Preparation and Novel One-electron Redox Reactions of a New Stable 4,7-Diisopropylbenzo[1,2-*d*][1,2,3]triselenole and its Radical Cation Salt

Satoshi Ogawa,[a] Takamasa Kikuchi,[a] Shigeya Niizuma[b] and Ryu Sato*[a]

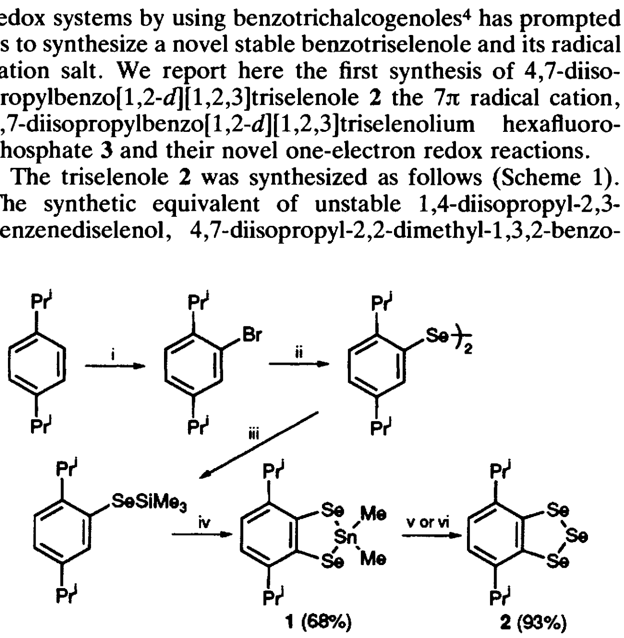
[a] *Department of Applied Chemistry and Molecular Science, Faculty of Engineering, Iwate University, Morioka 020, Japan*

[b] *College of Humanities and Social Science, Iwate University, Morioka 020, Japan*

Stable benzene-fused triselenide compounds, 4,7-diisopropylbenzo[1,2-*d*][1,2,3]triselenole **2** and its radical cation salt, 4,7-diisopropylbenzo[1,2-*d*][1,2,3]triselenolium hexafluorophosphate **3**, are prepared and undergo novel one-electron redox reactions.

1,2,3-Triselenoles may form an unusual 7π radical cation framework[1,2] by oxidation. Only three examples of triselenoles have been isolated due to the inherent lack of stability.[3] Our interest in the construction of reversible one-electron redox systems by using benzotrichalcogenoles[4] has prompted us to synthesize a novel stable benzotriselenole and its radical cation salt. We report here the first synthesis of 4,7-diisopropylbenzo[1,2-*d*][1,2,3]triselenole **2** the 7π radical cation, 4,7-diisopropylbenzo[1,2-*d*][1,2,3]triselenolium hexafluorophosphate **3** and their novel one-electron redox reactions.

The triselenole **2** was synthesized as follows (Scheme 1). The synthetic equivalent of unstable 1,4-diisopropyl-2,3-benzenediselenol, 4,7-diisopropyl-2,2-dimethyl-1,3,2-benzodiselenastannole **1**,† was prepared by a sequence of bromination,[5] selenation,[6] trimethylsilyl protection,[7] ortho lithiation[8] and dimethyltin protection.[9] Introduction of a selenium atom at the 2-position was performed by the following two methods. Stannole **1** (321 mg, 0.69 mmol) was treated with selenium tetrachloride (152 mg, 0.69 mmol) in THF at −78 °C under an Ar atmosphere. The mixture was stirred at −78 °C for 20 min and then at room temp. for 1 h and on work-up, the crude products were purified by column chromatography (silica gel, eluent hexane) to give **2**‡ in 50% yield. Alternatively, sequential treatment of stannole **1** (93 mg, 0.20 mmol) in THF (5 ml) under an Ar atmosphere at −78 °C with selenyl chloride (0.015 ml, 0.2 mmol) in THF (5 ml), trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.036 ml, 0.2 mmol) in THF (5 ml), 0.1 mol dm^{-3} samarium(II) iodide[10] (4.0 ml, 0.4 mmol) in THF followed by the same work-up and purification gave **2** in 93% yield.



