

Synthesis and Reactivity of η^5 -Germacyclopentadienyl Complexes of Iron

William P. Freeman, Jeffrey M. Dysard, and T. Don Tilley*

Department of Chemistry, University of California at Berkeley,
Berkeley, California 94720-1460

Arnold L. Rheingold*

Department of Chemistry, University of Delaware, Newark, Delaware 19716

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Reaction of 2 equiv of the previously reported germolyl anion $\text{Li}[\text{C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]$ with $\text{FeCl}_2(\text{THT})_{1.5}$ (THT = tetrahydrothiophene) at low temperature gave the new bis- η^5 -germolyl complex $[\eta^5\text{-C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]_2\text{Fe}$ (**1**), which was characterized by X-ray crystallography. Reaction of **1** with I_2 resulted in loss of the germolyl ligand as $\text{C}_4\text{Me}_4\text{Ge}(\text{I})[\text{Si}(\text{SiMe}_3)_3]$, while the reaction with MeLi produced the ferrocenophane *ansa*-(Me_3Si) $_2\text{Si}(\eta^5\text{-GeC}_4\text{Me}_4)_2\text{Fe}$ (**4**). X-ray crystallographic analysis of this compound revealed that the Ge atoms are displaced significantly out of the C_4 plane. Attempts to induce the ring-opening polymerization of **4** were unsuccessful.

Introduction

Recently, considerable attention has focused on the nature of potentially aromatic rings containing silicon and germanium.^{1,2} Our work in this area has produced examples of delocalized sila- and germacyclopentadienyl anions which are stabilized via coordination to a transition metal fragment.³ Electrochemical studies on the ruthenium germacyclopentadienyl (or germolyl) complex

$\text{Cp}^*\text{Ru}[\eta^5\text{-C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) suggested that the germolyl ligand might be significantly more electron donating than Cp^* , and studies on a related Hf system have shown that these ligands possess a rich reaction chemistry.^{3c,d} These factors have compelled us to further explore the coordination chemistry of these interesting new ligands to more fully understand their chemistry.

The chemistry of the group 15 element diheteroferrocenes has been well established, with isolation of numerous examples of complexes of the type $(\text{C}_4\text{R}_4\text{E})_2\text{-Fe}$, ($\text{E} = \text{P, As, Sb, or Bi}$; $\text{R} = \text{H, alkyl, or silyl}$).⁴ These complexes exhibit a variety of structural motifs and have been valuable in studies of aromaticity and π -bonding between carbon and heavier main group elements. It therefore seemed that it should be possible to obtain complexes involving the heavier congeners of the group 14 elements. In this contribution we report on the synthesis and structural characterization of the first

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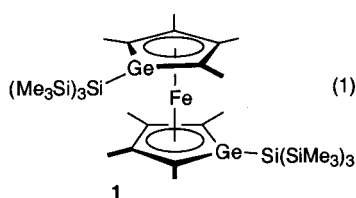
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examples of diheteroferrocenes possessing germacyclopentadienyl ligands.

