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Synthesis and Molecular Structure of a Tricyclic Stannasiloxane Containing a Novel $SiSn_3O_3F_2$ Structural Motif[†]

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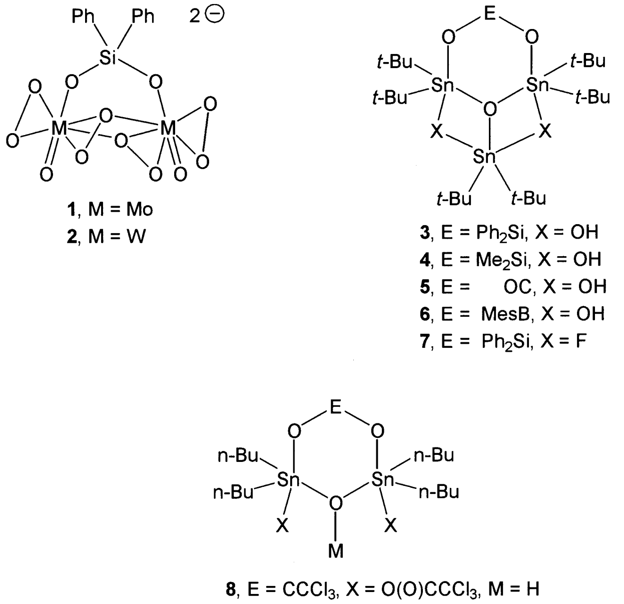
*Summary: The synthesis of the fluorine-substituted stannasiloxane complex cyclo-$Ph_2Si(OSn$t-$Bu_2)_2O{\cdot}$t-Bu_2SnF_2 (**7**) is reported, and its molecular structure has been determined by single-crystal X-ray diffraction analysis.*

Introduction

Molecular metallasiloxanes have attracted considerable attention, due to their potential as precursors for the preparation of ceramic materials and model compounds that effectively mimic heterogeneous silica-supported catalysts.[1−4] In academic research, the interest has been mostly directed toward the rich structural diversity, which is a result of the preferred coordination around the metal centers.[1−4] A general synthetic approach for the preparation of metallasiloxanes involves the removal of the acidic protons in organosilanols, such as $Ph_2Si(OH)_2$ and $HO(SiPh_2O)_nH$ ($n = 1-4$), by a base prior to reaction with suitable metal reagents. There are fewer reports in which organosilanols directly react with metal oxides to produce metallasiloxanes. One example is the reaction of $Ph_2Si(OH)_2$ with hydrated MoO_3 or WO_3 in the presence of H_2O_2, which almost quantitatively provided complexes of the type $Ph_2Si[OM(O)(O_2)_2]_2^{2-}$ (**1**, M = Mo; **2**, M = W) (Chart 1).[5] Recently, we reported the reaction of $Ph_2Si(OH)_2$ with (t-$Bu_2SnO)_3$, providing in high yield the stannasiloxane complex [*cyclo*-$Ph_2Si(OSn$-t-$Bu_2)_2O{\cdot}t$-$Bu_2Sn(OH)_2$] (**3**),[6] which is structurally related to the corresponding dimethylsilyl-, carbonyl-, and mesitylboryl-substituted derivatives **4**,[7] **5**,[8] and **6**,[9] respectively (Chart 1). The reaction of Ph_2SiF_2 with *cyclo*-(t-$Bu_2SnO)_3$ did not afford the related fluorine-substituted complex [*cyclo*-$Ph_2Si(OSn$-t-$Bu_2)_2O{\cdot}t$-Bu_2SnF_2] (**7**) but gave the open-chain stannasiloxane t-$Bu_2Sn(OSi$-t-$Bu_2F)_2$ and t-Bu_2SnF_2 instead.[10]

Chart 1



1, M = Mo
2, M = W

3, E = Ph_2Si, X = OH
4, E = Me_2Si, X = OH
5, E = OC, X = OH
6, E = MesB, X = OH
7, E = Ph_2Si, X = F

8, E = $CCCl_3$, X = $O(O)CCCl_3$, M = H

In this note, we report the synthesis and structure of [*cyclo*-$Ph_2Si(OSn$-t-$Bu_2)_2O{\cdot}t$-Bu_2SnF_2] (**7**) (Chart 1).