Scheme 1 *Reagents*: i, Br_2–Fe, CCl_4; ii (*a*) Mg, Et_2O (*b*) Se, (*c*) H^+/H_2O, (*d*) [O]; iii, (*a*) $LiAlH_4$, (*b*) H^+/H_2O, (*c*) NaH, (*d*) Me_3SiCl; iv, (*a*) tetramethylethylenediamine (tmen), Bu^{n}Li (4 equiv.), hexane, (*b*) Se, (*c*) Me_2SnCl_2; v, $SeCl_4$, THF; vi, (*a*) $SeOCl_2$, THF, (*b*) TMSOTf, THF, (*c*) SmI_2, THF

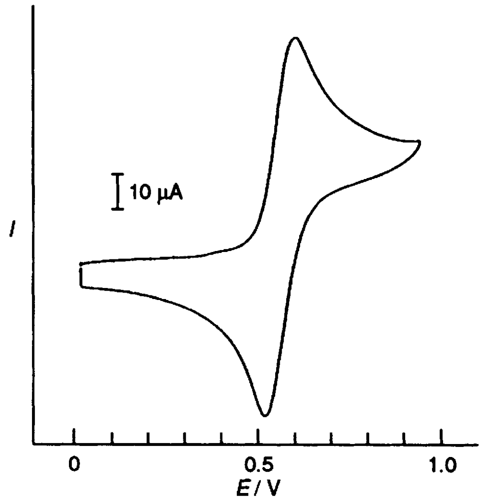
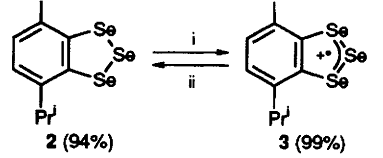


Fig. 1 Cyclic voltammogram of **2** (2 mmol dm^{-3}) in MeCN at 20 °C, 0.1 mol dm^{-3} NBu$^n_4$Cl supporting electrolyte, glassy-carbon working electrode, ferrocene external standard, potential *vs* Ag/0.01 mol dm^{-3} $AgNO_3$ reference; scan rate, 100 mV s^{-1}

Cyclic voltammetry of **2** in MeCN at 20 °C under Ar exhibited a well-defined reversible one-electron oxidation wave at $E_{1/2}$ = 0.56 V *versus* Ag/Ag$^+$ (Fig. 1). This result implies that **2** provides a stable radical cation even at room temperature.

The novel triselenolium radical cation salt **3**§ was isolated in the one-electron oxidation of **2** with 1 equiv. of $NOPF_6$ as a one-electron oxidant in ether–acetonitrile (Scheme 2). The