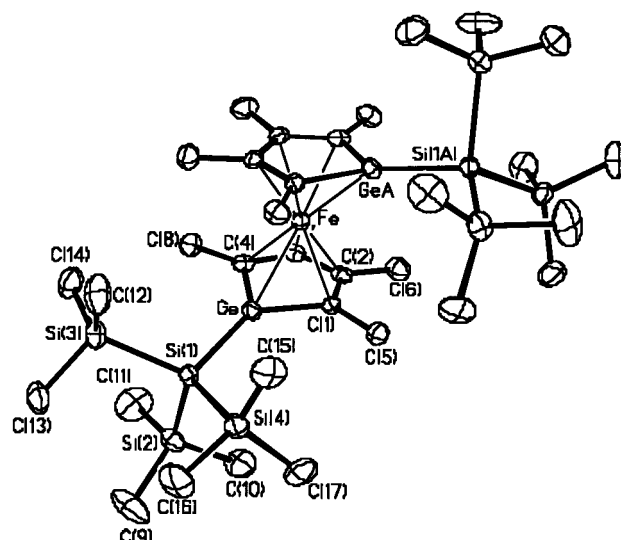
Results and Discussion

Several years ago we reported the synthesis of the germacyclopentadienyl anion $\text{Li}[\text{C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]$ and its reaction with 0.25 equiv of $[\text{Cp}^*\text{RuCl}]_4$ to give the η^5 -germacyclopentadienyl complex $\text{Cp}^*\text{Ru}[\eta^5\text{-C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]$.^{3d} Our initial synthetic strategy for the formation of a ferrocene derivative also relied on this methodology. Reaction of 2 equiv of $\text{Li}[\text{C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]$, generated in situ from the treatment of $\text{C}_4\text{Me}_4\text{Ge}(\text{H})\text{Si}(\text{SiMe}_3)_3$ with $n\text{BuLi}$, with $\text{FeCl}_2(\text{THT})_{1.5}$ (THT = tetrahydrothiophene) at -80°C in THF resulted in formation of a deep red solution from which $\text{Fe}[\eta^5\text{-C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]_2$ (**1**) was isolated in 65% yield (eq 1).



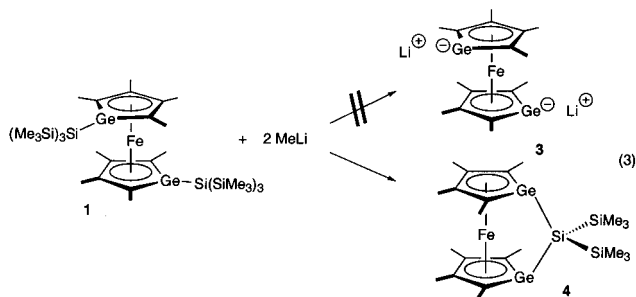
The ^1H NMR spectrum for **1** is consistent with C_2 symmetry on the NMR time scale, as indicated by three single resonances for the germolyl ligands at δ 0.36, 1.74, and 2.50 for the $\text{Si}(\text{SiMe}_3)_3$ and ring methyl groups, respectively. In addition, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** exhibits resonances at δ 79.51 and 89.86 for the carbon atoms of the coordinated germolyl ring. For comparison, the corresponding carbon atoms in the bond-localized germolyl anion $\text{Li}[\text{C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]$ resonate at δ 132.89 and 146.45, while in the η^5 -germolyl complex $\text{Cp}^*\text{Ru}[\eta^5\text{-C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]$ the analogous carbon shifts are δ 80.23 and 87.82.^{3d} An irreversible oxidation wave was observed for **1** at $E_{1/2} = -0.45$ V (vs SCE) by cyclic voltammetry (dichloromethane, 0.1 M $[\text{N}(n\text{Bu})_4]\text{ClO}_4$ as the supporting electrolyte). These data suggest that the germacyclopentadienyl ligands in **1** are more electron donating than Cp^* , as decamethylferrocene exhibits an oxidation wave at 0.28 V (vs SCE) under similar conditions.⁵

X-ray-quality crystals of **1** were grown from a concentrated pentane solution cooled to -40°C . The molecular structure of **1** (Figure 1) consists of two coplanar η^5 -germolyl rings bound in a "sandwich" fashion to the iron center. The angle between the least-squares planes of these rings is 5° , and they both lie 1.69 Å from the iron center. For comparison, the germolyl ring in $\text{Cp}^*\text{Ru}[\eta^5\text{-C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]$ lies 1.81 Å from the ruthenium center, and the analogous distance in decamethylferrocene is 1.657 Å.^{3d,6} The germanium atoms deviate by only 0.04 Å from the C_4Ge least-squares planes, and the bulky $\text{Si}(\text{SiMe}_3)_3$ group is bent out of these planes by 12.4° . For comparison, these



unsuccessful.¹⁴ The SiMe₃ protons in **2** resonate at δ 0.12, while the ring methyl protons appear as singlets at δ 1.53 and 1.87. In addition, the ring carbon atoms in **2** give rise to two singlets in the ¹³C NMR spectrum at δ 141.5 and 148.52, which are similar to the same values found for the analogous chloride derivative (δ 133.63 and 146.02) but quite different from those for an η^5 -germoyl ligand bound to a late transition metal.^{3d}

