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Regioselective Si-C Bond Activation in Silicon-Bridged Ansa-Cycloheptatrienyl-Cyclopentadienyl Complexes*

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1. Experimental Section

General: All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. Tropicene has been prepared from $[(\eta\text{-C}_5\text{H}_5)\text{TiCl}_3]$ and cycloheptatriene according to published procedures.^[1] Elemental analyses (C, H, N) were performed on a Elementar Vario EL elemental analyzer. ^1H and ^{13}C NMR spectra were measured on Jeol JNM GX 270, Jeol JNM GX 400 or Bruker DPX 400 spectrometers using the solvent as internal standard. The assignment of all resonances was supported by two-dimensional NMR spectroscopy (COSY and COLOC experiments). EPR spectroscopic details are reported in chapter 2 (*vide infra*).

2a: A solution of *n*-butyllithium (25 mL of a 2.5 M solution in hexane, 62.5 mmol) and of tmeda (8.54 g, 11.1 mL, 73.5 mmol) in 80 mL hexane was slowly treated with solid tropicene (5.0 g, 24.5 mmol) and stirred overnight. The resulting brownish slurry, containing $[(\eta\text{-C}_7\text{H}_6\text{Li})\text{Ti}(\eta\text{-C}_5\text{H}_4\text{Li})]\cdot 2\text{tmeda}$, was cooled to $-78\text{ }^\circ\text{C}$, and a solution of dichlorodimethylsilane (6.36 g, 6.0 mL, 49.3 mmol) in 150 mL hexane was added dropwise over a period of 6 h. The reaction mixture was allowed to reach ambient temperature overnight. After filtration through Celite, the solvent was removed in vacuo. The oily residue was suspended in a few mL of hexane, and the solvent decanted off via a cannula. Drying the residue in high vacuum afforded **1** as a blue-green solid (2.50 g, 39%), which can be purified by crystallization from a thf/hexane mixture at $-78\text{ }^\circ\text{C}$. δ_{H} (C_6D_6): 5.89 (m, 4H; C_7H_6), 4.87 (m, 4H; C_5H_4), 4.75 (dm, 2H; C_7H_6), 0.41 (s, 6H; SiCH_3). δ_{C} (C_6D_6): 101.2 (C_7H_6), 101.0 (C_5H_4), 100.6 (C_5H_4), 89.7 (C_7H_6), 87.6 (C_7H_6), 83.6 (*i*- C_5H_4), 61.6 (*i*- C_7H_6), -5.9 (SiCH_3). δ_{Si} (C_6D_6): -4.79 (SiCH_3).

[1] a) H. O. van Oven, H. J. Liefde Meijer, *J. Organomet. Chem.* 1970, **23**, 159-163; b) B. Demerseman, P. H. Dixneuf, J. Douglade, R. Mercier, *Inorg. Chem.* 1982, **21**, 3942-3947.

Anal. Calcd. for $C_{14}H_{16}SiTi$: C, 64.61; H, 6.20; Found: C, 63.44; H, 6.49. UV/vis (CH_2Cl_2):
 $\lambda_{max} (\epsilon) = 663 (105)$.

2b: A schlenk flask was charged with a suspension of 1.45 g (7.0 mmol) trovacene in 40 mL hexane. After addition of 2.44 g (3.17 mL, 21.0 mmol) tmeda and 7.0 mL *n*-butyllithium (2.5M solution in hexane, 17.5 mmol) the reaction mixture was stirred for 15 h at room temperature. The resulting suspension was cooled to $-78^\circ C$ and a solution of 1.81 g (1.7 mL, 14.0 mmol) Me_2SiCl_2 in 100 mL hexane was added dropwise over a period of 6 h. After reaching room temperature overnight, the violet solution was filtered to remove precipitated LiCl and evaporated to a quarter of the original volume. Cooling down to $-25^\circ C$ yielded 0.99 g (3.76 mmol; 54 %) [1]silatrovacenophane in pure form. Further evaporation and cooling of the supernatant solution yielded additional less pure product. The total yield was 1.31 g (71%). Anal. Calcd. for $C_{14}H_{16}SiV$: C, 63.86; H, 6.12. Found: C, 62.44; H, 6.37. MS (CI, 70 eV): 263.1 (M^+).

