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Synthesis, structure and catalytic properties of bis[2-(trifluoromethyl)phenyl]silanediol[†]

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1 | INTRODUCTION

Silanols are the silicon analogues of alcohols and therefore are of fundamental importance.^[1] Due to their relative acidity compared to their carbon analogues, the binding interactions of organosilanols have been employed for catalytic purposes quite recently.^[2] Silanediols acting as hydrogen-bonding organocatalysts in Diels–Alder reactions were first reported by Franz and co-workers.^[2b] The activity of the silanediol catalyst in such reactions is correlated with the acidity of the

A novel trifluoromethylaryl-substituted disilanol, bis[(2-trifluoromethyl)phenyl] silanediol, was prepared by hydrolysis of the precursor dichloride and fully characterized. Single-crystal X-ray diffraction indicates doubly linked hydrogen bonded dimers and also hydrogen bonding to tetrahydrofuran solvent. The acidity of the silanol functions is enhanced by the presence of the trifluoromethyl groups and the compound is found to be active in promoting a standard Diels–Alder reaction, increasing yields by a factor of three.

KEYWORDS

catalysis, Diels-Alder, hydrogen bond, silanediol, trifluoromethyl

silanol, which can be increased by the presence of one electron-withdrawing group at silicon.^[2c] Here we report the synthesis of a novel silanediol bearing two electron-withdrawing 2-(trifluoromethyl)phenyl units at silicon and its catalytic properties with respect to a standard Diels–Alder reaction.

2 | RESULTS AND DISCUSSION

We anticipated that bis[(2-trifluoromethyl)phenyl] dichlorosilane (1) should be a reasonable precursor for the preparation of the corresponding silanediol (3).

[†]Dedicated to Prof. Bob West on the occasion of his 90th birthday

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Starting from 1-bromo-2-(trifluoromethyl) benzene, dichlorosilane **1** was obtained via metal-halogen exchange with n-BuLi and subsequent twofold salt metathesis with SiCl₄ (Scheme 1). In addition to the envisaged dichlorosilane, the corresponding trichlorosilane **2** was formed which could be separated by distillation. Dichlorosilane **1** was isolated in moderate yield as a colourless and sublimable solid.

To ensure complete metallation of the aryl precursor, an excess of *n*-BuLi (2 eq.) was used in agreement with published procedures for related compounds.^[3] We did not isolate the lithiated intermediate and reacted further *in situ* with SiCl₄. Again 2 eq. of SiCl₄ was used to ensure that all metallated species were quenched prior to the distillation step. Heating of metallated organofluorine compounds or mixtures of organofluorine and organolithium compounds might cause potential hazards. Since the reactivity of the Si–Cl functionalities in **1** and **2** precludes standard quenching procedures with protic reagents, we have chosen this counterintuitive approach. In synthetic procedures for the related 2-(trifluoromethyl)phenylphosphanes, this issue has been circumvented via either complete substitution or the use of protecting groups.^[4]

²⁹Si NMR chemical shifts are 4.4 ppm for **1** and -2.7 ppm for **2** which are comparable to those for other aryl-substituted di- and trichlorosilanes.^[5] The ¹⁹F NMR chemical shifts, -56.76 ppm for **1** and -56.60 ppm for **2**, as well as the ¹*J*_{CF} coupling constant of 31.9 Hz, are in the expected range for *o*-CF₃-substituted arylchlorosilanes.^[6] In contrast to the observations of Batsanov *et al.* who encountered Cl/F exchange in the reactions of 2,4,6-tris-trifluoromethylphenyllithium and 2,6-bis-trifluoromethylphenyllithium with SiCl₄, no such exchange was observed in the preparation of **1** and **2**.^[6a] Recrystallization of **1** from benzene afforded single crystals suitable for X-ray diffraction. Compound **1** crystallizes in the monoclinic space group *Pc* (Figure 1).

