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# Synthesis and Intermediates in the Formation of a Terphenyl-Substituted Silanetriol: Activation through Hypervalency

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According to previous work, 2,6-dimesitylphenyl trifluorosilane does not hydrolyze to the corresponding silanetriol. However, the formation of this product can be achieved by first converting the trifluorosilane into the corresponding hypervalent fluorosilicate. Conversion into the corresponding lithium and rubidium terphenyl tetrafluorosilicates prior to hydrolysis leads to an increased reactivity of the Si−F bonds compared to 2,6-dimesitylphenyl trifluorosilane, which allows controlled stepwise fluorine displacement depending on the nature of the countercation and eventual formation of the silanetriol. The intermediates in this process, i.e., the corresponding difluorosilanol and fluorosilanediol, can be identified and isolated depending on the reaction conditions. For the terphenylfluorosilicates the observed reactivity is more closely related to the corresponding trichlorosilane than to the trifluorosilane. As its crystal structure shows, 2,6-$Mes_2C_6H_3Si(OH)_3$ forms unique hydrogen-bridged dimers in the solid state that also persist in solution.

## Introduction

In fluorosilanes a high electrophilicity at silicon is combined with a relatively high silicon−halogen bond strength (565 kJ/mol).[1] Recently we described the reactivity of the sterically hindered trifluorosilane 2,6-$Mes_2C_6H_3$-$SiF_3$ (**1**) toward water under neutral and basic conditions, where no silanetriol is formed due to the high Si−F bond strength, which favors condensation over hydrolysis.[2] In contrast, the corresponding trichlorosilane (**2**) exclusively yields silanetriol 2,6-$Mes_2C_6H_3$-$Si(OH)_3$ (**5**) under hydrolytic conditions, since the opposite situation favoring hydrolysis over condensation is observed. For fluorosilicates it is known from the literature that in certain cases hypercoordination can cause an increase in reactivity of Si−F bonds compared to the corresponding tetracoordinated silanes.[3,4] This prompted us to check whether transformation of the sterically hindered trifluorosilane **1** into the corresponding hypervalent fluorosilicates prior to hydrolytic Si−F cleavage would significantly affect the course of reaction. As a result, we found a substantial increase of reactivity, i.e., an activation of the Si−F bonds, for the fluorosilicate, which due to the competition between hydrolysis and condensation also affects the direction of the reaction. Thus, starting from fluorosilicate **6** eventually yields the same final product, silanetriol **5**, as is obtained from **2**. This means its reactivity is essentially closer to that of the corresponding trichlorosilane than to that of the trifluorosilane. Nevertheless, the reactivity of **6** is still reduced compared to that of **2**, which allows the identification of the major intermediates in the stepwise fluorine displacement in **1**, which are difluorosilanol **3** and fluorosilanediol **4**. The degree of activation can be gradually controlled by the countercation, which allowed us to obtain either of the intermediates **3** and **4** as the major product. Complete hydrolysis yields 2,6-$Mes_2C_6H_3Si(OH)_3$ (**5**), which is also structurally characterized. In the solid state the molecule forms hydrogen-bonded dimers, which according to our results are also retained in solution.

## Results and Discussion

To activate the Si−F bonds in 2,6-$Mes_2C_6H_3SiF_3$,[5] we reacted **1** with alkalimetal fluorides in acetone solution. By reacting lithium fluoride and rubidium fluoride with **1** in equimolar ratio in the presence of water, Si−F bonds are cleaved and displaced by hydroxyl groups. Under the reaction conditions the fluorine atoms in **1** are replaced successively, which allowed the identification of the intermediates 2,6-$Mes_2C_6H_3SiF_2OH$ (**3**) and 2,6-$Mes_2C_6H_3SiF(OH)_2$ (**4**) (Scheme 1), besides 2,6-$Mes_2C_6H_3Si(OH)_3$ (**5**). The latter product can also be obtained exclusively by mild hydrolysis of the corresponding terphenyl trichlorosilane (**2**).

