

## Notes

## Silylene and Disilene Additions to Hexa-2,4-diyne: Formation of a Propynylsilirene and of Bicyclic Compounds<sup>1</sup>

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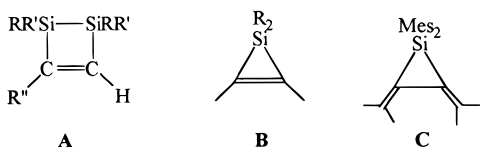
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**Summary:** Tetra-*tert*-butyldisilene and di-*tert*-butylsilylene, generated by photolysis of hexa-*tert*-butylcyclo-trisilane (**1**), react with the triple bonds of hexa-2,4-diyne to provide the addition products octa-*tert*-butyl-2-methyl-ene-5-methyl-3,4,7,8-tetrasilabicyclo[4.2.0]oct-1(6)-ene (**5**) and di-*tert*-butyl-2-methyl-3-propynylsilirene (**6**). Further treatment of **6** with **1** is thought to proceed via a bis(silirene) derivative to furnish the rearranged tetra-*tert*-butyl-3,6-dimethyl-2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene (**12**). The structures of **5** and **12** were determined by X-ray crystallography.

### Introduction

The formation of stable disilacyclobutenes of type **A** from thermally stable or marginally stable disilenes and unsymmetrically substituted alkynes is well-documented in the literature.<sup>2–5</sup> The stepwise course of the



reaction through diradical or dipolar intermediates was concluded from the formation of stereoisomeric products in the addition of (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene to phenylacetylene.<sup>4</sup>

(1) Silicon Compounds with Strong Intramolecular Steric Interactions. 65. Part 64: Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. *Angew. Chem.* **1997**, *109*, 2612; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2503.

(2) Fink, M. J.; DeYoung, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

(3) Schäfer, A.; Weidenbruch, M.; Pohl, S. *J. Organomet. Chem.* **1985**, *282*, 305.

(4) DeYoung, D. J.; West, R. *Chem. Lett.* **1986**, 883.

(5) DeYoung, D. J.; Fink, M. J.; West, R.; Michl, J. *Main Group Met. Chem.* **1987**, *10*, 19.

The additions of silylenes with sterically demanding substituents to C–C triple bonds proceed equally smoothly to furnish thermally stable or even air-stable silirenes of the type **B**.<sup>6–13</sup> Recently, Ando et al. reported on the synthesis and structural elucidation of a bis(alkylidene)silirane (**C**) possessing a system of conjugated double bonds with a significantly shortened C–C single bond within the three-membered ring.<sup>14</sup> This prompted us to investigate whether the reactions of 1,3-diyne with silylenes or disilenes would provide an access to compounds in which, in contrast to **C**, the two double bonds are part of a three- or four-membered ring. Hence, we now report on the attempted syntheses of bis(silirenes) and of C–C-linked bis(disilacyclobutenes), which led in part to unexpected rearrangement products.

### Results and Discussion

Tetra-*tert*-butyldisilene (**2**) and di-*tert*-butylsilylene (**3**) were chosen as the disilene and silylene components; both compounds are accessible by photolysis of hexa-*tert*-butylcyclo-trisilane (**1**) and have since been employed

(6) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715.  
(7) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 6382.

(8) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C12.  
(9) Ishikawa, M.; Nakagawa, K.; Kumada, M. *J. Organomet. Chem.* **1980**, *190*, 117.