We have previously shown that nucleophilic cleavage of Ge–Si bonds in certain germole derivatives leads to the formation of germoyl anions.¹⁴ It seemed that such reactions might be useful for the generation of the bis-(germoyl) dianion **3**. However, treatment of **1** with MeLi (THF, 0 °C) did not lead to the expected product (**3**, eq 3) but instead gave the novel bis(germoyl) ferrocenophane derivative *ansa*-Fe(η^5 -C₄Me₄Ge)₂Si(SiMe₃)₂ in 55% isolated yield (**4**, eq 3).



The ¹H NMR spectrum of **4** exhibits three resonances at δ 1.58, 1.49, and 0.50 for the two sets of ring methyl groups and the SiMe₃ groups, respectively. Interestingly, the ¹³C{¹H} NMR resonances for the germoyl ring carbon atoms (δ 101.08 and 126.62) are quite shifted from those in **1**, suggesting that the germoyl ligand is bound in more of a “diene-like” fashion to the iron center. Finally, the ²⁹Si{¹H} NMR spectrum for **4** exhibits two distinct resonances for the bridging silicon atom (δ 17.56) and trimethylsilyl groups (δ –7.50).

Slow evaporation of a concentrated benzene-*d*₆ solution resulted in X-ray quality crystals of **4**, and the molecular structure is shown in Figure 2. Complex **4** possesses approximate C_{2v} symmetry and can best be described as an *ansa*-ferrocene with two eclipsed germoyl rings bridged by an Si(SiMe₃)₂ group. Interestingly, that the Ge atoms in **4** lie 0.42 Å above the C₄ least-squares planes and the sum of the angles about Ge (296.1°) both suggest that this center is sp³-hybridized. Presumably this bending of the Ge atoms away from one another is the result of an electrostatic repulsion between the two, formally negatively charged Ge atoms. This is not seen for **1**, as the Ge atoms are not required to reside in an eclipsed conformation and can avoid close contacts with one another by rotation about the metal–ring bond. Finally, the Fe–Ge bond lengths in **4** (2.536(3) and 2.539(3) Å) are somewhat longer than the corresponding values in **1** (2.415(1) Å) but are much shorter than the analogous distance of

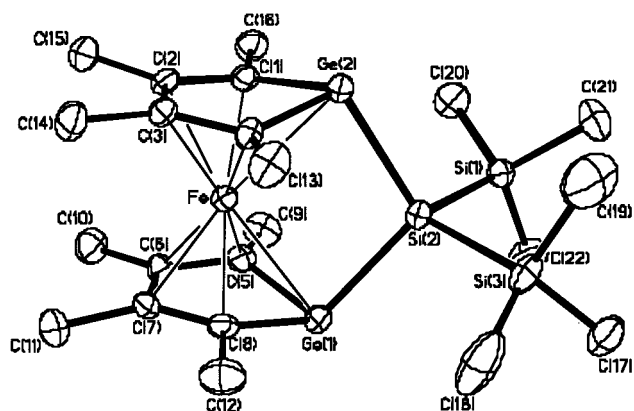


Figure 2. ORTEP diagram for *ansa*-Fe(η^5 -C₄Me₄Ge)₂Si(SiMe₃)₂ (**4**).

2.867(2) Å in the related germole complex [η^4 -C₄Ph₄Ge(F)Me]Fe(CO)₃.¹⁰ Also, the structure of **4** is related to that of a lithocenophane derivative of a trisgermole dianion, reported by the group of Boudjouk.¹⁴

One possible mechanism for the formation of **4** is shown in Scheme 1. Presumably, the first step in this reaction is nucleophilic cleavage of a Si–Si bond in **1** to produce a silyl anion (**A**, Scheme 1). The resulting anionic silicon center could then attack the other germoyl ring via nucleophilic displacement of LiSi(SiMe₃)₃ to produce **4**. This mechanism is supported by the observed reactivity of **1** with LiCH₂Ph (THF-*d*₈, room temperature), which cleanly produced Me₃SiCH₂Ph, **4**, and Li[Si(SiMe₃)₃] as the only products observed by ¹H NMR spectroscopy.

