

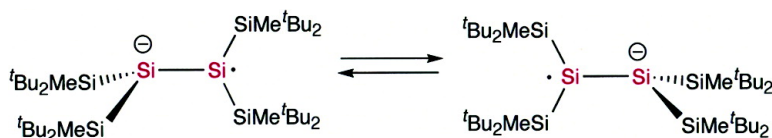
Article

Isolable Anion Radical of Blue Disilene (BuMeSi)SiSi(SiMeBu) Formed upon One-Electron Reduction: Synthesis and Characterization

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Isolable Anion Radical of Blue Disilene (^tBu₂MeSi)₂Si=Si(SiMe^tBu₂)₂ Formed upon One-Electron Reduction: Synthesis and Characterization

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Abstract: The highly twisted tetrakis(di-*tert*-butylmethylsilyl)disilene **4** was prepared and reacted with ^tBuLi in THF, producing disilene anion radical **5** upon one-electron reduction. The anion radical **5** was isolated in the form of its lithium salt as extremely air- and moisture-sensitive red crystals. The molecular structure of **5** was established by X-ray crystallography, which showed a nearly orthogonal structure (twisting angle of 88°) along the central Si–Si bond, with a length of 2.341(5) Å, which is 3.6% elongated relative to that of **4**. The interesting feature of **5** is that one of the central Si atoms has radical character, whereas the other Si atom has silyl anion character. An electron spin resonance (ESR) study of the hyperfine coupling constants of the ²⁹Si nuclei indicates that rapid spin exchange occurs between these central Si atoms on the ESR time scale.

Introduction

The introduction of a silyl group to a π system causes remarkable steric and electronic perturbations.¹ The unusual chemical and physical properties of tetrakis(trimethylsilyl)-ethylene (**1**) and its derivatives arising from the distorted nonplanar structure around the C=C double bond have been reported.² An interesting feature of **1** is that a cation radical was readily generated upon oxidation with aluminum trichloride, and also an anion radical and, subsequently, a dianion were formed by reduction with alkali metals.^{3,4} Disilenes with an Si=Si double bond are also known to undergo reduction because of their low-lying LUMOs compared with those of the corresponding alkene analogues.^{5,6} Meanwhile, we have reported the effective steric protection by di-*tert*-butylmethylsilyl groups that permits us to successfully isolate various types of unsaturated compounds of heavier Group 14 elements.^{7,8} Therefore, it is quite interesting to introduce four bulky ^tBu₂MeSi groups on the sp² Si atoms of a disilene to cause steric and electronic perturbations, as found in **1**. Herein, we report our study of the synthesis of the highly twisted tetrakis(di-*tert*-butylmethylsilyl)-disilene (**4**) and its unusual reaction with ^tBuLi resulting in the clean formation of the isolable anion radical of **5** upon one-

electron reduction. ESR studies on tetra-*tert*-butyldisilene and tetramesityldisilene anion radicals, which were generated during reduction of the corresponding 1,2-dichlorodisilanes, have been reported by Weidenbruch et al.⁹ Later, Kira et al. demonstrated the direct reduction of the disilene derivatives to form the corresponding anion radicals.¹⁰ However, these results report only on ESR spectra, and no structural study has been reported. The anion radical of **5** presented here is the first example of an anion radical isolable in a pure form that has been fully characterized, including X-ray crystallography.¹¹

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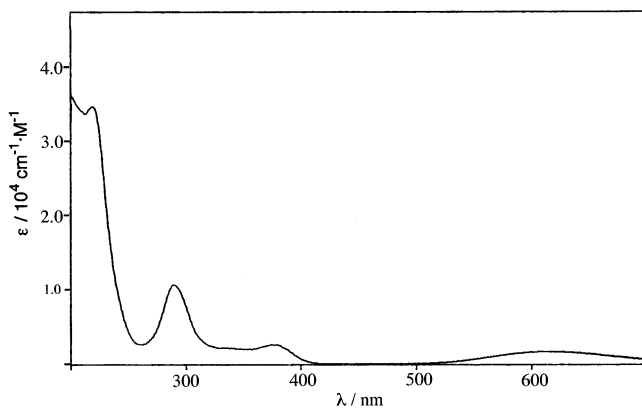
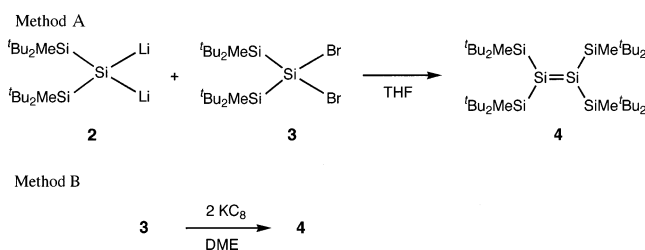


