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Facile hydrosilylation of norbornadiene by silanes R_3SiH and R_2SiH_2 with molybdenum catalysts

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ABSTRACT

Photochemically activated $[Mo(CO)_6]$ and $[Mo(CO)_4(\eta^4\text{-nbd})]$ have been demonstrated to be very effective catalysts for hydrosilylation of norbornadiene (nbd) by tertiary (Et_3SiH, Cl_3SiH) and secondary (Et_2SiH_2 and Ph_2SiH_2) silanes to give 5-silyl-2-norbornene, which under the same reaction conditions transform in ring-opening metathesis polymerization (ROMP) to unsaturated polymers and to a double hydrosilylation product, 2,6-bis(silyl)norbornane. The yield of a particular reaction depends very strongly on the kind of silane involved. The reaction products were identified by means of chromatography (GC–MS) and ^{1}H and ^{13}C NMR spectroscopy. In photochemical reaction of $[Mo(CO)_4(\eta^4\text{-nbd})]$ and Ph_2SiH_2 in cyclohexane-d_{12}, η^2-coordination of the Si—H bond to the molybdenum atom is supported by ^{1}H NMR spectroscopy due to the detection of two equal-intensity doublets with $^2J_{H-H} = 5.4$ Hz at δ 6.12 and -5.86 ppm.

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1. Introduction

Over the last several decades organosilicon chemistry has developed into a very important field of organometallic, inorganic, and organic synthesis. Hydrosilylation of olefins and acetylenes is widely used in organosilicon chemistry, organic synthesis, and polymer production [1–4]. This reaction is carried out with various transition-metal catalysts, which are able to activate the Si—H bond of silanes and coordinate unsaturated hydrocarbon molecules. The interaction of the Si—H bond of silanes with photochemically generated $M(CO)_5$ moieties (M = Cr, Mo, W) has recently been observed by spectroscopic methods (IR, NMR) in solution at low temperature [5–10]. The η^2-coordination of silane to a metal center has significant consequences for the activation of the Si—H bond in transition-metal-catalyzed hydrosilylation of olefins. The mechanism proposed for hydrosilylation of olefins involves the coordination of silane and olefin to a metal center, to give the intermediate complex $[MH(SiR_3)((^2\text{-olefin})L_n]$. However, in the catalytic system such a complex is very unstable and its characterization is very difficult and to the best of our knowledge has not been documented. Group 6 metal carbonyls can very easily substitute carbonyl ligands for silane or olefin ligands under photochemical conditions and used as catalysts for hydrosilylation of 1,3-dienes [11,12]. This inspired us to test the catalytic activity

of $[Mo(CO)_6]$ (**1**) and $[Mo(CO)_4(\eta^4\text{-nbd})]$ (**2**) in hydrosilylation of a bicyclic diene, norbornadiene (nbd), which can give 5-silyl-2-norbornene (Si-nbe), similar to reaction catalyzed by chloroplatinic acid [13]. One of the most interesting reactions of silicon compounds containing olefin bonds is metathesis, in which a new olefin or an unsaturated polymer can be obtained [14–19]. The ring-opening metathesis polymerization (ROMP) of norbornenes with a silicon-containing substituent has been investigated by several research groups because silicon-containing polynorbornenes are characterized by considerably enhanced permeability and diffusion coefficients for light gases, compared with polynorbornene [14–16].

In this paper we present a one-pot reaction, the hydrosilylation of nbd by Et_3SiH (**3**), Cl_3SiH (**4**), Et_2SiH_2 (**5**), and Ph_2SiH_2 (**6**) to give 5-silyl-2-norbornene (Si-nbe) and ROMP of Si-nbe to provide poly-5-silyl-norbornenes (poly-Si-nbe). In reaction of nbd with the secondary silane **5**, the Si-nbe formed in the first step undergoes subsequent hydrosilylation to give 2,6-bis(silyl)norbornane (bis-Si-nba) together with the ROMP polymer. However, the Si-nbe formed in reaction of nbd with **6** transformed mainly to 2-silylnorbornane (Si-nba) (Scheme 1).

2. Experimental

2.1. General remarks

All reactions were performed with standard Schlenk techniques under an atmosphere of nitrogen and with freshly distilled substrates and solvents. $Mo(CO)_6$ (**1**) (Aldrich) was used as

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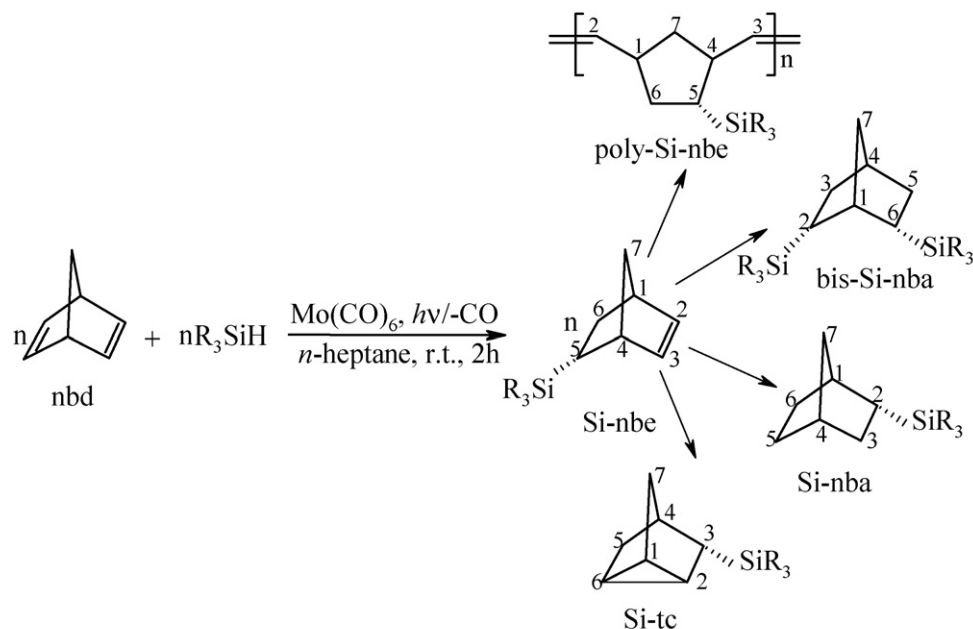
Scheme 1. Transformation of norbornadiene in the presence of photochemically activated $Mo(CO)_6$ (**1**) and silanes R_3SiH (R_3 = Et_3, Cl_3, Et_2H, Ph_2H).

received. The norbornadiene compound $[Mo(CO)_4(\eta^4\text{-nbd})]$ (**2**) was obtained from a photochemical reaction of $Mo(CO)_6$ and nbd in n-heptane solution and purified by sublimation [20–22]. The photolysis source was an HBO 200 W high-pressure Hg lamp.

^1H, ^{13}C NMR and two-dimensional ^1H–^1H COSY and ^1H–^{13}C HMQC NMR spectra were recorded with a Bruker AMX 300 or 500 MHz instrument. All proton and carbon chemical shifts were referenced to the residual proton signal for ^1H NMR (δ 7.24 $CDCl_3$ and 1.40 C_6D_{12}) or the natural abundant carbon signal of the solvent for ^{13}C NMR (δ 77.0 $CDCl_3$ and 26.4 C_6D_{12}). ^{95}Mo NMR chemical shifts were calibrated relative to $Mo(CO)_6$ (δ = −1856). ^{29}Si NMR chemical shifts were referenced relative to Ph_2SiH_2 (δ 37.08) used as external standard. IR spectra were measured with a Nicolet-400 FT-IR instrument in solution and KBr pellets. Analyses of the reaction products were performed on a Hewlett-Packard GC–MS system. The average molecular weights M_n and M_w of the polymers were determined by gel permeation chromatography (GPC) of the solution in $CHCl_3$ on a Hewlett-Packard 1090II instrument, equipped with a refractive index detector HP 1047A and Plgel 10 μ MIXED-B or Plgel 5 μ MIXED-C columns, previously calibrated with a use of commercially available polystyrene standards, in the molecular mass range 11.6×10^3 to 2.9×10^6. A polydispersity (PDI = M_w/M_n) was calculated from the weight average molecular weight (M_w) and the number average molecular weight (M_n) by the non-commercial computer programme examining the peaks at high molecular weight in the gel permeation chromatograms (GPC).

