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A highly stereoselective synthesis of new styryl- π -conjugate organosilicon compounds

Mariusz Majchrzak^{a,*}, Milena Hybsz^a, Sylwia Kostera^a, Maciej Kubicki^a, Bogdan Marciniec^{b,*}

^a Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland ^b Center of Advanced Technology, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

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ABSTRACT

This work describes very precise and controlled catalytic transformations as useful tools for the synthesis of new *trans*- π -conjugated molecular and macromolecular organosilicon compounds. Several distyryl-arenes were obtained efficiently via silylative coupling in high yields and with excellent selectivity for new *E*,*E*-bis(silyl)arenes.

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The search for new, highly selective methods to synthesize linear and branched organosilicon compounds has generated significant interest. Both molecular and macromolecular compounds containing silylene–arylene fragments are synthesized via Würtz polycondensation (using Grignard reagents)^{1,2} or by reactions catalysed by transition metals, for instance: Sonogashira,^{1c} Suzuki³ or Heck.⁴

Silylative coupling (SC) has been developed in our group over the last two decades. It is the reaction of olefins with vinyl-substituted organosilicon compounds, taking place in the presence of complexes containing initially, or generating in situ, metal–hydrogen [M–H] and metal–silicon [M–Si] bonds.⁵ The process occurs via cleavage of the =C–Si bond in the vinylsilane and the C–H bond in the olefin, and is catalysed by transition metal complexes [TM–H] or silyl [TM–Si] ligands (silicometallics) (where TM = Ru, Rh, Ir, Co).^{6,7}

Silylative coupling appears to be a unique, effective and highly regio- and stereoselective method for the functionalization of molecular and macromolecular compounds that have one or a few vinyl groups connected to the silicon atom. Without any doubt, this reaction is a powerful and convenient tool for the synthesis of unsaturated, highly π -conjugated compounds.

We have described the synthesis of polymers and copolymers containing arylene–silylene–vinylene and arylene–silylene–vinylene–phenylene–vinylene units with divinylbenzene, respectively, with well-defined structures.^{8–11}

In this Letter, we present a highly efficient, stereoselective method for the preparation of new π -conjugated distyryl-arylene silicon derivatives through silylative coupling catalysed by a well-defined ruthenium(II) complex.

The starting dienes were prepared in a highly efficient Suzuki– Miyaura coupling reaction catalysed by the very active palladium complex $[Pd(\eta^2-dba)(PCy_3)_2]$ **1**, as shown in Scheme 1.

Typically, the crude mixture was extracted with $CH_2Cl_2/water$ and a small amount of sodium chloride to disperse the slurry. The mixture was then left over sodium sulfate for six hours.¹² In the next step, we used the obtained olefin for the silylative coupling reaction. The catalytic process between distyrylarene and trimethylvinylsilane was conducted following the original procedure: $[RuH(CO)Cl(PCy_3)_2]^{13}$ (catalyst **2**), toluene, sealed ampoule, argon atmosphere.

In order to optimize the reaction conditions with respect to activity, selectivity, catalyst loading, time and temperature, the model reaction between 4,4-divinyl-*p*-biphenyl and vinyltrimethylsilane (after redistillation) at different molar ratios (from 1:2 to 1:5), was studied (Scheme 2).¹⁴

Since the reactive substrate contains a styryl group, the reaction conditions were optimized to eliminate possible uncontrolled,





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^{*} Corresponding authors. Tel.: +48 61 8291407; fax: +48 61 8291508.

E-mail addresses: mariusz.majchrzak@amu.edu.pl (M. Majchrzak), marcinb@ amu.edu.pl (B. Marciniec).



Pd = Pd(dba)(PCy₃)₂; R = H₂C=CH- or Br Ar = 0, arene

Scheme 1. Synthesis of distyrylarenes via Suzuki-Miyaura coupling.

radical polymerization. All the catalytic details are presented in Table 1.

The search for the optimum combination of reaction conditions established that the best conditions were an elevated temperature (around 90 °C) with 2 or 1 mol % of catalyst **2** in a closed flask (the ethylene elimination stage is irreversible⁷). The use of a higher amount of ruthenium catalyst **2** reduced the reaction time to 8 h. The use of the catalyst in a lower amount (0.25 mol %) gave a lower yield of the desired product (yield 45% at 70 °C and 79% at 90 °C after 24 h). We also used 2 mol % of catalyst **2** at 70 °C achieving a very good yield of the order of 96% (GC–MS analysis) in a short time (12 h).

