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4,5-Dicyano-3,6-diethylbenzo-1,2-diselenete, a Highly Stable 1,2-Diselenete: Its Preparation, Structural Characterization, Calculated Molecular Orbitals, and Complexation with Tetrakis(triphenylphosphine)palladium

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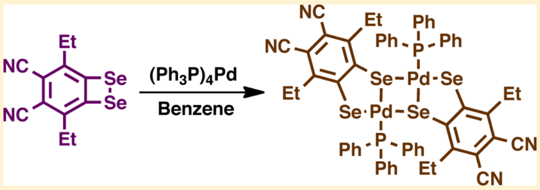
Supporting Information

ABSTRACT: The first isolable benzo-1,2-diselenete, 4,5-dicyano-3,6-diethylbenzo-1,2-diselenete (**4**), was prepared by the reaction of 4,5-(*o*-xylylenediseleno)-3,6-diethylphthalonitrile (**3**) with aluminum chloride in toluene. X-ray crystallographic analysis demonstrated that **4** contains a trapezoidal diselenide ring rather than a benzo-1,2-diselenone structure. In crystal form, **4** undergoes self-assembly and generates structures based on layered molecular sheets since the unit cell contains only one molecule. While the cyclic voltammogram of **4** exhibited only one irreversible peak (E_p = 1.59 V) during oxidation and two quasireversible couples during reduction, three peaks were observed in the differential pulse voltammogram of the reduction couples ($E_{1/2}$ = −1.19, −0.75, and −0.69 V). Although a THF solution of **4** in the presence of sodium metal was EPR silent, various signals were readily observed in its ^{1}H, ^{13}C, and ^{77}Se NMR spectra. Molecular orbital calculations for **4** demonstrated that the HOMO orbital is primarily localized at the two selenium atoms and four of the benzene carbon atoms while the LUMO orbital is situated solely on the diselenete ring. It appears that the HOMO and LUMO orbitals of **4** receive significant stabilization from the nitrile groups compared to the level of stabilization in the unsubstituted benzo-1,2-diselenete (**BDS**). The reaction of **4** with tetrakis(triphenylphosphine)palladium in benzene was found to produce a dinuclear palladium complex (**8**), and the structure of this complex was determined by X-ray crystallographic analysis. The central four membered ring of **8** consists of the Pd1, Se2, Pd2, and Se3 atoms and is not planar but rather adopts a folded arrangement.



INTRODUCTION

Recently, considerable attention has been focused on three or four membered dichalcogenide ring systems, due to their strained structures and high reactivities.[1] The smallest cyclic disulfide, 1,2-dithiiran, was first isolated and reported by Ishii et al. in 1994.[2] Since then, many related compounds have been prepared, and studies of their structures and reactivities have accumulated. In addition, both saturated and unsaturated four membered cyclic disulfides, the 1,2-dithietanes and 1,2-dithietes, have been investigated by many organic chemists.[1] On the basis of these studies, it is known that these ring systems are quite unstable and that 1,2-dithiete incorporates more steric strain than does 1,2-dithietane. Although the cyclic disulfides exhibit high reactivities, several 1,2-dithietanes[3] and 1,2-dithietes,[4] along with their oxidized derivatives,[4b,5] can be isolated in stable forms. There have also been many reports of unstable benzo-annelated 1,2-dithietes, the benzo-1,2-dithietes.[1] To date, several examples of stable benzo-1,2-dithietes have been described,[6] and it has been demonstrated that these compounds are stabilized either by steric protection or by fusion with the 1,2-benzoquinone skeleton. Although there are no actual examples of three membered diselenide ring systems, there exist several reports of four membered selenium derivatives, the 1,2-diselenetes and benzo-1,2-diselenetes.[7] However, these studies have involved either unstable or theoretical derivatives. The detection of 1,2-diselenete, for example, required photolysis of 1,4-diselenin derivatives at low temperature (−196 °C) using an argon matrix.[7a] A possible exception is 3,4-bis(trifluoromethyl)-1,2-diselenete, which was found to be stable at low temperatures but to slowly dimerize at 0 °C to form the corresponding 3,4,7,8-tetrakis-(trifluoromethyl)-1,2,5,6-tetraselenocin.[7b] In these reports, 1,2-dithiete and 1,2-diselenete are considered to be in equilibrium with their ring-opening valence isomers, 1,2-dithione and 1,2-diselenone, respectively. In addition, benzo-1,2-diselenete is expected to be extremely unstable because of the steric strain caused by fusing with the benzene ring.

Previously, we have reported the preparation, structural determination, and optical and electrochemical properties of several phthalocyanines and tetraazaporphyrins with peripheral sulfur- or selenium-based functional groups.[8] In that prior work,

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we used 5,6-dibromo-4,7-diethylbenzotrithioles and the corresponding selenium derivatives as precursors to phthalocyanines. In related work with phthalocyanines having four diselenadithiafulvalene units,[9] we observed the formation of a reddish-purple solid when 5,6-dicyano-4,7-diethylbenzo[1,3]diselenole-2-one (**5**) was prepared by the sequential treatment of 4,5-(*o*-xylylenediseleno)-3,6-diethylphthalonitrile (**3**) with aluminum chloride in toluene followed by carbonyl diimidazole. Unexpectedly, the reddish-purple product was determined to be a benzo-1,2-diselenete, specifically 4,5-dicyano-3,6-diethylbenzo-1,2-diselenete (**4**). Compound **4** is an unprecedented example of a stable benzo-1,2-diselenete and represents the first four membered diselenide ring system examined by X-ray crystallography. This Article reports the preparation, structural determination, and electrochemical properties of **4**, along with molecular orbital calculations based on density functional theory (DFT). In addition, the complexation reaction of **4** with tetrakis(triphenylphosphine)palladium and the structural analysis of the resulting complex are also reported.

■ EXPERIMENTAL SECTION

General. NMR spectra were obtained with a Bruker AVANCE 500 III spectrometer. Mass spectra were acquired using a JEOL JMS-700 mass spectrometer based on fast atom bombardment mass spectrometry (FAB MS) and electron ionization high-resolution mass spectrometry. UV−vis spectra were recorded with a JASCO Ubest V-570 spectrophotometer, and IR spectra were obtained employing a JASCO FT/IR-4200 spectrometer. A Hokuto Denko Co. model HAB-151 apparatus and a Cypress Systems CS-1200 galvanostat/potentiostat apparatus were used when measuring oxidation and reduction potentials, and elemental analysis was performed using a Yanako MT-6 analyzer.