It has been shown that silicon-bridged ferrocenophanes are very good precursors for the preparation of high molecular weight polyferrocenes.¹¹ This chemistry relies on the high ring strain in metallocenophane monomers that possess a single silicon atom bridge between the two cyclopentadienyl ligands. These silicon-bridged ferrocenophanes can be polymerized thermally or via anion-initiated or transition-metal-catalyzed ring-opening polymerizations.¹¹ Given the similarity between these ferrocenophanes and our *ansa*-bis(germoyl) ferrocene complex, it seemed that **4** might be a precursor to iron-germoyl-containing polymers. However, thermolysis of solid **4** up to 260 °C in an evacuated sealable reaction vessel for 18 h did not result in the formation of any polymeric materials, and only unreacted **4** was recovered. The anionic polymerization of **4** was attempted using either (Et₂O)LiCH₂Ph or ⁿBuLi as an initiator (in THF or benzene, room temperature). Unfortunately, no polymeric materials were detected in either of these reactions (by gel permeation chromatography; THF solvent). Presumably, the presence of the germanium atoms in **4**, and their displacements out of their respective germoyl C₄ planes, relieves ring strain that might otherwise exist.

In this contribution we have shown that it is possible to form bis- η^5 -germoyl transition metal complexes.

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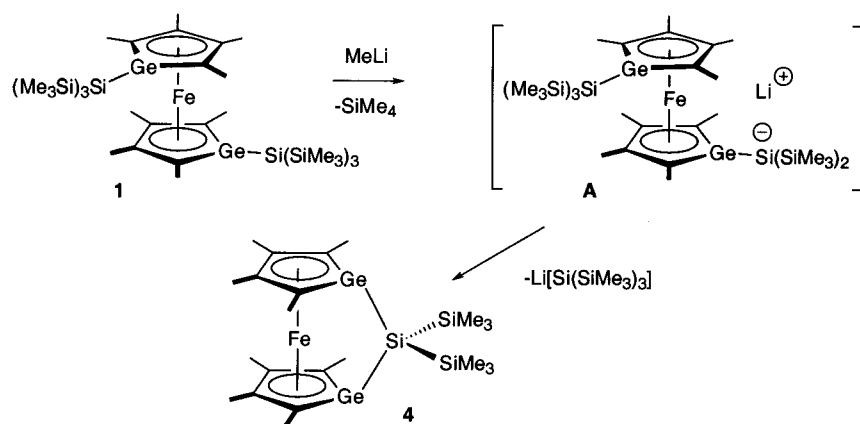
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Scheme 1



Structural, as well as NMR spectroscopic, analyses of the bisgermolyl ferrocene complex $\text{Fe}[\eta^5\text{-C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]_2$ (**1**) indicate that the η^5 -germolyl rings possess a significant amount of aromatic character. In addition, this compound was shown to be reactive toward nucleophiles, which cleave a Si–Si bond to form the novel ferrocenophane derivative *ansa*- $\text{Fe}(\eta^5\text{-C}_4\text{Me}_4\text{Ge})_2\text{Si}(\text{SiMe}_3)_2$ (**4**). Structural characterization of this complex revealed severe perturbations in the aromaticity of the germolyl rings. We are currently exploring the reactivity of these complexes in the hopes of establishing novel reactivity patterns and structural motifs for this class of heterole ligands.

Experimental Section

All manipulations were conducted under an atmosphere of nitrogen using either standard Schlenk techniques or a glovebox. Dry, deoxygenated solvents were employed for all manipulations. All solvents were distilled from Na/benzophenone ketyl, except benzene- d_6 and toluene- d_8 , which were purified by vacuum distillation from Na/K alloy. $\text{C}_4\text{Me}_4\text{Ge}(\text{H})\text{Si}(\text{SiMe}_3)_3$ ^{3d} was prepared according to literature procedures. ⁿButyllithium and methyllithium were purchased from Aldrich Chemical Company and used without further purification. Elemental analyses were performed by Desert Analytics and by the College of Chemistry Microanalytical Laboratory, U.C. Berkeley. NMR spectra were recorded on either a GE QE-300 or Bruker AMX-300 spectrometer at 300 MHz (¹H), 75.5 MHz (¹³C), or 59.6 MHz (²⁹Si) or on a Bruker AMX-400 spectrometer at 400 MHz (¹H) and 100 MHz (¹³C). All IR absorptions are reported in cm^{-1} and were recorded with a Perkin-Elmer 1330 spectrometer.