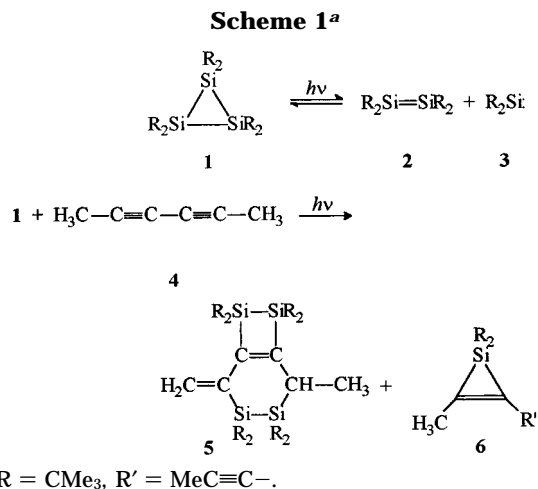
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(12) Hirotsu, K.; Higushi, T.; Ishikawa, M.; Sugisawa, H.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 726.

(13) Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281.

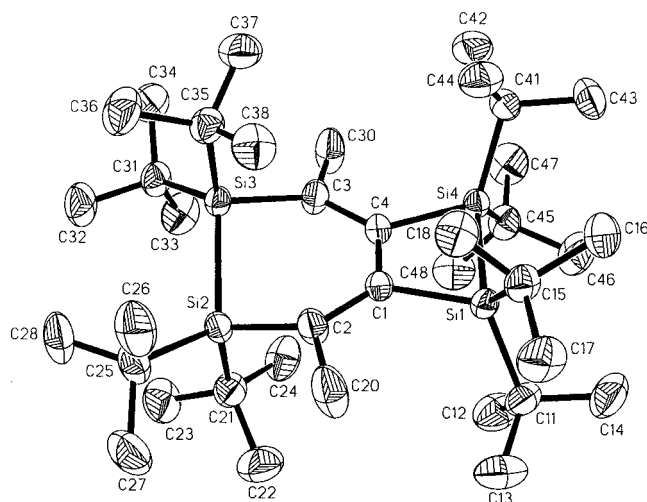
(14) Yamamoto, T.; Kabe, Y.; Ando, W. *Organometallics* **1993**, *12*, 1996.



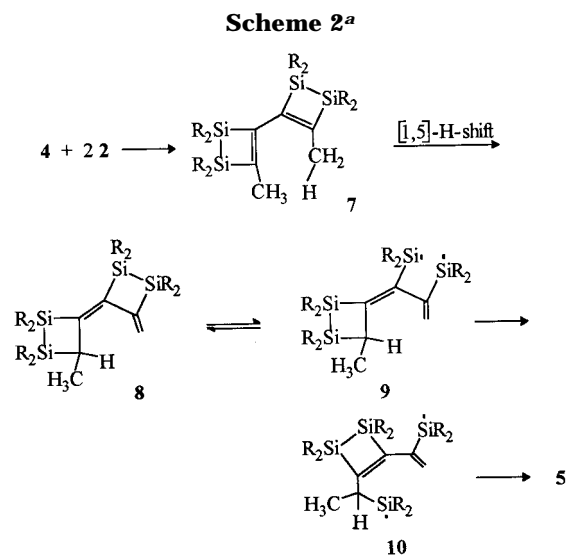
in numerous addition reactions (Scheme 1).<sup>15</sup> Irradiation of a solution of **1** in the presence of excess of hexa-2,4-diyne resulted in a smooth reaction that was complete within a few hours. First of all, a colorless, air-sensitive oil was obtained in 77% yield by fractional distillation and was assigned the constitution of the propynylsilirene **6** on the basis of its <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra. In comparison with the spectra of other silirenes, the <sup>29</sup>Si NMR signal (−63.78) is shifted to lower field. However, this is not unusual, since other three-membered-ring compounds bearing *tert*-butyl groups at the silicon atom such as, for example, siliranes<sup>17–21</sup> or cyclotrisilanes,<sup>15</sup> show a similar deshielding. Although the elemental analysis results of **6** confirmed its purity, the presence of additional, low-intensity signals in the NMR spectra are presumably indicative of the beginnings of rearrangement (see below).