X-ray Crystallographic Analysis. X-ray crystallographic data were acquired with a Rigaku Saturn724 diffractometer using graphite monochromated Mo Kα radiation. Diffraction patterns were collected at −172 ± 1 °C to a maximum 2θ value of 55.0°. Data were collected and processed using the CrystalClear software package (Rigaku), and the structures were solved by a direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package, except in the case of refinement, which was performed using SHELXL-97.

Oxidation−Reduction Potentials. All oxidation−reduction measurements were performed by cyclic voltammetry using Ag/AgNO$_3$ (0.01 mol dm^{-3}) as a reference electrode, glassy carbon as a working electrode, and Pt as a counter electrode (scan rate: 200 mV s^{-1}). A solution of n-Bu$_4$NClO$_4$ in CH$_3$CN (0.1 mol dm^{-3}) was used as the electrolyte. The oxidation potential of ferrocene was found to be $E_{1/2}$ = 0.09 V using this apparatus without applying any correction.

*5,6-Dibromo-4,7-diethylbenzotriselenole (**1**).* Compound **1** was prepared by the procedure described previously.[8a]

*1,2-(o-Xylylenediseleno)-4,5-dibromo-3,6-diethylbenzene (**2**).* To a solution of **1** (263.9 mg, 0.5 mmol) and K$_2$CO$_3$ (70 mg, 0.5 mmol) in 30 mL of THF and 10 mL of MeOH was added NaBH$_4$ (80 mg, 2.1 mmol) slowly, and the solution was stirred for 10 min. Xylylenedichloride (106 mg, 0.6 mmol) was added, and the solution was stirred at room temperature for 24 h. After addition of aqueous HCl and evaporation of the solvent, the product was extracted with CHCl$_3$ and the solvent was dried and evaporated. The residue was purified by column chromatography (Wakogel C-300HG, n-hexane/CHCl$_3$) to produce **2** in 73% yield (203.1 mg). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.10 (t, J = 7.4 Hz, 6H), 3.19 (q, J = 7.4 Hz, 4H), 4.37 (s, 4H), 6.89−6,96 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 13.5, 30.3, 35.6, 127.2, 128.1, 129.6, 135.4, 139.0, 148.0. ^{77}Se NMR (95 MHz, CDCl$_3$): δ = 412.7. HRMS calcd for C$_{18}$H$_{18}$^{79}Br$_2$^{80}Se$_2$ = 551.8106; found m/z = 551.8104 (M$^+$).

4,5-(o-Xylylenediseleno)-3,6-diethylphthalonitrile. Compound **2** (6.72 g, 12 mmol) and CuCN (4.33 g, 48 mmol) were placed in a glass reactor, DMF (50 mL) was added under Ar, and the solution was stirred at 140 °C for 5.5 h. After cooling the reactor, aqueous FeCl$_3$·6H$_2$O solution was added, and the solution was stirred at 70 °C for 15 min. After filtration, the residue was dissolved with CHCl$_3$. The solution was dried, and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, n-hexane/CHCl$_3$ = 1:1) to produce **3** in 12% yield (659 mg). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.19 (t, J = 7.5 Hz, 6H), 3.10 (q, J = 7.5 Hz, 4H), 4.46 (s, 4H), 6.94 (s, 4H). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 14.8, 30.9, 31.5, 114.8, 115.1, 127.8, 129.6, 135.0, 146.7, 151.8. ^{77}Se NMR (95 MHz, CDCl$_3$): δ = 406.9. HRMS calcd for C$_{20}$H$_{18}$N$_2$^{80}Se$_2$ = 445.9800; found m/z = 445.9797 (M$^+$).

*3,6-Diethyl-4,5-dicyanobenzo-1,2-diselenete (**4**).* To a mixture of **3** (60.9 mg, 0.14 mmol) and AlCl$_3$ (136 mg, 1.02 mmol) was added toluene (18 mL) under Ar, and the solution was stirred at room temperature for 2 h. To the solution was added H$_2$O. The product was extracted with toluene, and the solvent was evaporated. The product was purified with column chromatography (Wakogel C-300HG, CHCl$_3$) to produce **4** in 63% yield (29.3 mg): red-purple crystal; mp 192−195 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.29 (t, J = 7.7 Hz, 6H, CH$_3$), 2.62 (q, J = 7.7 Hz, 4H, CH$_2$). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 13.2, 24.3, 111.6, 114.9, 137.8, 143.6. ^{77}Se NMR (95 MHz, CDCl$_3$): δ = 685.3. IR (KBr): $\tilde{\nu}$ = 2219.7 cm^{-1} (CN). UV−vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 346.5 (10 900), 421.5 nm (183). HRMS calcd for C$_{12}$H$_{10}$N$_2$^{80}Se$_2$ = 341.9174; found m/z = 341.9168 (M$^+$). X-ray data: red platelet crystal, triclinic $P1$ (No. 1); a = 5.205(3) Å, b = 6.870(4) Å, c = 8.803(5) Å, α = 106.190(7)°, β = 91.612(7)°, γ = 103.098(6)°, V = 293.1(3) Å^3, Z = 1, D_{calc} = 1.927 g/cm^3, μ(Mo Kα) = 62.807 cm^{-1}. Temperature for data collection = −172.8 °C. Number of reflections measured = total, 2253; unique, 1737 (R_{int} = 0.0464); reflection/parameter ratio = 11.90; R1 [$I > 2.00\sigma(I)$] = 0.0291; wR2 (all reflections) = 0.0732; GOF = 1.062; maximum peak in the final difference Fourier map = 0.69 e/Å^3.

3,6-Diethyl-4,5-dicyano-1,2-benzenedithiol. To a mixture of 4,5-(*o*-xylylenedithio)-3,6-diethylphthalonitrile (178.1 mg, 0.5 mmol) and AlCl$_3$ (400 mg, 1.02 mmol) was added toluene (18 mL) under Ar, and the solution was stirred at room temperature for 2 h. To the solution was added H$_2$O. The product was extracted with toluene, and the solvent was evaporated. The product was purified with column chromatography (Wakogel C-300HG, CHCl$_3$) to produce the corresponding dithiol in 74% yield (93.6 mg), as a light-yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.29 (t, J = 7.6 Hz, 6H, CH$_3$), 3.09 (q, J = 7.6 Hz, 4H, CH$_2$), 4.36 (s, 2H, SH). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 13.0, 29.0, 113.1, 114.9, 139.2, 145.8. HRMS calcd for C$_{12}$H$_{12}$N$_2$S$_2$ = 248.0442; found m/z = 248.0441 (M$^+$).

