

Photochemical Reaction of Silyl-Substituted 1,4-Disila(Dewar-benzene) with Isocyanide and Phenylacetylene

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ABSTRACT: *The irradiation of silyl-substituted 1,4-disila(Dewar-benzene) **1** with light of wavelength $\lambda > 320$ nm in the presence of 2,6-dimethylphenylisocyanide or phenylacetylene produced 1,4-bis(di-tert-butylmethylsilyl)-2,3,5,6-tetraethyl-7-(2,6-dimethylphenylimino)-1,4-disilabicyclo[2.2.1]hepta-2,5-diene **5** or 1,4-bis(di-tert-butylmethylsilyl)-2,3,5,6-tetraethyl-1-(2-phenylethynyl)-1,4-disilacyclohexa-2,5-diene **6**, respectively. The molecular structures of **5** and **6** were determined by spectroscopic data and X-ray crystallography. © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:87–92, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20411*

INTRODUCTION

Several sila-aromatic compounds have recently been synthesized, and their unique structures, reactivity, and aromaticity have been extensively studied [1–3]. Very recently, we have succeeded in isolating a stable 1,2-disilabenzene derivative for the

first time (see [3]). In contrast, 1,4-disilaaromatics have never been isolated as stable compounds, although there are some reports of the direct observation by UV–vis spectroscopy of the parent 1,4-disilabenzene in a frozen Ar matrix at 10 K [4] and of the chemical trapping of intermediate 1,4-disilabenzenes with MeOH or acetylene derivatives [5]. Moreover, Ando et al. have characterized 1,4-disila(Dewar-benzene) and 2,5-disilabenzvalene, that is, valence isomers of 1,4-disilabenzene, by isomerizations of bis(silacyclopropene) [6].

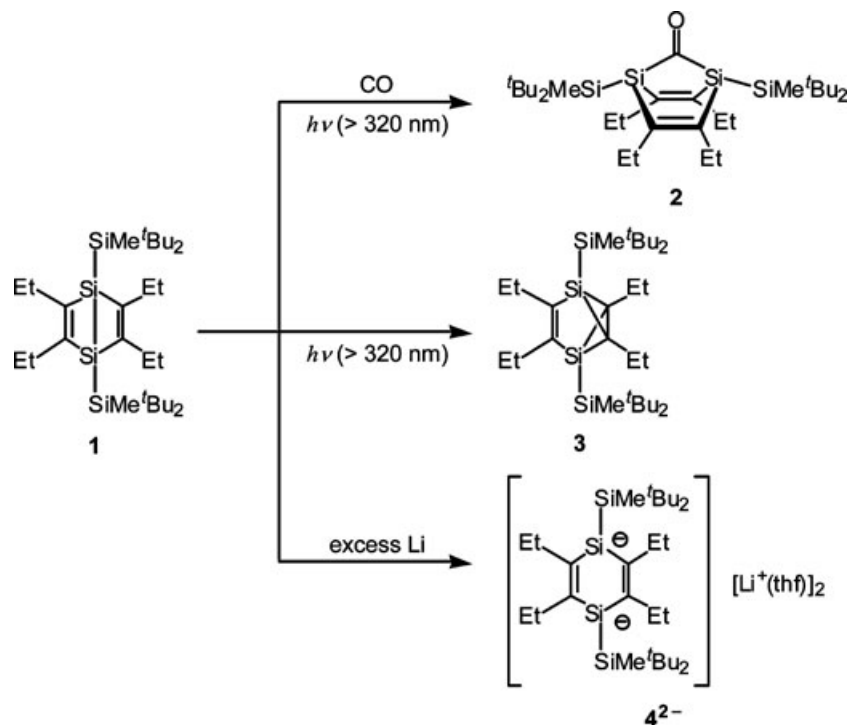
Despite its very interesting reactivity and the highly strained structure, the chemistry of 1,4-disila(Dewar-benzene) derivatives is very limited because of synthetic difficulties. Quite recently, we have developed a new and simple synthetic method for silyl-substituted 1,4-disila(Dewar-benzene) (**1**), together with the unexpected insertion reaction of CO into the strained Si–Si bond of **1**, to form a stable cyclic disilyl ketone (**2**) and the photochemical isomerization of **1** to produce the corresponding 2,5-disilabenzvalene (**3**) [7]. In addition, we have reported the reduction of **1** with metallic lithium leading to the formation of the corresponding dianionic derivative (**4**²⁻), representing a nonaromatic 8 π -electron cyclic system (Scheme 1) [8]. As the extension of reactivity of 1,4-disila(Dewar-benzene) **1**, we describe here the unique photochemical reactivity of **1** in the presence of 2,6-dimethylphenylisocyanide and phenylacetylene.