2.2. General reaction procedure

In the reaction presented in Scheme 1, compound **1** (*ca.* 0.01 g, 0.038 mmol), silane (**3–6**) (*ca.* 0.2 cm³, 1.9 mmol), and norbornadiene (*ca.* 0.17 g, 1.9 mmol) (1:50:50 molar ratio) in n-heptane solution (20 cm³) were stirred and irradiated with a mercury lamp at room temperature for 2 h. Photolysis of the reaction mixture resulted in the immediate formation of yellow solution and white precipitate. The precipitate (polymer) was then separated from the solution, dried under vacuum and weighed. The filtrate obtained after the separation of the polymer was analyzed by GC–MS and by NMR spectroscopy.

2.3. General procedure for NMR experiments

The reaction course presented in Scheme 1 was also followed by ^1H NMR spectroscopy. In the general procedure for NMR experiments, complex **2** (*ca.* 0.01 g, 0.03 mmol) was weighed into an NMR tube. The tube was then capped with a septum. A portion of silane (*ca.* 0.03 cm³) and C_6D_{12} (0.7 cm³) was then added to the NMR tube via a syringe. The tube was periodically irradiated and monitored by ^1H NMR spectroscopy at the desired time.

2.4. Identification by GC–MS and spectroscopic characteristic of hydrosilylation products

The hydrosilylation products of nbd were detected in photochemical reaction of nbd and silane **3–6** carried out in a cyclohexane-d_{12} and n-heptane solution containing molybdenum complex **1** or **2**.

5-Triethylsilyl-2-norbornene (**3**-Si-nbe), $C_{13}H_{24}Si$, M_r = 208.42, m/z (relative intensity): 43 (6), 59 (30), 66 (80), 85 (49), 87 (48), 113 (100), 115 (38), 121 (4), 151 (8), 179 (42), 208 (M^+, 3) for *endo*-**3**-Si-nbe; 43 (7), 59 (56), 66 (28), 85 (34), 87 (100), 113 (78), 115 (53), 121 (9), 151 (34), 179 (70), 208 (M^+, 7) for *exo*-**3**-Si-nbe. ^1H NMR (C_6D_{12}, 500 MHz) δ = 5.93 (t, $J_{H–H}$ = 1.5 Hz, 2H, $HC^{2,3}$), 2.96 (s, 1H, HC^4), 2.83, (s, 1H, HC^1), 1.88 (ddd, $J_{H–H}$ = 10.9, 9.8, 3.9 Hz, 1H, H_2C^6), 1.44 (dd, $J_{H–H}$ = 7.5, 1.6 Hz, 1H, H_2C^7), 1.18 (ddd, $J_{H–H}$ = 9.8, 5.9, 3.1 Hz, 1H, H_2C^5), 1.12 (d, $J_{H–H}$ = 7.5 Hz, 1H, H_2C^7), 1.06 (ddd, $J_{H–H}$ = 10.9, 5.9, 1.9 Hz, 1H, H_2C^6), 0.96 (t, $^3J_{H–H}$ = 7.9 Hz, 9H, CH_3-Et), 0.5 (dq, $^3J_{H–H}$ = 7.9, 4.0 Hz, 6H, CH_2-Et); $^{13}C\{^1H\}$ NMR (C_6D_{12}, 126 MHz) δ = 136.0, 134.9 (2C, $HC^{2,3}$), 52.3 (1C, H_2C^7), 45.7 (1C, HC^4), 43.1 (1C, HC^1), 28.2 (1C, H_2C^6), 23.2 ($^1J_{Si–C}$ = 56 Hz, 1C, HC^5), 8.1 (3C, CH_3-Et), 4.5 ($^1J_{Si–C}$ = 50 Hz, 3C, CH_2-Et); $^{29}Si\{^1H\}$ NMR (C_7D_8, 99 MHz) δ = 3.4 for *endo*-**3**-Si-nbe.

5-Trichlorosilyl-2-norbornene (**4**-Si-nbe) [14,17], $C_{13}H_{24}Si$, M_r = 227.59, m/z (relative intensity): 39 (8), 51 (2), 66 (100), 91 (7), 133 (3), 228 (M^+, 0.15) for *endo*-**4**-Si-nbe; 39 (5), 51 (1), 66 (100), 91 (8), 133 (4), 228 (M^+, 0.5) for *exo*-**4**-Si-nbe; ^1H NMR (C_6D_{12}, 500 MHz) δ = 6.05 (s, 2H, $HC^{2,3}$), 3.21 (s, 1H, HC^4), 2.98 (s, 1H, HC^1), 2.02 (ddd, $J_{H–H}$ = 11.5, 9.5, 3.5 Hz, 1H, H_2C^6), 1.84 (ddd, $J_{H–H}$ = 9.5, 5.2, 3.2 Hz, 1H, HC^5), 1.53 (ddd, $J_{H–H}$ = 8.4, 3.6, 2.0 Hz, 1H, H_2C^7),

1.36 (ddd, J_{H-H} = 11.7, 5.6, 3.0 Hz, 1H, H_2C^6), 1.18 (d, J_{H-H} = 7.9 Hz, 1H, H_2C^7); $^{13}C\{^1H\}$ NMR (C_6D_{12}, 126 MHz) δ = 137.3, 133.3 (2C, $HC^{2,3}$), 51.5 (1C, H_2C^7), 46.0 (1C, HC^4), 43.7 (1C, HC^1), 34.7 (1C, HC^5), 27.7 (1C, H_2C^6); $^{29}Si\{^1H\}$ NMR (C_6D_{12}, 99.4 MHz) δ = −48.7 for *endo*-**4**-Si-nbe. ^1H NMR (C_6D_{12}, 500 MHz) δ = 6.17 (m, 1H, HC^3), 6.08 (m, 1H, HC^2), 3.10 (s, 1H, HC^4), 3.01 (s, 1H, HC^1), 1.91, (ddd, J_{H-H} = 11.8, 9.6, 3.6 Hz, 1H, HC^5), 1.52 (m, 1H, H_2C^7), 1.32 (m, 2H, $H_2C^{6,7}$), 1.12 (ddd, J_{H-H} = 9.0, 6.0, 2.5 Hz, 1H, H_2C^6). $^{13}C\{^1H\}$ NMR (C_6D_{12}, 126 MHz) δ = 138.1 (1C, HC^3), 136.2 (1C, HC^2), 47.2 (1C, H_2C^7), 44.2 (1C, H^4), 43.4 (1C, HC^1), 34.4 (1C, HC^5), 27.5 (1C, H_2C^6) for *exo*-**4**-Si-nbe.

