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Structural Characterization of Areneselenenyl Chloride Stabilized by the Stereoelectronic Effect of an Intramolecular Nitrogen Atom

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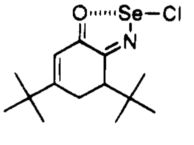
The first X-ray structural characterization of areneselenenyl chloride (ArSeCl) was achieved with a single crystal obtained from a 1:2 mixture of 2,2′-diselenobis[*N,N*-di[2-(2-pyridyl)ethyl]benzylamine] (**3**) and copper(II) chloride. The structure of the complex, $\mathbf{4} = \mathbf{3}\cdot 2\mathrm{Cl}\cdot 2\mathrm{CuCl_2}\cdot 2\mathrm{CHCl_3}$, contained a Se−Cl bond strongly stabilized by an intramolecular tertiary nitrogen atom. Selected bond parameters were Se−Cl = 2.432(3) Å, Se−C = 1.919(12) Å, Se···N = 2.191(8) Å, $\angle$C−Se−Cl = 96.5(3)°, and $\angle$Cl−Se···N = 178.4(2)°. In order to characterize the observed Se···N interaction, the electronic structure around the selenium was investigated by MO and NBO methods at various basis set levels using model compound **6**. The optimized geometries, obtained at 3-21G* and LANL1DZ basis set levels, were reasonably consistent with the results of the X-ray analysis of **4**. The shape of the LUMO and the large NBO deletion energy (47 kcal) between the Se−Cl bond and N suggested that the observed Se···N interaction arises from the orbital interaction between a low-lying unoccupied σ^* orbital of the selenium and the nitrogen lone pair electrons, showing that the electronic structure around the selenium is similar to the transition-state of a bimolecular nucleophilic substitution at selenium.

Introduction

Although the versatility of areneselenenyl chlorides (ArSeCl) is well recognized in selective organic synthesis,[1] their precise structural properties around the selenium remain undetermined because of their intrinsic high reactivity. The cambridge X-ray crystallographic database[2] contains no aryl selenyl chlorides but does contain two inorganic selenyl chlorides that bear Se−N covalent bonds (**1** and **2**).[3,4] Their characteristic features are the presence of stereoelectronic stabilization by a nearby heteroatom (O or Cl⁻) that coordinates the electron-deficient divalent selenium atom as well as the almost linear alignment of the Se−Cl bond with the coordinating atom. Such strong van der Waals contacts are attributed to interatomic interaction arising from the hypervalent nature of selenium.



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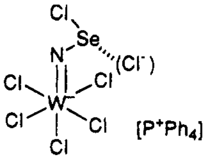

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Recently, Barton et al.[5] discussed the electronic structure of one of these inorganic selenenyl chlorides, **1**, and showed that the nature of the O···Se−Cl interaction is a three-center-four-electron bond (hypervalent bond). Their conclusion was that electron withdrawal from the Se by Cl increases the Se···O interaction. We have been interested in the nature of an analogous Se···N interaction[6] in connection with the catalytic mechanism of a selenium-containing antioxidant enzyme, glutathione peroxidase,[7] as well as in whether Barton's conclusion can be successfully applied to Se···N interaction.

In contrast to the lack of structural data for ArSeCl, there are some data in the literature for areneselenenyl bromide (ArSeBr). The molecular structures of benzeneselenenyl bromide[8] and its 2-nitro derivative[9] were determined by electron diffraction in the gas phase, and that of 2-formylbenzeneselenenyl bromide[10] was determined by X-ray diffraction in the solid state. It was found that the deviation of the Se−Br bond from the phenyl plane is significantly reduced by substituents at the *ortho*-position, accompanied by an increase in the Se−Br bond length. These phenomena may be explained by assuming that the oxygen atom of the substituent interacts intramolecularly with the selenium atom, forc-