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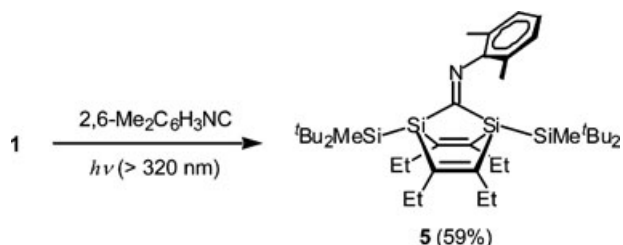
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SCHEME 1

RESULTS AND DISCUSSION

Irradiation of a THF solution of 1,4-disila(Dewarbenzene) **1** with light of wavelength $\lambda > 320$ nm in the presence of an isocyanide 2,6-Me₂C₆H₃NC resulted in the formation of the corresponding cyclic disilylimine, 1,4-bis(di-*tert*-butylmethylsilyl)-2,3,5,6-tetraethyl-7-(2,6-dimethylphenylimino)-1,4-disilabicyclo[2.2.1]hepta-2,5-diene (**5**), which was isolated as pale yellow crystals in 59% yield (Scheme 2). *tert*-Butylisocyanide was also reacted with **1** under irradiation, and an NMR analysis of the photolysate showed the formation of the corresponding disilylimine derivative. However, because

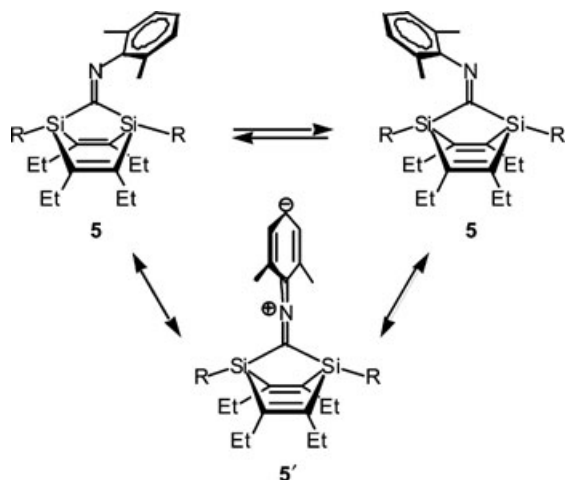


SCHEME 2

of its instability the product was not isolated in a pure form.

Disilylimine **5** was fully characterized by IR and NMR spectroscopy. The ¹³C NMR chemical shift of the imine carbon for **5** (213.6 ppm) is shifted downfield from those of normal aliphatic imines (165–170 ppm) [9] and is quite similar to those of three-membered ring disilylimine, disilacyclopropanimine (214.0 ppm) [10] and the six-membered ring compound, pentasilacyclohexanimine (215.9 ppm) [11]. In the IR spectrum, the C=N stretching frequency for **5** (1639 cm⁻¹) was observed at a higher wave number compared to those of reported cyclic disilylimines (1540–1580 cm⁻¹) [10–12].

With the electropositive silyl groups on C atom and the electronegative aryl group on N atom of the C=N group in **5**, a small inversion barrier would be expected due to electronic reasons [13]. The activation parameters for the syn-anti isomerization of *N*-alkyl and *N*-fluoroalkylimines of hexafluoroacetone have been reported to show relatively low barriers to inversion (e.g., $\Delta G_{298}^\ddagger = 18.5 \pm 0.2$ kcal mol⁻¹, $\Delta H^\ddagger = 19.2 \pm 0.7$ kcal mol⁻¹, and $\Delta S^\ddagger = 1.9 \pm 1.9$ cal mol⁻¹K⁻¹ for (CF₃)₂C=N^{*i*}Pr), which has been explained in terms of steric rather than the electronic effect [13]. Indeed, the ¹H NMR spectrum of