The identity of the products is established on the basis of heteronuclear NMR spectroscopy and by high-resolution mass spectrometry. In the $^{29}$Si NMR spectra

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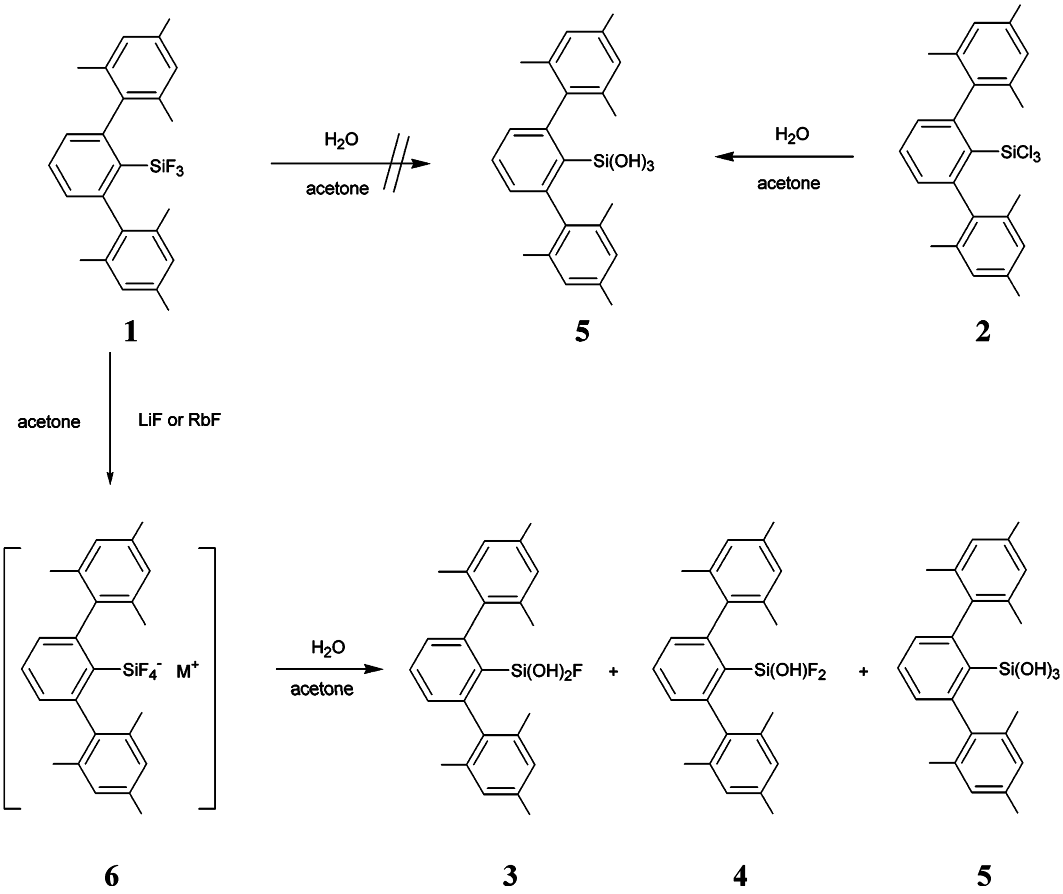
**Scheme 1. Silanol Formation Starting from 1 and 2**



compounds **3** and **4** show signals at −64.2 and −56.9 ppm, respectively, which are split into characteristic multiplets due to coupling with the fluorine nuclei present in the silane units. Thus for **3** a triplet is observed with a coupling constant of $^1J_{SiF} = 261$ Hz, and the signal of **4** is split into a doublet showing a coupling constant of $^1J_{SiF} = 257$ Hz. In the $^{19}$F NMR spectra **3** and **4** show singlets at −132.9 and −123.0 ppm, respectively. Moreover, both signals are accompanied by $^{19}$F−$^{29}$Si satellites, which are split with the above-mentioned coupling constants.