$\text{Fe}[\eta^5\text{-C}_4\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3]_2$ (1**).** A hexane solution of *n*-butyllithium (0.308 mL, 0.491 mmol) was slowly added to a cold solution (-80°C) of $\text{C}_4\text{Me}_4\text{Ge}(\text{H})\text{Si}(\text{SiMe}_3)_3$ (0.201 g, 0.468 mmol) in 100 mL of THF. The reaction solution became yellow and was stirred for 1 h at -80°C . This solution was then added via cannula to a 200 mL round-bottomed Schlenk flask containing a precooled (-80°C) solution of $\text{FeCl}_2(\text{THT})_{1.5}$ (0.052 g, 0.234 mmol) in 50 mL of THF. The reaction solution became amber and then deep red. After 5 min the cold bath was removed and the reaction solution was allowed to slowly warm over 1.5 h. After this time the volatile materials were removed under dynamic vacuum and the residue was extracted with pentane (3×25 mL). The combined pentane extracts were reduced in volume (25 mL), and the resulting solution was cooled to -80°C to give red crystals of **1** in 65% yield (0.138 g, 0.152 mol). ¹H NMR (benzene- d_6): δ 2.50, 1.74 (s, 12 H, $\text{C}_4\text{Me}_4\text{Ge}$), 0.36 (s, 54 H, $\text{Si}(\text{SiMe}_3)_3$). ¹³C{¹H} NMR (benzene- d_6): δ 89.86, 79.51 (s, $\text{C}_4\text{Me}_4\text{Ge}$), 18.55, 17.68 (s, $\text{C}_4\text{Me}_4\text{Ge}$),

Table 1. Crystallographic Data for Compounds 1 and 4

	1	4
(a) Crystal Parameters		
formula	$\text{FeGe}_2\text{Si}_8\text{C}_{34}\text{H}_{78}$	$\text{FeGe}_2\text{Si}_3\text{C}_{22}\text{H}_{42}$
fw	912.7	591.9
size (mm)	$0.38 \times 0.52 \times 0.54$	$0.33 \times 0.21 \times 0.11$
cryst syst	orthorhombic	triclinic
space group	<i>Pbcn</i>	<i>P1</i>
<i>a</i> (Å)	28.858(6)	10.256(3)
<i>b</i> (Å)	11.277(2)	12.210(3)
<i>c</i> (Å)	15.362(3)	13.786(6)
α, β, γ (deg)	90, 90, 90	69.17(3), 64.94(3), 63.18(3)
<i>V</i> (Å ³)	4999.2(18)	1366(1)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.213	1.438
<i>F</i> ₀₀₀	1963	612
(b) Data Collection		
temp (°C)	-145.0	25.0
no. of unique/total reflns	4409/5021	4803/5018
<i>R</i> _{int}	0.0476	0.0156
<i>T</i> _{max} / <i>T</i> _{min}	na	0.9986/0.6323
(c) Refinement		
no. of variables	204	253
reflection/param ratio	12.4	12.4
$R = \sum F_o - F_c / \sum F_o $	0.0409	0.0364
$R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$	0.0490	0.0448
goodness of fit	1.00	0.98
$(\sum w(F_o - F_c)^2 / (N_o - N_c))^{1/2}$		
max. and min. peaks in final diff map (e ⁻ /Å ³)	0.37/-0.35	0.44/-0.41

2.69 (s, $\text{Si}(\text{SiMe}_3)_3$, ²⁹Si{¹H}) (benzene- d_6): δ -9.3 (s, $\text{Si}(\text{SiMe}_3)_3$), -118.9 (s, $\text{Si}(\text{SiMe}_3)_3$). Anal. Calcd for $\text{C}_{34}\text{H}_{78}\text{FeGe}_2\text{Si}_8$: C, 44.73; H, 8.63. Found: C, 44.71; H, 8.67. IR (toluene, NaCl): 2368 w, 1962 w, 1873, w, 1811, w, 1661 m, 1254 m, 1439 w, 865 sh, 847 s, 635 sh, 511 m.