The *E*-silyl by-product was identified on the basis of mass spectrometry. The reaction was carried out in the presence of 0.25 and 0.5 mol % of **2** in the ratio 1:2. Probably, a small amount of vinyltrimethylsilane evaporated during the test. Therefore, we have identified mainly by-product and 23% of the desired product. These reaction parameters have a significant impact on the total control of the process.

The optimized conditions for the model reaction allowed us to use the most effective catalytic system for selectively controlled synthesis of a range of new bis(silyl)substituted distyrylarenes, (Scheme 3).¹⁵

The silylative coupling of 1,4-di(styryl)benzene with vinyltrimethylsilane (2.5 equiv) was accomplished following the welldefined procedure: ruthenium catalyst [RuH(CO)Cl(PCy₃)₂] (**2**) (1 mol % per olefin molecule), toluene, 90–95 °C for 10 h (up to 100% conversion of divinylarylene derivative), 'Schlenk closed

Table 1 Optimizat

ptimization	of the	silylative	coupling	reaction	conditions
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Entry	Catalyst amount ^b (mol %)	Temperature (°C)	Time (h)	Yield ^c (%)
1	2	70	8	83
			12	96
		90	8	>99
2	1	70	8	65
			12	74
		90	8	95
			12	>99
3	0.5	70	8	34, 4 ^d
			24	61, 10 ^d
		90	8	74
			24	95
4	0.25	70	8	24, 8 ^d
			24	45, 14 ^d
		90	8	49
			24	79, 9 ^d

^a [olefin]/[ViSi] = 1:2.5; closed system under Ar.

^b Per olefin molecule.

^c Determined by GC and GC-MS methods.

^d *E*-silyl by-product was observed.

system' to give selectively one isomer of the *E*,*E*-bis[(dimethylsilyl)vinylene]arenes in very good isolated yields 87–98%, except for the thiophene derivative (55%). The ¹H NMR spectrum of 4,4bis[(*E*)-2-(trimethylsilyl)vinyl]-*p*-terphenyl (**4**) (Fig. 1) testifies to the formation of a clean, new organosilicon compound which was isolated using simple and convenient flash filtration (glass filter/silica gel/Celite).

Signals A and B and their coupling constants (19.2 Hz) result from typical *E*-isomer vinylene–silylene fragments between silicon and the aromatic part. In addition, the X-ray crystallographic structure of new compound **8** was determined.¹⁶ As far as we are aware, this is the first example of the crystallographic characterization of this type of compound (Fig. 2).

The molecule of **8** is C_i -symmetrical, as it occupies a special position in the space group P-1; the middle point of the central phenyl ring lies in the inversion centre. As a consequence, the two symmetry-related phenyl rings (C4–C9 and its counterpart)



Scheme 2. Stereocontrolled silylative coupling of 4,4-divinyl-p-biphenyl with vinyltrimethylsilane for the synthesis of novel compound 3.



Scheme 3. Synthesis of new bis(trimethylsilyl)arenes.



Figure 1. ¹H NMR spectrum of **4** in CDCl₃ at 25 °C.



Figure 2. A perspective view of **8** together with the labelling scheme. The ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres with arbitrary radii. The unlabelled part of the molecule is related with the labelled section by the symmetry operation: -x, -y, -z.

are exactly coplanar, and form a dihedral angle of $51.63(18)^\circ$ with the plane of the central ring. The bond lengths and angles are quite typical, the crystal structure almost exclusively being determined by weak, largely non-specific van der Waals interactions and some very weak C—H···F contacts.

In this way, several new π -conjugated organosilicon compounds **3–8** were synthesized with almost 100% selectivity (GC– MS analysis). The above presented results on the synthesis of molecular bis(silyl)arenes formed the basis for the synthesis of an exemplary new arylene–vinylene–silylene copolymer **9**. Due to the low solubility of the anthracenyl derivative of the olefin, the reaction was carried out as a 0.125 M solution instead of 0.5 M as before. In addition, the low concentration of the reagents prevented the olefin from polymerizing. The reaction of copolycondensation was run according to Scheme 4. Analysis of the proton spectrum confirmed the formation of an oligomer made up of only *trans*-vinylene fragments in mers '-AB-AB-AB-AB-AB-' (coupling constants for the protons of the $-Me_2Si-HC=CH-C<$ unit, J_{HH} = 19.2 Hz and 18.6 Hz). Standard analysis using high pressure gel permeation chromatography (GPC) allowed the determination of the basic mass parameters such as the numerical average molecular weight (*Mn*), average molecular weight (*Mw*) and polydispersity (PDI) (*Mw/Mn*), which due to the heterogeneous nature ('ragged') of the GPC curve appeared in the following ranges: *Mn* = 1475–5952, *Mw* = 1491–8702 for PDI = 1.03–1.46.

