Cite this: New J. Chem., 2011, 35, 2743–2746

A new selective approach to unsymmetrical siloxanes and germasiloxanes via O-metalation of silanols with 2-methylallylsilanes and 2-methylallylgermanes

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Received (in Victoria, Australia) 17th July 2011, Accepted 29th September 2011 DOI: 10.1039/c1nj20624a

A scandium(III) trifluoromethanesulfonate-catalyzed *O*-metalation of silanols with 2-methylallylsilanes and 2-methylallylgermanes leading to siloxane or germasiloxane bond formation under mild conditions with evolution of isobutylene is described.

The functionalized, unsymmetrical disiloxanes and germasiloxanes have attracted much attention as precursors for the preparation of various functional materials, such as liquid crystalline polymers or resins for fabrication of high refractive index and low dielectric constant materials and components of biocompatible oils.¹

Conventional approaches to unsymmetrical siloxanes and germasiloxanes involve condensation of silanols with chloro-, amino-, acyloxy- or alkoxysilanes/germanes and cohydrolysis of two chloro- or alkoxysilanes/germanes.² In recent years not only stoichiometric reactions, but also catalytic methods such as rhodium(1)-catalyzed dehydrocoupling of silanols with hydrosilanes,³ or dealkylative coupling of hydrosilanes with alkoxysilanes⁴ have been reported for disiloxane bond formation. Unsymmetrical siloxanes were also obtained from silanols and hydrosilanes using a phase transfer catalytic system.⁵ The catalytic method for SiO–Ge bond formation based on the $B(C_6F_5)_3$ -catalyzed dealkylative coupling of hydrosilanes with alkoxygermanes or hydrogermanes with alkoxysilanes has also been reported.⁶

During the course of our recent studies on the catalytic activation of O–H bonds of silanols and alcohols by vinylmetalloids we have developed new catalytic routes for efficient *O*-silylation of silanols with vinylsilanes catalyzed by $[RuHCl(CO)(PCy_3)_2]^7$ and *O*-germylation of silanols with vinylgermanes catalyzed by $[Ru_3(CO)_{12}]$.⁸ Recently we have focused our research on the use of 2-methylallylsilanes and 2-methylallylgermanes as metalating agents and hydrogen acceptors for the *O*-metalation of silanols to form disiloxane or germasiloxane bonds, respectively.

There are several reports on the successful silulation of alcohols with allylsilanes catalyzed by p-toluenesulfonic acid⁹

iodine¹⁰ or trifluoromethanesulfonic acid¹¹ and scandium(III) trifluoromethanesulfonate¹² leading to silyl ethers as well as the silylation of SiO–H groups of the silica surface with 2-methylallylsilanes catalyzed by scandium(III) trifluoromethane-sulfonate.¹³ Nevertheless, to the best of our knowledge, no examples of a method for the synthesis of functionalized, unsymmetrical disiloxanes or germasiloxanes from the corresponding silanols and 2-methylallylsilanes/2-methylallylgermanes in the presence of a catalytic amount of Sc(OTf)₃ have been described to date.

Herein, we report a new facile and selective protocol for the synthesis of functionalized, unsymmetrical disiloxanes and germasiloxanes that involves activation of the O–H bond in silanols by 2-methylallylsilanes or 2-methylallylgermanes occurring in the presence of scandium(III) trifluoromethanesulfonate with elimination of isobutylene (Scheme 1).

The metalation of silanols by 2-methylallylsilanes or 2-methylallylgermanes with the formation of isobutylene as a neutral and harmless by-product could be very attractive since a wide variety of silanols is commercially available. The silyl- and germylsubstituted olefins were easily prepared by the reaction of (2-methylallyl)magnesium chloride with the corresponding chlorosilane or chlorogermane.

The silulation reactions were examined in the presence of scandium trifluoromethanesulfonate (Sc(OTf)₃) known to be active in the silulation of alcohols and SiO–H groups on the silica surface with methylallylsilanes.^{9–13} Both reported reactions were performed under similar conditions (catalyst loading -0.5-5 mol%, MeCN or EtCN as a solvent, 0.5–12 h, room temperature).