Scheme 2 *Reagents*: i, $NOPF_6$, MeCN–diethylether; ii, SmI_2 in THF

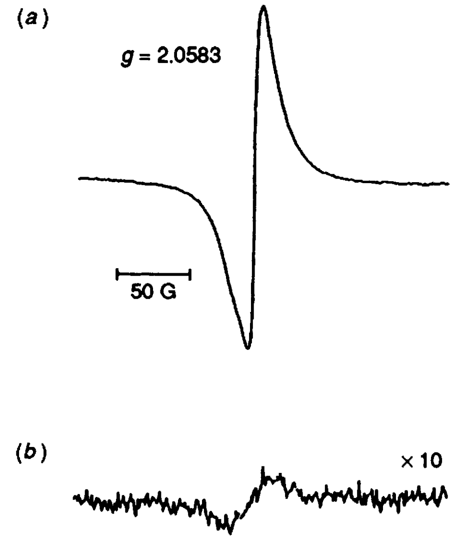


Fig. 2 ESR spectra of **3** at 16 °C (*a*) and −70 °C (*b*) in THF

dark blue salt **3** was stable and the structure of **3** in solution was analysed by ^{31}P NMR and ESR spectroscopy. The salt **3** dissolved readily in THF to give a red–purple solution. The ESR spectrum of the solution showed the presence of a singlet peak (g = 2.0583 G) attributable to a triselenolium radical cation. Valuable-temperature ESR studies on this species afforded decreasing of the intensities of the signal at low temperature. At −70 °C the signal almost disappeared and the colour of the solution changed to dark blue, presumably as a result of partial dimerization[2] of the radicals (Fig. 2). Interestingly, the salt **3** undergoes one-electron reduction to give **2** quantitatively by treatment with samarium(II) iodide (Scheme 2).[11]

Thus, the facile interconversion in the redox reaction of **2** and **3** are ascribed to the destabilization of the distorted neutral triselenide framework by lone pair–lone pair repulsion and the stabilization of the oxidized radical cation by 7π-aromaticity.

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Footnotes

† Compound **1**: Colourless plates (hexane); mp 160.5–162.0 °C [Found: C, 35.85; H, 4.78. $C_{14}H_{22}Se_2Sn$ requires C, 36.01; H, 4.75%]; ν_{max} (KBr)/cm^{-1} 2963, 2867, 1872, 1694, 1463, 1385, 1363, 1183, 1158, 902 and 816; δ_H (400 MHz, $CDCl_3$) 1.06 (6H, s, Me), 1.27 (12H, d, *J* 6.8, *Me*$_2$CH), 3.51 (2H, spt., *J* 6.8, Me$_2$C*H*) and 7.04 (2H, s, ArH); δ_C (100 MHz, $CDCl_3$) 1.0, 23.4, 37.6, 122.9, 138.5 and 148.3; δ_{Se} (76 MHz, $CDCl_3$, relative to neat $SeMe_2$) 83.2 [$J(^{77}Se^{117}Sn)$ 1061, $J(^{77}Se^{119}Sn)$ 1110]; δ_{Sn} (149 MHz, $CDCl_3$, relative to neat $SnMe_4$) 62.9 [$J(^{119}Sn^{77}Se)$ 1110]; *m/z* 440 (M^+, ^{80}Se, ^{120}Sn).

‡ Compound **2**: Reddish brown oil [Found: (M^+, 100%, $^{80}Se^{80}Se^{78}Se$) 397.8743 and (84.5%, $^{80}Se^{80}Se^{80}Se$) 399.8682. $C_{12}H_{16}Se_3$ requires (M^+, 100%, $^{80}Se^{80}Se^{78}Se$) 397.8761 and (86.2, $^{80}Se^{80}Se^{80}Se$) 399.8753]; ν_{max} (neat)/cm^{-1} 2958, 2865, 1885, 1754, 1462, 1385, 1367, 1323, 1160, 1104, 906 and 820; δ_H (400 MHz, $CDCl_3$) 1.24 (12H, d, *J* 6.8, *Me*$_2$CH), 3.02 (2H, d, *J* 6.8, Me$_2$C*H*) and 7.05 (2H, s, ArH); δ_C (100 MHz, $CDCl_3$) 23.4, 38.7, 125.0, 141.5 and 146.3; δ_{Se} (76 MHz, $CDCl_3$, relative to neat $SeMe_2$) 440.9 [$J(^{77}Se^{77}Se)$258] and 547.0 [$J(^{77}Se^{77}Se)$258]

§ Compound **3**: Blue powder (ether); mp 166.0–172.0 °C (decomp.); [Found: C, 26.78; H, 3.29. $C_{12}H_{16}F_6PSe_3$ requires C, 26.59; H, 2.97%]; δ_P (162 MHz, [$^2H_8$]THF, relative to H_3PO_4) −144.0 [spt., $J(^{31}P^{19}F)$706]

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