*Bis(4,5-dicyano-3,6-diethylbenzodiselenolato)bis(triphenylphosphine)dipalladium (**8**).* To a mixture of **4** (42.7 mg, 0.13 mmol) and tetrakis(triphenylphosphine)palladium (148 mg, 0.13 mmol) was added dry benzene (15 mL) under Ar, and the solution was stirred at room temperature for 16 h. After the solvent was evaporated, the residue was purified with column chromatography (Wakogel C-300HG, CHCl$_3$) to produce **8** in 84% yield (75 mg): dark brown crystal; mp 273−275 °C (decomp). ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.94 (t, J = 7.5 Hz, 6H, CH$_3$), 1.11 (t, J = 7.5 Hz, 6H, CH$_3$), 1.80 (dq, J = 13.9, 7.5 Hz, 2H, CH$_2$), 2.29 (dq, J = 13.9, 7.5 Hz, 2H, CH$_2$), 2.72 (dq, J = 13.7, 7.5 Hz, 2H, CH$_2$) 2.78 (dq, J = 13.7, 7.5 Hz, 2H, CH$_2$), 7.28−7.35 (m, 12H, ArH), 7.39−7.45 (m, 6H, ArH), 7.52−7.60 (m, 12H, ArH). ^{31}P NMR (202 MHz, CDCl$_3$): δ = 27.1 (s, $J_{\text{P−Se}}$ = 120, 103, 37 Hz as satellite coupling constants). ^{77}Se NMR (95 MHz, CDCl$_3$): δ = 349.7 ($J_{\text{Se−P}}$ = 120, 103 Hz), 604.952, 604.956 ($J_{\text{Se−P}}$ = 37 Hz). FABMS m/z = 1424 (M$^+$). Anal. Calcd for C$_{60}$H$_{54}$N$_4$P$_2$Pd$_2$Se$_4$: C, 50.69; H, 3.83; N, 3.94%. Found: C, 50.55; H, 3.52; N, 3.61%. X-ray data: red platelet crystal, triclinic $P\bar{1}$ (No. 2); a = 14.3131(17) Å, b = 15.8611(15) Å, c = 16.521(2) Å, α = 70.492(4)°, β = 86.635(5)°, γ = 66.389(4)°, V = 3227.0(6) Å^3, Z = 2, D_{calc} = 1.705 g/cm^3, μ(Mo Kα) = 31.54 cm^{-1}, temperature for data collection = −172.8 °C, number of reflections measured = total, 21 165; unique, 10 563 (R_{int} = 0.0299); reflection/parameter ratio = 13.46, R1 [I >

$2.00\sigma(I)$] = 0.0365, wR2 (all reflections) = 0.0919, GOF = 1.074, maximum peak in the final difference Fourier map = 1.42 e/Å^3.

Computational Methods. All calculations were performed using the Gaussian 09 program. Optimized structures, HOMO and LUMO energies and NMR shielding constants for **4**, **7**, benzo-1,2-diselenete (**BDS**), 3,6-diethylbenzo-1,2-diselenete (**BDSET**) and 4,5-dicyanobenzo-1,2-diselenete (**BDSCN**) were calculated using density functional theory (DFT) at the B3LYP/6-311++G (d, p) level.[10]

■ RESULTS AND DISCUSSION

As a precursor to compound **4**, 4,5-(*o*-xylylenediseleno)-3,6-diethylphthalonitrile (**3**) was prepared from 5,6-dibromo-4,7-diethylbenzotriselenole (**1**)[8a] via 1,2-(*o*-xylylenediseleno)-4,5-dibromo-3,6-diethylbenzene (**2**) (Scheme 1). In the process, the cyanation reaction of **2** unfortunately produced a low yield compared to the results obtained with sulfur derivatives, likely due to the lower bond energy of the Se−C bond compared with that of the S−C bond. As reported in a previous paper, the 1,3-diselenole-2-one derivative **5** (Chart 1) was obtained when **3** was treated with aluminum chloride in toluene followed by carbonyl diimidazole.[9] In contrast, treatment of **3** with aluminum chloride in toluene without the application of carbonyl diimidazole gave product **4** in 63% yield. This process, which is a modification of Decurtins' procedure, is the Friedel−Crafts-like deprotection reaction of the xylylene group from **3**.[11,12] Compound **4** appears to be highly stable at room temperature. The similar treatment of 4,5-(*o*-xylylenedithio)-3,6-diethylphthalonitrile with aluminum chloride in toluene gave the corresponding 1,2-benzenedithiol in 74% yield. These results suggest that the benzo-1,2-diselenete ring was formed by the oxidation of the corresponding 1,2-benzenediselenolate after elimination of the xylylene group.

Scheme 1. Preparation of 4 by the Reaction of 3 with Aluminum Chloride in Toluene

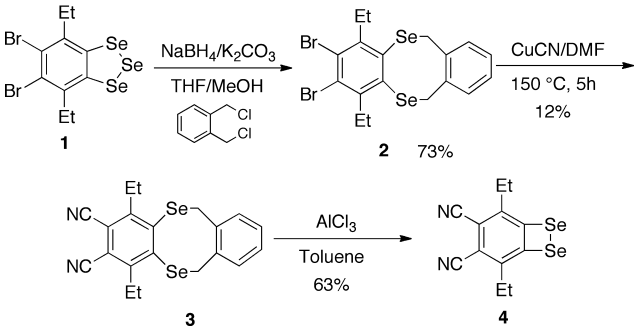
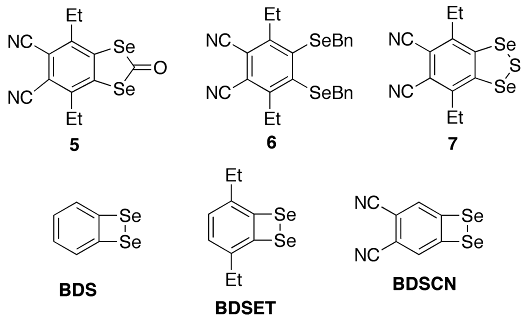