Figure 1. UV-vis spectrum of **4** in hexane at room temperature.

Scheme 1



Results and Discussion

Synthesis and Structure of Tetrakis(di-tert-butylmethylsilyl)disilene (4). ^tBu₂MeSi-substituted disilene **4** was successfully synthesized by two routes. Since we have demonstrated the utility of 1,1-dilithiosilane in the preparation of a variety of doubly bonded derivatives of heavier Group 14 elements, we first examined the reaction of bis(di-tert-butylmethylsilyl)dilithiosilane (**2**)^{8a,12} with 2,2-dibromo-1,1,3,3-tetra-tert-butyl-1,3-dimethyltrisilane (**3**) (Scheme 1, method A). Indeed, the reaction proceeds very smoothly to give **4**, which was isolated as blue crystals in 97% yield. An easier and simpler method to access **4** is the direct reaction of **3** with alkali metals. Thus, the reaction of **3** with 2 equiv of potassium graphite (KC₈) in dimethoxyethane (DME) produced **4** in 96% yield (Scheme 1, method B). Disilene **4** is stable, even in air, due to the effective steric protection around the Si=Si double bond. The interesting feature of **4** is its intense blue color. Indeed, the longest-wavelength absorption peak of **4** was observed at 612 nm (1300), together with absorption peaks at 375 (2000), 290 (8200), and 220 (26 500), as shown in Figure 1.

The crystal structure of **4** was determined by X-ray crystallography (Figure 2, Tables 1 and 2). The Si=Si double bond length (2.2598(18) Å) lies in the reported range (2.138–2.289 Å)¹³ but is longer than that for the known silyl-substituted disilenes (2.196–2.251 Å)¹⁴ due to steric reasons. The most interesting feature of **4** is the twisting of the Si=Si bond; the torsional angles of Si–Si=Si–Si are 48.8° and 62.9°. The twisting angle is 54.5°, as determined by the angles between the mean plane of Si3–Si1–Si4 and Si5–Si2–Si6, leading to

Table 1. Crystallographic Data and Experimental Parameters for the Crystal Structure Analysis of **4** and **5**

	4	5
empirical formula	C ₃₆ H ₈₄ Si ₆	C ₅₂ H ₁₁₆ LiO ₄ Si ₆
formula mass (g mol ⁻¹)	685.57	980.93
collection temperature (K)	150	200
λ (Mo Kα) (Å)	0.71070	0.71070
cryst syst	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
unit cell param		
<i>a</i> (Å)	21.702(1)	12.0720(3)
<i>b</i> (Å)	11.470(1)	21.5670(10)
<i>c</i> (Å)	18.3010(9)	24.2500(11)
α (°)	90.00	90.00
β (°)	94.783(5)	90.00
γ (°)	90.00	90.00
<i>V</i> (Å ³)	4539.7(7)	6313.7(4)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.003	1.032
μ (mm ⁻¹)	0.205	0.169
<i>F</i> (000)	1536	2188
cryst dimensions (mm)	0.60 × 0.50 × 0.10	0.3 × 0.3 × 0.3
θ range (°)	2.10–27.89	2.07–28.02
index ranges	0 ≤ <i>h</i> ≤ 28 0 ≤ <i>k</i> ≤ 15 –23 ≤ <i>l</i> ≤ 23	0 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 28 –0 ≤ <i>l</i> ≤ 31
collected reflns	42353	61161
independent reflns	10337	7793
<i>R</i> _{int}	0.1770	0.0450
reflns used	10337	7793
params	380	574
<i>S</i> ^a	1.020	1.027
weight params <i>a/b</i> ^b	0.1069/11.1422	0.0927/0.9517
<i>R</i> ₁ ^c [<i>I</i> > 2σ(<i>I</i>)]	0.0877	0.0526
<i>wR</i> ₂ ^d (all data)	0.2560	0.1514

