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Tetrafunctional Silanes of the Formula Type $Si(CH_2X)_4$ (X = SAc, SH, OAc, OH, Br, I)[§]

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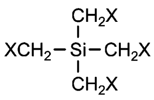
*Summary: The tetrafunctional silanes $Si(CH_2SAc)_4$ (**1**), $Si(CH_2SH)_4$ (**2**), $Si(CH_2OAc)_4$ (**3**), $Si(CH_2OH)_4$ (**4**), $Si(CH_2Br)_4$ (**5**), and $Si(CH_2I)_4$ (**6**) were synthesized, starting from $Si(CH_2Cl)_4$. Compounds **1**−**6** were characterized by NMR studies (^1H, ^{13}C, ^{29}Si) and elemental analyses, and the silanes **4**−**6** were additionally studied by single-crystal X-ray diffraction. Compounds **1**−**6** are challenging starting materials for the synthesis of further tetrafunctional silanes of the general formula type $Si(CH_2X)_4$, including compounds with different substituents X.*

Introduction

Recently, we have reported on the synthesis of a series of multifunctional (chloromethyl)silanes.[1] Tetrakis(chloromethyl)silane, $Si(CH_2Cl)_4$, was one of the compounds synthesized. In continuation of these studies, we have been interested in the synthetic potential of $Si(CH_2Cl)_4$ for the preparation of further tetrafunctional silanes of the general formula type $Si(CH_2X)_4$. We report here on the syntheses of compounds **1**−**6**, starting from $Si(CH_2Cl)_4$, and the structural characterization of **4**−**6** by single-crystal X-ray diffraction. Preliminary results of these studies have already been reported elsewhere.[2]



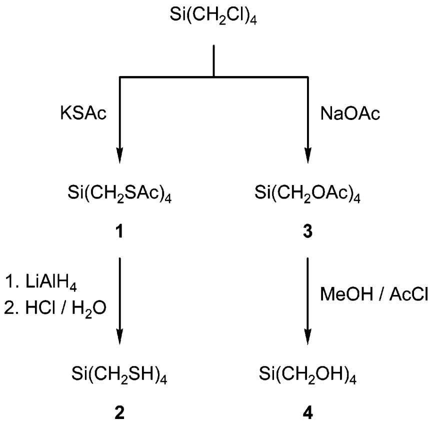
$$XCH_2-\overset{\displaystyle CH_2X}{\underset{\displaystyle CH_2X}{Si}}-CH_2X$$

	X
1	SAc
2	SH
3	OAc
4	OH
5	Br
6	I

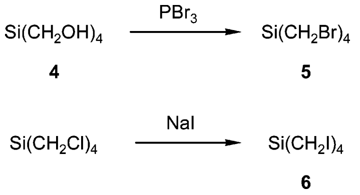
Results and Discussion

Syntheses. Tetrakis(mercaptomethyl)silane (**2**) and tetrakis(hydroxymethyl)silane (**4**) were synthesized according to Scheme 1, starting from tetrakis(chloromethylsilane). Thus, treatment of $Si(CH_2Cl)_4$ with potassium thioacetate gave tetrakis(acetylthiomethyl)silane (**1**) (yield 80%), which upon reduction with lithium aluminum hydride, followed by workup with hydrochloric acid, afforded **2** (yield 93%). Treatment of $Si(CH_2Cl)_4$ with sodium acetate gave tetrakis(acetoxymethyl)silane (**3**) (yield 77%), which upon methanolysis in the presence of acetyl chloride yielded **4** (yield 73%). Tetrakis(hydroxymethyl)silane (**4**) is a sila-analogue of pentaerythritol, $C(CH_2OH)_4$.

Scheme 1



Scheme 2



Tetrakis(bromomethyl)silane (**5**) and tetrakis(iodomethyl)silane (**6**) were synthesized according to Scheme 2. Thus, treatment of **4** with phosphorus tribromide gave **5** (yield 75%), and reaction of $Si(CH_2Cl)_4$ with sodium iodide afforded **6** (yield 81%).

Compounds **1**−**3** were isolated as colorless liquids, whereas **4**−**6** were obtained as colorless crystalline solids. The identities of all these compounds were established by elemental analyses and NMR studies (^1H, ^{13}C, ^{29}Si), and **4**−**6** were additionally characterized by crystal structure analyses.