3a: A solution of **2a** (0.074 g, 0.28 mmol) in 20 mL toluene was added dropwise to a solution of $Pt(PEt_3)_3$ (0.155 g, 0.28 mmol) in 20 mL toluene at room temperature. The resulting green solution was evaporated to dryness and the residue was extracted with 40 mL hexane. Evaporation of the extract to 2 mL and cooling down to $-25^\circ C$ afforded **3a** (0.05 g, 26 %) as a green crystalline solid. δ_H (C_6D_6): 5.87 (m, 4H, β - C_7H_6 and γ - C_7H_6), 5.78 (m, 2H, α - C_5H_4), 5.62 (m, $^3J_{PtH} = 67$ Hz, 2H, α - C_7H_6), 5.09 (m, 2H, β - C_5H_4), 1.62 (m, 6H, PCH_2CH_3), 1.24 (m, 6H, PCH_2CH_3), 0.93 (m, 9H, PCH_2CH_3), 0.81 (m, 9H, PCH_2CH_3), 0.77 (m, 6H, $^2J_{PtH} = 24$ Hz, $^3J_{PH} = 2.3$ Hz, $SiCH_3$). δ_C (C_6D_6): 120.3 (*i*- C_5H_4), 102.4 (α - C_5H_4), 97.0 (β - C_5H_4), 91.5 (m, $^2J_{PtC} = 79$ Hz, $^3J_{PtP} = 9.2$ Hz, α - C_7H_6), 90.7 (m, $^3J_{PtC} = 33$ Hz, β - C_7H_6), 89.0 (dd, $^2J_{CP} = 104$ Hz and 15 Hz, *i*- C_7H_6), 86.4 (γ - C_7H_6), 18.3 (m, $^2J_{PtC} = 28$ Hz, $^1J_{CP} = 27$ Hz, $^3J_{CP} = 5$ Hz, PCH_2CH_3 *trans* to C_7H_6 group), 15.3 (m, $^1J_{CP} = 17.7$, $^2J_{PtC} = 12.2$ Hz, PCH_2CH_3 *trans* to silyl

group), 8.8 (m, $^3J_{\text{PtC}} = 22.7$ Hz, PCH_2CH_3 *trans* to C_7H_6), 8.0 (m, $^3J_{\text{PtC}} = 10.9$ Hz, PCH_2CH_3 *trans* to silyl group), 7.5 (m, $^2J_{\text{PtC}} = 76.8$ Hz, $^3J_{\text{CP}} = 11.7$ Hz and 1.5 Hz, SiCH_3). δ_{P} (C_6D_6): 11.23 (m, $^1J_{\text{PtP}} = 994$ Hz, $^2J_{\text{SiP}} = 193$ Hz, $^2J_{\text{PP}} = 17$ Hz, PEt_3 *trans* to silyl group), 8.54 (m, $^1J_{\text{PtP}} = 2108$ Hz, $^2J_{\text{PP}} = 17$ Hz, PEt_3 *trans* to C_7H_6). δ_{Pt} (C_6D_6): -4630.0 (dd, $^1J_{\text{PtP}} = 2109$ Hz, $^1J_{\text{PtP}} = 992$ Hz). Anal. Calcd. for $\text{C}_{26}\text{H}_{46}\text{P}_2\text{PtSiTi}$: C, 45.15; H, 6.70. Found: C, 45.57; H, 6.85.

3b: A toluene solution of $\text{Pt}(\text{PEt}_3)_3$ ^[2] (0.296 g, 0.54 mmol) was treated with a solution of **2b** (0.142, 0.54 mmol) in toluene at room temperature. The resulting greyish solution was kept at 50°C for about 15 h. Evaporation to 3 mL and cooling down to -25°C afforded **3b** (0.125 g, 33 %) as a greyish crystalline solid, which was washed three times with 1 mL portion of hexane. Single crystals, suitable for X-ray diffraction were obtained by slow cooling a saturated thf/hexane solution of **3b** to -14°C. Anal. Calcd. for $\text{C}_{26}\text{H}_{46}\text{P}_2\text{PtSiV}$: C, 44.95; H, 6.67. Found: C, 44.96; H, 6.75.