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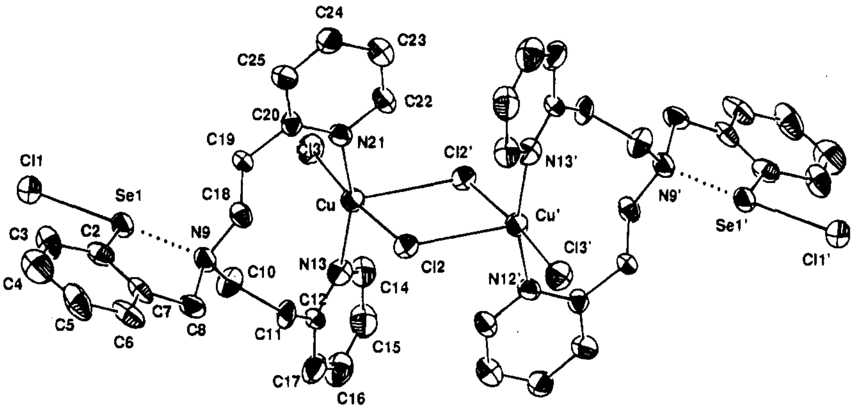


Figure 1. ORTEP plot for the 1:2 copper(II) complex of **3** (**4** = $\mathbf{3}\cdot 2Cl\cdot 2CuCl_2\cdot 2CHCl_3$) at the 50% probability level omitting $CHCl_3$.

Table 1. Molecular Structure of Selenenyl Chlorides Determined by X-ray Diffraction Methods along with That of Selenane 5 for Comparison

compd	Se−Cl (Å)	Se−C (Å)	Se··N (Å)	∠C−Se−Cl (deg)	∠Cl−Se··N (deg)	ref
1	2.302		(2.079)[a]		(174.7)[b]	3
2	2.430		(2.607)[c]		(165.9)[d]	4
4	2.432	1.919	2.191	96.5	178.4	this work
5	2.295	1.955[e]	2.191	95.2[e]	174.3	13

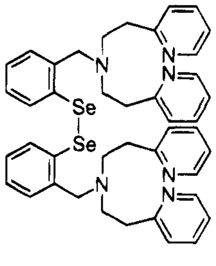
[a] Se··O interatomic distance. [b] ∠Cl−Se··O. [c] Se··Cl⁻ interatomic distance. [d] ∠Cl−Se··Cl⁻. [e] An averaged value.

ing the Se−Br bond into the phenyl plane and lengthening the Se−Br bond. A similar situation may occur for ArSeCl though no experimental evidence to support this assumption has appeared.

In this paper, the first X-ray structural characterization of ArSeCl, where the Se−Cl bond is stereoelectronically stabilized by strong intramolecular N··Se−Cl interaction, is presented. We shall discuss the electronic structure of such hypervalent selenium species based on *ab initio* MO calculations at various levels of the basis set and natural bond orbital (NBO) analysis using a model selenenyl chloride having a tertiary amino group.

Results and Discussion

Diselenide **3** acts as a catalyst in the conversion of simple olefins into allylic ethers or esters in the presence of copper(II) ion.[11] In order to characterize active intermediates of the catalytic cycle, we attempted to synthesize a copper(II) complex of **3**. After several unsuccessful attempts, we obtained a metal complex[12] from methanol solution containing a 1:2 mixture of **3** and $CuCl_2\cdot 2H_2O$ in low yield (7%). The molecular structure of the complex was determined by X-ray analysis of a dark blue single crystal recrystallized from chloroform.



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The obtained molecular structure (**4** = $\mathbf{3}\cdot 2Cl\cdot 2CuCl_2\cdot 2CHCl_3$) is shown in Figure 1 (chloroform molecules are omitted for clarification). The complex no longer has an Se−Se covalent bond but contains two selenium atoms (Se1 and Se1′), each of which has an areneselenenyl chloride form covalently bonded to chlorine Cl1 and Cl1′, respectively. This bond cleavage might occur through interaction between the Se−Se bond and the copper(II) ion, captured by pyridyl moieties. An inversion center exists at the middle point of the two copper ions (Cu and Cu′), which adopt a square pyramidal structure coordinated by two pyridine nitrogens and three chloride anions.