In the solid state the molecules of **1** show a low symmetry owing to the orientations of the phenyl rings which are non-coplanar with an interplanar angle of 79.71 (11)° giving rise to axial chirality. Similar to [2,4-(CF₃)₂C₆H₃]₂SiCl₂^[6a] the Si…F distances in **1** are rather short: Si(1)…F(13) = 2.863(2) Å; Si(1)…F(23) = 3.086(2) Å. The C–Si–C and C–Si–Cl bond angles in **1** are comparable with those in other dichlorosilanes,^[6,7] while the Cl–Si–Cl bond angle of 105.74(3)° is the smallest of



SCHEME 1 Preparation of 1 and 2



FIGURE 1 ORTEP plot of the crystal structure of **1** with ellipsoids drawn at 30% probability level (hydrogen atoms omitted for clarity)

these. As in other CF_3 -substituted aryldichlorosilanes,^[6a] the Si–Cl bond lengths of 2.0483(8) and 2.0536(8) Å are slightly shorter than those in non-perfluoro-substituted aryldichlorosilanes.^[6a,8]

Controlled hydrolysis of dichlorosilane 1 in the presence of two equivalents of NEt₃ in Et₂O affords bis[(2trifluoromethyl)phenyl] silanediol (3) in moderate yield as a crystalline solid after workup (Scheme 2). The ²⁹Si NMR chemical shift of -38.2 ppm is within the expected range for diarylsilanediols.^[5b] The ¹⁹F NMR chemical shift of the o-CF₃ unit in **3** (-56.93 ppm) is comparable to that in the recently reported silanediol $[2,5-(CF_3)_2C_6H_3]_2Si$ (OH)₂.^[6b] The infrared (IR) spectrum of **3** show a vibrational band at 3326 cm^{-1} characteristic for the Si–OH unit. Recrystallization of 3 from tetrahydrofuran (THF) afforded single crystals suitable for X-ray diffraction. Silanediol 3 crystallizes as a dimeric 1:1 THF adduct in triclinic space group P-1 (Figure 2). In addition to the hydrogen bonding towards the THF molecule, dimer formation by two silanediols takes place via two intermolecular hydrogen bonding interactions resulting in discrete units of the type $[3 \cdot \text{THF}]_2$ (Figure 3).

The O–H bond lengths were fixed at 0.84 Å and the hydrogen atoms were refined without any constraints to the bond angles. The OH···O distances range between 1.839(3) and 1.9112 (13) Å. The O···O (THF) distances are 2.6454 (13)–2.6843 (12) Å, which are shorter than the O···O distances resulting from the intermolecular interaction between two silanediol molecules (2.7479 (12)–2.7483 (12) Å). The O–H···O (THF) angles are smaller than the remaining O–H···O angles (160.3(9)–160.8(13)° versus 173.9(6)–176.8(7)°). A survey of all hydrogen bonding interactions in **3** is summarized in Table 1.



SCHEME 2 Hydrolytic formation of 3 from 1



FIGURE 2 ORTEP plot of the crystal structure of **3** with ellipsoids drawn at 30% probability level (aryl and THF hydrogen atoms omitted for clarity)



FIGURE 3 Hydrogen bonded dimers in the crystal structure of **3** with ellipsoids drawn at 30% probability level (aryl and THF hydrogen atoms omitted for clarity)

 TABLE 1
 Survey of hydrogen bonding interactions in 3

| $D-H\cdots A^{a}$ | d (D— H) (Å) | d (H…A) (Å) | d (D…A) (Å) | ∠(DHA) (°) |
|-----------------------------------|--------------|-------------|-------------|------------|
| $O(1)-H(1)\cdots O(2)^{(i)}$ | 0.84 | 1.9092 (12) | 2.7483 (12) | 176.8(7) |
| O(2)—H(2)····O(51) | 0.84 | 1.877(4) | 2.6843 (12) | 160.8(13) |
| O(3)—H(3)····O(4) ⁽ⁱⁱ⁾ | 0.84 | 1.9112 (13) | 2.7479 (12) | 173.9(6) |
| O(4)—H(4)····O(61) | 0.84 | 1.839(3) | 2.6454 (13) | 160.3(9)° |

^aSymmetry transformations used to generate equivalent atoms: (i) 1 - x, 1 - y, 2 - z; (ii) 2 - x, 1 - y, 1 - z.

The Si–O bond lengths range between 1.6229(9) and 1.6411(9) Å and the Si–Cl-bond lengths between 1.8817 (12) and 1.8882 (12) Å. The Si–O distances of the OH groups coordinated to the THF molecules (1.6407(9), 1.6411(9) Å) are significantly longer than the other two

Si–O bonds (1.6229(9), 1.6232(9) Å) which form the dimers. This is closely related to the situations in other adducts between silanols and solvents.^[9] In general, bond distances and angles are comparable to those for $(2,5-(CF_3)_2C_6H_3)_2Si(OH)_2$.^[6b]



SCHEME 3 Diels–Alder model reaction to assess the activation of carbonyl compounds by silanediol **3**