A second product was also isolated in 80% yield in the form of colorless crystals, the analytical data of which indicate formation of a 2:1 adduct of **2** and **4**. However, it can be deduced from both <sup>1</sup>H and <sup>13</sup>C NMR spectra that one of the two methyl groups in **4** has been converted into a methylene group. The results of an X-ray crystallographic analysis (Figure 1) finally demonstrated that the bicyclic compound **5** was the product of the reaction between **2** and **4**.

Formally, compound **5** consists of a hexa-1,3-diene chain with disilene bridging units between positions 3 and 4 and between positions 2 and 5. Although the Si–Si and Si–C bond lengths are stretched somewhat, the lengthening of these bonds must be considered as rather small in view of the actual substituent pattern. The terminal groups C=CH<sub>2</sub> and CHCH<sub>3</sub> are disordered, with the CH<sub>2</sub> and CH<sub>3</sub> carbon atoms occupying positions



**Figure 1.** Structure of **5** in the crystal (hydrogen atoms of the CMe<sub>3</sub> groups are omitted). Ellipsoids are drawn at 30% probability. Selected bond lengths (pm) and bond angles (deg): Si1–Si4, 243.4(1); Si1–C1, 192.8(2); C1–C4, 137.9(2); C4–Si4, 191.8(2); C1–C2, 150.4(2); C2–Si2, 191.4(2); Si2–Si3, 242.4(1); Si3–C3, 191.0(2); C3–C4, 150.1(3); C3–C30, 137.7(3); C2–C20, 142.1(3); Si1–C1–C4, 105.6(1); C1–C4–Si4, 106.3(1); C4–Si4–Si1, 74.1(1); Si4–Si1–C1, 74.0(1); C1–C2–Si2, 122.4(2); C2–Si2–Si3, 97.6(1); Si2–Si3–C3, 97.3(1); Si3–C3–C4, 123.4(1); C3–C4–C1, 128.3(1); C4–C1–C2, 128.4(2).



that cannot be separated into split positions. Two different bond lengths of 137.7(3) and 142.1(3) pm result which do not correspond with the typical bond distances of C/C single and double bonds. The disorder of these groups should thus deviate from an occupancy ratio of 1:1.

In accord with the structure determination, the <sup>29</sup>Si NMR spectrum contains four different signals, while the <sup>1</sup>H and <sup>13</sup>C NMR spectra reveal separate signals for the eight *tert*-butyl groups.

At present we can only speculate about the mechanism of formation of **5** (Scheme 2). A plausible rationale would be the addition of two molecules of disilene **2** across the C–C triple bonds to give the cycloadduct **7**. This compound could undergo a thermally allowed 1,5-hydrogen sigmatropic shift to move the requisite hy-

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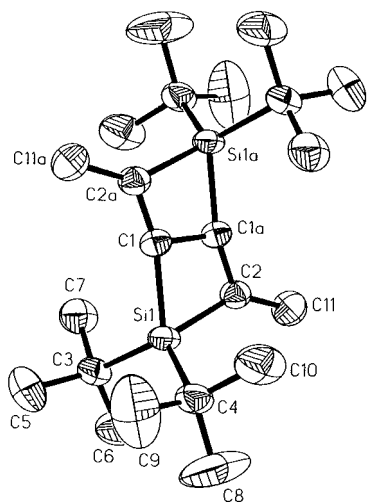
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(19) Kroke, E.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Organometallics* **1995**, *14*, 5695.

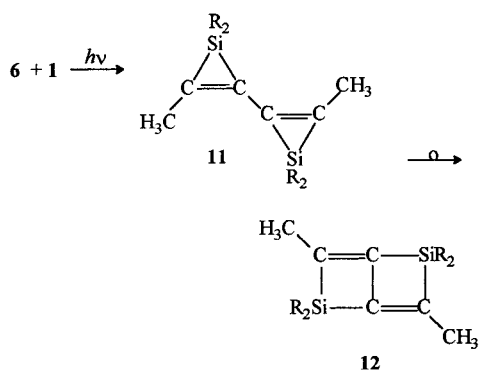
(20) Kroke, E.; Willms, S.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Tetrahedron Lett.* **1996**, *37*, 3675.