The selected bond parameters of **4** determined by X-ray analysis are listed in Table 1 along with those of inorganic selenenyl chlorides previously reported in the literature. The table also contains the molecular structure of selenane **5**[13] for comparison. The short interatomic distance between the selenium (Se1) and the amino nitrogen (N9) (Se1··N9 = 2.191 Å) observed in **4** clearly shows the existence of a strong nonbonded interaction between these two atoms, forming a slightly bent envelop-type five-membered ring (∠C2−C7−C8−N9 (ω) = 26°). The distance is only 0.35 Å longer than the standard Se−N(sp^3) single bond length (1.84 Å)[14] and about 1.3 Å shorter than the van der Waals contact (3.5 Å).[15] The linear alignment of the Se−Cl covalent bond and the coordinating nitrogen (∠N9··Se1−Cl1 = 178.4°) should allow an effective orbital interaction between the nitrogen lone pair and σ^* orbital of the Se−Cl bond, which may cause the elongation of the Se−Cl bond. Indeed, the observed Se−Cl bond length (Se1−Cl1 = 2.432 Å) seems quite long when compared with benzeneselenenyl bromide (PhSeBr, Se−Br = 2.325 Å) determined by electron diffraction.[8] Recently, Fujihara and Furukawa reported

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[12] On the basis of the UV and ^{77}Se NMR spectral changes, it was found that **3** forms a 1:1 stoichiometric complex with copper(II) in methanol and that within the complex the Se−Se covalent bond of **3** undergoes disproportionation to produce an electron-deficient selenium species and an electron-rich one. Their ^{77}Se NMR signals appeared at δ 600 and 270 ppm, respectively, as broad band absorptions. This 1:1 complex may be a real active intermediate. However, the complex could not be isolated due to low stability.

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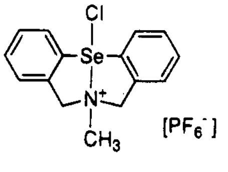
an analogous linear N^+–Se(<)–Cl hypervalent bond of **5**,[13] in which the N^+–Se bond length (2.191 Å) is the same as the Se··N interatomic distance observed in **4** and the Se–Cl bond (2.295 Å) is slightly shorter than that observed in **4**, probably due to the difference in the valence state of the selenium. The structural similarity reasonably confirms the hypervalent nature of the N··Se–Cl interaction in **4**.



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Since the Se–Cl bond length reflects the electronic environment around the selenium, it should offer a reasonable index of the extent of the electron delocalization from the coordinating atom to the selenium. The observed Se–Cl bond of the complex with N··Se–Cl interaction was longer by 0.13 Å than that of inorganic selenenyl chloride **1** with O··Se–Cl interaction, where Barton et al.[5] concluded that the major component of the interaction is orbital interaction, i.e., a three-center-four-electron bond. This indicates that the nitrogen lone pair electrons of the complex delocalize into the Se–Cl bond to form a more advanced three-center-four-electron bond. Thus, the increase of the Se–Cl bond length strongly suggests resemblance of the electronic character of the selenium to the transition state of bimolecular nucleophilic substitution (S_N2) at the selenium.

The observed bond parameters around the selenium of the complex (ArSeCl) were very similar to those of PhSeBr[8] and 2-$NO_2C_6H_4SeBr$[9] determined by electron diffraction. 2-$NO_2C_6H_4SeBr$ has an approximately planar structure with a slightly longer Se–Br bond than PhSeBr due to the O··Se–Br interaction. A similar phenomena was observed in ArSeCl with the N··Se–Cl interaction as discussed above. However, the Se–C bond of ArSeCl (1.919 Å) seemed to be slightly longer than that of ArSeBr (1.876–1.899 Å) and the C–Se–Cl angle of ArSeCl (96.5°) seemed to be a little smaller than that of ArSeBr (98.0–99.8°).