Our initial studies were carried out with the tris(trimethylsiloxy)silanol and 2-methylallyldimethyl-vinylsilane. After several attempts we found that the *O*-silylation reaction of

$$\mathbf{R_3'Si-O-H} + \mathbf{H_2C} \underbrace{\overset{Me}{\leftarrow} \mathbf{ER_3}}_{CH_3CN, 0.22^{\circ}C, 1h} \mathbf{R_3'Si-O-ER_3} + \mathbf{H_2C} \underbrace{\overset{Me}{\leftarrow}}_{Me}$$

$$\mathbf{E} = \mathbf{Si}, \mathbf{Ge}$$

$$\mathbf{R} = \mathbf{H} \text{ alkenyl and singulations}$$

Scheme 1 The O-metalation of silanols by 2-methylallylsilanes-(germanes) catalyzed by Sc(OTf)₃.

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tris(trimethylsiloxy)silanol (1 equiv.) with 2-methylallyldimethylvinylsilane (1.2 equiv.) in the presence of 2 mol% $Sc(OTf)_3$ in an open system conducted in acetonitrile at room temperature afforded exclusively 1,1,1,5,5-pentamethyl-5-vinyl-3,3-bis(trimethylsiloxy)-trisiloxane (1) after 1 hour (Table 1, entry 1).

The presence of a $Sc(OTf)_3$ catalyst is crucial for this transformation. In the absence of a Lewis acidic catalyst, no reaction took place. As may be expected, lowering of the catalyst loading to 1 mol% resulted in decrease of the reaction rate (74% conversion of tris(trimethylsiloxy)silanol after 4 hours), but not of product selectivity.

These optimal conditions were applied to other silanols (triethylsilanol, dimethylphenylsilanol, and triisopropylsilanol), 2-methylallylsilanes (2-methyl-allyltriisopropylsilane, 2-methyl-allyltris(trimethylsiloxy)-silane, 2-methylallyldiiso-propylsilane) and 2-methyl-allyltriethylgermane providing the desired products in high isolated yields (79–96%) (Scheme 1, Table 1).

Most of the reactions examined proceeded selectively in very good yield to form the respective siloxanes or germasiloxanes. However, in some cases when triethylsilanol and dimethylphenylsilanol were used, a silanol homo-condensation by-product was observed (20–30%). However two- or three-fold excess of olefin and decreasing the reaction temperature to 0 °C allowed minimizing the formation of side products, which could be easily separated by column chromatography. All germasiloxane and siloxane products were isolated and characterized spectroscopically.

The attractiveness of this selective *O*-germylation and *O*-silylation of silanols by allylsilanes and allylgermanes stems from the fact that it permits synthesis of functional compounds with hydrogen atoms or vinyl groups, which may be used as reagents for further catalytic transformations.¹⁴

As an extension to the present study we investigated the hydrosilylation reaction of 1,1,1,5,5-pentamethyl-5-vinyl-3,3bis(trimethylsiloxy)trisiloxane (1) with heptamethyltrisiloxane in the presence of a platinum Karstedt catalyst known for its high catalytic activity for a number of hydrosilylation reactions.^{15,16} The reaction was carried out under typical