(21) Very recently, four di-*tert*-butylsilirenes with chemical shifts of  $\delta$  −65.3 to −71.7 were reported: Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824.



**Figure 2.** Structure of **12** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 30% probability. Selected bond lengths (pm) and bond angles (deg): Si1–C1, 188.7(3); Si2–C2, 190.0(3); C1–C1a, 148.5(6); C2–C1, 150.3(5); C1–C2a, 133.9(4); C1–Si1–C2, 75.1(1); Si1–C2–C1a, 89.6(2); C1–C1a–C2, 109.5(3); Si1–C1–C1a, 85.9(2); Si1–C2–C11, 142.4(3); C1a–C2–C11, 128.0(3).

**Scheme 3<sup>a</sup>**



<sup>a</sup> R = CMe<sub>3</sub>.

drogen. Homolysis of the resulting strained silacyclobutane **8** would form the silyl diradical **9**, which could undergo two successive cyclizations to provide the isolated product **5** via compound **10**.<sup>22</sup>

To obtain a bis(silirene)<sup>23</sup> and to clarify the already mentioned tendency of **6** to undergo rearrangement, the silirene **6** was again subjected to photolysis in the presence of **1**. A colorless, crystalline product was obtained, and its analytical and NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopic data were in accord with the constitution of the bis(silirene) **11** (Scheme 3). However, its stability toward air and, above all, the position of its <sup>29</sup>Si NMR signal at 34.5 ppm, which is far removed from the typical range for silirenes<sup>16</sup> and is even shifted by ca. 100 ppm to lower field than the signal of **6**, are not compatible with the putative structure **11**. The structure of this product was finally elucidated by X-ray crystallography (Figure 2) to be that of the 2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene **12**.

(22) We thank one of the reviewers for this suggestion.

(23) Recently, a bis(silirene) was mentioned as a possible intermediate in the photochemical reaction of 1,4-bis(pentamethyldisilyl)butadiyne with methanol: Lee, S. T.; Baek, E. K.; Shim, S. C. *Organometallics* **1996**, *15*, 2182.

The molecule of **12** possesses a crystallographic center of inversion at the midpoint of the C1–C1a bond. The atoms C1, C1a, C2, and C2a form a plane with the two silicon atoms minimally protruding above and below this plane by about 2.4 pm. Despite the substitution by the bulky *tert*-butyl groups, both the endocyclic and the exocyclic Si–C bond lengths are only slightly increased. The steric influence of these groups does, however, noticeably affect the two methyl groups which, as demonstrated by the bond angle Si1–C1–C11 of 142.4°, are clearly deflected away from these voluminous groups.

Although the mechanism of formation of the bicyclic compound **12** cannot be proven experimentally, the following proposal seems to be reasonable. The [2 + 1] addition of a second silylene molecule to the silirene **6** should lead at first to the bis(silirene) **11**, which then rearranges to the markedly less strained bicyclic product **12** by cleavage and re-formation of only two Si–C bonds.

Even though the targeted syntheses of bis(silirenes) and C–C-linked bis(disilacyclobutenes) could not be realized, the present investigations have led to the preparation of the first examples of an alkynylsilirene and to the complete structural elucidation of two remarkable rearrangement products.

## Experimental Section

**General Procedures.** All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. Photolyses were carried out at room temperature by using a high-pressure mercury immersion lamp (Heraeus TQ 150).