Dimeric association via hydrogen bonding has been identified as a potential aspect in the preorganization of substrate and catalyst in silanol-mediated reactions along with the acidity of the catalytic silanol.^[10] As an indication of the acidity, the proton resonance of silanediol **3** in THF- d_8 is clearly deshielded (6.37 ppm) compared with the resonance of its non-fluorinated analogue Ph₂Si (OH)₂ in the same solvent (5.95 ppm). The catalytic activity of silanediol **3** concerning Diels–Alder reactions was therefore explored for a model reaction which has been used before to assess silanol catalysts (Scheme 3).^[2b]

 TABLE 2
 Crystal data and structure refinement for 1 and 3

| | 1 | 3 |
|--|----------------------|--|
| Formula | $C_{14}H_8Cl_2F_6Si$ | $\begin{array}{c} C_{14}H_{10}F_6O_2Si\\ \cdot C_4H_8O\end{array}$ |
| Formula weight | 389.19 | 424.41 |
| Temperature (K) | 100 | 100 |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic |
| Space group | Pc | <i>P</i> -1 |
| Unit cell dimensions | | |
| a (Å) | 7.9481(2) | 9.0357(3) |
| <i>b</i> (Å) | 7.9115(2) | 13.6360(6) |
| c (Å) | 12.2892(3) | 16.0306(6) |
| α (°) | | 105.6495 (18) |
| β (°) | 104.1011(8) | 90.2620 (15) |
| γ (°) | | 105.2280 (15) |
| Volume (Å ³) | 749.48(3) | 1829.09 (12) |
| Ζ | 2 | 4 |
| Density (calcd) (Mg m ⁻³) | 1.725 | 1.541 |
| $\mu(\text{mm}^{-1})$ | 0.571 | 0.204 |
| θrange for data collection (°) | 2.57-30.00 | 2.34-30.00 |
| Goodness-of-fit on F^2 | 1.040 | 1.060 |
| Data/parameters | 3496/210 | 10623/533 |
| Final <i>R</i> indices R_1 [$I > 2\sigma(I)$] | 0.0245 | 0.0368 |
| <i>R</i> indices wR_2 (all data) | 0.0573 | 0.1009 |
| CCDC number | 1826249 | 1826250 |

This model reaction is based on carbonyl activation in the Diels-Alder reaction of methacrolein and Rawal's diene at -70 °C in a non-polar solvent such as toluene. so the acidity of the silanol is not levelled by the basicity of a donor solvent. In the presence of 3, the yield of the model reaction increases by a factor of three compared with the reaction under identical conditions without the silanol. Interestingly this moderate increase is in the average range of that of silanediol catalysts for this reaction but inferior to that of BINOL, which is a superior catalyst for this reaction under otherwise identical conditions, but has no silanol functionalities at all.^[2c] Although a mechanism similar to that proposed by Franz and co-workers,^[2b] via hydrogen-bonding-based activation of the carbonyl oxygen, seems likely, a disadvantage of increasing the acidity via incorporation of trifluoromethyl units is reduced π -stacking ability of the aryl groups in 3.

3 | CONCLUSIONS

In summary, we prepared and fully characterized a fluoro-substituted silanediol, bis[2-(trifluoromethyl)phenyl]silanediol. X-ray diffraction studies revealed that hydrogen bonding occurs between pairs of adjacent molecules resulting in the formation of doubly linked dimers in the solid state. According to our findings, this compound is active in catalysing Diels–Alder reactions.

4 | EXPERIMENTAL

Unless otherwise noted, all manipulations were carried out under strict exclusion of moisture and air in an inert argon atmosphere using standard Schlenk techniques where appropriate. ¹H NMR, ¹³C NMR and ²⁹Si NMR spectra were recorded with a Bruker Avance III at a Larmor frequency of 300 MHz for ¹H using tetramethylsilane as reference and C_6D_6 as solvent (dried over potassium and distilled prior to use). 1-Bromo-2-(trifluoromethyl)benzene was purchased from ABCR while other reagents were obtained from Sigma-Aldrich. Mass spectra were recorded with an Agilent 5975C using direct insertion of the sample into the ionization source (EI) or with a micrOTOF (Bruker Daltonics) using an Apollo[™]Ion Funnel electrospray ionization (ESI) source. Combustion analyses were performed with a HEKAtech Euro EA. Attenuated internal reflectance IR spectra were recorded with a Bruker Alpha Platinum ATR-IR spectrophotometer using neat samples.