In order to estimate the strength of the N··Se–Cl interaction as well as to investigate the electronic structure around the selenium, *ab initio* MO calculations[16] and NBO analysis[17] were performed on the model compound **6**. The fully optimized geometry parameters obtained at various basis set levels are listed in Table 2. Comparison of the results from different levels of calculations with those of the X-ray structure of **4** may give valuable information on the accuracy of calculations of pseudo high-valent selenium species. The semiempirical PM3 calculation overestimated the Se··N nonbonded interaction significantly (Se··N 1.977 Å, ω 11.3°), which was underestimated when the *ab initio* calculation using an STO-3G basis set was employed (Se··N 2.771 Å, ω 47.0°) due to limited extension of valence orbitals on Se. The differences in optimized geometries at 3-21G and polarized 3-21G* basis set[18] levels were clear. The discrepancy suggests that vacant 4*d* orbitals on Se may partially participate in the Se··N nonbonded interaction, weakening it. The use of an effective core potential (LANL1MB),[19] which includes some relativistic effects, was very efficient with respect to the use of STO-3G. The more accurate LANL1DZ basis set,[19] which does not include *d* orbitals, gave approximately the same results as 3-21G*. The results from 3-21G* and LANL1DZ were roughly consistent with the partial X-ray structure of complex **4**, indicating that these basis set levels are the minimum limits to treat pseudo high-valent selenium species. The differences between the optimized geometries of **6** and the X-ray molecular structure of **4**, for example, the difference in interatomic Se··N distance, may be partially attributed to the crystal packing force in the solid state.

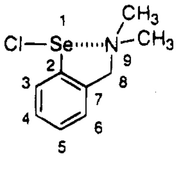

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Table 2. Molecular Structures and NBO Deletion Energies of 6 Obtained by MO Calculations at Various Basis Set Levels with the Result from X-ray Analysis of Complex 4

method[a]	Se–Cl (Å)	Se··N (Å)	∠Cl–Se··N (deg)	ω[b] (deg)	ΔE_{del}[c] (kcal)
PM3	2.225	1.977	173.7	11.3	
STO-3G	2.216	2.771	171.1	47.0	
3-21G	2.529	2.182	174.6	32.2	
3-21G*[d]	2.290	2.331	174.6	35.6	47.0
LANL1MB[e]	2.547	2.278	173.0	31.4	
LANL1DZ[f]	2.448	2.359	174.4	32.9	47.4
X-ray[g]	2.432	2.191	178.4	26	

[a] Details are described in the Experimental Section. [b] A dihedral angle of C2–C7–C8–N9. [c] NBO deletion energy between an Se–Cl moiety and an amino nitrogen atom. [d] A 3-21G basis set with *d* polarization functions for Se and Cl.[18] [e] Los Alamos ECP+MB basis set for Se and Cl and STO-3G for N, C, and H. [f] Los Alamos ECP+DZ basis set for Se and Cl and Dunning/Huzinaga valence double-ζ basis set for N, C, and H. [g] Molecular structure of **4** determined by X-ray analysis.

NBO deletion analysis is a useful method for quantitating the orbital interaction energy between specific atoms or groups.[17] The results of NBO deletion analysis (Table 2) suggested that the orbital interaction between the Se–Cl bond and N is fairly strong (47.0 kcal at 3-21G* and 47.4 kcal at LANL1DZ). The energy is quite large compared to the estimated value of the Se–Br bond dissociation energy (61.7 kcal).[20] The result indicates that the predominant force of the Se··N interaction is the orbital interaction between the Se–Cl bond and N, although other effects such as dipole or quadrupole moment and high polarizability of the Se–Cl bond may also be involved in the N··Se–Cl interaction. The major factor in this stabilization is the n–σ^* type orbital interaction between the N lone pair (n_N) and the σ^* orbital of the Se–Cl bond (σ^*_{Se-Cl}) because when the off-diagonal NBO Fock matrix elements between the N and Se–Cl were deleted, the occupancy of n_N increased by 0.133 e (electron) or 0.116 e and that of σ^*_{Se-Cl} decreased by 0.143 e or 0.141 e at the 3-21G* or the LANL1DZ level,

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(16) Details of MO calculations are described in the Experimental Section.