Results and Discussion

The reaction of equimolar amounts of the dimeric tetraorganodistannoxane [t-$Bu_2(F)SnOSn(F)t$-$Bu_2]_2$[11] and the eight-membered stannasiloxane *cyclo*-(Ph_2SiOSn-t-$Bu_2O)_2$[10] provided the tricyclic stannasiloxane [cyclo-$Ph_2Si(OSn$-t-$Bu_2)_2O{\cdot}t$-Bu_2SnF_2] (**7**) in good yield (eq 1). Compound **7** was obtained as a colorless crystalline chloroform adduct. However, once isolated from the mother liquor, the compound rapidly loses the chloro-

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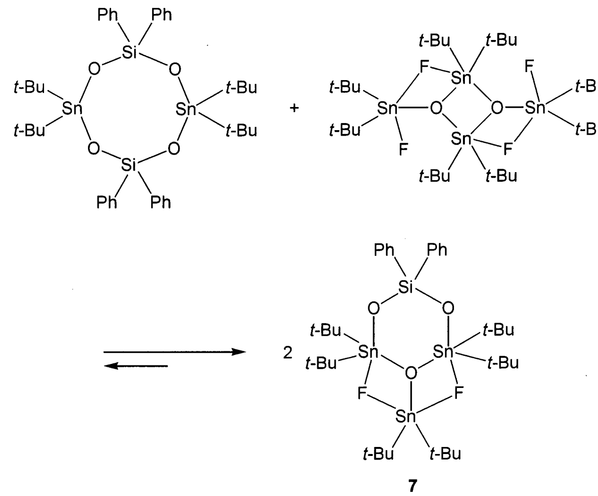

(1)

form and turns into an amorphous material. Unlike the related hydroxy-substituted derivative [*cyclo*-$Ph_2Si(OSn\text{-}t\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2$],[6] compound **7** is extremely sensitive toward moisture and reacts irreversibly with water to give [$t\text{-}Bu_2Sn(OH)F$]$_2$[12] and *cyclo*-($Ph_2SiOSn\text{-}t\text{-}Bu_2O$)$_2$.[10] The identity of the hydrolysis products was confirmed by comparison with authentic samples prepared according to the literature.[10]

The molecular structure of the fluorine-substituted tricyclic stannasiloxane **7** (as its $CHCl_3$ adduct) is shown in Figure 1, and selected bond lengths and angles are given in Table 1. The $Sn_3SiO_3F_2$ structural motif is almost planar, with the largest deviation from the plane being 0.206(3) Å for O(1). All three tin atoms show distorted-trigonal-bipyramidal geometries (geometrical goodness[13] $\Delta\Sigma(\theta) = 65.9°$ for Sn(1), 64.5° for Sn(2), 88.2° for Sn(3)), in which two carbon atoms and an oxygen atom occupy the equatorial positions (C(1), C(5), and O(3) for Sn(1); C(11), C(15), and O(3) for Sn(2); C(21), C(25), and O(3) for Sn(3)). The axial positions are occupied either by an oxygen and a fluorine atom (O(1) and F(1) for Sn(1) and O(2) and F(2) for Sn(2)) or by two fluorine atoms (F(1) and F(2) for Sn(3)). Interestingly, the Sn(3)−F(1) and Sn(3)−F(2) distances of 2.074(3) and 2.073(3) Å, respectively, are much shorter than the Sn(1)−F(1) and Sn(2)−F(2) distances of 2.399(3) and 2.353(3) Å, respectively, suggesting compound **7** to be formally interpreted as a $t\text{-}Bu_2SnF_2$ adduct of *cyclo*-$Ph_2Si(OSn\text{-}t\text{-}Bu_2)_2O$.[6,10]