Chart 1



The ^{1}H NMR spectrum of **4** in chloroform-*d* exhibits signals attributed to the ethyl groups at 1.29 and 2.62 ppm, while the methylene signal is situated at a higher magnetic field than the corresponding signals of 5,6-dicyano-4,7-diethylbenzo[1,2,3]-triselenole (**7**) (Table 1).[8a] In addition, the ^{13}C NMR spectrum of **4** shows signals due to the ethyl carbons at 13.2 and 24.3 ppm, while these signals in the spectrum of **7** appear at 14.0 and 33.2 ppm. Finally, the ^{77}Se NMR spectrum of **4** exhibits a singlet peak at 685.3 ppm, at a lower magnetic field than the two selenium signals of **7**. The IR spectrum of **4** has a nitrile peak at 2219.7 cm^{-1}, slightly below the position of the corresponding peak in the spectrum of **7** (2222.6 cm^{-1}). The UV−vis spectrum of **4** in THF showed λ_{max} values at 346.5 nm (ε = 10 900) and 421.5 nm (ε = 183).

Table 1. Partial Summary of Observed and Calculated NMR Data for 4 and 7[a]

	4 δ (ppm)		7 δ (ppm)	
	obsd	calcd	obsd	calcd
^{1}H	1.29, 2.62	1.26, 2.58	1.29, 3.01	1.30, 2.97
^{13}C	13.2, 24.3	16.1, 29.1	14.0, 33.2	16.1, 38.9
^{77}Se	685.3		463.5, 563.5	

[a] Calculated chemical shifts were obtained by the DFT method (*vide infra*).

It was found that 4,5-bis(benzylseleno)-3,6-diethylphthalonitrile (**6**), a precursor to 2,3,9,10,16,17,23,24-octakis-(benzylseleno)phthalocyanine,[8a] gradually decomposed both in the solid state and in solution to give **4**. On monitoring the decomposition reaction of **6** via ^{1}H NMR in chloroform-*d* at room temperature, the signals associated with **6** disappeared while the signals attributed to the ethyl group of **4** appeared and increased in intensity, together with new signals due to benzaldehyde. Although the reaction mechanism is not clear, **4** and benzaldehyde may be produced via the oxidation of selenide **6** with oxygen, followed by a Pummerer-type reaction.

The structure of **4** was determined by X-ray crystallography, which indicated unexpected variations in the molecular arrangements within the crystals. Compound **4** therefore appears to exhibit crystal polymorphism.[13] Since **4** is crystallizing in a triclinic form with the space group *P*1 (No. 1) and *Z* = 1, the crystal contains a unique molecular structure in the unit cell. The ORTEP drawing indicates that the 4,5-dicyanobenzo-1,2-diselenete skeleton is planar in the crystal (Figure 1A). In addition, the two ethyl groups of **4** are situated such that they extend in opposite directions. The bond lengths of the Se1−Se2, Se1−C1, Se2−C2, and C1−C2 bonds are 2.3736(13), 1.915(5), 1.905(6), and 1.376(7) Å, respectively [see Supporting Information (SI)]. The Se−Se bond of **4** is longer than those of either the diaryl diselenide or **7** while the Se−C bonds of **4** and the diaryl diselenide are similar in length.[14] The Se−Se and Se−C bond lengths of bis-(pentafluorophenyl) diselenide are 2.319(4) and 1.910 Å (a mean value), respectively, and those of **7** are 2.319 and 1.94 Å (mean values). The bond angles of **4** at the Se2−Se1−C1, Se1−Se2−C2, Se1−C1−C2, and Se2−C2−C1 junctions are 74.52(15)°, 75.21(13)°, 105.3(4)°, and 104.9(4)°, respectively. X-ray crystallographic analysis demonstrated that **4** contains a trapezoidal diselenide ring rather than a benzo-1,2-diselenone structure in the crystal.

It appears that **4** has small intermolecular distances between neighboring molecules in the crystal. For example, the two

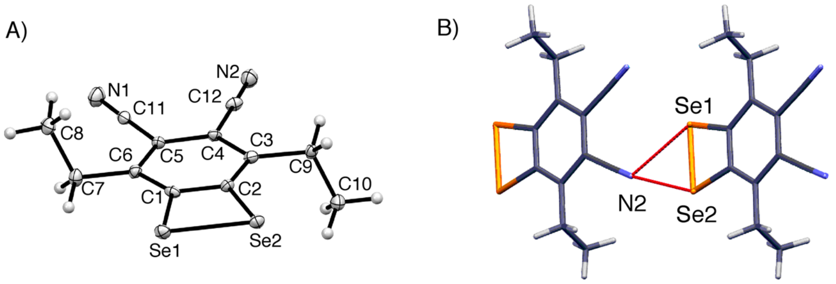


Figure 1. (A) ORTEP drawing of **4** viewed along the *b* axis. The thermal ellipsoids are drawn at the 50% probability level. (B) Short contact distances of **4** viewed along the *a* axis: Se1−N2, 3.124(6) Å; Se2−N2, 3.049(6) Å.

selenium atoms, Se1 and Se2, are close to nitrogen atom N2 of the nitrile group on the adjacent molecule, as shown in Figure 1B. The intermolecular distances between the Se1−N2 and Se2−N2 atoms are 3.124(6) and 3.049(6) Å, respectively, which are less than the sum of the van der Waals radii of selenium and nitrogen atoms (3.45 Å).[15] It is expected that these interactions between selenium and nitrogen atoms strongly affect the molecular arrangement of **4** in the crystal. As a result, the unit cell contains only one molecule (Supporting Information Figure S2), and the molecules of **4** can undergo self-assembly and form molecular sheets (Supporting Information Figures S3 and S4).

The oxidation−reduction potentials of **4** were measured by cyclic voltammetry using Ag/AgNO$_3$ as a reference electrode (solvent, CH$_3$CN; scan rate, 200 mV s^{-1}). The voltammogram showed one irreversible peak potential (E_p = 1.59 V) during oxidation and two quasireversible peaks during reduction (Figure 2). Since the shapes of the two reduction couples were not clear, we measured the reduction potentials using differential pulse voltammetry. As shown in the inset of Figure 2, we observed one overlaid peak for the first reduction couple ($E_{1/2}$ = −0.75 and −0.69 V) and one peak for the second reduction couple ($E_{1/2}$ = −1.19 V), suggesting that the first reduction couple in the cyclic voltammogram contains two one-electron-transfer processes. While the first reduction potential of **4** is similar to that of **7** ($E_{1/2}$ = −0.68 V), the oxidation potential is higher than that of **7** ($E_{1/2}$ = 0.87 V).