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker AM 300 or Bruker AMX 500 spectrometer using C<sub>6</sub>D<sub>6</sub> as solvent. The assignment of the <sup>1</sup>H and <sup>13</sup>C NMR signals was confirmed by DEPT and COSY spectra. The <sup>29</sup>Si NMR spectra were recorded on a Bruker AMX 300 spectrometer. IR spectra were taken on a Bio-Rad FTS-7 spectrometer. Mass spectra were recorded on a Varian MAT 212 or Finnigan MAT 95 instrument. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

The cyclotrisilane **1** was prepared according to the literature procedure.<sup>24</sup>

**Photolysis of 1 in the Presence of Hexa-2,4-diyne (4).** A solution of **1** (1.02 g, 2.4 mmol) and **4** (0.64 g, 8.2 mmol) in *n*-hexane (80 mL) was irradiated for 5 h. After this time, the reaction was shown to be complete by the disappearance of **1** (TLC monitoring). The solvent was removed by vacuum distillation, and the oily residue was transferred to a molecular still. Distillation at 60 °C/1.5 mbar yielded 0.41 g (77%) of **6**.

The distillation residue was redissolved in a minimum amount of *n*-hexane. Cooling to –25 °C provided 0.52 g (80%) of colorless crystals of **5**.

**3,3,4,4,7,7,8,8-Octa-*tert*-butyl-2-methylene-5-methyl-3,4,7,8-tetrasilabicyclo[4.2.0]oct-1(6)-ene (5):** colorless crystals, mp 284 °C; <sup>1</sup>H NMR (318 K) δ 1.26 (s, 9 H), 1.28 (s, 9 H), 1.30 (s, 9 H), 1.33 (s, 9 H), 1.34 (s, 9 H), 1.40 (s, 9 H), 1.41 (s, 9 H), 1.42 (s, 9 H), 2.00 (d, 3 H, CH<sub>3</sub>, <sup>3</sup>J = 7.7 Hz), 2.99 (q, 1 H, CH), 5.83 (d, 1 H, CH<sub>2</sub>, <sup>2</sup>J = 2.3 Hz), 6.05 (d, 1 H, CH<sub>2</sub>); <sup>13</sup>C NMR δ 22.09–25.35 (accumulation of signals, C<sub>q</sub>), 30.10 (C<sub>p</sub>), 31.26 (C<sub>p</sub>), 32.38 (C<sub>p</sub>), 32.60 (C<sub>p</sub>), 32.87 (C<sub>p</sub>), 33.02 (C<sub>p</sub>), 33.14 (C<sub>p</sub>), 33.71 (C<sub>p</sub>), 134.41 (CH<sub>2</sub>), the quaternary C=C atoms could not be observed (C<sub>p</sub> and C<sub>q</sub> refer to primary and quaternary carbon atoms); <sup>29</sup>Si NMR δ –8.49, 4.12, 26.45, 32.24; mass

(24) Weidenbruch, M.; Schäfer, A.; Lesch, A. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Thieme Verlag: Stuttgart, Germany, 1996; Vol. 2, p 210.

**Table 1. Crystallographic Data for 5 and 12**

	<b>5</b>	<b>12</b>
empirical formula	C <sub>38</sub> H <sub>78</sub> Si <sub>4</sub>	C <sub>22</sub> H <sub>42</sub> Si <sub>2</sub>
fw	647.38	362.75
<i>a</i> (pm)	918.65(6)	879.22(5)
<i>b</i> (pm)	1062.8(1)	1290.5(1)
<i>c</i> (pm)	2370.1(1)	1169.63(6)
$\alpha$ (deg)	98.918(7)	
$\beta$ (deg)	91.612(6)	108.821(4)
$\gamma$ (deg)	113.673(7)	
<i>V</i> (pm <sup>3</sup> )	2083.2 × 10 <sup>6</sup>	1256.1 × 10 <sup>6</sup>
<i>Z</i>	2	2
<i>D</i> (calcd) (g cm <sup>-3</sup> )	1.032	0.959
cryst size (mm)	0.95 × 1.15 × 0.35	0.5 × 0.55 × 0.6
cryst syst	triclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>
data collection mode	$\omega$ scan	$\omega$ scan
2 $\theta_{\max}$ (deg)	55	55
no. of rflns measd	11312	3206
no. of unique rflns	9527	2882
no. of rflns <i>F</i> > 3 $\sigma$ ( <i>F</i> )	8069	2391
lin abs coeff (mm <sup>-1</sup> )	0.17	0.14
data to param ratio	20.64	21.74
<i>R</i> ( <i>R</i> <sub>w</sub> )	0.046 (0.045)	0.076 (0.083)
residual electron density (e nm <sup>-3</sup> )	+630, -320	+450, -470