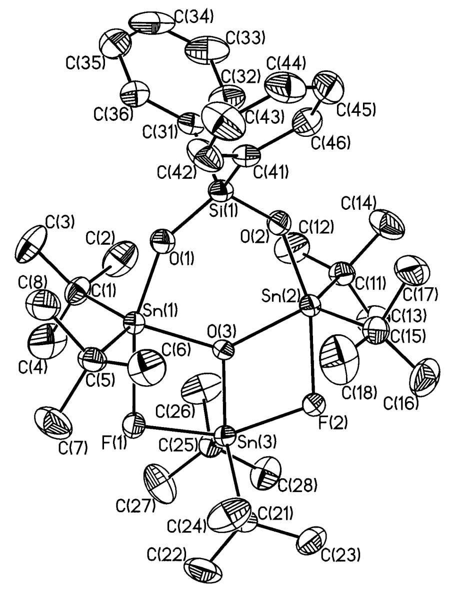

Figure 1. General view (SHELXTL[19]) of a molecule of [*cyclo*-$Ph_2Si(OSnt\text{-}Bu_2)_2O\cdot t\text{-}Bu_2SnF_2$] (**7**) showing 30% probability displacement ellipsoids and the atom numbering.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 7

Sn(1)−O(1)	1.981(4)	Sn(1)−O(3)	2.098(4)
Sn(1)−C(1)	2.183(6)	Sn(1)−C(5)	2.183(6)
Sn(1)−F(1)	2.399(3)	Sn(2)−O(2)	1.999(4)
Sn(2)−O(3)	2.109(4)	Sn(2)−C(15)	2.167(6)
Sn(2)−C(11)	2.184(6)	Sn(2)−F(2)	2.353(3)
Sn(3)−O(3)	2.064(4)	Sn(3)−F(1)	2.074(3)
Sn(3)−F(2)	2.073(3)	Sn(3)−C(21)	2.177(6)
Sn(3)−C(25)	2.177(6)	Si(1)−O(1)	1.621(4)
Si(1)−O(2)	1.599(4)	Si(1)−C(31)	1.881(7)
Si(1)−C(41)	1.848(6)		

O(1)−Sn(1)−O(3)	95.29(15)	O(1)−Sn(1)−C(1)	100.9(2)
O(1)−Sn(1)−C(5)	93.9(2)	O(3)−Sn(1)−C(1)	111.9(2)
O(3)−Sn(1)−C(5)	120.8(2)	C(1)−Sn(1)−C(5)	123.3(3)
O(1)−Sn(1)−F(1)	162.50(14)	O(3)−Sn(1)−F(1)	68.30(12)
C(1)−Sn(1)−F(1)	91.3(2)	C(5)−Sn(1)−F(1)	89.78(19)
O(2)−Sn(2)−O(3)	94.72(15)	O(2)−Sn(2)−C(11)	95.6(2)
O(2)−Sn(2)−C(15)	100.8(2)	O(3)−Sn(2)−C(11)	121.8(2)
O(3)−Sn(2)−C(15)	111.9(2)	C(11)−Sn(2)−C(15)	121.9(3)
O(2)−Sn(2)−F(2)	162.67(14)	O(3)−Sn(2)−F(2)	68.68(12)
C(11)−Sn(2)−F(2)	89.5(2)	C(15)−Sn(2)−F(2)	90.4(2)
O(3)−Sn(3)−F(1)	75.64(13)	O(3)−Sn(3)−F(2)	75.23(13)
F(2)−Sn(3)−F(1)	150.82(13)	F(1)−Sn(3)−C(25)	99.70(19)
F(2)−Sn(3)−C(25)	96.39(19)	F(1)−Sn(3)−C(21)	96.5(2)
F(2)−Sn(3)−C(21)	97.64(19)	O(3)−Sn(3)−C(21)	122.5(2)
O(3)−Sn(3)−C(25)	120.5(2)	C(21)−Sn(3)−C(25)	117.0(2)
O(1)−Si(1)−O(2)	111.7(2)	O(1)−Si(1)−C(31)	109.4(3)
O(2)−Si(1)−C(31)	109.7(3)	O(1)−Si(1)−C(41)	108.4(3)
O(2)−Si(1)−C(41)	111.2(3)	C(41)−Si(1)−C(31)	106.2(3)
Sn(1)−F(1)−Sn(3)	102.21(13)	Sn(2)−F(2)−Sn(3)	103.27(13)
Sn(1)−O(3)−Sn(2)	133.39(18)	Sn(1)−O(3)−Sn(3)	113.85(16)
Sn(1)−O(1)−Si(1)	139.6(3)	Sn(2)−O(2)−Si(1)	140.6(2)
Sn(2)−O(3)−Sn(3)	112.76(17)		