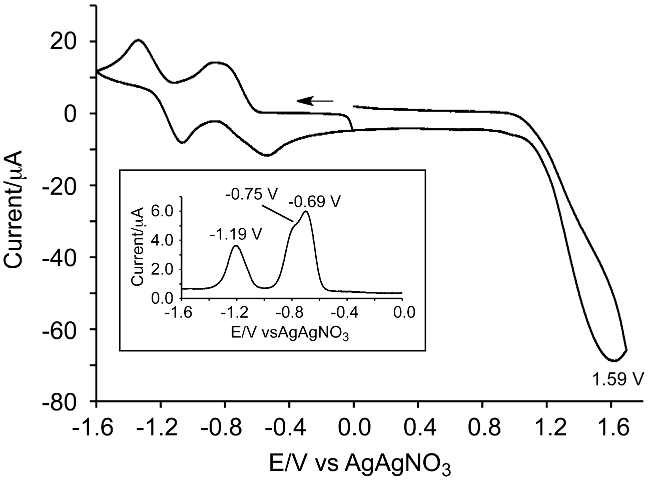


Figure 2. Oxidation−reduction potentials of **4** as measured by cyclic voltammetry using Ag/AgNO$_3$ as a reference electrode. Inset: differential pulse voltammetry data.

It was anticipated that, while it exhibits low reactivity with an oxidizing reagent, **4** would be readily reduced with a reducing reagent. On treatment of **4** with sodium metal in a THF solution, the compound took on a reddish-brown coloration and the UV−vis absorption spectrum of the resulting solution exhibited λ_{max} values of 347.0 nm (ε = 9120) and 424.0 nm (ε = 3970). In solution, the absorption of **4** is slightly shifted to lower energies while the molar absorption coefficient at 421.5 is increased from 183 to 3970 (424.0 nm). Although this solution was also analyzed using EPR at room temperature, no signals were observed in the resulting spectrum. When the ^{1}H NMR spectrum of **4** in THF-d_8 was acquired following treatment with sodium metal, the spectrum of the reddish-brown solution contained a sharp triplet and a broadened quartet at δ = 1.12 and 2.67 ppm, respectively, such that the quartet was at a slightly lower magnetic field position than the equivalent peaks in the spectrum of unreacted **4**. Since the quasireversible first reduction couple in the cyclic voltammogram is caused by a two-electron transfer, the species in the NMR tube must have been generated by the reduction of **4** with the two electrons. Under similar conditions, the ^{13}C NMR spectrum showed six signals at δ = 13.8, 30.5, 111.5, 115.9, 142.8, and 145.2 ppm. Although no signals were observed in the ^{77}Se NMR spectrum acquired at room temperature, a singlet peak was present at 622.5 ppm in the spectrum obtained at −40 °C, suggesting that there may be an equilibrium between the ring-opening and the ring-closing forms. This peak appeared at a higher magnetic field position than the equivalent peak in the spectrum of unreacted **4**. After quenching the THF solution with hydrochloric acid, compound **4** was recovered. These results suggest that **4** produced an anionic rather than a radical anionic species in the THF solution.

The optimized structures, HOMO and LUMO energies, and NMR shielding constants for **4** and for the related compounds, benzo-1,2-diselenete (**BDS**), 3,6-diethylbenzo-1,2-diselenete (**BDSET**), 4,5-dicyanobenzo-1,2-diselenete (**BDSCN**), and **7**, were calculated using the Gaussian 09 program (Chart 1).[10] The structures of these compounds were optimized using the DFT method at the B3LYP/6-311++G (d, p) level.

The calculated structure of **4** is completely planar, which is similar to the results obtained from X-ray crystallography. The bond lengths calculated for **4** were 2.4291 (Se1−Se2), 1.9226 (Se1−C1 and Se2−C2), and 1.3958 (C1−C2) Å; these values are slightly longer than those determined by X-ray crystallography. The Se−C bond of **4** is longer than that calculated for benzohexaselenone,[7d] suggesting that the four membered diselenide ring is more favorable than the benzo-1,2-diselenone structure.[16] The calculated bond angles at the Se2−Se1−C1 (Se1−Se2−C2) and Se1−C1−C2 (Se2−C2−C1) junctions of **4** are 74.41° and 105.59°, respectively, and these angles are in

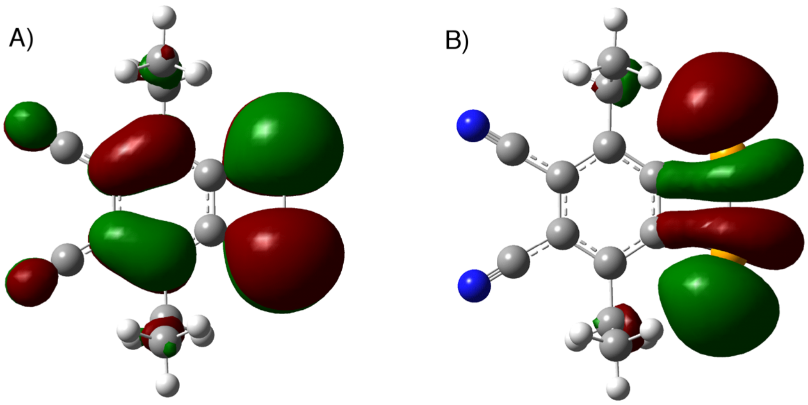


Figure 3. Molecular orbitals of **4**: (A) HOMO and (B) LUMO.

good agreement with the X-ray crystallography data. The calculated HOMO and LUMO orbitals of **4** are shown in Figure 3. While the HOMO orbital is primarily localized at the two selenium atoms and four of the benzene carbon atoms, the LUMO orbital is situated solely on the diselenete ring. The HOMO orbital exhibits antibonding character between the Se1−Se2 and C4−C5 bonds, while the LUMO orbital shows antibonding character between the Se1−Se2 and C1−C2 bonds. On the basis of this result, it is expected that anionic species generated from **4** in the THF/Na solution may have a ring-opening structure.