spectrum (CI, NH<sub>3</sub>) *m/z* 665 (MNH<sub>3</sub><sup>+</sup>, 100), 648 (M<sup>+</sup>, 40). Anal. Calcd for C<sub>38</sub>H<sub>78</sub>Si<sub>4</sub>: C, 70.46; H, 12.14. Found: C, 70.22; H, 12.38.

**1,1-Di-*tert*-butyl-2-methyl-3-propynyl-1-silacyclopropane (6)**: colorless, air-sensitive oil; <sup>1</sup>H NMR  $\delta$  0.99 (s, 18H), 1.82 (s, 3H), 2.19 (s, 3H) (minor signals at 1.29 and 1.48); <sup>13</sup>C NMR  $\delta$  4.50 (CH<sub>3</sub>), 5.04 (CH<sub>3</sub>), 21.86 (C<sub>q</sub>), 29.74 (C<sub>p</sub>), 73.98 (C≡C), 98.39 (C≡C), 136.58 (C=C), 160.41 (C=C) (minor signals at 17.19, 28.13, 78.87, 104.23); <sup>29</sup>Si NMR  $\delta$  -63.78 (minor signal at -20.34); IR (KBr)  $\nu$  2182 (C≡C) cm<sup>-1</sup>; mass spectrum (CI, isobutane) *m/z* 221 (MH<sup>+</sup>, 100). Anal. Calcd for C<sub>14</sub>H<sub>24</sub>Si: C, 76.28; H, 10.97. Found: C, 76.08; H, 10.98.

**2,2,5,5-Tetra-*tert*-butyl-3,6-dimethyl-2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene (12)**. A solution of silirene **6** (0.53

g, 2.4 mmol) and **1** (0.53 g, 1.2 mmol) in *n*-hexane (80 mL) was irradiated for 4 h. The solvent was removed by vacuum distillation and the oily residue transferred to a molecular still. Distillation at 50 °C/0.01 mbar provided 0.12 g of a colorless oil, which was dissolved in 10 mL of ethyl acetate and cooled to -25 °C. Recrystallization of the precipitate from a minimum amount of ethyl acetate at room temperature provided 0.080 g (18%) of colorless crystals of **12**: mp 135 °C; <sup>1</sup>H NMR  $\delta$  1.14 (s, 36 H), 1.96 (s, 6 H); <sup>13</sup>C NMR  $\delta$  20.23 (CH<sub>3</sub>), 20.40 (C<sub>q</sub>), 28.26 (C<sub>p</sub>), 150.23 (C=C), 174.77 (C=C); <sup>29</sup>Si NMR  $\delta$  35.05; mass spectrum (CI, isobutane) *m/z* 362 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>22</sub>H<sub>42</sub>Si<sub>2</sub>: C, 72.87; H, 11.68. Found: C, 72.59; H, 11.72.

**Crystallographic Analyses.** Crystal and numerical data of the structure determinations are given in Table 1. The colorless crystals of **5** and **12** were grown by slow evaporation of solutions in dimethoxyethane (**5**) or ethyl acetate (**12**) at room temperature. In each case, the crystal was mounted in a thin-walled glass capillary. Data collection was performed at 296(2) K on a Siemens P4 diffractometer using graphite-monochromated Mo K $\alpha$  radiation.

The structures were solved by direct phase determination using the Siemens SHELXTL-PLUS program system and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically.

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**Supporting Information Available:** Tables of crystal data, atomic coordinates for H atoms, bond lengths, bond angles, and anisotropic displacement coefficients for **5** and **12** (16 pages). Ordering information is given on any current masthead page.

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