The $^{29}$Si NMR spectra of **5** shows a signal at −51.2 ppm, and the absence of line splitting due to fluorine coupling confirms the complete displacement of all fluorine atoms at silicon. A single crystal suitable for X-ray diffraction could be obtained by recrystallization from a *m*-xylene solution. The crystal structure shows dimers of **2**, each connected by two hydrogen bridges (Figure 1; Tables 1, 2). The third hydroxyl group of each silanetriol unit is involved in hydrogen bonding toward an adjacent mesityl ring. Each dimer is discrete, with no further interactions with neighboring dimers. The distance Si1−O2 for the silanol group acting as hydrogen donor (1.6111(13) Å) is slightly shorter than for the other two Si−O distances [1.6366(12), 1.6380(13) Å]. Nevertheless, these values and the O−Si−O angles [103.77(7)°, 111.51(7)°, 109.72(7)°] are in the expected range of normally observed values for silanetriols.[6] The hydrogen atoms of the silanol groups could be located from a difference Fourier map and were refined with tetrahedral Si−O−H angles, enabling rotation around the Si−O bond, with O−H distances fixed at 0.98 Å, and with individual isotropic displacement parameters. The hydrogen-bonding interactions lead to a O2···O3′ distance of 2.8587(18) Å and an O2−H2···O3′ angle of

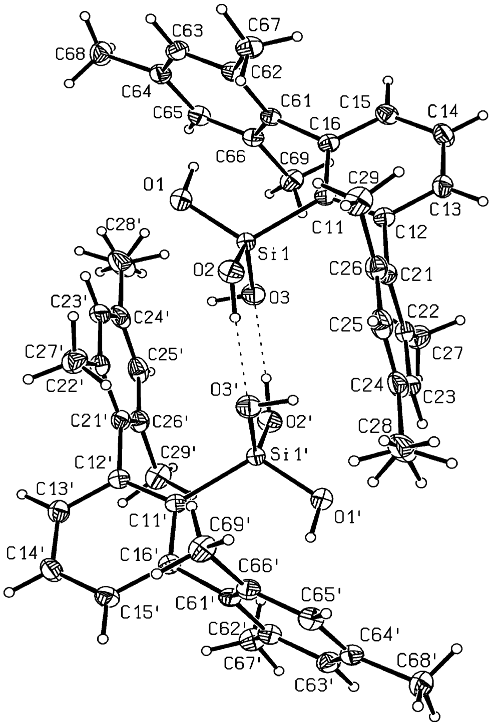


**Figure 1.** Crystal structure of 2,6-$Mes_2C_6H_3Si(OH)_3$ (**5**). Thermal ellipsoids are shown at the 50% level.

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168.4(1)° and their symmetry equivalents, which is in the range of moderately strong hydrogen bridges.[7] By hydrogen-bonding interactions an eight-membered ring $(O-Si-O-H)_2$ is formed that is nearly planar, with the largest deviation at Si1/Si1′ (0.166(9) Å).

The geometry of this ring is very similar to the one found in related silanediols.[8] Another notable feature of the structure is that H1 is directed toward the mesityl $\pi$-system of the adjacent terphenyl substituent. The H1−C61 distance is only 2.08 Å, and the distance to the neighboring carbon atoms (C62 and C66) are 2.24 and 2.43 Å, respectively. Similar interactions have been described in a related silanediol.[8] The dimeric arrangement found in **2** is a novel structural motif in the chemistry of silanetriols. So far all structures could be divided into three groups, in which the silanetriol molecules are connected by hydrogen networks to form sheets, cages, or in one single case no hydrogen bonding at all.[9,10] Obviously the size of the 2,6-dimesitylphenyl substituent interferes with the silanetriols' tendency to form hydrogen bonds with all three silanol groups. Therefore the structure of **2** is a borderline case between the existing types of completely isolated silanetriols and sheet/cage-like hydrogen-bonded networks.

Indications for the dimeric structure are also found in the IR spectra of **2**, where two bands indicative for the OH units can be observed in the solid state. A sharp absorption at 3589 cm$^{-1}$ and a less intense broader absorption around 3516 cm$^{-1}$ are attributed to the unassociated and the associated silanol groups, respectively. In contrast, in the high-resolution mass spectra only the monomeric unit of **2** can be detected.