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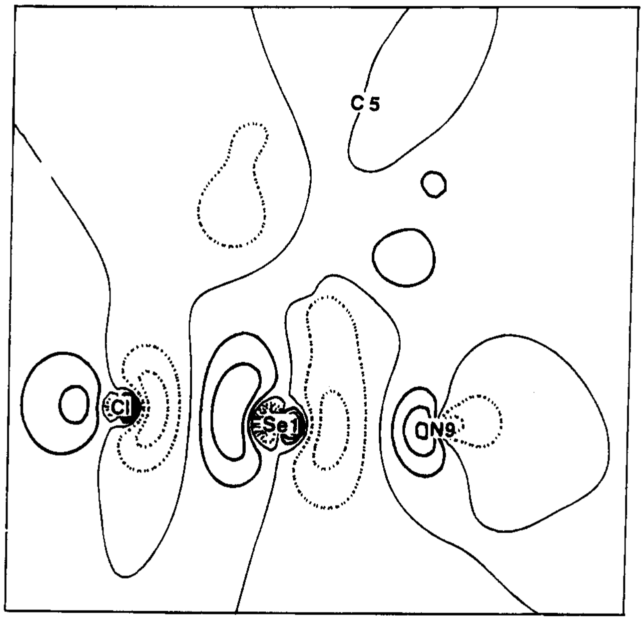

Figure 2. Contour plot of LUMO for **6** using a 3-21G* basis set at the plane on Se1, N9, and C5 with a line interval of 0.05. Thin solid lines mean intersection of the nodal surface.

respectively. These values were significantly larger than the occupancy changes of other NBO's, which were approximately equal to zero (<0.01 e). At the 3-21G* level, one Rydberg orbital of d function on Se lost 0.011 e when the Se···N orbital interaction was eliminated, indicating a minor contribution of vacant d orbitals in forming the Se···N interaction.

The shape of the LUMO for **5** reasonably supports the above NBO deletion results. Figure 2 shows the contour plot of the LUMO using a 3-21G* basis set at the plane on Se1, N9, and C5. It can be seen that the nitrogen lone pair strongly interacts with the σ^* orbital of the Se−Cl bond in an antibonding way. This orbital interaction causes effective stabilization in the total electronic energy accompanied by significant charge transfer from the the N to Se−Cl bond, to weaken the Se−Cl bond considerably. The fact that the LUMO expansion around the Cl is almost the same as that around the N is in accordance with the assumption that the strength of the Se−Cl bond is counter-balanced with the magnitude of the Se···N interaction, which may well be compared to the S_N2 transition state at a divalent selenium.

In summary, we succeeded in the first X-ray crystallographic characterization of an ArSeCl strongly stabilized by the intramolecular N···Se−Cl nonbonded interaction. This interaction may be the primary origin of the planar structure of ArSeCl as well as the observed elongation of the Se−Cl bond, previously discussed for 2-substituted ArSeBr.[9,10] The magnitude of the Se−Cl bond elongation and the calculated n−σ^* orbital interaction (47 kcal) between Se and N suggest that the nature of the observed N···Se−Cl interaction is most likely a three-center-four-electron bond. Since the extent of electron delocalization from N to Se−Cl was significantly large, the electronic structure around the selenium may most probably be similar to the S_N2 transition state at a divalent selenium.

Experimental Section

2,2′-Diseleno-bis[*N*,*N*-bis[2-(2-pyridyl)ethyl]benzylamine] (3).[11] 2,2′-diselenobis(benzyl chloride)[6d] (5.0 g, 12 mmol), bis[2-(2-pyridyl)ethyl]amine[21] (5.46 g, 24 mmol), and triethylamine (8.36 mL, 60 mmol) were dissolved in dry benzene, and the solution was refluxed for 2 h. After the reaction mixture was concentrated under reduced pressure, **3** was obtained as yellow viscous oil in 37% yield (3.51 g) from the residue by column chromatography on a silica gel using CH_2Cl_2−MeOH (10:1) as eluent. Spectral data for **3**: ^{1}H-NMR at 500 MHz in $CDCl_3$ δ 3.03 (s, 16H), 3.86 (s, 4H), 7.08 (m, 14H), 7.53 (td, 4H), 7.68 (m, 2H), 8.48 (dt, 4H); ^{13}C-NMR at 125.65 MHz δ 34.9, 52.4, 59.9, 121.0, 123.2, 125.8, 128.0, 128.5, 131.3, 133.7, 136.1, 139.1, 149.0, 160.3; ^{77}Se-NMR at 95.35 MHz δ 424.4; IR (neat) 747, 1435, 1478, 1590, 2840 cm^{-1}; mass spectrum *m/e* 396 ($M^+/2$), 106 (base).