4: A schlenk tube was charged with a solution of **2a** (0.102 g, 0.392 mmol) and **3a** (8.1 mg, 11.76 μmol , 3 mol-%) in benzene (1 mL) and heated to 80°C for 64 h. The resulting suspension was evaporated to dryness and the residue extracted with 5 mL CH_2Cl_2 . The extract was added dropwise to a rapidly stirring solution of hexane (80 mL) precipitating a light-green solid. Filtration and subsequent washing with hexane yielded 0.094 g (92 %) of poly(troticenyilsilane). δ_{H} (C_6D_6): 5.54 (br m, 6H, C_7H_6), 5.15 (br m, 4H, C_5H_4), 0.52 (br s, 6H, SiCH_3). δ_{C} (C_6D_6): 110.9 (*i*- C_5H_4), 103.8 (C_5H_4), 100.5 (C_4H_5), 95.7 (*i*- C_7H_6), 91.2 (C_7H_6), 89.1 (C_7H_6), 87.7 (C_7H_6), -0.4 (SiCH_3). δ_{Si} (C_6D_6): -6.43 (SiCH_3). Anal. Calcd. for $(\text{C}_{14}\text{H}_{16}\text{SiTi})_n$: C, 64.61; H, 6.20. Found: C, 64.84; H, 6.65.

[2] T. Yoshida, T. Matsuda and S. Otsuka, *Inorg. Synth.*, 1990, **28**, 119.

2. Selected NMR Spectra of **3a** and **4**

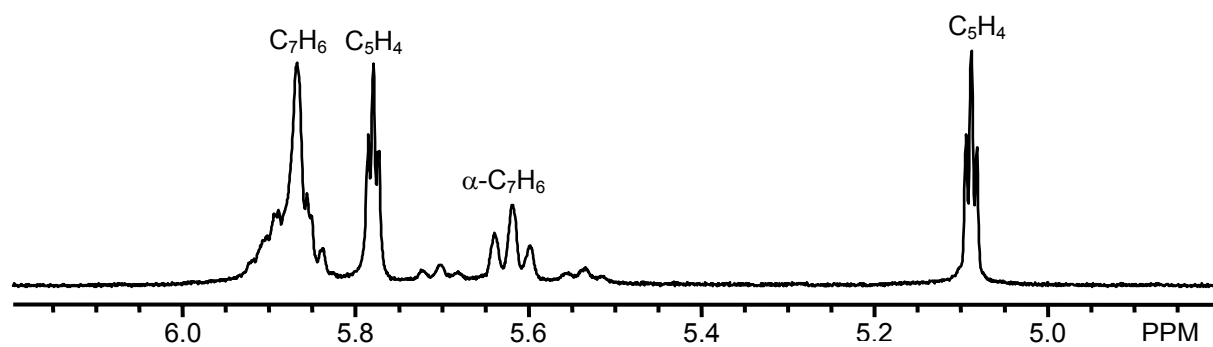


Figure 1. ¹H NMR spectrum of **3a** in C₆D₆ at room temperature.

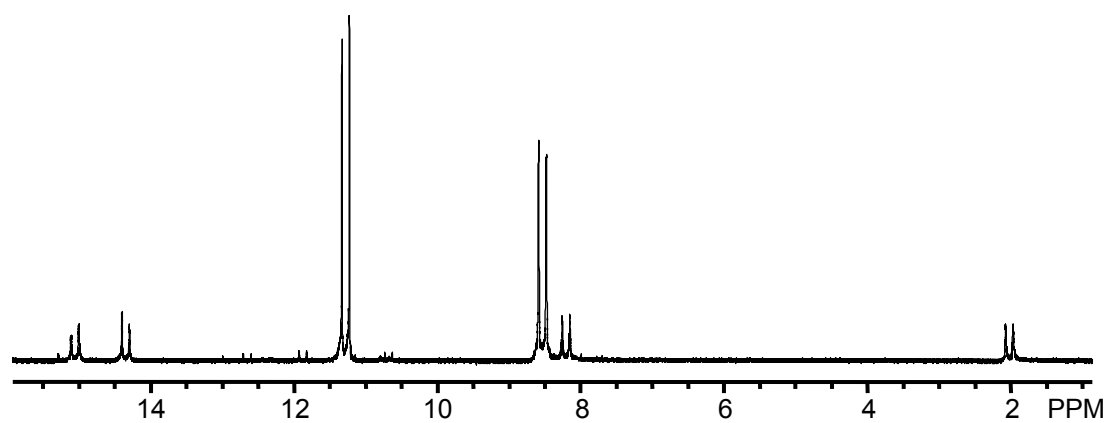


Figure 2. ³¹P NMR spectrum of **3a** in C₆D₆ at room temperature.