4.1 | Synthesis of Bis[2-(trifluoromethyl) phenyl] dichlorosilane (1) and [(2-Trifluoromethyl)phenyl] trichlorosilane (2)

1-Bromo-2-(trifluoromethyl)benzene (14.41 g, 64 mmol, 1 eq.) dissolved in 60 ml of Et_2O was cooled to -90 °C and slowly treated with 51 ml of *n*-BuLi (2.5 M in hexane, 128 mmol, 2 eq.). Upon addition the reaction mixture was slowly warmed to room temperature and further stirred for 2 h. The mixture was then cooled to -80 °C and SiCl₄ (15 ml, 21.74 g, 128 mmol, 2 eq.) was added. Stirring was continued for 12 h while slowly warming to room temperature. The solvent was evaporated under reduced pressure and the residue extracted with pentane. Eliminated salts were removed by filtration and the pentane was evaporated under reduced pressure. The product mixture was separated by fractional distillation affording **1** and **2**.

4.1.1 | Analytical details for 1

Yield: 3.41 g (8.8 mmol; 27%). Sublimation: 97 °C/ 0.1 mbar. IR (cm⁻¹): 1313 (s); 1169 (s); 1120 (s); 1049 (s); 819 (s); 769 (s); 559 (s); 537 (s); 484 (s); 434 (s). MS/ EI: m/z (%) = 388 (30) [M]⁺; 243 (100) [M - C₇H₄F₃]⁺; 45 (15) $[C_7H_4F_3]^+$; 77 (20) $[C_6H_6]^+$. HRMS/ESI(+) upon quenching with methanol: $m/z = 403.0559 [M + Na]^+$; calcd for $[C_{16}H_{14}F_6O_2SiNa]^+ = 403.0565$. Elemental analysis: calcd for C₁₄H₈Cl₂F₆Si (%): C: 43.20; H: 2.07; found (%): C: 43.90; H: 2.29. ¹H NMR (400 MHz; C₆D₆; δ, ppm): 8.23 (m; 2H; Aryl-H); 7.27 (m; 2H; Aryl-H); 6.99 (m; 2H; Aryl-H); 6.85 (tm; 2H; Aryl-H). ¹³C NMR (100.5 MHz; C₆D₆; δ, ppm): 136.7 (CH); 134.2 (q; ${}^{2}J_{CF} = 32$ Hz, C–CF₃); 131.9 (CH); 131.5 (CH); 130.3 (m; C_a); 127.1 (q; ${}^{3}J_{CF} = 7$ Hz; CH); 125.0 (q; ${}^{1}J_{CF} = 274$ Hz, CF₃). ¹⁹F NMR (376.3 MHz; C₆D₆; δ, ppm): -56.76. ²⁹Si NMR (59.6 MHz; C₆D₆; δ, ppm): 4.4.

4.1.2 | Analytical details for 2

Yield: 2.31 g (8.3 mmol; 13%). Boiling point: 43 °C/ 0.1 mbar. ¹H NMR (300 MHz; C₆D₆; δ , ppm): 7.89 (m; 1H; Ar—H); 7.40 (m; 1H; Ar—H); 7.14 (m; 2H; Ar—H). ¹³C NMR (75.4 MHz; C₆D₆; δ , ppm): 136.7 (CH); 134.6 (q; ²J_{CF} = 32 Hz; C—CF₃); 133.0 (CH); 131.5 (CH); 128.0 (q; ³J_{CF} = 2 Hz; C_q); 127.5 (q; ³J_{CF} = 5 Hz; CH); 124.3 (q; ¹J_{CF} = 274 Hz; CF₃). ¹⁹F NMR (282.2 MHz; C₆D₆; δ , ppm): -56.60. ²⁹Si NMR (59.6 MHz; C₆D₆; δ , ppm): -2.7.

4.2 | Synthesis of Bis[2-(trifluoromethyl) phenyl] silanediol (3)

Bis[(2-trifluoromethyl)phenyl] dichlorosilane (0.61 g, 1.6 mmol, 1 eq.) dissolved in 10 ml of Et₂O was slowly

added to a cooled solution (0 °C) of NEt₃ (0.32 g, 3.2 mmol, 2 eq.) and water (0.06 g, 3.2 mmol, 2 eq.) in 30 ml of Et₂O. Stirring was continued for 12 h while slowly warming to room temperature. Eliminated salts were removed by filtration and extracted with further portions of Et₂O. From the combined extracts the solvent was evaporated under reduced pressure. The colourless solid product, **3**, was washed several times with pentane and dried to constant weight.