$\text{C}_4\text{Me}_4\text{Ge}(\text{I})\text{Si}(\text{SiMe}_3)_3$ (2**).** To a solution of **1** (0.033 g, 0.036 mmol) in 0.35 mL of THF- d_8 was added I_2 (0.018 g, 0.072 mmol). The resulting solution was placed in an NMR tube, which was shaken for 10 min to give **2** exclusively. ¹H NMR (THF- d_8): δ 1.87, 1.53 (s, 12 H, $\text{C}_4\text{Me}_4\text{Ge}$), 0.12 (s, 27 H, $\text{Si}(\text{SiMe}_3)_3$). ¹³C{¹H} NMR (THF- d_8): δ 148.52, 141.51 (s, $\text{C}_4\text{Me}_4\text{Ge}$), 21.92, 17.95 (s, $\text{C}_4\text{Me}_4\text{Ge}$), 5.93 (s, $\text{Si}(\text{SiMe}_3)_3$).

***ansa*- $\text{Fe}(\eta^5\text{-C}_4\text{Me}_4\text{Ge})_2\text{Si}(\text{SiMe}_3)_2$ (**4**).** An ethereal solution of methyllithium (0.409 mL, 0.573 mmol) was added to a 200 mL round-bottomed Schlenk flask containing a cold (0 °C) solution of **1** (0.498 g, 0.546 mmol) in 50 mL of THF. The cold bath was removed, and the reaction solution was stirred for 90 min. The original red color of the reaction solution still remained after this time. The volatile materials were then

removed under dynamic vacuum, and the residue was extracted with pentane (3×40 mL). The combined extracts were concentrated to 25 mL and cooled to -80 °C to afford **4** as black crystals in 55% yield (0.178 g, 0.301 mmol). ^1H NMR (benzene- d_6): δ 1.58, 1.49 (s, 12 H, $\text{C}_4\text{Me}_4\text{Ge}$), 0.50 (s, 18 H, $\text{Si}(\text{SiMe}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6): δ 126.62, 101.08 (s, $\text{C}_4\text{Me}_4\text{Ge}$), 18.45, 14.30 (s, $\text{C}_4\text{Me}_4\text{Ge}$), 4.44 (s, $\text{Si}(\text{SiMe}_3)_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6): δ 17.6 (s, $\text{Si}(\text{SiMe}_3)_2$), -7.5 (s, $\text{Si}(\text{SiMe}_3)_2$). Anal. Calcd for $\text{C}_{22}\text{H}_{42}\text{FeGe}_2\text{Si}_3$: C, 44.64; H, 7.17. Found: C, 44.45; H, 7.08. IR (toluene, NaCl): 2363 w, 1957 w, 1876 w, 1812 w, 1659 w, 1461 w, 1307 w, 1253 m, 1145 w, 1018 w, 937 w, 874 sh, 847 s, 585 m, 504 s.

Crystallographic Structural Determinations. Crystallographic data are collected in Table 1. Crystals of both **1** and **4** were mounted in fine capillary tubes in an inert atmosphere and studied on a Siemens P4 diffractometer. Crystals of **1** were uniquely assigned to the orthorhombic space group *Pbcn* based on diffraction symmetry and systematic absences in the data. Crystals of **4** showed no symmetry higher than triclinic, and the centrosymmetric option was selected on the basis of its

much greater probability and subsequently affirmed by the results of refinement. Both structures were corrected for absorption by empirical methods, solved by direct methods, refined with anisotropic thermal parameters for all non-hydrogen atoms, and incorporated hydrogen atoms as idealized contributions. All software was contained in versions of the SHELXTL library of programs (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: Tables of crystal data collection and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **1** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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