 $\label{eq:table_$

Entry	-ER ₃	-SiR'3	Molar ratio [CH ₂ ==C(CH ₃)CH ₂ ER ₃]:[HOSiR' ₃]	Product	Isolated yield (%)
1	-SiMe ₂ CH=CH ₂	-Si(OSiMe ₃) ₃	1.2:1	Si ^{CC} Si(OSiMe ₃) ₃ Me Me 1	95
2	-SiMe ₂ CH=CH ₂	-Si(<i>i</i> -Pr) ₃	1.2:1	Me Me 2	97
3	-SiMe ₂ CH=CH ₂	-SiEt ₃	3:1	Me Me 3	83 ^{<i>a</i>}
4	-SiMe ₂ CH=CH ₂	-SiMe ₂ Ph	3:1	Me Si ^C SiPhMe ₂ Me 4	81 ^{<i>a</i>}
5	-Si(OSiMe ₃) ₃	-Si(OSiMe ₃) ₃	1.2:1	(Me ₃ SiO) ₃ Si ^{_O_} Si(OSiMe ₃) ₃	92
6	-Si(OSiMe ₃) ₃	-Si(<i>i</i> -Pr) ₃	1.2:1	(Me₃SiO)₃Si ^{∽O} ∽Si(<i>i</i> -Pr)₃ ₆	95
7	-Si(OSiMe ₃) ₃	-SiEt ₃	3:1	(Me₃SiO)₃Si ^{∕O} ∕SiEt₃ ₇	86 ^{<i>a</i>}
8	-Si(<i>i</i> -Pr) ₃	-Si(OSiMe ₃) ₃	3:1	$(i-Pr)_3Si^{O}Si(OSiMe_3)_3_6$	93
9	-Si(<i>i</i> -Pr) ₃	-Si(<i>i</i> -Pr) ₃	1.2:1	(<i>i</i> -Pr)₃Si ^{∕O} ∕Si(<i>i</i> -Pr)₃ 8	98
10	-Si(<i>i</i> -Pr) ₃	-SiMe ₂ Ph	1.2:1	$(i-Pr)_3Si^{O_SiPhMe_2}$	79 ^{<i>a</i>}
11	-SiH(<i>i</i> -Pr) ₂	-Si(OSiMe ₃) ₃	1.2:1	$(i\text{-}Pr)_2HSi^{O}Si(OSiMe_3)_3 10$	90
12	-GeEt ₃	-Si(OSiMe ₃) ₃	1.2:1	Et ₃ Ge ^{_O_} Si(OSiMe ₃) _{3 11}	94
13	-GeEt ₃	-Si(<i>i</i> -Pr) ₃	1.2:1	Et ₃ Ge ^{-O} -Si(<i>i</i> -Pr) ₃ 12	96
14	-GeEt ₃	-SiEt ₃	2:1	$Et_3Ge^{-O_s}SiEt_{3}$	88 ^a
15	-GeEt ₃	-SiMe ₂ Ph	2:1	Et ₃ Ge ^{_O_} SiPhMe ₂ 14	80 ^a
Reaction	conditions: acetonitrile	(0.1 M), room temp	erature, catalyst loading—2 mol%. ^a React	tion performed at 0 $^{\circ}$ C.	

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conditions used for hydrosilylation of vinylsiloxanes (toluene, 60 $^{\circ}$ C, 4 h), and the product was isolated as a viscous oil with excellent yield (94%).

The trisiloxane (1) can be also functionalized *via* the silylative coupling reaction. The silylation reaction was examined in the presence of a ruthenium-hydride catalyst: RuHCl(CO)(PCy₃)₂— known to be active in silylative coupling of vinylsilanes with olefins.¹⁷ In a typical procedure, trisiloxane (1), trimethylvinyl-silane (1:3 ratio) and RuHCl(CO)(PCy₃)₂ catalyst (2 mol%) were dissolved in toluene (0.1 M concentration) and heated in a Schlenk bomb flask fitted with a plug valve at 110 °C for 24 h to yield functionalized vinylsiloxane with good yield (89%) and high stereoselectivity (E/Z = 98/2) (Scheme 2).

In conclusion, we have developed a new catalytic route for efficient O-silylation and O-germylation of silanols with 2-methylallylsilanes and 2-methylallylgermanes, in which the unsaturated compound acts as a metalating agent and hydrogen acceptor to form the SiO–Si or SiO–Ge bond with evolution of isobutylene. Mild conditions, good functional group compatibility and the simplicity of the experimental technique of this new catalytic approach to functionalized siloxanes and germasiloxanes are favorable features of the reaction. Further application of this protocol for the synthesis of polysiloxanes is currently under study.