An interesting question in this context is whether the dimeric structure of **2** is also retained in solution. At room temperature the silanetriol unit of **2** gives rise to a single resonance at 4.7 ppm in the proton NMR spectra in chloroform solution. However, this equivalence could also be a consequence of rapid proton exchange relative to the NMR time scale. To investigate the association behavior of **2** in solution, we used the cryoscopic method to determine the effective molecular weight, by measuring the freezing point depression for solutions of **2** in cyclohexane versus the pure solvent. The resulting van't Hoff factor was $i = 0.52$, which indicates that the dimeric structure of **2** is retained also in solution.

To obtain the $^{29}$Si NMR spectra of mixtures of several fluorinated silanes, we found it especially helpful to employ the well-known refocused INEPT technique[11] in a modified form. Since in all our terphenylsilanes the $^1$H nuclei that would be available for polarization transfer show only small coupling constants to the $^{29}$Si nucleus ranging over four or more bonds, we obtained much better results by employing the $^{19}$F nuclei, which are directly bound to the silicon atom and show large $^1J_{SiF}$ coupling constants. By this method we obtained a reduction of recording time by a factor of 200 compared to the regular inverse gated technique. While this method of data acquisition is valuable to get information about the product distribution, it is less suitable if accurate quantitative signal integration is required, due to alterations of the signal intensities caused by the NOE.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5**

| | | | |
|---|---|---|---|
| Si(1)−O(1) | 1.6366(12) | O(1)−Si(1)−O(2) | 103.77(7) |
| Si(1)−O(2) | 1.6111(13) | O(1)−Si(1)−O(3) | 109.72(7) |
| Si(1)−O(3) | 1.6380(13) | O(1)−Si(1)−C(11) | 112.66(7) |
| Si(1)−C(11) | 1.9056(16) | O(2)−Si(1)−O(3) | 111.51(7) |
| O(2)···O(3)′ | 2.8587(18) | O(2)−Si(1)−C(11) | 113.39(7) |
| O2−H2···O3′ | 168.4(1) | O(3)−Si(1)−C(11) | 105.89(7) |

**Table 2. Crystal Data and Structure Refinement for 5**

| | |
|---|---|
| formula | $C_{24}H_{28}O_3Si$ |
| fw | 392.55 |
| temp, K | 95 |
| wavelength | 0.71073 |
| cryst syst | triclinic |
| space group | $P\bar{1}$ |
| unit cell dimens | |
| $a$, Å | 9.232(3) |
| $b$, Å | 11.013(3) |
| $c$, Å | 12.051(3) |
| $\alpha$, deg | 67.26(2) |
| $\beta$, deg | 74.90(2) |
| $\gamma$, deg | 69.31(2) |
| volume, Å$^3$ | 1046.2(5) |
| $Z$ | 2 |
| density(calcd), Mg/m$^3$ | 1.246 |
| $\mu$ (mm$^{-1}$) | 0.134 |
| $\theta$ range for data collection, deg | 2.62 to 30.01 |
| goodness-of-fit on $F^2$ | 1.051 |
| R1 (obsd data) | 0.0471 |
| wR2 (all data) | 0.1166 |

To quantitatively analyze the product distribution, we integrated the $^{19}$F NMR spectra to obtain the relative amounts of **1**, **3**, and **4**, while taking into account the different number of fluorine atoms in these compounds. Since silanetriol **5** contains no fluorine, its relative amount is determined by integration of the $Si(OH)_3$ signal in the $^1$H NMR spectra compared to that of **4**. The results obtained by this method are summarized in Table 1. Alternative approaches, such as the integration of the $^1$H NMR signals of the different terphenyl groups, as well as the determination via GC turned out to be unsuccessful.

Generally, the intermediate fluorosilicates have been prepared in situ and were not isolated prior to the subsequent hydrolysis reaction. Nevertheless their formation is plausible, and the corresponding potassium fluorosilicates have been studied in the solid state and in solution under aprotic conditions before.[5,12,13] The nature of the countercation and its solvation are known to affect the stability of fluorosilicates. Metal fluorides providing cations with higher ion potential are known to form less stable adducts with fluorosilanes, in part due to the increased metal−fluorine bond strength.[4,14] Also in our case the efficiency of the hydrolytic exchange reaction in **1** depends on the nature of the metal cation.