Crystal Structure Analyses. Compounds **4**−**6** were structurally characterized by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for these studies are given in Table 1. The molecular structure of **4** is depicted in Figure 1; selected interatomic distances and bond angles are given in the figure legend.

Compound **4** crystallizes in the space group $I4_1/a$. The asymmetric unit contains only one "quarter" of the $Si(CH_2OH)_4$ molecule. The structure of **4** is not isostructural to that of its carbon analogue $C(CH_2OH)_4$, which crystallizes in the space group $I\bar{4}$.[3]

Compound **5** crystallizes in the space group $P\bar{4}2_1c$. The asymmetric unit contains only one "quarter" of the $Si(CH_2Br)_4$

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[§] Dedicated to Professor Ulrich Schubert on the occasion of his 60th birthday.

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10.1021/om0580497 CCC: $33.50

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 4−6

	4	**5**	**6**
empirical formula	$C_4H_{12}O_4Si$	$C_4H_8Br_4Si$	$C_4H_8I_4Si$
formula mass, g mol^{-1}	152.23	403.83	591.79
collection T, K	173(2)	173(2)	193(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst syst	tetragonal	tetragonal	orthorhombic
space group (No.)	$I4_1/a$ (88)	$P\bar{4}2_1c$ (114)	$P2_12_12_1$ (19)
a, Å	11.8617(14)	8.7291(12)	9.3971(5)
b, Å	11.8617(14)	8.7291(12)	9.4013(8)
c, Å	5.6519(7)	6.8619(14)	27.0781(14)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	90	90	90
V, Å^3	795.22(17)	522.86(15)	2392.2(3)
Z	4	2	8
D(calcd), g cm^{-3}	1.271	2.565	3.286
μ, mm^{-1}	0.248	15.439	10.461
F(000)	328	372	2064
cryst dimens, mm	0.5 × 0.4 × 0.3	0.5 × 0.2 × 0.1	0.4 × 0.3 × 0.3
2θ range, deg	10.54−55.42	6.60−55.84	4.34−49.96
index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-6 \le l \le 7$	$-11 \le h \le 11$, $-11 \le k \le 11$, $-8 \le l \le 9$	$-11 \le h \le 11$, $-11 \le k \le 11$, $-32 \le l \le 32$
no. of collected reflns	2511	8765	23 226
no. of indep reflns	466	636	4167
R_{int}	0.0243	0.0425	0.0322
no. of reflns used	466	636	4167
no. of params	30	21	164
S[a]	1.125	1.169	1.097
weight params a/b[b]	0.0449/0.2300	0.0286/0.6121	0.0125/14.5453
$R1$[c] [$I > 2\sigma(I)$]	0.0249	0.0234	0.0215
$wR2$[d] (all data)	0.0733	0.0611	0.0479
abs struct param		0.00(3)	−0.01(5)
max./min. resid electron density, e Å^{-3}	+0.306/−0.119	+0.294/−0.412	+0.636/−0.647

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

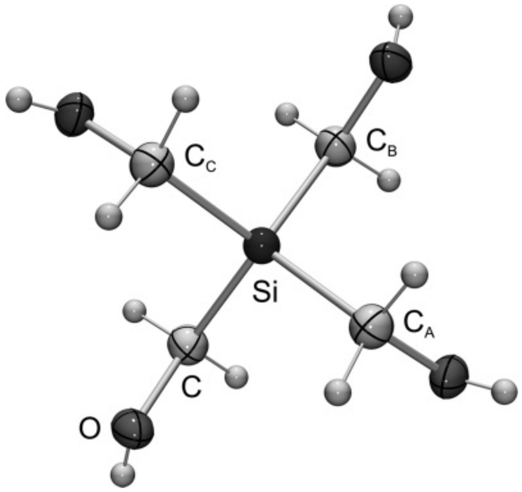

Figure 1. Molecular structure of **4** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si−C 1.8826(10), C−O 1.4433(13), C−Si−C_A 109.93(7), C−Si−C_B 109.24(3), C−Si−C_C 109.24(3), C_A−Si−C_B 109.24(3), C_A−Si−C_C 109.24(3), C_B−Si−C_C 109.93(7), Si−C−O 107.67(7). The silicon atom lies on a special position (1, 0.25, 0.125).

molecule. The structure of **5** is not isostructural to that of its carbon analogue $C(CH_2Br)_4$, which crystallizes in the space group $P2_1/c$,[4] but isostructural to that of $Si(CH_2Cl)_4$.[1]