Experimental section

The reagents and $Sc(OTf)_3$ as well as the Karstedt catalyst used for experiments were purchased from Sigma-Aldrich Co. and Gelest Inc. and used without further purification. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a Varian XL 300 spectrometer using C₆D₆ as a solvent. GC analyses were performed on a Varian 3400 with a Megabore column (30 m) and TCD.

Synthesis of siloxanes and germasiloxanes

The structures of synthesized siloxanes and germasiloxanes **5**, **11** and **14** were confirmed by GC-MS and NMR spectroscopy matching data reported in the literature.^{8,18}

General method. A mixture consisting of 1.5 mmol of silanol, 1.8–4.5 mmol of 2-methylallylsilanes or 2-methylallyltriethylgermane (according to conditions indicated in Table 1), 14.8 mg (0.03 mmol) of Sc(OTf)₃ and 15 ml of acetonitrile were placed in a 50 ml one-necked round-bottomed flask and stirred at room temperature (for triethylsilanol and dimethylphenylsilanol at 0 °C) for 1 h. After this time the solvent was evaporated and the



Scheme 2 Synthetic application of 1,1,1,5,5-pentamethyl-5-vinyl-3,3-bis(trimethylsiloxy)trisiloxane.

product was purified by column chromatography on silica gel, eluting with *n*-hexane to give corresponding compounds **1–14**.

1,1,1,5,5-Pentamethyl-5-vinyl-3,3-bis(trimethylsiloxy)-trisiloxane (1). ¹H NMR (300 MHz, C₆D₆); δ (ppm): 0.23 (s, 27H, OSiCH₃), 0.29 (s, 6H, SiCH₃), 5.81–5.90 (dd, J = 4.0, 20.2 Hz, 1H, CH=CH₂), 5.93–6.00 (dd, J = 4.0, 14.9 Hz, 1H, CH=CH₂), 6.21–6.33 (dd, J = 14.9, 20.2 Hz, 1H, CH=CH₂). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) 0.3 (SiCH₃), 1.8 (OSiCH₃), 132.2 (CH=CH₂), 139.2 (CH=CH₂). Anal. calcd for C₁₃H₃₆O₄Si₅: C, 39.34; H, 9.14%. Found: C, 39.49; H, 9.06%.

1,1-Dimethyl-3,3,3-triisopropyl-1-vinyldisiloxane (2). ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.24 (s, 6H, SiCH₃), 0.94–1.03 (m, 3H, SiCH), 1.07–1.09 (m, 18H, SiCH(CH₃)₂), 5.73–5.79 (dd, J = 4.0, 20.2 Hz, 1H, CH=CH₂), 5.89–5.94 (dd, J = 4.0, 14.9 Hz, 1H, CH=CH₂), 6.18–6.27 (dd, J = 14.9, 20.2 Hz, 1H, CH=CH₂), 1³C NMR (75 MHz, C₆D₆): δ (ppm) 0.7 (SiCH₃), 13.1 (SiCH), 18.1 (SiCH(CH₃)₂), 131.7 (CH=CH₂), 140.0 (CH=CH₂). Anal. calcd for C₁₃H₃₀OSi₂: C, 60.39; H, 11.70%. Found: C, 60.50; H, 11.62%.

1,1,1-Triethyl-3,3-dimethyl-3-vinyldisiloxane (3). ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.24 (s, 6H, SiCH₃), 0.61–0.66 (q, 6H, SiCH₂), 0.97–1.03 (t, 9H, SiCH₂CH₃), 5.72–5.78 (dd, J = 3.9, 20.1 Hz, 1H, CH=CH₂), 5.90–5.94 (dd, J = 3.9, 14.8 Hz, 1H, CH=CH₂), 6.18–6.26 (dd, J = 14.8, 20.1 Hz, 1H CH=CH₂). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) 0.7 (SiCH₃), 7.5 (SiCH₂), 8.8 (SiCH₂CH₃), 131.8 (CH=CH₂), 139.8 (CH=CH₂). Anal. calcd for C₁₀H₂₄OSi₂: C, 55.48; H, 11.18%. Found: C, 55.69; H, 11.09%.