endo,endo-2,6-bis(hydrodiethylsilyl)norbornane   (bis(**5**-Si)-nba), $C_{15}H_{32}Si_2$, *rac* and *meso* diastereoisomers, M_r = 268.59; *m/z* (relative intensity): 59 (66), 87 (38), 123 (41), 151(55), 180 (20), 239 (100), 269 (M^+, 0.1). ^1H NMR (CDCl$_3$, 500 MHz) δ = 3.85 (pd, $^3J_{H-H}$ = 3.5, 2.0 Hz, $^1J_{Si-H}$ = 182 Hz, 2H, H–Si), 2.42 (s, 1H, HC^1), 2.30 (s, 1H, HC^4), 1.74 (ddd, J_{H-H} = 11.1, 10.1, 4.7 Hz, 2H, $H_2C^{3,5}$), 1.34 (s, 2H, H_2C^7), 1.07 (ddd, J_{H-H} = 11.8, 5.8, 3.1 Hz, 2H, $H_2C^{3,5}$), 1.02 (d, J_{H-H} = 9.9 Hz, 2H, 1H$C^{2,6}$), 0.96 (t, $^3J_{H-H}$ = 7.8 Hz, 6H, CH_3-Et), 0.94 (t, $^3J_{H-H}$ = 7.8 Hz, 6H, CH_3-Et), 0.65 (qd, $^3J_{H-H}$ = 7.8, 2.0 Hz, 4H, CH_2-Et), 0.49 (qd, $^3J_{H-H}$ = 7.8, 2.0 Hz, 4H, CH_2-Et). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 126 MHz) δ = 46.1 (1C, H_2C^7), 43.1 (1C, HC^1), 37.0 (1C, HC^4), 33.8 (2C, $H_2C^{3,5}$), 26.8 ($^1J_{Si-C}$ = 54 Hz, 2C, $HC^{2,6}$), 8.4 (2C, CH_3-Et), 8.2 (2C, CH_3-Et), 3.4 ($^1J_{Si-C}$ = 51 Hz, 2C, CH_2-Et), 2.9 ($^1J_{Si-C}$ = 51 Hz, 2C, CH_2-Et). $^{29}Si\{^1H\}$ NMR (CDCl$_3$, 99 MHz) δ = −5.8.

5-Hydrodiphenylsilyl-2-norbornene   (**6**-Si-nbe), $C_{19}H_{20}Si$, M_r = 276.45; *m/z* (relative intensity): **6**-Si-nbe: 44 (18), 53 (10), 79 (10), 105 (44), 131 (9), 179 (9), 183 (100), 198 (19), 209 (30), 248 (36), 276 (M^+, 16). ^1H NMR (C_6D_{12}, 500 MHz) δ = 6.01 (dd, J_{H-H} = 5.7, 3.2 Hz, 1H, HC^3), 5.81 (dd, J_{H-H} = 5.7, 2.8 Hz, 1H, HC^2), 4.47 (d, $^2J_{H-H}$ = 6.0 Hz, $^1J_{Si-H}$ = 203 Hz, 1H, H–Si), 2.96 (s, 1H, HC^4), 2.91, (s, 1H, HC^1), 2.19 (ddd, J_{H-H} = 11.4, 9.6, 3.6 Hz, 1H, HC^6), 1.71 (ddd, J_{H-H} = 11.4, 5.8, 3.4 Hz, 1H, HC^5), 1.44 (d, J_{H-H} = 7.9 Hz, 1H, H_2C^7), 1.31 (m, 1H, H_2C^6), 1.20 (d, J_{H-H} = 7.9 Hz, 1H, H_2C^7). $^{13}C\{^1H\}$ NMR (C_6D_{12}, 126 MHz) δ = 137-128 (12C, Ph), 136.7 (1C, HC^3), 134.2 (1C, HC^2), 51.2 (1C, H_2C^7), 46.1 (1C, HC^4), 43.7 (1C, HC^1), 29.7 (1C, H_2C^6), 23.7 (1C, $^1J_{Si-C}$ = 63 Hz, HC^5).

2-Hydrodiphenylsilylnorbornane   (**6**-Si-nba), $C_{19}H_{22}Si$, M_r = 278.46; *m/z* (relative intensity): 53 (3), 79 (4), 105 (23), 122 (4), 172 (17), 183 (100), 200 (39), 278 (M^+, 2). ^1H NMR (CDCl$_3$, 500 MHz) δ = 7.35-6.90 (m, 10H, Ph), 4.83 (d, $^3J_{H-H}$ = 6.3 Hz, 1H, H–Si), 2.37 (s, 1H, HC^1), 2.30 (s, 1H, HC^4), 1.88, (dd, J_{H-H} = 11.4, 3.5 Hz, 1H, H_2C^3), 1.68 (m, 1H, H_2C^6), 1.58 (m, 1H, HC^2), 1.54 (m, 1H, H_2C^5), 1.43 (m, 1H, H_2C^6), 1.33 (m, 2H, H_2C^7), 1.29 (m, 1H, H_2C^3), 1.15 (m, 1H, H_2C^5). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 126 MHz) δ = 137-128 (12C, Ph), 41.2 (1C, H_2C^7), 38.8 (1C, HC^1), 37.0 (1C, HC^4), 33.4 (1C, H_2C^3), 29.8 (1C, H_2C^5), 27.3 (1C, $^1J_{Si-C}$ = 54 Hz, HC^2), 24.7 (1C, H_2C^6).

2.5. Spectroscopic characteristics of poly(5-silyl-2-norbornene) (poly-Si-nbe)

The microstructure of poly-Si-nbe was investigated by ^1H and ^{13}C NMR spectroscopy.

Poly(5-triethylsilyl-2-norbornene) (poly-**3**-Si-nbe): ^1H NMR (CDCl$_3$, 500 MHz) δ = 5.32 ($HC^{2,3}$, *trans*), 5.21 ($HC^{2,3}$, *trans*, *cis*), 5.09 ($HC^{2,3}$, *cis*), 3.12 ($HC^{1,4}$, *cis*), 2.74 ($HC^{1,4}$, *cis*, *trans*), 2.38 ($HC^{1,4}$, *trans*), 2.02, 1.78, 1.27, 1.19, 1.05 (H_2C^7, H_2C^6, HC^5), 0.90 (CH_3-Et), 0.53 (CH_2-Et). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 126 MHz) δ = 134-132 ($HC^{2,3}$), 45.5-44.8 ($HC^{1,4}$, *trans*), 40.2-38.8 (H_2C^7), 36.6, 36.1 ($HC^{1,4}$, *cis*), 29.8, 29.7, 29.0 (HC^5, $H_2C^{6,7}$), 7.7 (CH_3-Et), 3.7 (CH_2-Et).

Poly(5-hydrodiethylsilyl-2-norbornene) (poly-**5**-Si-nbe): ^1H NMR (CDCl$_3$, 500 MHz) δ = 5.31 ($HC^{2,3}$, *trans*), 5.23 ($HC^{2,3}$, *trans*, *cis*) 5.11 ($HC^{2,3}$, *cis*), 3.61, 3.53 ($^1J_{Si-H}$ = 180 Hz, H–Si), 3.10 ($HC^{1,4}$,

cis), 2.71 ($HC^{1,4}$, *cis*, *trans*), 2.34 ($HC^{1,4}$, *trans*), 1.96 (H_2C^7), 1.78 (H_2C^6), 1.32 (HC^5), 1.19 (H_2C^6), *ca.* 1.0 (H_2C^7), 0.90 (CH_3-Et), 0.54 (CH_2-Et). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 125 MHz) δ = 133.8, 133.3, 132.8, 132.5, ($HC^{2,3}$), 45.2, 44.6, ($HC^{1,4}$, *trans*), 42.3, 41.5 (H_2C^7), 40.0, 39.2 ($HC^{1,4}$, *cis*), 37.2, 36.6 (H_2C^6), 28.1, (HC^5), 7.3-6.2 (Et). $^{29}Si\{^1H\}$ NMR (CDCl$_3$, 99 MHz) δ = −6.6.

2.6. GPC analysis of poly-**5**-Si-nbe

The molecular weight of poly-**5**-Si-nbe was determined by GPC (CHCl$_3$, r.t.) with polystyrene standards. The polymers samples presented bimodal GPC curves, with higher (M_w = 550000, PDI = 1.9) and lower (M_w = 15200, PDI = 1.3) molecular weight.