^a *S* = {Σ[w(*F*_o² – *F*_c²)]/(*n* – *p*)^{0.5}}, *n* = number of reflection; *p* = number of parameters. ^b *w* = 1/[σ(*F*_o²) + (*aP*)² + *bP*], with *P* = (*F*_o² + 2*F*_c²)/3. ^c *R*₁ = Σ||*F*_o| – |*F*_c||/Σ|*F*_o|. ^d *wR*₂ = Σ[w(*F*_o² – *F*_c²)]/Σ[w(*F*_o²)]^{0.5}.

the most twisted Si=Si bond reported so far.^{5,13} However, the sp² Si atoms have nearly planar geometry, the sum of the bond angles being 359.7° for Si1 and 359.6° for Si2. Similar silyl-substituted (R₃Si)₂Si=Si(SiR₃)₂ (R₃Si = ^tPr₂MeSi, ^tBuMe₂Si, ^tPr₃Si, ^tBuMe₂Si/^tPr₂MeSi) have been synthesized and their X-ray structures have been reported.¹⁴ However, there is a very large structural difference between **4** and the reported compounds, since a large twisting is observed for **4** (54.5°) compared to those of the others (0–8.9°).¹⁴

Synthesis and Structure of Tetrakis(di-tert-butylmethylsilyl)disilene Anion Radical (5). The highly twisted disilene **4** showed an unexpected reaction with ^tBuLi. When a mixture of **4** and 1.2 equiv of ^tBuLi in THF was stirred from –78 °C to room temperature over 2 h, the color of the reaction mixture immediately changed from dark blue due to **4** to an intense red, from which the disilene anion radical **5** was isolated in the form of its lithium salt in 58% yield as red crystals (Scheme 2). The anion radical **5** is extremely air- and moisture-sensitive, with a melting point of 164–166 °C (dec). The formation of **5** can be rationalized by assuming a single-electron transfer process because the formation of isobutene was observed. The choice of the reducing reagent is crucial, and only the use of ^tBuLi produces **5**. When disilene **4** was reacted with LiNp or Li, the cleavage reaction of the central Si–Si took place, probably via two-electron reduction.

The crystal structure of **5** was unambiguously determined by X-ray crystallography (Figure 3, see also Tables 1 and 2). The lithium cation of **5** is coordinated by four THF molecules, and the closest distance between the lithium ion and a silicon atom

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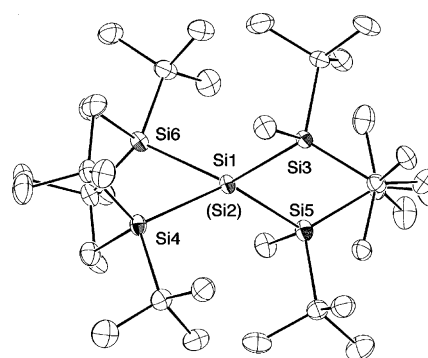
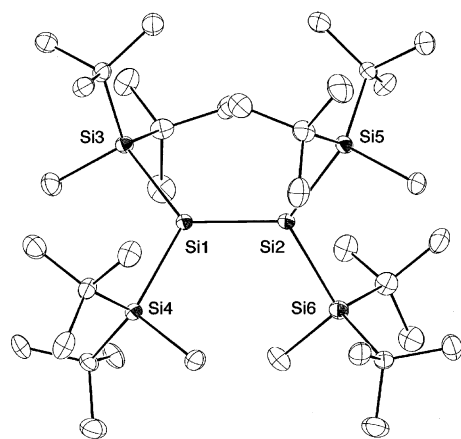