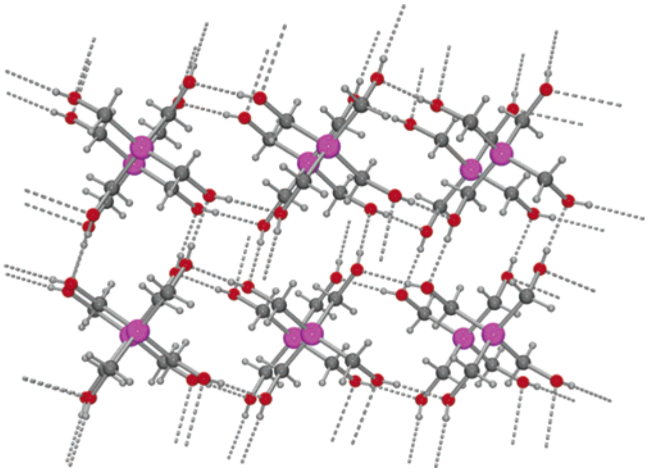

Figure 2. Three-dimensional hydrogen-bonding network in the crystal of **4**.[7]

Compound **6** crystallizes in the space group $P2_12_12_1$. The asymmetric unit contains two $Si(CH_2I)_4$ molecules, with very similar structures. To the best of our knowledge, reliable crystal structure data of the carbon analogue $C(CH_2I)_4$ have not yet been reported.[5,6]

The bond lengths and angles determined for compounds **4**−**6** are all in the expected range and do not need further comments. However, the hydrogen-bonding system observed in the crystal of **4** deserves a short discussion. As shown in Figure 2, all four OH groups of the silane **4** act as both proton donors and proton acceptors, leading to a three-dimensional network consisting of strong O−H···O hydrogen bonds (O−H, 0.731(16) Å; H···O, 1.953(16) Å; O···O, 2.6826(11) Å; O−H···O, 176.5(18)°).[7] Each molecule is hydrogen-bonded to four neighboring molecules by eight hydrogen bonds. One observes a 4-fold crystallographic screw axis, whereby the hydrogen bonds form regular infinite helices (···HO···HO···HO···) along the direction [001], with left- and right-handed helices alternating. In contrast to this, the hydrogen-bonding system of the carbon analogue $C(CH_2OH)_4$, where each molecule is hydrogen-bonded to four neighboring molecules in the basal plane by eight hydrogen bonds, is characterized by quadrilaterals around the $\bar{4}$ axes in the [001] planes.[3]

Conclusions

With the synthesis of the tetrafunctional silanes **1**−**6**, a series of versatile symmetric building blocks of the formula type $Si(CH_2X)_4$ have been made accessible. These compounds can react with either nucleophiles (in the case of X = Br, I) or electrophiles (in the case of OH, SH). Additionally, reaction of **2** and **4** with nucleophilic bases such as *n*-butyllithium should lead to the corresponding lithiated species. All these tetrafunctional silanes offer the possibility to synthesize a huge variety of further symmetric C-functional tetraorganylsilanes of the formula type $Si(CH_2X)_4$. They are of great interest as "cores"

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(7) The hydrogen-bonding system was analyzed by using the program system *PLATON*: Spek, A. L. *PLATON*; University of Utrecht: Utrecht, The Netherlands, 1998.

for the synthesis of dendrimers and as precursors for the synthesis of multifunctional silicon-based drugs. The title compounds can also serve as building blocks for the synthesis of unsymmetric C-functional tetraorganosilanes of the formula type $Si(CH_2X)_4$, with different substituents X. Further studies are in progress to elucidate the synthetic potential of this chemistry.

Experimental Section

General Procedures. All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. A Büchi GKR 50 apparatus was used for the bulb-to-bulb distillations. Melting points were determined with a Büchi B-540 melting point apparatus using samples in open glass capillaries. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz; compounds **1**, **2**, **4**, and **6**), Avance 400 NMR spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz; compound **3**), or Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz; compound **5**). $CDCl_3$, CD_2Cl_2, or [D$_6$]DMSO was used as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), $CHDCl_2$ (^{1}H, δ 5.32; CD_2Cl_2), CD_2Cl_2 (^{13}C, δ 53.8; CD_2Cl_2), [D$_5$]DMSO (^{1}H, δ 2.49; [D$_6$]DMSO), [D$_6$]DMSO (^{13}C, δ 39.5; [D$_6$]DMSO), or external TMS (^{29}Si, δ 0; $CDCl_3$, CD_2Cl_2, [D$_6$]DMSO). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments.