2.7. Photochemical reaction of **1**, 2-norbornene (nbe) and silane **3** in n-heptane

A solution of **1** (0.01 g, 0.038 mmol), **3** (0.22 g, 1.9 mmol) and nbe (0.18 g, 1.9 mmol) in *n*-heptane (20 cm^3) was irradiated at room temperature for 2 h. Photolysis of the reaction mixture resulted in the immediate formation of yellow solution and white precipitate. The precipitate was then separated from the solution, dried under vacuum and weighed. The filtrate obtained after the separation of solid was evaporated and the residue analyzed by ^1H and ^{13}C NMR spectroscopy in CDCl$_3$ solution showed spectral characteristics of poly(1,3-cyclopentylenevinylene) (poly-nbe) similar to previously described by Ivin et al. [14,23]. The overall yield of the poly-nbe determined by mass was *ca.* 100%. The microstructure of poly-nbe was investigated by ^1H and ^{13}C NMR spectroscopy [13]. ^1H NMR (CDCl$_3$, 500 MHz) δ = 5.31 ($HC^{2,3}$, *trans*), 5.19 ($HC^{2,3}$, *cis*), 2.77 ($HC^{1,4}$, *cis*), 2.40 ($HC^{1,4}$, *trans*), 1.82 (H_2C^7), 1.75 ($H_2C^{5,6}$), 1.32 ($HC^{5,6}$), 1.05 (H_2C^7), $^{13}C\{^1H\}$ NMR (CDCl$_3$, 125 MHz) δ = 134.0, 133.9, 133.8, 133.7, ($HC^{2,3}$), 43.4, 43.1, ($HC^{1,4}$, *trans*), 42.1, 41.4, 40.7 (H_2C^7), 38.6, 38.4 ($HC^{1,4}$, *cis*), 33.1, 32.9, 32.4, 32.2 ($H_2C^{5,6}$).

2.8. Photochemical reaction of **1** with cyclic olefins in n-heptane

2.8.1. Formation and identification of norbornene complexes: [Mo(CO)$_5$(^{2}-nbe)] and trans-[Mo(CO)$_4$(^{2}-nbe)$_2$]

A solution of **1** (0.2 g, 0.75 mmol) and nbe (0.4 g, 4.5 mmol) in *n*-heptane (30 cm^3) was irradiated at room temperature. The course of the reaction was monitored by IR measurements in solution, and photolysis was stopped when the IR bands of pentacarbonyl moiety at 2079 cm^{-1} reached its maximum intensity (about 0.5 h). The volatile materials (solvent and unreacted **1**) were then removed from the reaction mixture under reduced pressure at room temperature. The residue was analyzed by IR and NMR spectroscopy. At this stage of the synthesis, the ^1H NMR method showed *ca.* 80% of [Mo(CO)$_5$((^{2}-nbe)] and 20% of *trans*-[Mo(CO)$_4$((^{2}-nbe)$_2$]. However, ^1H NMR monitoring of these compounds in CDCl$_3$ solution showed the complete disappearance of pentacarbonyl complex and the formation of poly-nbe over period of 24 h. In toluene-d_8 solution the pentacarbonyl complex is much more stable.

[Mo(CO)$_5$((^{2}-nbe)]: IR (*n*-heptane): 2079 (w), 1959 (vs), 1947 (s) cm^{-1}; ^1H NMR (CDCl$_3$, 500 MHz, −20 °C) δ = 5.07 (s, $^1J_{C-H}$ = 170 Hz, 2H, $HC^{2,3}$), 2.87 (s, $^1J_{C-H}$ = 146 Hz, 2H, $HC^{1,4}$), 1.71 (d, J_{H-H} = 8 Hz, 2H, *exo*-$H_2C^{5,6}$), 1.26 (dd, J_{H-H} = 8, 2 Hz, 2H, *endo*-$H_2C^{5,6}$), 1.00 (d, J_{H-H} = 10 Hz, 1H, *syn*-H_2C^7), 0.73 (d, J_{H-H} = 10, Hz, 1H, *anti*-H_2C^7). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 126 MHz, −20 °C) δ = 211.5 (1C, CO), 205.3 (4C, CO), 95.6 (2C, $HC^{2,3}$), 41.6 (2C, $HC^{1,4}$), 37.4 (1C, H_2C^7), 25.5 (2C, $H_2C^{5,6}$). ^{95}Mo NMR (C_7D_8, 32 MHz) δ = −1724.

trans-[Mo(CO)$_4$((^{2}-nbe)$_2$]: IR (*n*-heptane): 1989 (w), 1940 (vs) cm^{-1}; ^1H NMR (CDCl$_3$, 500 MHz, −20 °C) δ = 3.50 (s, $^1J_{C-H}$ = 160 Hz, 2H, $HC^{2,3}$), 2.69 (s, $^1J_{C-H}$ = 150 Hz, 2H, $HC^{1,4}$), 1.71 (d, J_{H-H} = 8 Hz, 2H, *exo*-$H_2C^{5,6}$), 1.16 (dd, J_{H-H} = 8, 2 Hz, 2H, *endo*-$H_2C^{5,6}$), 0.91 (d,

J_{H-H} = 10 Hz, 1H, *syn*-H_2C^7), 0.54 (d, J_{H-H} = 10, Hz, 1H, *anti*-H_2C^7). $^{13}C\{^1H\}$ NMR (CDCl₃, 126 MHz, −20 °C) δ = 210.7 (4C, CO), 69.6 (2C, $HC^{2,3}$), 41.2 (2C, $HC^{1,4}$), 34.1 (1C, H_2C^7), 27.9 (2C, $H_2C^{5,6}$). ^{95}Mo NMR (C_7D_8, 32 MHz) δ = −2029.

2.8.2. Formation and spectroscopic characteristic of [Mo(CO)₄((⁴-nbd)] (2)

The norbornadiene compound **2** was obtained in photochemical reaction of **1** and nbd in *n*-heptane solution and purified by sublimation. IR (*n*-heptane): 2045 (m), 1959 (vs), 1913 (s) cm⁻¹; ^1H NMR (CDCl₃, 500 MHz) δ = 4.91 (s, 4H, $HC^{2,3,5,6}$), 3.79 (s, 2H, $HC^{1,4}$), 1.32 (s, 2H, H_2C^7). $^{13}C\{^1H\}$ NMR (CDCl₃, 126 MHz) δ = 218.0 (2C, CO), 214.3 (2C, CO), 78.1 (4C, $HC^{2,3,5,6}$), 65.0 (1C, H_2C^7), 49.0 (2C, $HC^{1,4}$). ^{95}Mo NMR (CDCl₃, 32 MHz) δ = −1587.

3. Results and discussion

3.1. Hydrosilylation of nbd with silanes initiated by photochemically activated 1 or 2

The hydrosilylation of nbd by triethylsilane **3** in the presence of a catalytic amount (*ca.* 2 mol %) of the molybdenum complex **1** or **2** gave 5-triethylsilyl-2-norbornene (**3**-Si-nbe), which was identified by NMR as a 99:1 mixture of *endo*-**3**-Si-nbe and *exo*-**3**-Si-nbe (Fig. 1), similar to reaction catalyzed by platinum compounds [13,18]. However, under the reaction conditions, the **3**-Si-nbe that is formed is next transformed to the ROMP polymer poly(5-triethylsilyl-2-norbornene) (poly-**3**-Si-nbe) (Table 1). The disappearance of **3**-Si-nbe and the formation of poly-**3**-Si-nbe (slower in C_6D_{12} than in CDCl₃ solution) was observed even in the dark.

The hydrosilylation of nbd by trichlorosilane **4** gave 5-trichlorosilyl-2-norbornene (**4**-Si-nbe), which was identified by NMR as a mixture containing 87% of *endo*-**4**-Si-nbe and 13% of *exo*-**4**-Si-nbe (Fig. 2) [13,18]. However, the yield of **4**-Si-nbe is low due to its high conversion to the ROMP polymer poly(5-trichlorosilyl-2-norbornene) (poly-**4**-Si-nbe) (Table 1).

