium(II) chloride (30 mg, 0.04 mmol) and cuprous iodide (4 mg, 0.02 mmol) were stirred in 10 ml of diethylamine for 24 h. Concentration in vacuo and chromatography on silica gel (eluant hexanes) gave 1,4-bis(pentamethyldisilanyl)-1,3-butadiyne [12] (0.053 g, 0.17 mmol).

Acknowledgements

The authors are grateful to W.B. Hammond for providing 200 MHz NMR spectral data.

References and notes

- 1 M. Ishikawa, T. Fuchikami and M. Kumada, *J. Chem. Soc., Chem. Commun.*, (1977) 352.
- 2 M. Ishikawa, T. Fuchikami and M. Kumada, *J. Organomet. Chem.*, 142 (1977) C45.
- 3 M. Ishikawa, T. Nakagawa and M. Kumada, *J. Organomet. Chem.*, 131 (1977) C15.

- 4 M. Ishikawa, K. Nishimura, H. Sugisawa and M. Kumada, *J. Organomet. Chem.*, 194 (1980) 147.
- 5 M. Ishikawa, H. Sugisawa, K. Yamamoto and, M. Kumada, *J. Organomet. Chem.*, 179 (1979) 377.
- 6 M. Ishikawa, H. Sugisawa, O. Harata and M. Kumada, *J. Organomet. Chem.*, 217 (1981) 43.
- 7 M. Ishikawa, S. Matsuzawa, T. Higuchi, K. Hirotsu and S. Kamitori, *Organometallics*, 4 (1985) 2040.
- 8 M. Ishikawa, H. Sugisawa, T. Fuchikami, M. Kumada, T. Yamabe, H. Kawakami, K. Fukui, Y. Ueki and H. Shizuka, *J. Am. Chem. Soc.*, 104 (1982) 2872.
- 9 T.J. Barton and W.D. Wulff, *J. Am. Chem. Soc.*, 101 (1979) 2735.
- 10 H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama and C. Kabuto, *J. Organomet. Chem.*, 105 (1983) 3359.
- 11 H. Sakurai, Y. Eriyama, A. Hosomi, Y. Nakadaira and C. Kabuto, *Chem. Lett.*, (1984) 595.
- 12 U.S. 3 627 804, 1972; *Chem. Abstr.*, 76 (1972) P127998f.
- 13 *Jpn* 58,152,892, 1983; *Chem. Abstr.*, 100 (1983) 210118d.
- 14 *Jpn* 58,152,891, 1983, *Chem. Abstr.*, 100 (1983) 210119e.
- 15 *Jpn* 58,152,893, 1983, *Chem. Abstr.*, 100 (1983) 210120y.
- 16 L. Cassar, *J. Organomet. Chem.*, 93 (1975) 253.
- 17 H.A. Dieck and R.F. Heck, *J. Organomet. Chem.*, 93 (1975) 259.
- 18 K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, (1975) 4467.
- 19 S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, (1980) 627.
- 20 H. Sakurai, Y. Kamiyama and Y. Nakadaira, *Chem. Lett.*, (1975) 887.
- 21 H. Sakurai, Y. Kamiyama and Y. Nakadaira, *J. Am. Chem. Soc.*, 97 (1975) 931.
- 22 H. Sakurai, Y. Eriyama, Y. Kamiyama and Y. Nakadaira, *J. Organomet. Chem.*, 264 (1984) 229.
- 23 N.A. Bumagin, A.B. Ponomarev and I.P. Beletskaya, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 7 (1984) 1561.
- 24 N.A. Bumagin, I.O. Kalinovskii, A.B. Ponomarev and I.P. Beletskaya, *Dokl. Akad. Nauk. SSSR*, 265 (1981) 1138.
- 25 M. Kumada, M. Yamaguchi, Y. Yamamoto, J.-I. Nakajima and K. Shiina, *J. Org. Chem.*, 21 (1956) 1264.
- 26 H. Sakurai, Y. Kamiyama and Y. Nakadaira, *J. Organomet. Chem.*, 131 (1977) 147; H. Sakurai and M. Yamagata, *Chem. Commun.*, (1970) 1144.
- 27 C.S. Kraihanzel and M.L. Losee, *J. Organomet. Chem.*, 10 (1967) 427.
- 28 M. Ishikawa, H. Sugisawa, K. Yamamoto and M. Kumada, *J. Organomet. Chem.*, 179 (1979) 377.