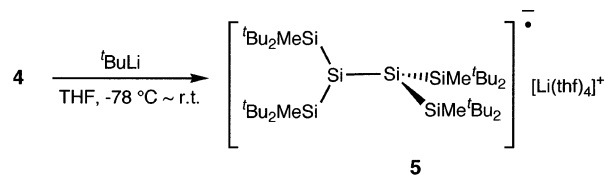
Figure 2. Molecular structure of **4** with thermal ellipsoids drawn at the 30% level (hydrogen atoms are omitted for the clarity): left, top view; right, side view.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of **4** and **5**^a

4		5	
Bond Lengths			
Si1–Si2	2.2598(18)	Si1–Si2	2.341(5)
Si1–Si3	2.416(2)	Si1–Si3	2.390(5)
Si1–Si4	2.4188(19)	Si1–Si4	2.392(5)
Si2–Si5	2.4132(19)	Si2–Si5	2.4122(13)
Si2–Si6	2.423(2)	Si2–Si6	2.4008(13)
Bond Angles			
Si2–Si1–Si3	124.68(8)	Si2–Si1–Si3	120.3(2)
Si2–Si1–Si4	116.66(8)	Si2–Si1–Si4	116.4(2)
Si3–Si1–Si4	118.36(7)	Si3–Si1–Si4	115.97(18)
Si1–Si2–Si5	124.18(7)	Si1–Si2–Si5	126.59(10)
Si1–Si2–Si6	117.15(7)	Si1–Si2–Si6	116.65(10)
Si5–Si2–Si6	118.23(7)	Si5–Si2–Si6	116.66(5)
Torsional Angles			
Si4–Si1–Si2–Si6	48.8(1)	Si3–Si1–Si2–Si5	70.5(2)
Si3–Si1–Si2–Si5	62.9(1)	Si3–Si1–Si2–Si6	113.2(2)
		Si4–Si1–Si2–Si5	78.4(2)
		Si4–Si1–Si2–Si6	97.9(2)

^a Atomic numbers are given in Figures 2 and 3. Standard deviations are in parentheses.

Scheme 2



of **5** is greater than 9 Å, indicating no interactions between them. The central Si1–Si2 bond length is 2.341(5) Å, which is 3.6% longer than that of **4** due to the lack of double-bond character. The most important feature is the twisting angle of the central Si–Si bond, which is 88°, as determined by the angles between the mean plane of Si2–Si1–Si4 and Si5–Si2–Si6. The geometry around the Si2 atom is nearly planar (the sum of the bond angles = 359.9°), whereas the Si1 atom has pyramidal geometry (the sum of the bond angles = 352.7°).¹⁶ These structural features of **5** show that the Si2 atom has radical character, whereas the Si1 atom has silyl anion character. This

(15) The addition of LiH across the E=E' bond (E, E' = Si, Ge) through single electron transfer was observed in the reaction of 2- and 1-disilagermirenes with ^tBuLi, see: Lee, V. Ya.; Sekiguchi, A. *Chem. Lett* **2004**, *33*, 84.

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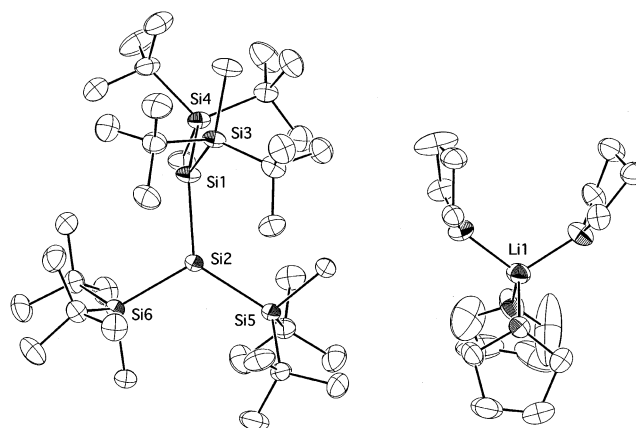


Figure 3. Molecular structure of **5** with thermal ellipsoids drawn at the 30% level (Si1 atom with occupancy factor of 0.516 is disordered). Hydrogen atoms are omitted for clarity.