SCHEME 3

5 in toluene- d_8 at 298 K does show a sharp signal for the methyl groups (0.26 ppm) of the ${}^t\text{Bu}_2\text{MeSi}$ groups because of rapid inversion at room temperature. Upon lowering the temperature, the ${}^1\text{H}$ signals of the methyl protons in the ${}^t\text{Bu}_2\text{MeSi}$ groups broadened and split into two singlets (0.04 and 0.38 ppm) at 238 K. The temperature-dependent change of the ${}^1\text{H}$ signals results from the inversion of the 2,6-dimethylphenyl group on the imino nitrogen atom. From the Arrhenius and Eyring plots, the values of the free energy of the activation at coalescence temperature T_c ($\Delta G_{250} = 11.9 \pm 0.1$ kcal mol $^{-1}$), $E_a = 14.2 \pm 1.8$ kcal mol $^{-1}$, $\Delta H^\ddagger = 13.7 \pm 1.8$ kcal mol $^{-1}$, and $\Delta S^\ddagger = 7.3 \pm 6.8$ cal mol $^{-1}$ K $^{-1}$ for the inversion can be estimated. This relatively low flipping barrier might be caused by the contribution of a linear transition state **5'**, which is stabilized by delocalization of a lone pair on the imino nitrogen atom over the aromatic ring (Scheme 3).

The molecular structure of **5**, which is shown in Fig. 1, was determined by X-ray crystallographic analysis. Selected bond lengths and bond angles of **5** are given in Table 1. The C1–N1 bond length (1.269(2) Å) is close to those of normal imines and disilylimines [11,12]. The Si1–C1 and Si2–C1 bond lengths (1.9647(17) and 1.9353(19) Å) in **5** are somewhat elongated compared with those of other Si–C bonds (Si1–C2 (1.9196(19) Å), Si1–C5 (1.9153(19) Å), Si2–C3 (1.9052(18) Å), Si2–C4 (1.9018(19) Å)) attached to C=C bonds. The Si1–C1–Si2 bond angle (93.75(8)°) is highly distorted from the normal sp^2 bond angle, 120°, and close to that reported for the cyclic disilyl ketone **2** (93.26(7)°) [7].

Earlier papers by West et al. have described the isolation of trapping products believed to arise from hexamethyl-1,4-disilabenzene, including several

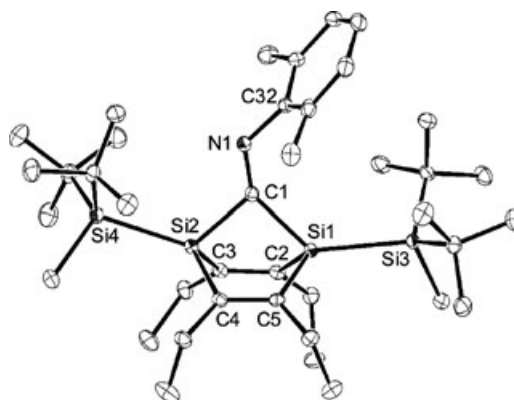


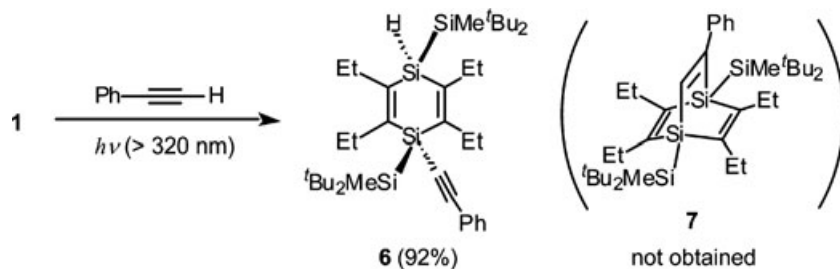
FIGURE 1 ORTEP drawing of **5** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity.