1,1,3,3-Tetramethyl-1-phenyl-3-vinyldisiloxane (4). ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.29 (s, 6H, SiCH₃), 0.44 (s, 6H, SiCH₃), 5.73–5.79 (dd, J = 4.0, 20.2 Hz, 1H, CH=CH₂), 5.92–5.96 (dd, J = 4.0, 14.7 Hz, 1H, CH=CH₂), 6.19–6.27 (dd, J = 14.7, 20.2 Hz, 1H, CH=CH₂), 7.23–7.32 (m, 3H, Ph), 7.56–7.61 (m, 2H, Ph). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) 0.3, 1.8 (SiCH₃), 128.1, 129.4, 130.5, 134.5 (Ph), 130.9 (CH=CH₂), 139.2 (CH=CH₂). Anal. calcd for C₁₂H₂₀OSi₂: C, 60.95; H, 8.53%. Found: C, 60.89; H, 8.42%.

1,1.1-Trimethyl-5,5,5-triisopropyl-3,3-bis(trimethyl-siloxy)trisiloxane (6). ¹H NMR (300 MHz, C_6D_6): δ (ppm) 0.24 (s, 27H, OSiCH₃), 0.93–1.07 (m, 3H, SiCH), 1.15–1.19 (m, 18H, SiCH(CH₃)₂). ¹³C NMR (75 MHz, C_6D_6): δ (ppm) 1.8 (SiCH₃), 13.1 (SiCH), 18.1 (SiCH(CH₃)₂). Anal. calcd for $C_{18}H_{48}O_4Si_5$: C, 46.10; H, 10.32%. Found: C, 46.12; H, 10.40%.

1,1,1-Triethyl-5,5,5-trimethyl-3,3-bis(trimethylsiloxy)-trisiloxane (7). ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.25 (s, 27H, OSiCH₃), 0.60–0.64 (q, 6H, SiCH₂), 1.00–1.04 (m, 9H, SiCH₂CH₃). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) 1.8 (SiCH₃), 6.6 (SiCH₂CH₃), 7.7 (SiCH₂CH₃), Anal. calcd for C₁₅H₄₂O₄Si₅: C, 42.20; H, 9.92%. Found: C, 42.13; H, 9.81%.

Hexaisopropyldisiloxane (8). ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.93–1.16 (m, 42H, SiCH, SiCH(CH₃)₂). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) 13.8 (SiCH), 18.4 (SiCH(CH₃)₂). Anal. calcd for C₁₈H₄₂OSi₂: C, 65.37; H, 12.80%. Found: C, 65.25; H, 12.41%. **1,1-Dimethyl-1-phenyl-3,3,3-triisopropyldisiloxane (9)**. ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.39 (s, 6H, SiCH₃), 0.93–1.02 (m, 3H, SiCH), 1.06–1.10 (m, 18H, SiCH(CH_3)₂), 7.24–7.33 (m, 3H, Ph), 7.56–7.62 (m, 2H, Ph). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) 1.7 (SiCH₃), 13.1 (SiCH), 18.2 (SiCH(CH_3)₂), 128.2, 129.4, 130.4, 134.2 (Ph). Anal. calcd for C₁₇H₃₂OSi₂: C, 66.16; H, 10.45%. Found: C, 66.19; H, 10.39%.

1,1,1-Trimethyl-5-hydrido-5,5-triisopropyl-3,3-bis(tri-methyl-siloxy)trisiloxane (10). ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.24 (s, 27H, OSiCH₃), 0.96–1.06 (m, 2H, SiCH), 1.10–1.18 (m, 12H, SiCH(CH_3)₂), 4.56 (s, 1H, SiH). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) 1.8 (OSiCH₃), 13.3 (SiCH), 17.3 (SiCH(CH_3)₂). Anal. calcd for C₁₅H₄₂O₄Si₅: C, 42.20; H, 9.92%. Found: C, 41.92; H, 9.80%.