The molecular orbital energies of **4** and the related compounds demonstrate that the HOMO and LUMO orbitals in these molecules are highly stabilized by the nitrile groups and slightly destabilized by the ethyl groups compared with the degree of stabilization in the unsubstituted benzo-1,2-diselenete (**BDS**), as shown in Table 2 and Figure 4. This finding suggests that the stability of the 1,2-diselenete rings of **4** and **BDSCN** is strongly affected by the two nitrile groups. The shielding constants of **4** were subsequently calculated using the same basis sets, and the results showed that the calculated ^{1}H and ^{13}C NMR chemical shifts of the ethyl groups of **4** are at higher magnetic field positions than those of **7** (Table 1). In addition, while the calculated ^{1}H NMR chemical shifts of **4** are at a slightly higher magnetic field than the measured values, the calculated ^{13}C NMR chemical shifts are at a slightly lower magnetic field than those obtained experimentally.

Table 2. Molecular Orbital Energies of 4 and Related Compounds (eV)[a]

	BDS	4	BDSET	BDSCN	7
LUMO − 2	−0.87	−1.84	−0.63	−2.24	−2.28
LUMO − 1	−1.12	−2.48	−0.96	−2.71	−2.81
LUMO	−2.90	−3.54	−2.75	−3.79	−3.22
HOMO	−6.03	−6.74	−5.84	−7.00	−6.41
HOMO − 1	−6.45	−7.20	−6.30	−7.44	−7.11
HOMO − 2	−7.81	−8.16	−7.23	−8.82	−7.77

[a] MO calculations were performed using Gaussian 09 with DFT, B3LYP6-311++G(d,p).

It is well-known that a zerovalent palladium atom can oxidatively add to the organo-disulfide, diselenide, and, ditelluride bonds to produce the corresponding Pd complexes.[17,18] It was therefore anticipated that **4** would react in the same manner with zerovalent palladium to produce the corresponding palladium complex. The reaction of **4** with tetrakis(triphenylphosphine)palladium in benzene at room temperature did in fact proceed, to give the palladium complex **8** in 84% yield (Scheme 2). This complex was stable under air and soluble in chloroform. We observed two ethyl signals as double quartet patterns as well as complex aromatic signals in the ^{1}H NMR spectrum of the product, suggesting that the ethyl and phenyl groups are sterically congested and that **8** has an unsymmetrical structure on the NMR time scale. In the ^{31}P NMR spectrum of this compound, a singlet signal at $\delta = 21.7$ ppm was found together with satellite peaks due to coupling with the selenium atoms (see Supporting Information). It is

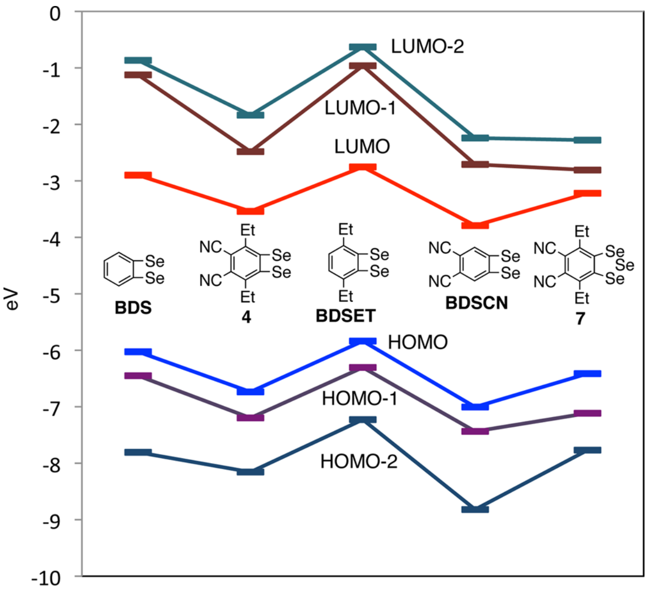
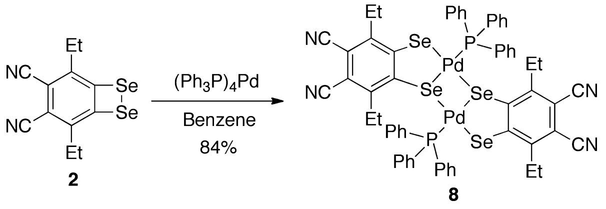


Figure 4. Molecular orbital energies of **4**, **BDS**, **BDSET**, **BDSCN**, and **7**.

Scheme 2. Reaction of 4 and Tetrakis(triphenylphosphine)palladium



expected that one phosphorus atom can affect four selenium atoms in terms of spin−spin coupling because of the unsymmetrical structure of **8** caused by steric hindrance, and the ^{77}Se NMR spectrum showed split signals at δ = 349.7 and 605.0 ppm at a higher magnetic field compared to the signal in the spectrum of **4**. However, since we were unable to observe spin−spin coupling between selenium atoms even after 20 000 times data acquisition, the corresponding coupling constants via the palladium atom must be extremely small. In contrast, the selenium atoms of **8** do exhibit spin−spin coupling with the phosphorus atom. In the case of the ^{31}P−^{77}Se coupling of **8**, the selenium peaks at δ = 349.7 ppm which are assigned to bridged selenium show two coupling constants: $J_{\mathrm{Se-P}}$ = 120 and 103 Hz (see Supporting Information). The peaks at δ = 605.0 ppm would be due to the outer selenium atom, and were observed as a doublet signal ($J_{\mathrm{Se-P}}$ = 37 Hz). Therefore, the ^{31}P NMR spectrum of **8** is expected to show one singlet peak together with satellite peaks based on interactions with the selenium atoms ($J_{\mathrm{P-Se}}$ = 120, 103, 37 Hz). A singlet-like signal was observed at δ = 605.0 ppm between the doublet signals in the ^{77}Se NMR spectrum, although the signal was not clear since it was obscured by the major doublet signals. This peak would be assigned to the outer selenium atom of **8** and may be split due to spin−spin coupling with another phosphorus atom ($^4J_{\mathrm{Se-P}}$). These results suggest that the dinuclear complex may have an asymmetric character at the central four membered ring. The structure of **8** was further supported by FAB MS data and by elemental analysis.