1,4-disilabarrelenes, by reaction with acetylenes [5]. Therefore, it is quite interesting to study the reactivity of **1** toward acetylenes. Thus, we examined the photolysis of **1** in the presence of phenylacetylene. Upon irradiation of a phenylacetylene solution of **1** in a sealed NMR tube with light of wavelength $\lambda > 320$ nm, the yellow color of **1** completely disappeared within 20 min. After removal of the solvent, 1,4-bis(di-*tert*-butylmethylsilyl)-2,3,5,6-tetraethyl-1-(2-phenylethynyl)-1,4-disilacyclohexa-2,5-diene **6** was unexpectedly obtained as colorless crystals in 92% yield (Scheme 4). No evidence for the formation of the corresponding 1,4-disilabarrelene derivative was found in this reaction.

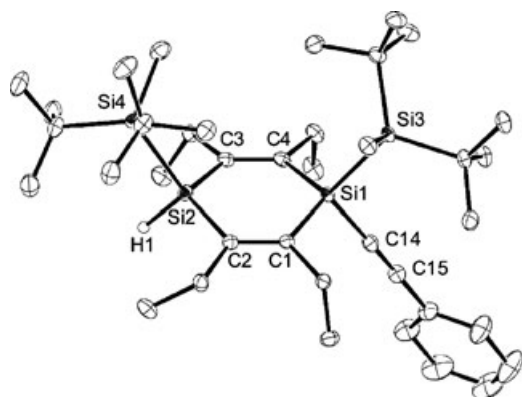
All NMR spectra of **6** were in complete accord with its asymmetrical structure. In the ${}^{29}\text{Si}$ NMR spectrum of **6**, the skeletal Si atoms in **6** are characteristically shifted upfield, appearing at -62.0 (Si–H) and -54.5 (Si–C \equiv C) ppm. Furthermore, we carried out an X-ray crystallographic analysis of **6** and confirmed that this compound has the *cis* configuration. An ORTEP drawing of **6** is shown in Fig. 2, together with selected bond lengths and angles (Table 2). The central disilacyclohexadiene ring

TABLE 1 Selected Bond Lengths (Å) and Bond Angles (deg) of **5**

Bond Lengths (Å)			
N1–C1	1.269 (2)	Si1–Si3	2.4525 (7)
Si2–Si4	2.4129 (7)	Si1–C1	1.9647 (17)
Si2–C1	1.9353 (19)	Si1–C2	1.9196 (19)
Si1–C5	1.9153 (19)	Si2–C3	1.9052 (18)
Si2–C4	1.9018 (19)	C2–C3	1.357 (3)
C4–C5	1.360 (3)		
Bond Angles (deg)			
Si1–C1–N1	142.96 (14)	Si1–C1–Si2	93.75 (8)
C1–Si1–Si3	131.18 (6)	Si2–C1–N1	123.16 (13)
C1–N1–C32	126.83 (15)	C1–Si2–Si4	118.25 (6)



SCHEME 4

FIGURE 2 ORTEP drawing of **6** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity.

of **6** has a boat conformation with a dihedral angle of 172.6° . The Si1–Si3 bond length (2.4197(6) Å) of **6** is slightly shortened compared with that of **5** (2.4525(7) Å) due to the lack of the bulky 2,6-dimethylphenyl group, whereas the Si2–Si4 bond length (2.4152(15) Å) remains essentially unchanged relative to that of **5** (2.4129(7) Å).

The formation of **5** and **6** clearly shows the formation of the intermediate biradical species **8** by the photolytic cleavage of the strained central Si–Si bond in **1**. The resulting **8** then undergoes a trapping