The fluorine atoms in compound **7** are chemically equivalent. They are magnetically equivalent as well with respect to one tin, but they are magnetically nonequivalent with respect to the other two tins, being part of the silicon-containing six-membered ring. Consequently, the ^{119}Sn NMR spectrum ($CDCl_3$) of **7** (crystalline sample) reveals a doublet of doublets centered at −222.2 ppm (($^1J(^{119}Sn-^{19}F) = 1171$ Hz, $^3J(^{119}Sn-OSn-^{19}F) = 7$ Hz) and flanked by $^2J(^{119}Sn-O-^{119/117}Sn)$ coupling satellites ($^2J(^{119}Sn-O-^{117}Sn) = 228$ Hz, $^2J(^{119}Sn-O-^{119/117}Sn) = 51$ Hz) and a triplet at −280.8 ppm (($^1J(^{119}Sn-^{19}F) = 2465$ Hz, $^2J(^{119}Sn-O-^{119/117}Sn) = 52$ Hz) with an integral ratio of 2:1 (total integral 88%), which indicates the structure in solution is rather similar to that observed in the solid state. In addition to the two major signals, a singlet at −149.5 ppm and two equally intense triplets at −226.3 ppm ($^1J(^{119}Sn-^{19}F) = 807$ Hz) and −290.4 ppm ($^1J(^{119}Sn-^{19}F) = 2450$ Hz) are observed (total integral 12%), which are unambiguously assigned to the starting compounds *cyclo*-($Ph_2SiO\text{-}t\text{-}Bu_2SnO$)$_2$ and [$t\text{-}Bu_2(F)SnOSn(F)\text{-}t\text{-}Bu_2$]$_2$, respectively.[10,11] The reason compound **7** in solution apparently is in equilibrium with the starting materials and does not, as suggested by its molecular structure (see discussion above), dissociate into *cyclo*-$Ph_2Si(OSn\text{-}t\text{-}Bu_2)_2O$

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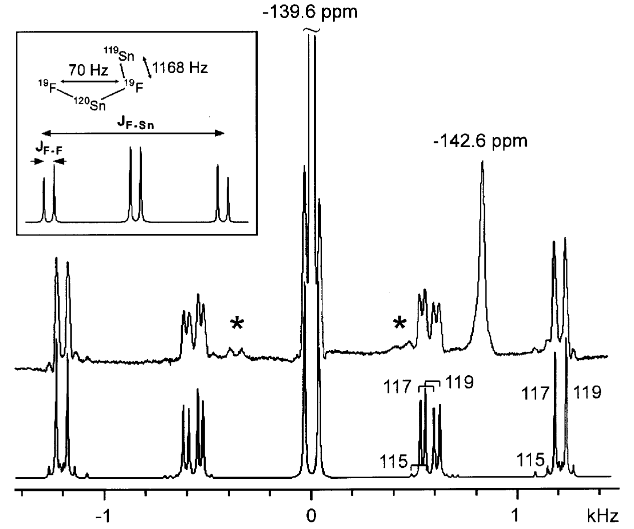

Figure 2. Experimental (top) and simulated (bottom) ^{19}F NMR spectra of [*cyclo*-$Ph_2Si(OSn$-*t*-$Bu_2)_2O$·*t*-Bu_2SnF_2] (**7**). The spectrum is a superposition of AX, AA′X, AA′XY, and AA′XX′ spectra, each weighted with the appropriate isotopic abundance of the three Sn isotopes. The signals labeled with an asterisk in the experimental spectrum constitute the high-frequency half of the set of satellites of the signal at −142.6 ppm belonging to [*t*-$Bu_2(F)SnOSn(F)$-*t*-$Bu_2]_2$ in equilibrium with **7**. The box in the upper left-hand corner shows the simulated spectrum of one isotopomer of **7**.