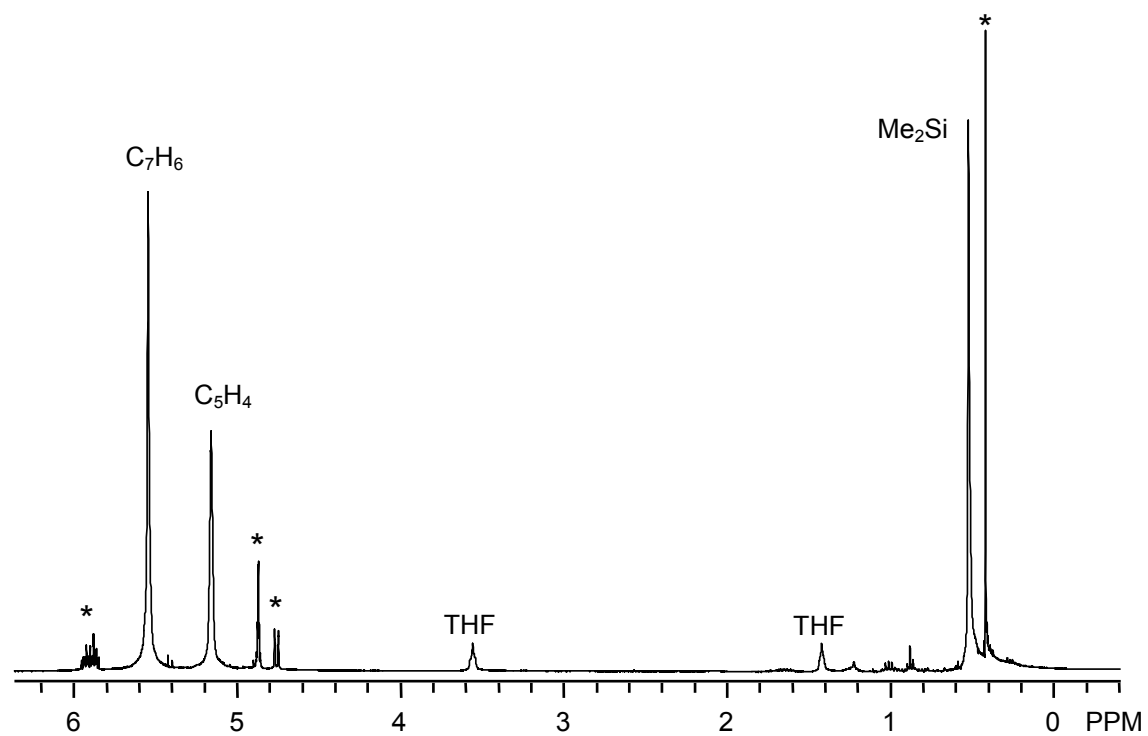


Figure 3. ¹H NMR spectrum of a mixture of oligomers **4** in C₆D₆ at room temperature; the resonances of the starting material **2a** are marked with an asterisk.

3. EPR Spectra of **2b** and **3b**

Continuous-wave EPR spectra were recorded on a JEOL JES-RE2X system at X-band frequency at a temperature of 285 K. The spectra were measured at a microwave frequency of *ca.* 9.05 GHz with a microwave power of 5 mW, modulation amplitude of 0.4 mT, time constant 0.1 s and a modulation frequency of 100 kHz. The *g* and *A* values were calibrated using DPPH (2,2-diphenyl-1-picryl-hydrazil; *g* = 2.00365) as standard. Experimental errors are: $\Delta g = \pm 0.002$, $\Delta A = \pm 3 \times 10^{-4} \text{ cm}^{-1}$. The isotropic *g*-factor for **2b** was found at $g_0 = 1.985$. The value for the hyperfine coupling is $a_0(^{51}\text{V}) = 6.8 \text{ mT} = 63 \times 10^{-4} \text{ cm}^{-1}$. The EPR spectrum of **3b** exhibits an isotropic *g*-factor of $g_0 = 1.987$ and a hyperfine coupling of $a_0(^{51}\text{V}) = 7.1 \text{ mT} = 66 \times 10^{-4} \text{ cm}^{-1}$.