The hydrosilylation of nbd by diethylsilane **5** gave 5-hydrodiethylsilyl-2-norbornene (**5**-Si-nbe) as the intermediate compound, which under the reaction conditions very quickly transformed to the ROMP polymer and to a double hydrosilylation product, identified by the GC–MS method as bis(hydrodiethylsilyl)norbornane, (bis(**5**-Si)-nba) ($C_{15}H_{32}Si_2$, M_r = 268.59) (Scheme 1). The latter compound may be formed as a mixture of different isomers. The stereochemistry of bis(**5**-Si)-nba isolated here was identified by NMR methods (^1H, $^{13}C\{^1H\}$, ^1H–^1H COSY and ^1H–^{13}C HMQC) [24–26]. The $^{13}C\{^1H\}$ NMR spectrum of bis(**5**-Si)-nba shows five carbon signals due to seven carbons of the norbornyl moiety at δ 46.1, 43.1, 37.0, 33.8, and 26.8 in an approximate intensity ratio of 1:1:1:2:2 (Fig. 3). The last signal clearly shows satellites due to coupling with the silicon atom ($^1J_{Si-C}$ = 54 Hz). This resonance can thus be assigned
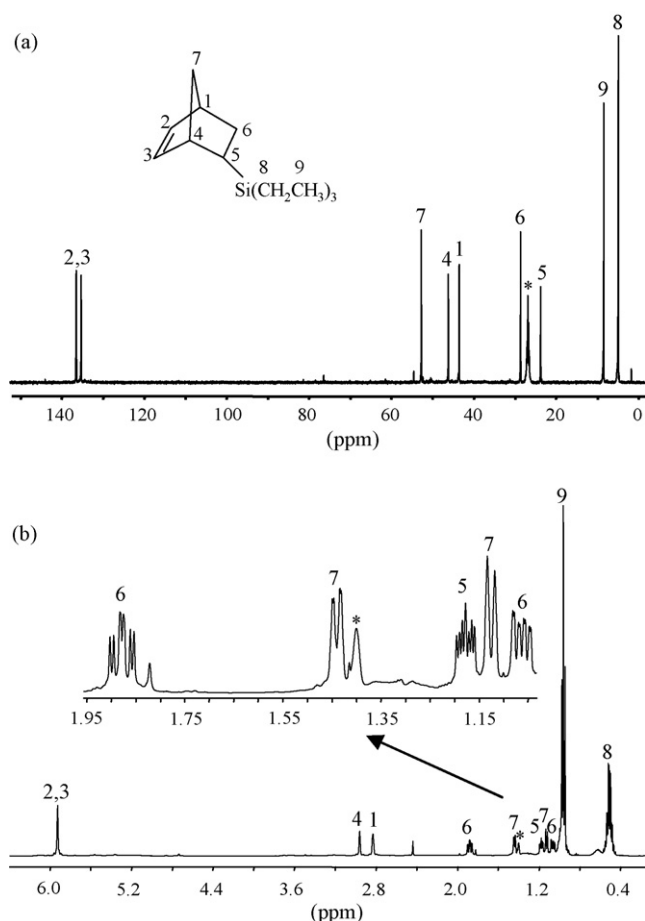
to two magnetically equivalent carbons adjacent to the silicon atom ($SiC^{2,6}$). Analysis of the two-dimensional ^1H–^{13}C HMQC NMR spectrum reveals a correlation between the singlet proton resonances at δ 2.42 and 2.30 and the ^{13}C resonances at δ 43.1 and 37.0, respectively. These resonances can thus be assigned to two bridgehead carbons ($HC^{1,4}$). The correlation between the resonance at δ 46.1 and the proton signal at δ 1.34 indicates a bridge carbon (H_2C^7) resonance. The methylene carbon ($H_2C^{3,5}$) resonance was detected at δ 33.8 due to correlation with two proton signals at δ 1.74 and 1.07 ppm, whose chemical shifts and magnitudes of splitting indicated *exo* and *endo* positions of protons, respectively [24,25]. Correlation can also be seen between the ^{13}C resonance at δ 26.8 ($SiHC^{2,6}$) and the proton resonance at δ *ca.* 1.0. Analysis of the two-dimensional ^1H–^1H COSY NMR spectrum reveals a correlation between resonances at δ 1.74, 1.07, and *ca.* 1.0 ppm.

Fig. 1. (a) $^{13}C\{^1H\}$ NMR spectrum (125 MHz, C_6D_{12}) and (b) ^1H NMR spectrum (500 MHz, C_6D_{12}) of **3**-Si-nbe (99% *endo* isomer). The characteristic proton signals are presented with the scale expansion. An asterisk denoted signal of C_6D_{12}.

Table 1
Data on formation of silicon containing compounds in reaction of nbd with silanes catalyzed by photochemically activated Mo(CO)₆ (**1**)[a]

Silane	Conversion of nbd (%)	Products distribution (%)[b]				
		Si-nbe (*endo*)	Poly-Si-nbe	bis-Si-nba	Si-nba	Si-tc
Et₃SiH (**3**)	31	98 (99)	2	–	–	–
Cl₃SiH (**4**)	23	40 (87)	60	–	–	–
Et₂SiH₂ (**5**)	40	–[c]	83	17	–	–
Ph₂SiH₂ (**6**)	100	35 (56)	5	–	44	16

[a] Reaction was carried out at room temperature in *n*-heptane (20 cm³) with continued photolysis (2 h) at Mo(CO)₆:silane:nbd = 1:50:50.

[b] See Scheme 1 for the structure and abbreviation of products.

[c] An unidentified compound in the isolated mixture of products, observed during the monitoring of the reaction by ^1H NMR.
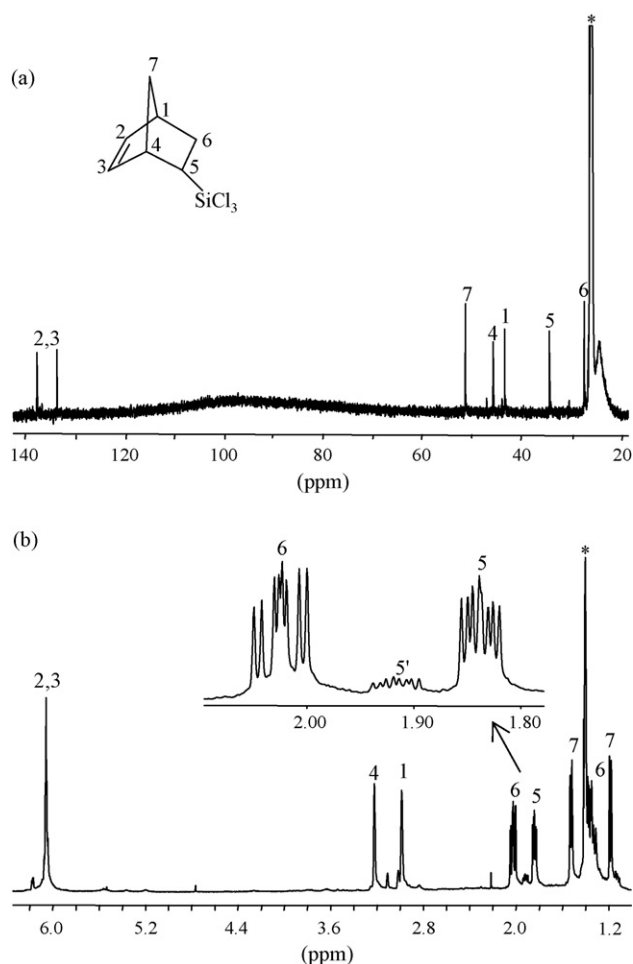
(a)

(b)

Fig. 2. (a) $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, C_6D_{12}) and (b) ^{1}H NMR spectrum (500 MHz, C_6D_{12}) of **4**-Si-nbe (*ca.* 90% *endo* isomer). The characteristic proton signals for H_2C^6 and $SiHC^5$ units are presented with the scale expansion. The proton signal denoted by 5′ is due to $SiHC^5$ unit of *exo* isomer. An asterisk denoted signal of C_6D_{12}.