is also reflected in the bond lengths of Si–Si attached to these Si atoms; the Si1–Si3 (2.390(5) Å) and Si1–Si4 (2.392(5) Å) bond lengths are shortened compared to those of **4** (av = 2.418 Å) due to delocalization of the negative charge over the Si3 and Si4 atoms, whereas the Si2–Si5 (2.4122(13) Å) and Si2–Si6 (2.4008(13) Å) bond lengths are similar to those of the tris-(di-*tert*-butylmethylsilyl)silyl radical (2.421(7) Å).¹⁷

The ESR spectrum of **5** measured at room temperature in 2-methyltetrahydrofuran showed a strong signal with a *g* value of 2.0061, accompanied by a pair of satellite signals (2.45 mT) due to coupling of the unpaired electron with the ²⁹Si nuclei, as shown in the top of Figure 4. The magnitude of the spin coupling by the ²⁹Si nuclei is half the value of the coupling observed in the tris(di-*tert*-butylmethylsilyl)silyl radical (5.80 mT).¹⁷ Kira et al. also observed hyperfine coupling constants of 2.45–3.18 mT for the silyl-substituted disilene anion radicals¹⁰ generated upon reduction of the corresponding disilenes with potassium in DME. On the basis of the observed hyperfine coupling constants of **5**, it is quite reasonable to assume that rapid spin exchange occurs between atoms Si1 and Si2 of **5** in solution on the ESR time scale, as depicted in Chart 1. Indeed, when the ESR spectrum of **5** was measured at 120 K in a glass matrix, we observed satellite signals with a coupling

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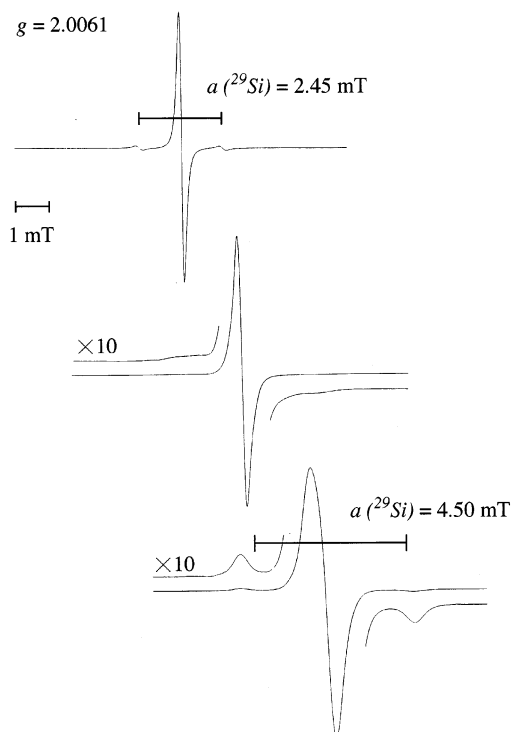
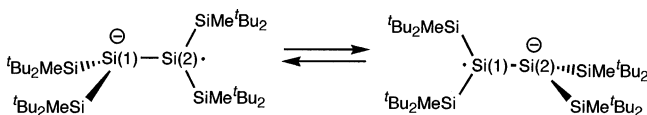


Figure 4. Variable temperature ESR spectra of **5** in 2-methyltetrahydrofuran: top, 298 K; middle, 155 K; bottom, 120 K.

Chart 1



constant of 4.50 mT (Figure 4). This indicates that the spin exchange was suppressed at low temperature.

Conclusions

We presented here the synthesis and molecular structure of a highly twisted tetrakis(di-*tert*-butylmethylsilyl)disilene **4** and its unique reactivity. The disilene **4** readily reacts with ^tBuLi in THF, producing stable anion radical **5**, representing the first isolable example of the heavy alkene analogues. The X-ray analysis of **5** showed a nearly orthogonal structure along the central Si–Si bond. The most interesting feature is that one of the central Si atoms has radical character, whereas the other Si atom has silyl anion character. ESR study indicates that rapid spin exchange occurs between these central Si atoms on the ESR time scale.