and *t*-Bu_2SnF_2 is not clear. The ^{29}Si NMR spectrum ($CDCl_3$) of **7** (same sample) shows a highly intense singlet at −40.8 ppm ($^2J(^{29}Si-O-^{119/117}Sn) = 51$ Hz) and a minor intense signal at −42.7 ppm, which are assigned to **7** and *cyclo*-(Ph_2SiO*t*-$Bu_2SnO)_2$, respectively. The ^{19}F NMR spectrum ($CDCl_3$) of **7** (same sample, but diluted) exhibits two singlets at −139.6 ppm (integral 92%) and −142.6 ppm (integral 8%) belonging to **7** and [*t*-$Bu_2(F)SnOSn(F)$-*t*-$Bu_2]_2$, respectively (Figure 2). The coupling pattern of the signal at −139.6 ppm is complex. Simulation of the spectrum (Figure 2)[14] confirms that this complexity is the result of the presence of a strongly non-first-order pattern arising from different isotopomers, in some of which the two fluorine atoms are magnetically nonequivalent. In a previous paper on the fluorine-containing tetraorganodistannoxane [*t*-$Bu_2(F)SnOSn(F)$-*t*-$Bu_2]_2$ we interpreted a ^{19}F NMR spectrum of similar complexity in terms of a dynamic wagging process.[11] Although the latter process is taking place, it is not formally established that it is related to the complex ^{19}F NMR spectrum observed.

Conclusion

This work shows that the novel fluorine-substituted stannasiloxane complex **7** (Chart 1) and the related compounds **3**−**6** (Chart 1) adopt a common structural motif. It also shows that certain functional groups (or atoms) can be replaced by isoelectronic groups (or atoms) with retention of the structural motif. One straightforward example is the formal substitution of a hydroxide ion in compound **3** by a fluoride ion in compound **7**. That this concept is even more general is demonstrated by compound **8** (Chart 1),[15] which can formally be interpreted as the product of the reaction of the tetraorganodistannoxane *n*-$Bu_2(X)SnOSn(X)$*n*-Bu_2 with HX (X = $O(O)CCCl_3$).

It appears likely that other atoms or functional groups can be replaced as well, which offers perspectives for the synthesis of a variety of novel compounds.

Experimental Section

Manipulations were performed under a dry atmosphere of nitrogen using standard Schlenk and vacuum-line techniques. All solvents were dried over appropriate desiccants and freshly distilled prior to use. [*t*-$Bu_2FSnOSnF$-*t*-$Bu_2]_2$[11] and *cyclo*-(Ph_2SiOSn-*t*-$Bu_2O)_2$[10] were synthesized according to literature procedures. NMR spectra were recorded in $CDCl_3$ solution on a Bruker DRX 400 (^1H, ^{13}C, ^{29}Si, ^{119}Sn) and a Bruker DPX 300 spectrometer (^{19}F) and were referenced to $SiMe_4$ (^1H, ^{13}C, ^{29}Si), $CFCl_3$ (^{19}F), or $SnMe_4$ (^{119}Sn). The elemental analysis was performed on an instrument from Carlo Erba Strumentazione (Model 1106).

Synthesis of [*cyclo*-$Ph_2Si(OSn$-*t*-$Bu_2)_2O$·*t*-Bu_2SnF_2] (7). A mixture of *cyclo*-(Ph_2SiOSn-*t*-$Bu_2O)_2$ (268 mg, 0.30 mmol) and [*t*-$Bu_2(F)SnOSn(F)$-*t*-$Bu_2]_2$ (520 mg, 0.50 mmol) was heated in chloroform (5 mL) for 2 h at 40 °C. The excess [*t*-$Bu_2(F)SnOSn(F)$-*t*-$Bu_2]_2$ was removed by filtration. The solvent was reduced in vacuo to a volume of approximately 2 mL. Upon cooling to −10 °C colorless crystals of **7**·$CHCl_3$ (460 mg, 0.48 mmol, 79%) were deposited. Isolated from the mother liquor, compound **7** slowly loses the crystal solvent.