TABLE 2 Selected Bond Lengths (Å) and Bond Angles (deg) of **6**

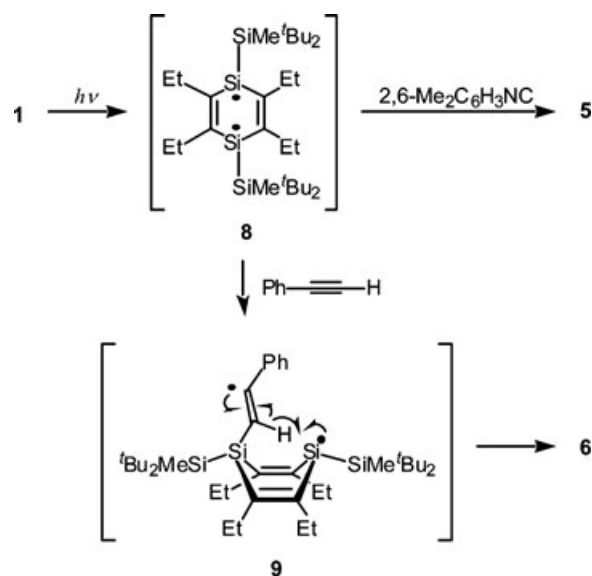
Bond Lengths (Å)			
Si1–C14	1.8527 (19)	Si1–Si3	2.4197 (6)
Si2–Si4	2.4152 (15)	Si1–C1	1.8741 (17)
Si1–C4	1.8689 (17)	Si2–C2	1.8932 (17)
Si2–C3	1.8946 (18)	C1–C2	1.357 (2)
C3–C4	1.349 (3)	C14–C15	1.208 (3)
Bond Angles (deg)			
C1–Si1–C4	112.29 (8)	C2–Si2–C3	111.84 (8)
Si3–Si1–C14	108.58 (6)		

reaction with isocyanide to produce the disilylimine **5**. In contrast, the formation of **6** can be explained by the reaction of **8** with phenylacetylene to give the vinyl radical **9**, which subsequently undergoes an intramolecular migration of the H atom in **9** to form the final product **6** (Scheme 5). The formation of **6** is quite different from the results reported in the earlier papers by West et al., which produced 1,4-disilabarrelene derivatives [5]. The formation of 1,4-disilabarrelene is unfavorable in the present case because of the steric factor, which prevents Si–C bond formation in the intermediate **9** as a result of the steric bulkiness of the SiMe^tBu₂ groups.

EXPERIMENTAL

General Procedures

All experiments were performed using high-vacuum line techniques or in an argon atmosphere of MBRAUN MB 150B-G glove box. All solvents were predried over sodium benzophenone ketyl



SCHEME 5

and finally dried and degassed over potassium mirror in vacuum prior to use. NMR spectra were recorded on a Bruker AC-300FT NMR spectrometer (^1H NMR at 300.1 MHz; ^{13}C NMR at 75.5 MHz; ^{29}Si NMR at 59.6 MHz). Infrared spectrum was obtained on a JASCO FT/IR-410 spectrophotometer. UV-spectra were recorded on a Shimadzu UV-3150 UV-vis spectrophotometer. The silyl-substituted 1,4-disila(Dewar-benzene) **1**, 1,4-bis(di-*tert*-butylmethylsilyl)-2,3,5,6-tetraethyl-1,4-disilabicyclo [2.2.0] hexa-2,5-diene, was prepared by the reaction of 1,4-*anti*-bis(di-*tert*-butylmethylsilyl)-1,4-dichloro-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene with potassium graphite [7].

Synthesis of 1,4-Disilabicyclo-[2.2.1]hepta-2,5-diene (**5**)

A THF (2 mL) solution of **1** (100 mg, 0.187 mmol) and 2,6-dimethylphenylisocyanide (24 mg, 0.183 mmol) in a glass tube was irradiated with a high-pressure Hg lamp (400 W, $\lambda > 320$ nm) for 24 h. After removal of the solvent in vacuo, the resulting residue was washed with pentane to give **5** (72 mg, 59%), which was obtained as pale yellow crystals. **5**: mp 171–172°C; ^1H NMR (C_6D_6 , 298 K, δ) 0.26 (s, 6H), 1.05 (t, $J = 7.5$ Hz, 12H), 1.13 (t, 36H), 2.08 (s, 6H), 2.53 (dq, $J = 13.3$ Hz, $J = 7.5$ Hz, 4H), 2.83 (dq, $J = 13.3$ Hz, $J = 7.5$ Hz, 4H), 6.77–6.91 (m, 3H); ^{13}C NMR (C_6D_6 , 298 K, δ) -3.9, 16.6, 19.2, 21.0, 26.3, 30.3, 122.7, 125.6, 128.6, 151.7, 161.6, 213.6 (C=N); ^{29}Si NMR (C_6D_6 , 298 K, δ) -36.4, 8.7. IR (KBr): $\nu(\text{C}=\text{N})$ 1639 cm^{-1} . UV-vis (hexane) λ_{max} (nm) (ϵ) 334 (4000); Anal. Calcd for $\text{C}_{39}\text{H}_{71}\text{NSi}_4$ C, 70.30; H, 10.74; N, 2.10. Found: C, 69.41; H, 10.69; N, 1.93; HRMS: calcd for $\text{C}_{39}\text{H}_{71}\text{NSi}_4$: 665.4664; found: 665.4666.