In conclusion, this is the first Letter of a highly selective method for the synthesis of new π -conjugated, distyrylarylene molecular organosilicon compounds **3–8**. The reactions take place with high yields and occur regio- and stereoselectively to give *E*,*E*-products. An example synthesis of a new high *trans*- π -conjugated linear copolymer **9** obtained via the silylative coupling is also disclosed. Further results on the use of these compounds for the synthesis of high-molecular weight π -conjugated organic compounds will be reported in due course.

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Supplementary data

Supplementary data (general synthetic procedure for polycondensation; characterization of **3**–**9**, analytical details: ¹H NMR, ¹³C NMR, ²⁹Si NMR, ¹⁹F NMR, MS, HRMS) associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.tetlet.2014.03.119.

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- 14. General procedure for the catalytic test of the silylative coupling: A 10 mL Schlenk system was charged under argon with distyrylarene (0.1 g, 4.85×10^{-4} mol), toluene (1.95 mL, 0.2 5 M solution of diene), vinyltrimethylsilane (an amount depending on the [ViSi]/[olefin] ratio, 1:2, 1:2.5, 1:3, 1:4 and 1:5) and [RuH(CO)Cl(PCy₃)₂] (2) (2, 1, 0.5 0.25 mol %, see details under Table 1). All components were added under argon. The final mixture was heated to 70–90 °C in an oil bath for 8–24 h. The reaction progress was monitored by TLC (eluent/CH₂Cl₂/*n*-hexane: 1:3). Conversion of the substrate and reaction selectivity were monitored by GC–MS chromatography. The final yields were calculated on the basis of the ¹H NMR spectra.
- 15. General procedure for the silylative cross-coupling: A mixture consisting of distyrylarylene derivative (0.48 mmol), dry toluene (0.25–0.125 M, depending on the combination of olefin), vinyltrimethylsilane (1.44 mmol) and $[RuH(CO)Cl(PCy_3)_2]$ (2) (0.00096 mmol) was placed under an argon atmosphere in a 10 mL Schlenk glass reactor (closed system) equipped with a stir bar and heated at 80–85°C for 20 h to complete the reaction (GC–MS analysis). Then, after cooling to room temperature, the volume was reduced using a vacuum pump and the crude residue was chromatographed on SiO₂ (eluent/CH₂Cl₂ in *n*-hexane = 0–20%, *R_f* = 0.24–0.46) to afford the analytically pure products.
- 16. X-Ray structure determination: X-ray diffraction data were collected at room temperature by the ω -scan technique on an Agilent Technologies SuperNova diffractometer with an Atlas detector and CuK_{\alpha} ($\lambda = 1.54178$ Å) radiation. The data were corrected for Lorentz-polarization as well as for absorption effects.¹⁷ Cell parameters were determined by least-squares fit of the 4848 strongest reflections chosen from the whole experiment. The calculations were mainly performed within the WinGX program system.¹⁸ The structures were solved with SIR92¹⁹ and refined with the full-matrix least-squares procedure on F² by SHELXL97.²⁰ Non-hydrogen atoms were refined anisotropically, hydrogen atoms were located at calculated positions and refined as a 'riding model' with isotropic thermal parameters fixed at 1.2 (1.5 for methyl groups) times the Ueq values of the appropriate carrier atom. *Crystal data of* **8**: C₂₈H₃₀F₄Si₂; M_r = 498.70; triclinic, P-1, *a* = 5.8907(3) Å, *b* = 10.7750(6) Å, *c* = 1.6208(9) Å, $\alpha = 107.150(5)^\circ$, $\beta = 94.885(5)^\circ$, $\gamma = 103.533(5)^\circ$, V = 675.73(7) Å³, *Z* = 1, *d*_x = 1.23 g cm⁻³. CuK_x ($\lambda = 1.54178$ Å), 5935 reflections measured, 2691 unique (*R*_{int} = 0.036), 2472 observed (*I* > 2 σ (*I*), final *R* = 5.79%, wR2 = 18.02%, *S* = 1.10. Maximum $\Delta \rho$ in the final difference Fourier map: +0.44/-0.20 e Å⁻³. CCDC-926523.
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