Triethyl(triisopropylsiloxy)germane (12). ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.82–0.85 (q, 6H, GeCH₂), 1.01–1.18 (m, 30H, GeCH₂CH₃, SiCH and SiCH(CH₃)₂) ¹³C NMR (75 MHz, C₆D₆): δ (ppm) 8.2 (GeCH₂CH₃), 9.1 (GeCH₂CH₃), 13.9 (SiCH), 18.6 (SiCH(CH₃)₂). Anal. calcd for C₁₅H₃₆GeOSi: C, 54.07; H, 10.89%. Found: C, 53.95; H, 10.78%.

Triethyl(triethylsiloxy)germane (13). ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.60–0.64 (q, 6H, SiCH₂), 0.81–0.84 (q, 6H, GeCH₂), 1.00–1.11 (m, 18H, GeCH₂CH₃, and SiCH₂CH₃). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) 6.5 (SiCH₂CH₃), 7.6 (SiCH₂CH₃), 8.1 (GeCH₂CH₃), 8.9 (GeCH₂CH₃). Anal. calcd for C₁₂H₃₀GeOSi: C, 49.51; H, 10.39%. Found: C, 49.45; H, 10.44%.

The hydrosilylation reaction of 1,1,1,5,5-pentamethyl-5-vinyl-3,3bis(trimethylsiloxy)-trisiloxane with heptamethyltrisiloxane

A mixture consisting of 0.2 g (0.5 mmol) of 1,1,1,5,5pentamethyl-5-vinyl-3,3-bis(trimethylsiloxy)trisiloxane, 0.12 g (0.55 mmol) of heptamethyltrisiloxane, 5×10^{-6} mol of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex and 5 ml of toluene was placed in a 20 ml Schlenk bomb flask fitted with a plug valve and heated at 60 °C for 4 h. Next, after cooling the reaction mixture to room temperature, the solvent was evaporated and the product was purified by column chromatography on silica gel, eluting with *n*-hexane to give the product in 94% yield as a colorless liquid.

¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.15–0.30 (m, 54H, OSiCH₃), 0.67–0.78 (m, 4H, SiCH₂). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) –0.5 (SiCH₃), 1.8, 2.1 (SiCH₃), 9.4, 9.9 (SiCH₂). Anal. calcd for C₂₀H₅₈O₆Si₈: C, 38.78; H, 9.44%. Found: C, 38.92; H, 9.39%.

The silylative coupling reaction of 1,1,1,5,5-pentamethyl-5-vinyl-3,3-bis(trimethylsiloxy)trisiloxane with trimethylvinylsilane

A mixture consisting of 0.2 g (0.5 mmol) of 1,1,1,5,5pentamethyl-5-vinyl-3,3-bis(trimethylsiloxy)trisiloxane, 0.15 g (1.5 mmol) of trimethylvinylsilane, 0.01 mmol of [RuHCl(CO)(PCy₃)₂] and 5 ml of toluene was placed in a 20 ml Schlenk bomb flask fitted with a plug valve and heated at 110 °C for 24 h. Next, after cooling the reaction mixture to room temperature, the solvent was evaporated and the product was purified by column chromatography on silica gel, eluting with *n*-hexane to give the product in 89% yield as a colorless liquid. ¹H NMR (300 MHz, C₆D₆): δ (ppm) 0.15 (s, 9H, SiCH₃), 0.24 (s, 27H, OSiCH₃), 0.34 (s, 6H, SiCH₃), 6.82 (d, J = 22.6, 1H, CH=CH), 6.95 (d, J = 22.6, 1H, CH=CH). ¹³C NMR (75 MHz, C₆D₆): δ (ppm) -1.6, 1.8, 1.9 (SiCH₃), 149.7, 152.0 (SiCH=). Anal. calcd for C₁₆H₄₄O₄Si₆: C, 40.97; H, 9.46%. Found: C, 41.15; H, 9.41%.

Acknowledgements

This work was made possible by a grant IP2010 013070 (*Iuventus Plus*) from Ministry of Science and Higher Education (Poland).

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