The structure of **8** was also examined by X-ray crystallography. The results showed that **8** is a dinuclear complex and that both Pd atoms are a four-coordinated structure which has an almost square planar geometry (Figure 5). The lengths of the Pd1−Se1 and Pd2−Se4 bonds are 2.3841(7) and 2.3796(6) Å (see Supporting Information). The Se2 and Se3 atoms coordinate to both the palladium atoms, and the lengths of the associated Pd−Se bonds are 2.4227(8) Å for Pd1−Se2, 2.4856(6) Å for Pd2−Se2, 2.5016(7) Å for Pd1−Se3, and 2.4271(6) Å for Pd2−Se3. The interatomic distance between the two Pd atoms is 3.0751(3) Å, and the lengths of the Pd2−Se2 and Pd1−Se3 bonds are longer than those of the Pd1−Se2 and Pd2−Se3 bonds. The bond angles at the Pd1−Se2−Pd2, Pd1−Se3−Pd2, Se2−Pd1−Se3, and Se2−Pd2−Se3 junctions are 77.58(2)°, 77.189(18)°, 77.28(2)°, and 77.505(17)°, respectively. As a result, the Pd2 atom deviates from the Se2−Pd1−Se3 plane, forming not a planar structure but rather a folded arrangement.

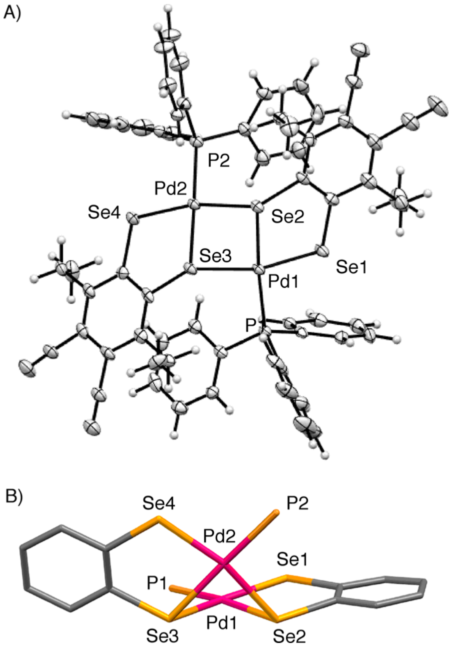


Figure 5. (A) ORTEP drawing of **8**. Two chloroform molecules and a water molecule are removed for clarity. The thermal ellipsoids are drawn at the 50% probability level. (B) Partial molecular structure showing the folded arrangement of the central Pd1−Se2−Pd2−Se3 ring.

The bond angles at the Se1−Pd1−Se3, Se2−Pd2−Se4, Se2−Pd1−P1, and Se3−Pd2−P2 junctions are 164.55(3)°, 166.16(2)°, 173.29(4)°, and 177.14(5)°, respectively. There have been several reports concerning similar complexes with a four membered Pd−Se−Pd−Se ring,[17] and it appears that the structure of the central four membered Pd−Se−Pd−Se ring of **8** is similar to that of the dinuclear Pd complex prepared by the reaction of cycloalkeno-1,2,3-selenadiazole or 1,4-diselenine derivatives with tetrakis(triphenylphosphine)palladium.[17c] However, while the lengths of the Pd−Se bonds within the central four membered ring of **8** are slightly longer than the equivalent bonds in Morley's complex, the bond angles in the ring structure of **8** are slightly smaller than those found in the Morley complex.

■ CONCLUSION

The highly stable benzo-1,2-diselenete derivative **4** was obtained by the reaction of **3** with aluminum chloride in toluene. The spontaneous and gradual decomposition of **6** also gave **4**. X-ray crystallographic analysis showed that **4** contains a trapezoidal four membered diselenide ring. In crystal form, **4** undergoes self-assembly to form layered molecular sheets since the unit cell contains only one molecule. Molecular orbital calculations for **4** demonstrated that the HOMO and LUMO energies are stabilized by the electron-withdrawing nitrile groups. The reaction of **4** with tetrakis(triphenylphosphine)-palladium resulted in the dinuclear palladium complex **8**, the structure of which was determined by X-ray crystallographic analysis. Since the Pd2 atom deviates from the Se2−Pd1−Se3 plane, **8** appears to adopt a folded arrangement at the central four membered Pd−Se−Pd−Se ring rather than a planar form.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data and NMR spectra of **4** and **8**.[19] This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Nakayama, J.; Ishii, A. *Advances in Heterocyclic Chemistry*; Katrizky, A., Ed.; Academic Press: San Diego, 2000; Vol. 77, pp 221−284. Ishii, A. *J. Synth. Org. Chem. Jpn.* **2006**, *64*, 359−405 (in Japanese). Kimura, T.; Ogawa, S.; Sato, R. *Mini.-Rev. Org. Chem.* **2007**, *4*, 15−29.

(2) Ishii, A.; Akazawa, T.; Ding, M.-X.; Honjo, T.; Nakayama, J.; Hoshino, M. *J. Am. Chem. Soc.* **1993**, *115*, 4914−4915. Ishii, A.; Akazawa, T.; Maruta, T.; Nakayama, J.; Hoshino, M.; Shiro, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 777−779.

(3) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Carroll, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 3802−3804. Nicolaou, K. C.; Hwang, C.-K.; DeFrees, S.; Stylianides, N. A. *J. Am. Chem. Soc.* **1988**, *110*, 4846−4869. Nicolaou, K. C.; DeFrees, S. A.; Hwang, C.-K.; Stylianides, N.; Carroll, P. J.; Snyder, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 3029−3039.

(4) (a) Krebs, A.; Golberg, H.; Hopfner, V.; Kinling, J.; Odenthal, J. *Heterocycles* **1979**, *12*, 1153−1156. (b) Nakayama, J.; Mizumura, A.; Yokomori, Y.; Krebs, A.; Schütz, K. *Tetrahedron Lett.* **1995**, *36*, 8583−8586. (c) Shimizu, T.; Murakami, H.; Kobayashi, Y.; Iwata, K.; Kamigata, N. *J. Org. Chem.* **1998**, *63*, 8192.