Tetrakis(chloromethyl)silane. This compound was synthesized according to ref 1.

Preparation of Tetrakis(acetylthiomethyl)silane (1). Tetrakis(chloromethyl)silane (5.15 g, 22.8 mmol) was added in one single portion at 20 °C to a stirred suspension of potassium thioacetate (15.6 g, 137 mmol) in tetrahydrofuran (150 mL), and the resulting mixture was stirred at 20 °C for 19 h. The solvent was removed under reduced pressure, diethyl ether (150 mL) and water (100 mL) were added, the organic layer was separated, and the aqueous phase was extracted with diethyl ether (2 × 50 mL). The organic extracts were combined, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (column dimensions, 60 × 5.5 cm; silica gel (32−63 μm, ICN 02826), 580 g; eluent, *n*-hexane/ethyl acetate (4:1 (v/v))) to afford a yellowish oily product. Charcoal (2.00 g) and *n*-hexane (300 mL) were added to this oil, and the resulting mixture was stirred under reflux for 30 min, cooled to 20 °C, and filtered. This purification step was repeated with another portion of charcoal (1.00 g), following the same protocol. The solvent was removed under reduced pressure to give **1** in 80% yield as a colorless liquid (7.00 g, 18.2 mmol). ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 8 H, CH_2), 2.32 (s, 12 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 9.5 (CH_2), 30.1 (CH_3), 195.3 (CO). ^{29}Si NMR ($CDCl_3$): δ 2.4. Anal. Calcd for $C_{12}H_{20}O_4S_4Si$: C, 37.47; H, 5.24. Found: C, 37.4; H, 5.2.

Preparation of Tetrakis(mercaptomethyl)silane (2). A solution of **1** (2.90 g, 7.54 mmol) in diethyl ether (40 mL) was added dropwise at 0 °C within 30 min to a stirred suspension of lithium aluminum hydride (2.86 g, 75.4 mmol) in diethyl ether (90 mL), and the resulting mixture was stirred at 0 °C for 70 min and then at 20 °C for 16 h. Hydrochloric acid (2 M, 55 mL) was added dropwise at 0 °C within 30 min, and the resulting mixture was then warmed to 20 °C. Water (350 mL) and diethyl ether (200 mL) were added, the organic phase was separated, the aqueous phase was extracted with diethyl ether (2 × 100 mL), the organic extracts were combined, the solvent was removed under reduced pressure, and the resulting residue was purified by distillation in a Kugelrohr apparatus (oven temperature 110 °C, 0.02 mbar) to give **2** in 93% yield as a colorless liquid (1.51 g, 6.97 mmol). ^{1}H NMR ($CDCl_3$): δ 1.41 (t, $^3J_{HH}$ = 7.5 Hz, 4 H, SH), 1.96 (d, $^3J_{HH}$ = 7.5 Hz, 8 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 1.9 (CH_2). ^{29}Si NMR ($CDCl_3$): δ 3.6. Anal. Calcd for $C_4H_{12}S_4Si$: C, 22.19; H, 5.59. Found: C, 22.1; H, 5.5.

Preparation of Tetrakis(acetoxymethyl)silane (3). Sodium acetate (5.88 g, 71.7 mmol) was added in one single portion at 20 °C to a stirred solution of tetrakis(chloromethyl)silane (2.70 g, 11.9 mmol) in dimethylformamide (40 mL), and the resulting mixture was stirred under reflux for 4 h. The solvent was removed under reduced pressure, diethyl ether (100 mL) and water (50 mL) were added, the organic layer was separated, and the aqueous phase was extracted with diethyl ether (2 × 50 mL). The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the resulting residue was purified by distillation in a Kugelrohr apparatus (oven temperature 130 °C, 0.05 mbar) to give **3** in 77% yield as a colorless liquid (2.96 g, 9.24 mmol). ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 12 H, CH_3), 3.88 (s, 8 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 20.4 (CH_3), 53.9 (CH_2), 172.0 (CO). ^{29}Si NMR ($CDCl_3$): δ −11.8. Anal. Calcd for $C_{12}H_{20}O_8Si$: C, 44.99; H, 6.29. Found: C, 44.7; H, 6.1.