The multiplicity of proton signals at δ 1.74 (ddd, $J_{H-H} = 11.1$, 10.1, 4.7 Hz) and the relatively large value of proton–proton coupling constants suggested the *endo* position of the silicon substituent and the *exo* position of the proton at the adjacent carbon atom ($HC^{2,6}Si$). On the basis of NMR data, the product of double hydrosilylation of norbornadiene by diethylsilane **5** may be described as *endo,endo*-2,6-bis(**5**-Si)-nba. Two chiral centers in a molecule of *endo,endo*-2,6-bis(**5**-Si)-nba make possible the formation of four chiral combinations of stereoisomers (both *rac* and *meso* stereoisomers) [27]. In this case, a 1:1 mixture of two diastereoisomers was identified by NMR due to two equal-intensity signals for the diastereotopic ethyl protons and carbons (Fig. 3). **5**-Si-nbe was only observed during the monitoring of photochemical reaction of **2** with **5** by ^{1}H NMR spectroscopy in C_6D_{12} solution. The olefinic proton signals of **5**-Si-nbe appear at the beginning of the reaction as two equal-intensity multiplets at $\delta = 6.08$ and 5.88. However, the yield of the concurrent ROMP reaction of **5**-Si-nbe to give poly(5-hydrodiethylsilyl-2-norbornene) (poly-**5**-Si-nbe) was higher than that of bis-hydrosilylation (Table 1).

The hydrosilylation reaction of nbd by diphenylsilane **6** in the presence of **1** gives a very complicated mixture of products because of the low stereoselectivity of the reaction and the number of isomers formed. The stereoselective formation of *endo*-5-hydrodiphenylsilyl-2-norbornene (**6**-Si-nbe) was only observed during the photochemical reaction of **2** with **6** (1:1 molar ratio)
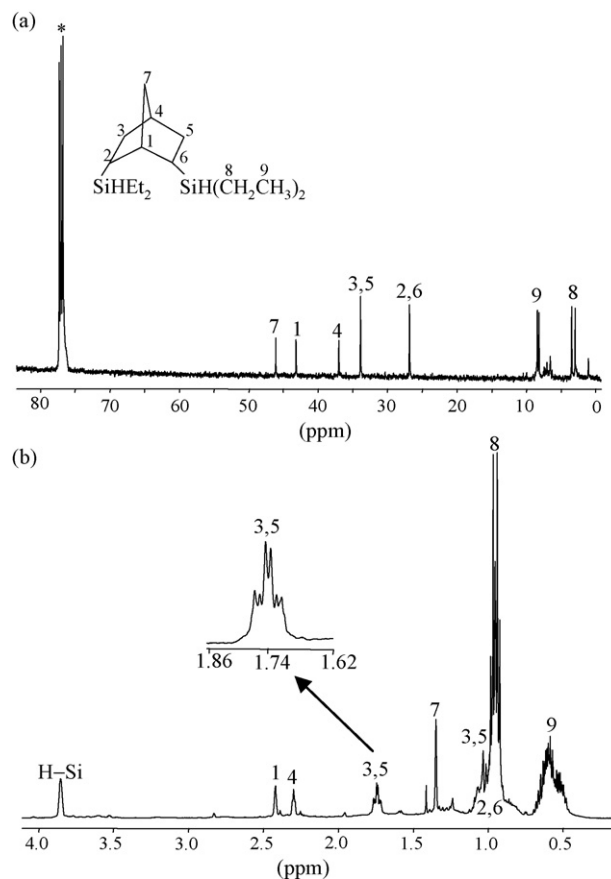
(a)

(b)

Fig. 3. (a) $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) and (b) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of bis(**5**-Si)-nba. The proton signal at δ 1.74 is presented with the scale expansion. An asterisk denoted signal of $CDCl_3$.

monitored by ^{1}H NMR spectroscopy (Fig. 4). In the mixture of products isolated from prolonged (2 h) reaction catalyzed by photochemically activated **1**, **6**-Si-nbe was detected with a yield no higher than 50%, as a mixture (*ca.* 1:1) of *endo* and *exo* stereoisomers due to four olefinic proton signals in the region of 6.0–5.8 ppm. The chiral nature of the latter compounds makes possible the formation of diastereoisomers. A 2:1:1 mixture of stereoisomers was identified by ^{1}H NMR due to three 2:1:1 intensity doublet signals at δ 4.48, 4.44, and 4.38 ppm ($^{3}J_{H-H} = 6.3$ Hz) for the Si–H bond of $SiHPh_2$ moieties. **6**-Si-nbe, similarly as other norbornenes containing silicon substituents, undergoes ROMP reaction. However, the yield of the polymerization reaction is rather low. The major product of the subsequent transformation of **6**-Si-nbe in the same reaction conditions was 2-(hydrodiphenylsilyl)norbornane (**6**-Si-nba) (Scheme 1, Table 1). Hydrodiphenylsilyltricyclene (**6**-Si-tc) was detected in reaction mixture by ^{13}C NMR spectroscopy due to characteristic three methine carbon signals at δ 12.9, 10.5 and 10.0 ppm [26].

3.2. Activation of the H–Si bond of silane in photochemical reaction of complex **2**

Monitoring by ^{1}H NMR spectroscopy the reaction of **2** with silane in C_6D_{12} solution allowed us to observe the decay of proton signals arising from the olefinic protons of η^4-nbd and the H–Si bond of silane and the appearance of proton signals at high field characteristic of the hydride ligands. In the photochemical reaction of **2** with **6** (1:1 molar ratio) monitored by ^{1}H NMR spectroscopy it was possible to observe the η^2-coordination of silane to
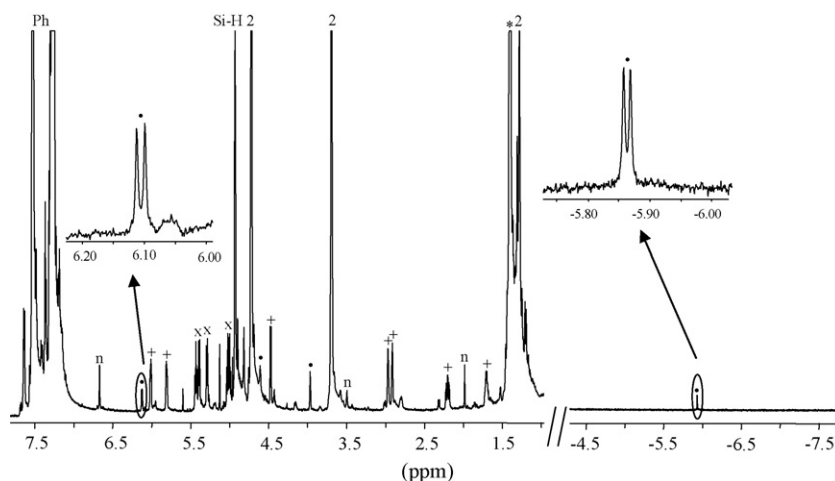
Fig. 4. ^{1}H NMR spectrum (500 MHz, C_6D_{12}) obtained during photochemical reaction of **2** with **6**-Si at 283 K. The proton signal at δ 6.12 and -5.86 ppm denoted by black points are presented with the scale expansion. The proton signals of **6**-Si-nbe are labeled by +, free norbornadiene by n and the proton signals of η^6-phenyl by x. An asterisk denoted signal of C_6D_{12}.