(5) Block, E.; Bazzi, A. A.; Revelle, L. K. *J. Am. Chem. Soc.* **1980**, *102*, 2490−2491. Block, E.; Bazzi, A. A.; Lambert, J. B.; Wharry, S. M.; Andersen, K. K.; Dittmer, D. C.; Patwardhan, B. H.; Smith, D. J. H. *J. Org. Chem.* **1980**, *45*, 4807−4810. Block, E.; Gillies, J. Z.; Gillies, C. W.; Bazzi, A. A.; Putman, D.; Revelle, L. K.; Wang, D.; Zhang, X. *J. Am. Chem. Soc.* **1996**, *118*, 7492−7501.

(6) Boar, R. B.; Hawkins, D. W.; McGhie, F. M.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 515−517. Drewnowski, T.; Leśniak, S.; Mlostoń, G.; Siedlecka, R.; Skarżewski, J. *Helv. Chim. Acta* **2006**, *89*, 991−999. Cherkasov, V. K.; Abakumov, G. A.; Fukin, G. K.; Klementyeva, S. V.; Kuropatov, V. A. *Chem.—Eur. J.* **2012**, *18*, 13821−13827.

(7) (a) Tokitoh, N.; Ishizuka, H.; Yabe, A.; Ando, W. *Tetrahedron Lett.* **1989**, *30*, 2955−2958. (b) Borisenko, K. B.; Broschag, M.; Harrgittai, I.; Klapötke, T. M.; Schröder, D.; Schulz, A.; Schwarz, H.; Tornieporth-Oetting, I. C.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1994**, 2705−2712. (c) Yoshida, S.; Bryce, M. R.; Chesney, A. *Chem. Commun.* **1996**, 2375−2376. (d) Nazari, F. *THEOCHEM* **2006**, *760*, 29−37.

(8) (a) Kimura, T.; Yomogita, A.; Matsutani, T.; Suzuki, T.; Tanaka, I.; Kawai, Y.; Takaguchi, Y.; Wakahara, T.; Akasaka, T. *J. Org. Chem.* **2004**, *69*, 4716−4723. (b) Kimura, T.; Kanota, N.; Matsui, K.; Tanaka, I.; Tsuboi, T.; Takaguchi, Y.; Yomogita, A.; Wakahara, T.; Kuwahara, S.; Nagatsugi, F.; Akasaka, T. *Inorg. Chem.* **2008**, *47*, 3577−3583. (c) Kimura, T.; Iwama, T.; Namauo, T.; Suzuki, E.; Fukuda, T.; Kobayashi, N.; Sasamori, T.; Tokitoh, N. *Eur. J. Inorg. Chem.* **2011**, 888−894.

(9) Kimura, T. *Heterocycles* **2014**, *88*, 207−212.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N. Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009.

(11) Loosli, C.; Jia, C.; Liu, S.-X.; Haas, M.; Dias, M.; Levillain, E.; Neels, A.; Labat, G.; Hauser, A.; Decurtins, S. *J. Org. Chem.* **2005**, *70*, 4988−4992. Donders, C. A.; Liu, S.-X.; Loosli, C.; Sanguinet, L.; Neels, A.; Decurtins, S. *Tetrahedron* **2006**, *62*, 3543−3549.

(12) Kimura, T.; Watanabe, D.; Namauo, T. *Heterocycles* **2008**, *76*, 1023−1026. Kimura, T.; Namauo, T.; Amano, K.; Takahashi, N.; Takaguchi, Y.; Hoshi, T.; Kobayashi, N. *J. Porphyrins Phthalocyanines* **2011**, *15*, 547−554.

(13) Compound **4** is capable of crystallizing in both a triclinic form (termed crystal A) with the space group $P1$ (No. 1) and a triclinic form (crystal B) with the space group $P\bar{1}$ (No. 2). While it is likely that crystal B consists of layered thin crystals, the structure of **4** in crystal B could be solved, and it was determined that the unit cell contains two independent molecules: R1 $[I > 2.00\sigma(I)] = 0.0862$, wR2 (all reflections) = 0.2270, GOF = 1.135. The two ethyl groups of **4** are both oriented in the same direction in crystal B. However, we could not overcome the problem of an alert level A associated with this crystal, and therefore, no crystal or structural data for crystal B are presented in this Article.

(14) Woodard, C. M.; Brown, D. S.; Lee, J. D.; Massey, A. G. *J. Organomet. Chem.* **1976**, *121*, 333−344.

(15) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(16) One of the referees has suggested that a “buttressing effect” by the ethyl groups may also favor the 1,2-diselenete form over the ring opened 1,2-diselenone valence isomer. Decouzon, M.; Ertl, P.; Exner, O.; Gal, J.-F; Maria, R.-C. *J. Am. Chem. Soc.* **1993**, *115*, 12071−12078.

(17) (a) Zanella, R.; Ros, R.; Graziani, M. *Inorg. Chem.* **1973**, *12*, 2736−2738. (b) Fukuzawa, S.; Fujinami, T.; Sakai, S. *Chem. Lett.* **1990**, 927−930. (c) Ford, S.; Khanna, P. K.; Morly, C. P.; Di Vaira, M. *J. Chem. Soc., Dalton Trans.* **1999**, 791−794. (d) Oilunkaniemi, R.; Laitinen, R. S.; Ahlgrén, M. *Chem. Commun.* **1999**, 585−586. (e) Oilunkaniemi, R.; Laitinen, R. S.; Ahlgrén, M. *J. Organomet. Chem.* **1999**, *587*, 200−206. (f) Oilunkaniemi, R.; Laitinen, R. S.; Ahlgrén, M. *J. Organomet. Chem.* **2001**, *623*, 168−175. (g) Nakata, N.; Ikeda, T.; Ishii, A. *Inorg. Chem.* **2010**, *49*, 8112−8116.

(18) Weigand, W.; Bräutigam, S.; Mloston, G. *Coord. Chem. Rev.* **2003**, *245*, 167−175. Ishii, A.; Kashimura, S.; Hayashi, Y.; Weigand, W. *Chem.—Eur. J.* **2007**, *13*, 4326−4333. Windhager, J.; Apfel, U.-P.; Yoshino, T.; Nakata, N.; Görls, H.; Rudolph, M.; Ishii, A.; Weigand, W. *Chem.—Asian. J.* **2010**, *5*, 1600−1610.

(19) The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as 967554 (**4**) and 967555 (**8**). These data can be obtained free of charge from CCDC via www.ccdc.cam.ac.uk/data_request/cif.