Synthesis of 7-(2-Phenylethynyl)-1,4-disilahexa-2,5-diene (**6**)

A phenylacetylene (1.0 mL) solution of **1** (50 mg, 0.094 mmol) in a sealed glass tube was irradiated with a high-pressure Hg lamp (400 W, $\lambda > 320$ nm) for 4 h. After removal of the solvent, the residue was recrystallized from carbon tetrachloride/hexane to give **6** (55 mg, 92%) as colorless crystals. **6**: mp 164–166°C (dec); ^1H NMR (C_6D_6 , 298 K, δ) 0.20 (s, 3H), 0.27 (s, 3H), 1.16 (s, 18H), 1.24 (t, $J = 7.2$ Hz, 6H), 1.29 (s, 18H), 1.40 (t, $J = 7.5$ Hz, 6H), 2.23 (dq, $J = 7.5$, 13.4 Hz, 2H), 2.56 (dq, $J = 7.2$, 13.4 Hz, 2H), 2.68–2.84 (m, 4H), 4.96 (s, 1H), 6.93–6.99 (m, 3H), 7.43–7.45 (m, 2H); ^{13}C NMR (C_6D_6 , 298 K, δ) -5.9, -5.8, 15.2, 16.0, 21.1, 21.8, 27.3, 27.6, 29.9, 30.3, 95.8, 109.1, 124.4, 128.6, 129.3, 131.6,

153.3, 154.1; ^{29}Si NMR (C_6D_6 , 298 K, δ) -62.0 (*Si*-H), -54.5 (*Si*-C \equiv C), 2.1 (*SiMe'*Bu $_2$), 4.0 (*SiMe'*Bu $_2$); Anal. Calcd for $\text{C}_{38}\text{H}_{68}\text{Si}_4$ C, 71.62; H, 10.75. Found: C, 71.52; H, 11.01.

X-Ray Crystallographic Analyses of Compounds **5** and **6**

Pale yellow cubic single crystals of **5** were grown by the slow evaporation of its saturated hexane solution. Colorless single crystals of **6** were grown from the saturated solution in carbon tetrachloride and hexane. The intensity data were collected at 150 K for **5** and 120 K for **6** on a Mac Science DIP2030 image plat diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo K α radiation ($\lambda = 0.71071$ Å). The structures were solved by direct methods (SIR97) [14] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97) [15]. Crystal data for **5**: formula $\text{C}_{39}\text{H}_{71}\text{NSi}_4$, MW = 666.33, monoclinic, space group $P2_1/c$, $a = 12.6950(6)$, $b = 20.8100(5)$, $c = 16.3160(8)$ Å, $\beta = 106.856(2)^\circ$, $V = 4125.2(3)$ Å 3 , $Z = 4$, $D_{\text{calcd}} = 1.073$ g cm^{-3} , $\mu = 0.170$ mm $^{-1}$; R_1 ($I > 2\sigma(I)$) = 0.0477, wR_2 (all data) = 0.1354, GOF = 1.024 for 9890 reflections and 398 parameters. Crystal data for **6**: formula $\text{C}_{38}\text{H}_{68}\text{Si}_4$, MW = 637.28, triclinic, space group $P1$, $a = 10.3930(4)$, $b = 13.7580(5)$, $c = 15.4480(3)$ Å, $\alpha = 110.5710(2)$, $\beta = 100.6110(2)$, $\gamma = 92.6310(2)^\circ$, $V = 2017.92(11)$ Å 3 , $Z = 2$, $D_{\text{calcd}} = 1.049$ g cm^{-3} , $\mu = 0.170$ mm $^{-1}$; R_1 ($I > 2\sigma(I)$) = 0.0437, wR_2 (all data) = 0.1179, GOF = 1.059 for 7013 reflections, 404 parameters and 1 restraint. CCDC no. 659376 for **5** and CCDC no. 659377 for **6** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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