Experimental Section

General Procedures. All reactions involving air-sensitive compounds were carried out under argon atmosphere using high-vacuum line and standard Schlenk techniques, as well as dry, oxygen-free solvents. 2,2-Dibromo-1,1,3,3-tetra-*tert*-butyl-1,3-dimethyltrisilane (**3**) was synthesized by the bromination of (tBu₂MeSi)₂SiH₂ with Br₂ in CH₂Cl₂ according to the literature procedure.¹⁷ Bis(di-*tert*-butylmethylsilyl)dilithiosilane was prepared starting from 1,1-bis(di-*tert*-butylmethylsilyl)-2,3-bis(trimethylsilyl)silacyclopentene with Li in THF.^{8a,12}

NMR spectra were recorded on a Bruker AC-300FT NMR spectrometer (¹H NMR at 300.13 MHz; ¹³C NMR at 75.47 MHz; ²⁹Si NMR at 59.63 MHz). Mass spectra were obtained on JEOL JMS SX-102 instrument (EI, 70 eV). UV/vis spectra were recorded on a Shimadzu UV-3150 UV/visible spectrophotometer in hexane. ESR spectra were recorded on a Bruker EXM-T ESR spectrometer.

Synthesis of 4 (Method A). Dry, oxygen-free THF (2.0 mL) was introduced by vacuum transfer to a mixture of dilithiosilane **2** (0.22 mmol) and 2,2-dibromo-1,1,3,3-tetra-*tert*-butyl-1,3-dimethyltrisilane **3** (104 mg, 0.21 mmol), and then the reaction mixture was allowed to warm from –78 °C to room temperature. The color of the reaction mixture immediately changed from reddish-brown to an intense blue color. The mixture was vigorously stirred at room temperature for 1 h. The solvent was replaced by hexane, and the reaction mixture was filtered to remove the resulting inorganic salt. The solvent was evaporated to give blue crystals of **4** (139 mg) in 97% yield. Mp 189–191 °C (dec); ¹H NMR (C₇D₈, 298 K, δ) 0.64 (s, 12 H), 1.23 (s, 72 H); ¹³C NMR (C₇D₈, 298 K, δ) 1.3, 23.9 (CMe₃), 31.4 (CMe₃); ²⁹Si NMR (C₇D₈, 200 K, δ) 21.1, 155.5 (Si=Si); UV/vis (hexane) λ_{max}/nm (ε) 220 (26 500), 290 (8200), 375 (2000), 612 (1300); HRMS calcd for C₃₆H₈₄Si₆ 684.5189, found 684.5188. The ²⁹Si NMR spectrum was measured at low temperature because of the very weak intensity, probably due to the biradical character of **4** resulting from the highly distorted structure.

Synthesis of 4 (Method B). Dry, oxygen-free DME (30 mL) was introduced by vacuum transfer to a mixture of **3** (4.02 g, 7.99 mmol) and KC₈ (2.35 g, 17.3 mmol), and then the reaction mixture was allowed to warm from –78 °C to room temperature with stirring over 5 h. The solvent was replaced by hexane, and the reaction mixture was filtered to remove the resulting potassium salt and graphite. The solvent was evaporated to give blue crystals of **4** (2.63 g, 3.84 mmol) in 96% yield.

Synthesis of 5. Crystals of **4** (216 mg, 0.32 mmol) and a powder of ^tBuLi (25 mg, 0.39 mmol) were placed in a reaction tube. Dry, oxygen-free THF (2 mL) was introduced by vacuum transfer, and the mixture was warmed from –78 °C to room temperature over 2 h. A rapid color change from blue to intense red was observed. The solvent was evaporated, and the resulting solids were washed with hexane several times in a glovebox. After evaporation of solvent, toluene (1.5 mL) was added, and the solution was cooled to –30 °C to give red crystals of **5** (179 mg, 0.17 mmol) in 58% yield. Mp 164–166 °C (dec); ESR (MeTHF) *g* = 2.0061; UV/vis (THF) λ_{max}/nm (ε) 291 (11 600), 436 (2100).

X-ray Crystal Structure Analyses. The single crystals of **4** for the X-ray diffraction study were grown from the saturated hexane solution. The single crystals of **5** for the X-ray diffraction study were grown from the saturated toluene solution at –30 °C in a sealed tube. Diffraction data were collected on a Mac Science DIP2030K image plate diffractometer employing graphite-monochromatized Mo K_α radiation (λ = 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using the SHELXL-97 program. The crystallographic and structural data are given in Tables 1 and 2.

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Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for **4** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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