^1H NMR (400.13 MHz): δ 7.8−7.2 (m, 10H; *Ph*), 1.44 (s, $^3J(^1H-CC-^{119/117}Sn) = .110$ Hz, 18H; C*Me*$_3$), 1.34 (s, $^3J(^1H-CC-^{119/117}Sn) = 110$ Hz, 36H; C*Me*$_3$). $^{13}C\{^1H\}$ NMR (100.64 MHz): δ 142.8, 134.6, 127.9, 126.9 (*i*-, *o*-, *p*-, *m*-Ph), 43.2 (t, $^1J(^{13}C-^{119}Sn) = 601$ Hz, $^2J(^{13}C-Sn-^{19}F) = 4$ Hz; *C*Me$_3$), 41.9 (t, $^1J(^{13}C-^{119}Sn) = 585$ Hz, $^2J(^{13}C-Sn-^{19}F) = 10$ Hz; *C*Me$_3$), 30.7 (C*Me*$_3$), 30.4 (C*Me*$_3$). $^{19}F\{^1H\}$ NMR (282.4 MHz): δ −139.6 (s, $^1J(^{19}F-^{119}Sn) = 2465$ Hz, $^1J(^{19}F-^{119}Sn) = 1168$ Hz, $^2J(^{19}F-^{19}F) = 70$ Hz). $^{29}Si\{^1H\}$ NMR (79.5 MHz): δ −40.8 (s, $^2J(^{29}Si-O-^{119/117}Sn) = 51$ Hz). $^{119}Sn\{^1H\}$ NMR (149.2 MHz): δ −222.2 (2Sn, dd, $^1J(^{119}Sn-^{19}F) = 1171$ Hz, $^2J(^{119}Sn-O-^{-17}Sn) = 228$ Hz, $^2J(^{119}Sn-O-^{119/117}Sn) = 51$ Hz, $^3J(^{119}Sn-^{19}F) = 7$ Hz), −280.8 (1Sn, t, $^1J(^{119}Sn-^{19}F) = 2465$ Hz, $^2J(^{119}Sn-O-^{119/117}Sn) = 52$ Hz). Anal. Calcd for $C_{36}H_{64}F_2O_3SiSn_3$ (967.19): C, 44.71; H, 6.67; Found: C, 44.8; H, 7.0.

Crystallography. A single crystal suitable for X-ray analysis was directly taken from the reaction mixture and sealed with some dry paraffin oil. Crystal data and structure solution details for **7**·$CHCl_3$: $C_{36}H_{64}F_2O_3SiSn_3 \cdot CHCl_3$, $M_r = 1086.40$, monoclinic, $P2_1/c$, $a = 20.492(1)$ Å, $b = 11.939(1)$ Å, $c = 19.263(1)$ Å, $\beta = 91.830(1)°$, $V = 4710.4(5)$ Å^3, $Z = 4$, $D_{exptl} = 1.532$ Mg m^{-3}, $F(000) = 2176$, λ(Mo Kα) = 0.710 69 Å, $\mu = 1.812$ mm^{-1}, $T = 291(1)$ K. The data were collected to a maximum $\theta = 25.00°$ with 360 frames via ω rotation ($\Delta/\omega = 1°$) at two times 10 s per frame on a Nonius Kappa CCD diffractometer with a completeness of 93.1% to θ_{max}. The structure was solved by direct methods (SHELXS97[16]) and successive difference Fourier syntheses and was refined by full-matrix least-squares calculations using all measured F^2 data and SHELXL97.[17] All non-H atoms were refined anisotropically. The H atoms were placed in geometrically calculated positions using the riding model (including free rotation about C−C bonds) with different isotropic temperature factors for alkyl and aryl H atoms (H_{alkyl}, C−H = 0.96 Å, $U_{iso} = 0.127(4)$ Å^2; H_{aryl}, C−H = 0.93 Å, U_{iso} =

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[14] The program used for the simulation can be obtained free of charge from http://e3.physik.uni-dortmund.de/~suter/sim/sim.html.

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0.105(9) Å^2). Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 18. R1 = 0.0399 for 4409 reflections ($(I > 2\sigma(I))$ and wR2 = 0.0903 for 7759 independent reflections. The maximum and minimum residual electron densities were 0.629 and −0.617 e Å^{-3}.

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Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for compound **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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