the photochemically activated complex **2** (Scheme 2). Two equal-intensity doublet signals ($^2J_{H-H} = 5.4$ Hz) were detected at δ 6.12 and -5.86 ppm for (^{2}-H—SiHPh$_2$) ligand (Fig. 4). These signals are in the similar region as observed by Heinekey and co-workwers [9] for [Mo(CO)$_5$(η^2-H—SiHPh$_2$)] (δ 6.04 and -6.49 ppm, $^2J_{H-H} = 11.8$ Hz), but the value of $^2J_{H-H}$ is *ca.* half that value for the complex containing the η^4-nbd ligand. With regard to the origin of this effect, the value of $^2J_{H-H}$ in ^{1}H NMR spectra correlates with the degree of metal ($d\pi$) → (η^2-H—Si) bond (σ^*) back-donation which is reflected in a higher value of $^2J_{H-H}$ for [Mo(CO)$_5$((^{2}-H—SiHPh$_2$)] and smaller value for compound [Mo(CO)$_3$((^{2}-H—SiHPh$_2$)(η^4-nbd)]. As nbd is a weaker π-acceptor than the carbonyl ligand, back-donation to the (^{2}-H—Si bond is much preferred in the norbornadienetricarbonyl than in the pentacarbonyl complex. To the best of our knowledge it is the first example of a complex containing olefin and the (^{2}-H—SiR$_3$) ligand that gives the hydrosilylation product, although similar complexes containing η^2-H—Si and η^2-olefin bonds of coordinated hydrovinylsilane have been described before [28,29]. The η^2-H—Si bond coordination to the molybdenum center leads to its activation and next addition to the olefinic bond of the η^4-nbd ligand. The reductive elimination of hydrosilylation product **6**-Si-nbe from the very unstable catalytically active tricarbonyl complex leads to the formation of a coordinatively unsaturated tricarbonyl moiety, Mo(CO)$_3$, which can undergo deactivation due to the η^6-coordination of the phenyl ring of the silane **6** or **6**-Si-nbe. The η^6-arene compounds were detected by NMR spectroscopy in all the investigated reactions of **6** (Fig. 4). The proton signals of the η^6-phenyl ring were observed in the region 5.43–5.00 ppm ($^3J_{H-H} = 6.3$ Hz) and the carbon signals in the range 101–89 ppm in spectra of C_6D_{12} solution, while the carbonyl carbon signal of the Mo(CO)$_3$ moiety was detected at *ca.* 220 ppm. Proton and carbon signals of other molybdenum complexes containing the η^6-arene and carbonyl ligands have been observed before in a similar range

of the NMR spectra [30,31]. Similar η^6-coordination of the phenyl ring has been observed before during the photochemical reaction of W(CO)$_6$ and Ph$_3$SiH [32].
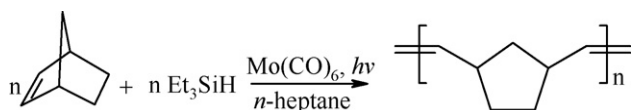
The oxidative addition of the H—Si bond to the molybdenum(0) centre and formation of two hydride ligands in reaction of silane **5** with the photochemically activated molybdenum complex **2** indicated two equal but very low intensity proton signals at $\delta = -7.90$ ($^1J_{Si-H} = 54$ Hz) and -9.52 ($^2J_{Si-H} = 93$ Hz), which appeared during all of the reactions monitored by ^{1}H NMR spectroscopy at room temperature (Scheme 3). Full NMR data of the latter compound were obtained from the spectra of a sample prepared in reaction of **2** and **5** in *n*-heptane solution. The four well-separated groups of signals of η^4-nbd ligand in a new molybdenum complex were detected at δ 5.05, 3.95, 3.84 and 1.71 ppm in an intensity ratio of 1:1:1:1. The absorption at δ 5.05 is due to two protons attached to one of the two double bonds, while the peak at δ 3.95 is due to two protons attached to the other double bond. The resonance of olefin protons is at a higher and lower field than that of the η^4-nbd ligand in **2** by 0.96 and 0.14 ppm ($\delta = 4.91$ for **2**), respectively, indicating asymmetrical weaker and stronger interactions of the olefin bonds with the molybdenum atom in a new complex. Similar conclusions can be drawn from ^{13}C NMR spectra which show two carbonyl resonances, at δ 214.8 and 210.4 ppm, in an intensity ratio of 1:2. The resonance at δ 210.4 can be assigned to the two carbonyls that are mutually *trans*. This resonance is slightly high-field shifted compared to the signal of the CO group that is approximately *trans* to the olefin unit of η^4-nbd. However, both signals of CO ligands are shifted compared to the signals of the CO groups of **2** observed here at δ 218.4 and 214.3 in an intensity ratio of 1:1. The olefin carbon signals of η^4-nbd ligand for a new compound were detected at δ 88.1 and 47.0 ppm, and their assignment was proved by 2D [13]C—[1]H HMQC spectra, in which the olefin proton signals at δ 5.05 and 3.95 ppm correlate with the carbon signals at δ 88.1 and 47.0 ppm, respec-
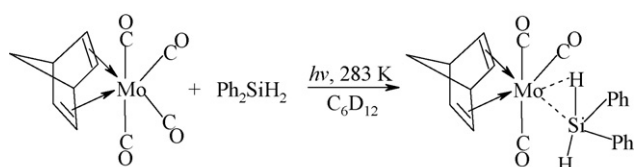
Scheme 2. Activation of the Si—H bond of Ph$_2$SiH$_2$ in photochemical reaction of the norbornadiene complex **2**.
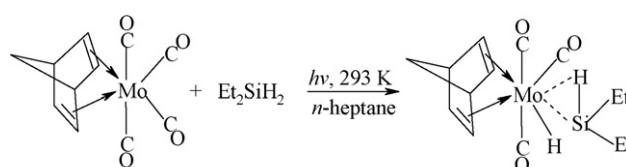
Scheme 3. Oxidative addition of the Si—H bond of Et$_2$SiH$_2$ to the molybdenum centre in complex **2** and the formation of [MoH(η^2-H—SiEt$_2$)(CO)$_3$(η^4-nbd)].

Scheme 4. Ring-opening metathesis polymerization of nbe by **1** in the presence of Et$_3$SiH.
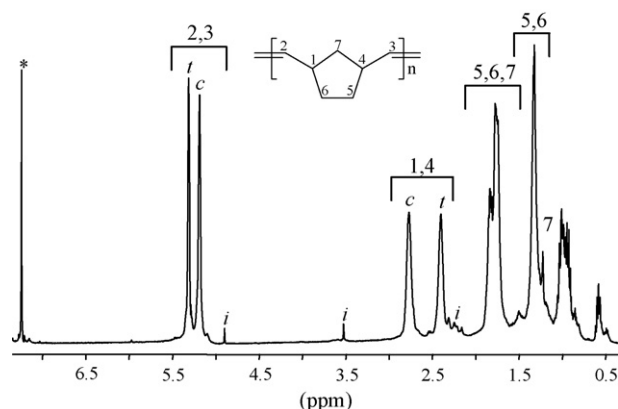

Fig. 5. ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of poly-(cyclopentylenevinylene) obtained in reaction of nbe initiated by **1** in *n*-heptane containing Et$_3$SiH. An asterisk denoted signal of CDCl$_3$ and *i* impurities. Signals denoted by *c* and *t* are due to *cis* and *trans* polymer units.

tively. The lower-field olefin carbon signal could be assigned to the carbons of the C=C unit *trans* to the CO group, and the signal at higher field to the carbons of the double bond *trans* to a ligand other than very good π-acceptor CO ligand, e.g. hydride or silyl ligand. The methylene carbon signal was detected at δ 64.0. These NMR data are closely related to the corresponding seven-coordinate norbornadiene complexes of molybdenum(II) ([MoCl(ECl$_3$)(CO)$_3$(η^4-nbd)], E = Ge, Sn), formed in photochemical reaction of complex **2** with GeCl$_4$ or SnCl$_4$. The molecular structure of those compounds was earlier revealed by X-ray diffraction studies of single crystal and by NMR and IR spectroscopic method in solution [33,34]. In the latter two compounds the η^4-nbd ligand is coordinated asymmetrically with one of the Mo—C(olefin) bond *trans* to CO longer by *ca.* 0.1 Å and a shorter one *trans* to the chloride ligand. The NMR data are in agreement with similar asymmetric coordination of the η^4-nbd ligand in all three seven-coordinate complexes of molybdenum(II). On the basis of NMR data the new compound can be formulated as [MoH(η^2-H–SiEt$_2$)(CO)$_3$(η^4-nbd)] (Scheme 3). The elimination of the nbd ligand from complex **2** in the presence of **5** gave the previously identified complex [{Mo(μ-(^{2}-H(SiEt$_2$)(CO)$_4$}$_2$] [35], which was detected by IR and NMR spectroscopy in all investigated reactions of **5** with carbonyl compounds **1** and **2**.