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**Table 3. Product Distribution (%) in the Fluoride-Assisted Partial Hydrolysis of 1**

| | 1 | 3 | 4 | 5 |
|---|---|---|---|---|
| LiF | 29 | 66 | 4 | 1 |
| RbF | 0 | 8 | 71 | 21 |

The relative number of displaced fluoride equivalents increases from lithium to rubidium (Table 3). This trend parallels the decrease of the strength of the metal−fluorine bond, as well as the increase of the solubility of the metal fluoride in the reaction medium.[15] Since the factors that are beneficial for the displacement of fluorine in **1** are in fact the same that favor the formation of fluorosilicates in general,[3,4,14] the crucial step in the metal−fluoride-assisted hydrolysis of **1** seems to be the formation of the intermediate fluorosilicate.

## Conclusion

In summary we showed that the reactivity of 2,6-$Mes_2C_6H_3SiF_3$ toward displacement reactions can be greatly increased by activation with alkali metal fluorides. The final product obtained by this method under hydrolytic conditions is silanetriol **5**. The crystal structure of 2,6-$Mes_2C_6H_3Si(OH)_3$ shows unique hydrogen-bridged dimers in the solid state that also persist in solution. For partial conversion the number of fluorine atoms that are displaced can be controlled by employing different metal fluorides, which allowed the identification and isolation of the key intermediates difluorosilanol **3** and fluorosilanediol **4**. For the terphenylfluorosilicates the observed reactivity is closely related to the corresponding trichlorosilane, hydrolysis is favored over condensation due to the reduced silicon−halogen bond strength, while it differs completely from that of the trifluorosilane, where condensation is favored over hydrolysis.

## Experimental Section

$^1H$, $^{13}C$, $^{29}Si$, and $^{19}F$ NMR spectra have been recorded on Bruker AMX 360 and Bruker Avance DRX 500 instruments. $^{29}Si\{^{19}F\}$ INEPT measurements have been performed on a Varian Unity 500 spectrometer. IR spectra were obtained with a Perkin-Elmer 1725X FT-IR spectrometer using KBr pellets. Mass spectra have been measured on a Masslab VG 12-250 using the electron impact ionization technique. Compounds **1** and **2** have been prepared according to published procedures.[5,16]

**Synthesis of 2,6-Dimesitylphenylsilanetriol (5). Route A.** 2,6-$Mes_2C_6H_3SiF_3$ (0.8 g, 2 mmol) is dissolved in 100 mL of acetone. To this mixture is added at room temperature a solution of 0.21 g (2 mmol) of RbF dissolved in 5 mL of water under vigorous stirring. This mixture is stirred for 14 days and subsequently evaporated to dryness. The resulting crystalline residue is recrystallized from 20 mL of benzene. From this extract **5** crystallizes as a colorless solid (0.2 g, 25%).

**Route B.** 2,6-$Mes_2C_6H_3SiCl_3$ (0.8 g, 1,8 mmol) is dissolved in 2 mL of benzene and added to 50 mL of acetone containing 20 wt % water at room temperature while stirring. After stirring for an additional 2 h the resulting solution is evaporated to dryness and the remaining residue is extracted with toluene. From this extract **2** crystallizes as colorless solid (0.6 g, 85%).

Mp: 177.6 °C. $^{29}Si$ (71.51 MHz; $C_6D_6$): $\delta$ −51.2 ppm (s). $^1H$ (360.13 MHz; $CDCl_3$): $\delta$ 7.55 (t, $^3J_{HH} = 7.5$ Hz; 1H, *p*-CH), 7.08 (d, $^3J_{HH} = 7.5$ Hz; 2H, *m*-CH), 6.99 (s, 4H, Mes-CH), 4.67 (br s, 3H, OH), 2.33 (s, 6H, *p*-$CH_3$), 2.05 (s, 12H, *o*-$CH_3$). $^{13}C$ (90.56 MHz; $CDCl_3$): $\delta$ 147.54 (Cq), 137.56 (Cq), 136.52 (Cq), 135.76 (CH), 130.65 (Cq), 128.45 (CH), 128.00 (CH), 127.45 (Cq), 21.03 (*p*-CH3), 20.57 (*o*-$CH_3$). IR (KBr): $\nu$ [$cm^{-1}$] 3589 (s), 2914 (s), 1610 (w), 1446 (s), 1124 (w), 852 (s), 809 (s), 467 (w). Anal. Calcd for $C_{24}H_{28}O_3Si$: C, 73.43; H, 7.19. Found: C, 73.53; H, 7.53. MS (EI): *m*/*z* 392.1810 (0.53 ppm dev.) [$M^+$], 374 [$M^+ - H_2O$], 314 [$TerH^+$].