Preparation of Tetrakis(hydroxymethyl)silane (4). Acetyl chloride (100 mg, 1.27 mmol) was added dropwise at 20 °C within 1 min to a stirred solution of **3** (2.89 g, 9.02 mmol) in methanol (140 mL), and the resulting mixture was heated under reflux for 7 h. The solvent was removed under reduced pressure, and the resulting solid was recrystallized from boiling acetonitrile (60 mL; crystallization at 20 °C over a period of 3 days). The product was isolated by removal of the solvent via a syringe and then dried in vacuo (0.001 mbar, 20 °C, 12 h) to give **4** in 73% yield as a colorless crystalline solid (1.00 g, 6.57 mmol); mp 81 °C. ^{1}H NMR ([D$_6$]DMSO): δ 3.36 (d, $^3J_{HH}$ = 4.4 Hz, 8 H, CH_2), 3.95 (t, $^3J_{HH}$ = 4.4 Hz, 4 H, OH). ^{13}C NMR ([D$_6$]DMSO): δ 47.9 (CH_2). ^{29}Si NMR ([D$_6$]DMSO): δ −9.9. Anal. Calcd for $C_4H_{12}O_4Si$: C, 31.56; H, 7.95. Found: C, 31.6; H, 7.7.

Preparation of Tetrakis(bromomethyl)silane (5). Phosphorus tribromide (709 mg, 2.62 mmol) was added dropwise at 20 °C within 5 min to a stirred suspension of **4** (200 mg, 1.31 mmol) in toluene (10 mL), and the resulting mixture was stirred at 20 °C for 18 h. The solvent was removed under reduced pressure, dichloromethane (50 mL) and water (50 mL) were added, the organic layer was separated, and the aqueous phase was extracted with dichloromethane (2 × 30 mL). The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the resulting solid was recrystallized from boiling *n*-hexane (20 mL; slow cooling to 20 °C over a period of 6 h, followed by crystallization at −20 °C over a period of 4 days). The product was isolated by removal of the solvent via a syringe and then dried in vacuo (0.001 mbar, 20 °C, 12 h) to give **5** in 75% yield as a colorless crystalline solid (399 mg, 988 μmol); mp 93 °C. ^{1}H NMR ($CDCl_3$): δ 2.82 (s, CH_2). ^{13}C NMR ($CDCl_3$): δ 9.2 (CH_2). ^{29}Si NMR ($CDCl_3$): δ −1.6. Anal. Calcd for $C_4H_8Br_4Si$: C, 11.90; H, 2.00. Found: C, 11.7; H, 1.9.

Preparation of Tetrakis(iodomethyl)silane (6). Tetrakis(chloromethyl)silane (100 mg, 442 μmol) was added in one single portion at 20 °C to a stirred solution of sodium iodide (531 mg, 3.54 mmol) in acetone (4 mL), and the resulting mixture was stirred at 20 °C for 17 h. The solvent was removed under reduced pressure, dichloromethane (40 mL) and water (20 mL) were added, the organic layer was separated, and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the resulting solid was recrystallized from boiling *n*-hexane (14 mL; crystallization at 20 °C over a period of 24 h). The product was isolated by removal of the solvent via a syringe and then dried in vacuo (0.001 mbar, 20 °C, 12 h) to give **6** in 81% yield as a colorless crystalline solid (211 mg, 357 μmol); mp 131 °C. ^{1}H NMR ($CDCl_3$): δ 2.40 (s, CH_2). ^{13}C NMR

($CDCl_3$): δ −20.7 (CH_2). ^{29}Si NMR ($CDCl_3$): δ 2.9. Anal. Calcd for $C_4H_8I_4Si$: C, 8.12; H, 1.36. Found: C, 8.2; H, 1.4.

Crystal Structure Analyses. Suitable single crystals of **4** were obtained by cooling of a solution of **4** (100 mg) in acetonitrile (60 mL) to −20 °C. Single crystals of **5** resulted directly from the preparation. Suitable single crystals of **6** were obtained by slow cooling of a boiling solution of **6** (643 mg) in *n*-heptane (20 mL) to 20 °C. The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å)). The structures were solved by direct methods.[8] All non-hydrogen atoms were refined anisotropically.[9] A riding model was employed in the refinement of the hydrogen atoms.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-283890 (**4**), CCDC-283892 (**5**), and CCDC-283891 (**6**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, (+44)1223/336033; e-mail, deposit@ccdc.cam.ac.uk).

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, bond lengths and angles for **4**−**6**, and the molecular structures of **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0580497

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