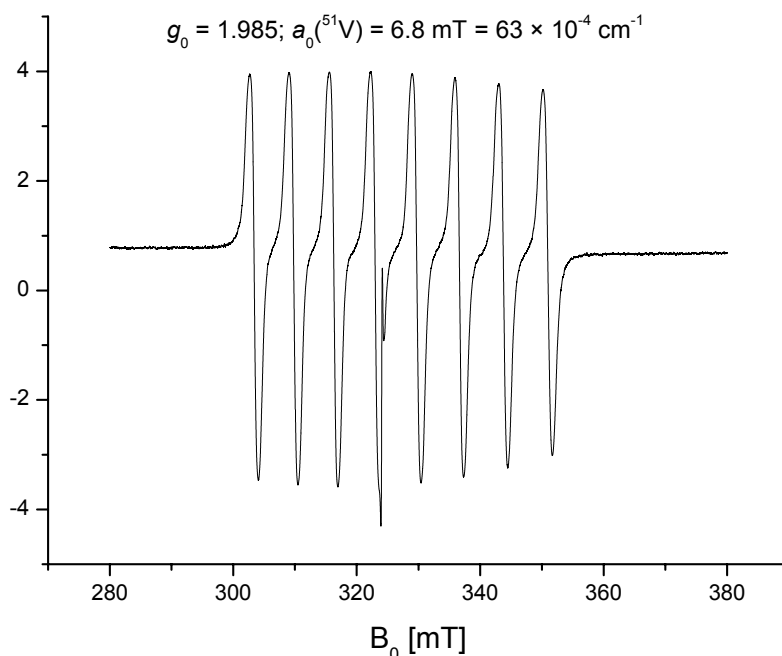


Figure 4. X-band EPR spectrum of **2b** in hexane solution at room temperature.

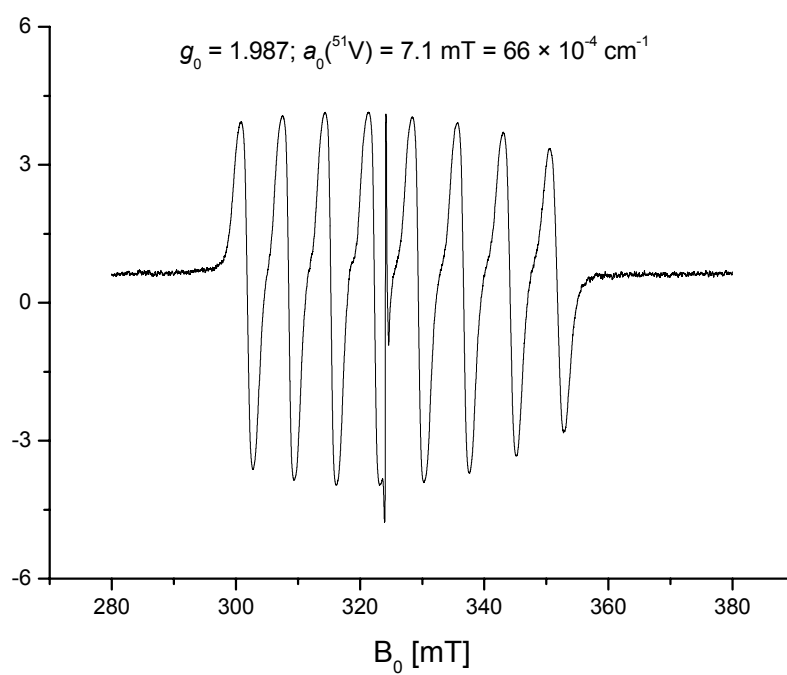


Figure 5. X-band EPR spectrum of **3b** in hexane solution at room temperature.