Di-μ-chlorobis[chloro[2-[[*N*,*N*-bis[2-(2-pyridyl)ethyl]amino]methyl]benzeneselenenyl chloride]copper(II)] (4 = 3·2Cl·2CuCl$_2$·2CHCl$_3$). **3** (159.1 mg, 0.20 mmol) and $CuCl_2{\cdot}2H_2O$ (68.3 mg, 0.40 mmol) were dissolved in methanol (10 mL). Precipitated green crystals were collected by filtration and recrystallized from $CHCl_3$. The molecular structure of the blue complex obtained as single crystals (18 mg, 7%) was determined by X-ray diffraction methods.

X-ray Analysis of the Complex. A Rigaku automated 4-cycle diffractometer was employed with the Mo Kα radiation monochromatized by graphite. The crystal data obtained are as follows: $C_{21}H_{22}ClN_3Se{\cdot}CuCl_2{\cdot}CHCl_3$, $M = 684.7$, triclinic, $a = 14.339(5)$ Å, $b = 11.544(3)$ Å, $c = 8.581(3)$ Å, $\alpha = 86.81(2)$, $\beta = 71.86(3)$, $\gamma = 75.10(2)°$, $V = 1304.0(7)$ Å^3, space group $P1-$, $Z = 2$, $D_c = 1.74$ g/mL (observed value; 1.70 g/mL). Number of variables was 299. The structure was solved by direct methods and was refined by the full-matrix least-squares method neglecting hydrogen atoms by using the UNICS III program.[22] The final *R* value was reduced to 0.058 for 2471 non-zero reflections. The selected bond parameters: Se1−Cl1, 2.432(3) Å; Se1−C2, 1.919(12) Å; Se1···N9, 2.191(8) Å; Cu−N13 2.05(1) Å; Cu−N21 2.02(1) Å; Cu−Cl2 2.289(3) Å; Cu−Cl3, 2.258(4) Å; Cu−Cl2′, 2.851(3) Å; Cu···Cu, 3.965(2) Å; ∠Cl1−Se1−C2, 96.5(3)°; ∠Cl1−Se1···N9, 178.4(2)°; ∠C2−Se1···N9, 82.3(4)°; ∠N13−Cu−Cl3, 90.4(3)°; ∠N13−Cu−N21, 161.3(3)°; ∠N13−Cu−Cl2, 92.3(3)°; ∠N13−Cu−Cl2′, 96.1(2)°; ∠Cl3−Cu−N21, 89.1(3;, ∠Cl3−Cu−Cl2, 173.2(1); ∠Cl3−Cu−Cl2′, 93.9(1); ∠N21−Cu−Cl2, 90.4(3); ∠N21−Cu−Cl2′, 102.6(2), ∠Cl2−Cu−Cl2′, 79.6(1)°.

MO Calculations. Gaussian 92[23] and Spartan 3.0[18] were used as source programs for MO calculations. The geometry of **6** was fully optimized at a Hartree−Fock level using various basis sets such as STO-3G, 3-21G, 3-21G* (3-21G with d polarization functions for Se and Cl),[18] LANL1MB (Los Alamos ECP+MB basis set[19] for Se and Cl and STO-3G for N, C, and H), and LANL1DZ (Los Alamos ECP+DZ basis set[19] for Se and Cl and Dunning/Huzinaga valence double-ζ basis set for N, C, and H). NBO analysis, which is included in Gaussian 92, was done on the optimized conformations obtained at HF/3-21G* and HF/LANL1DZ using the same basis set. The electron delocalization energy (ΔE_{del}) between Se−Cl and N was calculated by the NBO deletion method.[17]

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **3** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. The author has deposited atomic coordinates for **4** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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