3.3. Initiation of ROMP

The hydrosilylation of nbd by silane **3**–**6** in the presence of the molybdenum complex **1** gave silyl-2-norbornene, which was next transformed to the ROMP polymer (Scheme 1). The analogous photochemical reaction of nbe with **3** in the presence of **1** (the respective molar ratio of 50:50:1) gave the ROMP polymer with high yield (*ca.* 100% by mass) (Scheme 4). This experiment indicates that under the reaction conditions, the η^2-nbe ligand in the coordination sphere of the molybdenum atom can easily rearrange to give a carbene species initiating the ROMP reaction. The mechanism of this transformation most probably involves the formation of [Mo(CO)$_5$(η^2-nbe)] complex. The latter complex is formed readily in the photochemical reaction of **1** with nbe and has been characterized by IR and NMR spectroscopy in a separate experiment. It has been shown that this complex, similarly as the recently investigated complex of tungsten(0), [W(CO)$_5$((^{2}-nbe)] [10,36], very quickly decomposes in chloroform-d_1 solution to give quantitatively the ROMP polymer. This result provides direct evidence for the transformation of η^2-nbe to metallanorbornylidene. A similar η^2-olefin to alkylidene rearrangement was proposed by

others for such catalytic systems where the source of alkylidene species was only the olefin ligand [14]. The direct evidence for such alkene-to-alkylidene rearrangement was obtained by Wolczanski and co-workers [37].

The mechanism for the initiation of ROMP of Si-nbe can be analogues to that of nbe and involves coordination of Si-nbe to the molybdenum atom and its transformation to a molybdanorbornylidene species (Scheme 5). The ease of carbene formation from the η^2-Si-nbe ligand in the presence of silanes explains the high yield of ROMP reaction in the investigated system. It is worth pointing out that the detection of poly-Si-nbe provides direct evidence for the transformation of η^2-olefin to metallacarbene in the presence of silanes. It should be noted that the initiation of terminal alkene metathesis in photochemical reaction of group 6 metal carbonyls and secondary silanes has been recently observed by Bespalova et al. [38].

3.4. Characteristic of poly-Si-nbe

As was described earlier, the most useful spectroscopic method applied in elucidation of microstructure of ROMP polymers is ^{1}H and ^{13}C NMR spectroscopy [14,23].

A comparison of the integrals of the proton signals at δ 5.31 (*trans*) and 5.19 (*cis*) as well as the proton signals at δ 2.77 (*cis*) and 2.40 (*trans*) leads to the determination of the content of *trans* olefin units in the poly-nbe at *ca.* 50% (Fig. 5). Analyzing the NMR spectra of poly-Si-nbe, we expected to obtain an evidence of the fraction of *cis* double bond in the polymer chain, similarly as for poly-nbe. However, the NMR spectra of poly-Si-nbe are very complicated, although the methine and methylene carbon signals are very well assigned by analysis of ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC NMR spectra. In ^{1}H NMR spectrum of poly-**5**-Si-nbe, the *cis* and
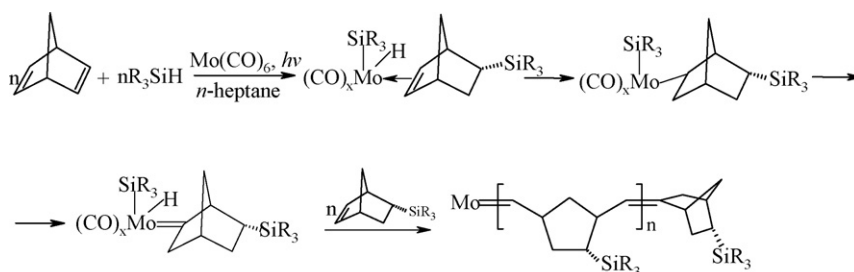
Scheme 5. The initiation of ROMP of Si-nbe and the formation of carbene species in photochemical reaction of **1** and silane (**3**–**6**) in *n*-heptane solution.
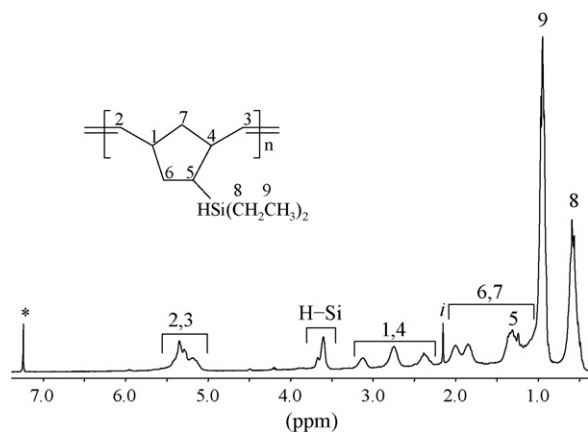
Fig. 6. ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of poly-**5**-Si-nbe obtained in photochemical reaction of **1**, nbd and **5** (1:50:50) in *n*-heptane. An asterisk denoted signal of CDCl$_3$ and *i* impurities.

trans (−HC=CH−) unit of polymer gives three broad signal at δ 5.32, 5.21 and 5.09 and the two methine (HC^{1,4}) units of poly-Si-nbe give three signals at δ 3.12, 2.74 and 2.38 ppm (Fig. 6). In the olefinic carbon region (134–132 ppm) of ^{13}C NMR spectrum one broad signal centered at *ca.* 133 ppm, was detected. On these NMR data poly-**5**-Si-nbe was characterized as containing *trans* (*ca.* 50%) and *cis* arrangements of olefinic protons.

The average molecular weight of poly-**5**-Si-nbe was determined by the gel permeation chromatography of the solution in CHCl$_3$. However, the GPC chromatograms showed bimodal curves with higher ($M_w = 550,000$, PDI = 1.9) and lower ($M_w = 15,200$, PDI = 1.3) molecular weight, which may result from different reactivity of the metal centre created from complex **1** or **2**. The polydispersity index of polymers (higher than 1), is typical for initiators which transform to catalytically active carbene species during the induction period [14].

The ROMP polymer poly(5-trichlorosilyl-2-norbornene) (poly-**4**-Si-nbe), isolated from the reaction mixture, lost solubility, which made it difficult to characterize it in solution by NMR spectroscopy. As suggested by elemental analysis (anal. found: C, 63.5, H, 5.7, Cl, 5.3 vs. calcd.: C, 36.9, H, 4.0, Cl, 46.7 for poly-**4**-Si-nbe), the low solubility of poly-**4**-Si-nbe most probably resulted from hydrolysis of the SiCl$_3$ unity of the polymer during the isolation process.

4. Conclusions

To sum up, we have succeeded in generating 5-silyl-2-norbornenes as a result of hydrosilylation reaction of nbd by tertiary and secondary silanes catalyzed by photochemically activated Mo(CO)$_6$. However, under the reaction conditions, the 5-silyl-2-norbornenes are smoothly transformed in the ROMP reaction to respective unsaturated polymers and in reaction of diethylsilane to the double hydrosilylation product, 2,6-bis(silyl)norbornane. All these transformations were observed step-by-step during the monitoring of the photochemical reaction of the norbornadiene complex **2** with silane by ^{1}H NMR spectroscopy in C$_6$D$_{12}$ solution. The initially formed η^2-silane intermediate complex [Mo(CO)$_3$(η^2-H−SiHPh$_2$)(η^4-nbd)] was detected by ^{1}H NMR spectroscopy. The oxidative addition of the H−Si bond of Et$_2$SiH$_2$ to the molybdenum center of complex **2** leads to the formation of seven-coordinate complex [MoH(η^2-H(SiEt$_2$)(CO)$_3$(η^4-nbd)], which was identified by NMR spectroscopy. Further investigations of the Si−H bond activation and hydrosilylation reaction using this methodology are underway.

It is worth pointing out that the formation of poly-Si-nbe provides direct evidence for the promoted by molybdenum complex transformation of olefin to molybdacarbene that is able to initiate the ROMP of Si-nbe.

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