4.2.1 | Analytical details for 3

Yield: 0.13 g (0.4 mmol; 23%). IR (cm⁻¹): 3326 (b): 1438 (s); 1163 (s); 1111 (s); 1050 (s); 1034 (s); 903 (s); 886 (s); 833 (s); 770 (s); 711 (s); 506 (s). MS/EI: m/z (%) = 352 (10) $[M]^+$; 207 (70) $[M - C_7H_4F_3]^+$; 161 (100) $[C_7H_4F_3O]$; 145 (5) $[C_7H_4F_3]^+$; 77 (20) $[C_6H_6]^+$. HRMS/ ESI(+): m/z = 375.0236 [M + Na]⁺; calcd for $[C_{10}H_{10}F_6O_2SiNa]^+ = 375.0251$. Elemental analysis: calcd for C₁₄H₁₀O₂F₆Si (%): C: 47.73; H: 2.86; found (%): C: 47.37; H: 2.87. ¹H NMR (300 MHz; THF-d₈; δ, ppm): 8.24 (m; 2H; Ar-H); 7.67 (m; 2H; Ar-H); 7.56 (m; 4H; Ar- H); 6.37 (b; 2H; - Si- OH). ¹³C NMR (100.5 MHz; THF-d₈; δ, ppm): 138.1 (CH); 136.5 (m; C_a); 135.7 (q; ${}^{2}J_{CF} = 31$ Hz, C_{q} – CF₃); 131.2 (CH); 130.4 (CH); 126.3 (q; ${}^{3}J_{CF} = 5$ Hz; CH);125.8 (q; ${}^{1}J_{CF} = 274$ Hz, CF₃). ${}^{19}F$ NMR (376.3 MHz; THF-*d*₈; δ, ppm): -56.93. ²⁹Si NMR (59.6 MHz; THF-*d*₈; δ, ppm): -38.2.

4.3 | Details for Catalytic Model Reaction

The procedure followed previous literature reports.^[2b,11] Catalyst 3 (42.44 mg, 0.10 mmol, 0.2 eq.) and methacrolein (41.5 µl, 0.50 mmol, 1.0 eq.) were dissolved in toluene (0.75 ml). The resulting solution was cooled to -70°C and *trans*-3-(*tert*-butyldimethylsiloxy)-N,Ndimethyl-1,3-butadien-1-amine (260 µl, 1.00 mmol, 2.0 eq.) was added. After stirring for 48 h at -70 °C, the reaction was quenched with LiAlH₄ (4.0 M, 0.50 ml, 2.0 mmol, 4.0 eq.) and stirred for 0.5 h at -70 °C and then 1.5 h at room temperature. Excess LiAlH₄ was quenched with water (0.5 ml) and the resulting solid was removed by filtration and washed with Et_2O (5 × 3 ml). The filtrate was concentrated under reduced pressure to yield a pale vellow oil, which was dissolved in acetonitrile (2.0 ml). After cooling to 0 °C, HF (70% in pyridine, 0.27 ml) was added and the materials were stirred for 8 h at room temperature. The mixture was then treated with 1.10 g of CaCl₂, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica (50:50 hexanes-ethyl acetate). Evaporation of the eluent afforded 4-hydroxymethyl-4methylcyclohex-2-en-1-one in a yield of 30 mg. In 6 of 6 WILEY Organometallic Chemistry

contrast, only 10 mg of product was obtained following the same procedure without addition of **3** under otherwise identical conditions. The spectral data for the product (4-hydroxymethyl-4-methylcyclohex-2-en-1-one) match the values reported in the literature.

4.4 | Crystallographic Details

The crystal structures were determined using a Bruker APEX-II CCD diffractometer using with graphitemonochromated Mo Ka radiation (0.71073 Å). All structures were solved by direct methods (SHELXS-97)^[12] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6).^[12] The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The hydrogen atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95 Å and common isotropic displacement parameters were refined for the hydrogen atoms of the same ring. For 3, the positions of the hydrogen atoms of the OH groups were taken from a difference Fourier map, the O-H distances were fixed to 0.84 Å and the hydrogen atoms were refined with individual isotropic displacement parameters without any constraints to the bond angles. The hydrogen atoms of the CH₂ groups of the solvent co-crystallizing with 3 were refined with common isotropic displacement parameters for the hydrogen atoms of the same group and idealized geometries with approximately tetrahedral angles and C-H distances of 0.99 Å. Table 2 summarizes the crystal data and refinement for the structures of 1 and 3. Crystallographic data for this paper can be obtained free of charge quoting CCDC 1826249-1826250 from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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