**Partial Hydrolysis to Fluorosilanols 3 and 4.** Following the above-mentioned procedure A, 1 equiv of trifluorosilane is reacted with 1 equiv of metal fluoride in acetone with water. To ensure partial hydrolysis, the reaction is stopped by evaporation of the solvent after 4 days. By employing LiF for activation difluorosilanol **3** is obtained as the major product. By employing RbF for activation fluorosilanediol **4** is obtained as the major product. Compounds **3** and **4** are obtained as mixtures of each other, which prevented determination of reliable melting points or microanalytical data for **3** and **4**. However, by picking different shaped crystals from this mixture separate high-resolution mass spectra for both intermediates could be obtained.

**Compound 3.** $^{29}Si$ (71.51 MHz; $C_6D_6$): $\delta$ −64.2 ppm (s). $^{19}F$ (470.53 MHz; $CDCl_3$): $\delta$ −132.9 (t, $^1J_{SiF} = 261$ Hz). MS (EI): *m*/*z* 396.1724 (0.71 ppm dev.) [$M^+$], 378 [$M^+ - H_2O$], 314 [$TerH^+$].

**Compound 4.** $^{29}Si$ (71.51 MHz; $C_6D_6$): $\delta$ −56.9 ppm (s). $^{19}F$ (470.53 MHz; $CDCl_3$): $\delta$ −123.0 (d, $^1J_{SiF} = 257$ Hz). $^1H$ (360.13 MHz; $CDCl_3$): $\delta$ 7.61 (t, $^3J_{HH} = 7.6$ Hz; 1H, *p*-CH), 7.13 (d, $^3J_{HH} = 7.6$ Hz; 2H, *m*-CH), 7.02 (s, 4H, Mes-CH), 4.58 (br s, 2H, OH), 2.36 (s, 6H, *p*-$CH_3$), 2.06 (s, 12H, *o*-$CH_3$). MS (EI): *m*/*z* 394.1770 (0.83 ppm dev.) [$M^+$], 376 [$M^+ - H_2O$], 314 [$TerH^+$].

**X-ray Crystallography.** A colorless crystal of **5** with dimensions 0.32 × 0.25 × 0.25 mm was coated in paraffin oil, mounted on a glass fiber, and placed under a cold stream of nitrogen. All the measurements were performed using graphite-monochromatized Mo Kα radiation at 95 K. A total of 7020 reflections were collected ($\theta_{max} = 30.0°$), from which 6085 were unique ($R_{int} = 0.0253$), with 4832 having $I > 2\sigma(I)$. Additional experimental details are given in Table 2. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against $F^2$ (SHELXL-97).[17,18] The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl rings were put at the external bisector of the C−C−C angle at a C−H distance of 0.95 Å, and common isotropic displacement parameters were refined for the H atoms for the same phenyl group. The H atoms of the other methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with tetrahedral angles, enabling rotation around the C−H bond, and C−H distances of 0.98 Å. The H atoms of the methyl group C28 are disordered over two orientations and were refined at two positions rotated from each other by 60°. The three H atoms of the OH groups could be undoubtedly located from a difference Fourier map and were refined with tetrahedral Si−O−H angles, enabling rotation around the Si−O bond, O−H distances fixed at 0.98 Å, and with individual isotropic displacement parameters. For 274 parameters final *R* indices of $R = 0.0471$ and wR2 = 0.1166 (GOF = 1.051) were obtained. The largest peak in a

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difference Fourier map was 0.337 e Å$^{-3}$. CCDC reference number 232388.

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**Supporting Information Available:** Details of the X-ray crystallographic studies for **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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