1,4-Diselenine synthesis by Diels–Alder reaction of a novel exocyclic 1,2-diselone: X-ray crystal structure of (5,6-dimethoxycarbonyl-1,4-diselenine-2,3-dithiolate)Ni(dppe) [dppe = 1,2-($Ph_2P)_2C_2H_4$]

Antony Chesney, Martin R. Bryce,* Andrei S. Batsanov and Judith A. K. Howard

Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE

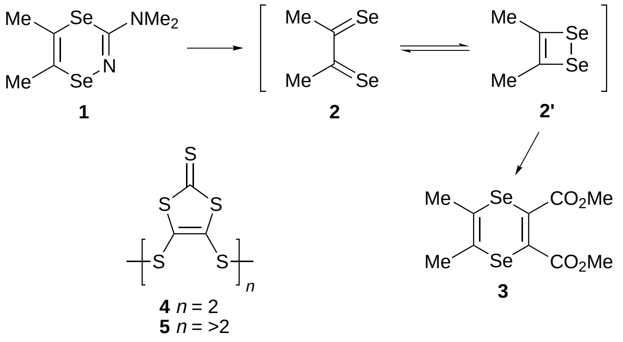
The salt $(NBu_4)_2[Zn(dsit)_2]$ 6 has been converted into the polymer $(C_3S_3Se_2)_n$ 7 which is a source of the reactive 1,2-diselone 8, trapping of which with dimethyl acetylenedicarboxylate affords the 1,4-diselenine derivative 9, which is subsequently transformed into the 1,4-diselenine-2,3-dithiolate species 11, characterised by the X-ray crystal structure of a nickel complex 12.

The synthesis of unusual organoselenium heterocycles, especially *via* cycloaddition chemistry of reactive N=Se[1] and C=Se[2] bonds, has recently attracted considerable attention. For example, the low-yielding synthesis of 1,4-diselenine derivative **3** from the unstable 1,4,2-diselenazine **1** was presumed to occur *via* the transient 1,2-diselone intermediate **2**, or the 1,2-diselenete tautomer **2′** (Scheme 1).[2c] We now report an entirely different approach to an exocyclic 1,2-diselone intermediate and its efficient trapping reaction to yield the highly-functionalised bicyclic 1,4-diselenine system **9** which is subsequently transformed into the nickel complex **12**.

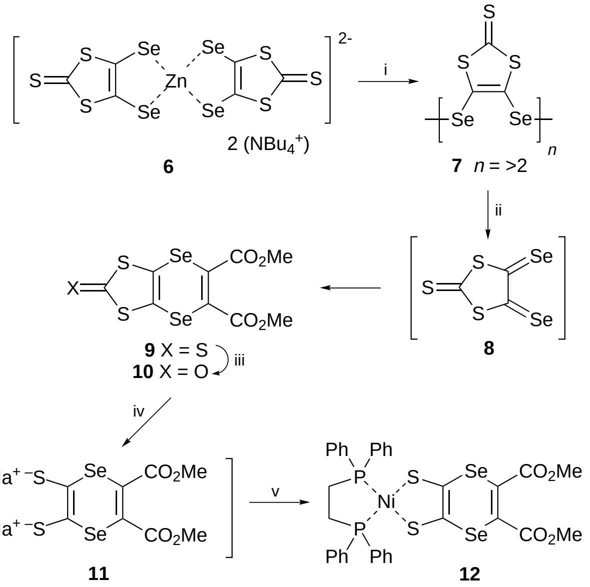
1,4-Dithiine synthesis by reactions of either the dimer **4**[3] or the polymer **5**[4] of the C_3S_5 unit[4b,5] has been reported. We chose to investigate the selenium-containing salt $(NBu_4)_2[Zn(dsit)_2]$ (dsit = 1,3-dithiole-2-thione-4,5-diselenolate) **6**[6] as a novel precursor for 1,2-diselones. Zinc salt **6** was easily prepared on a multi-gram scale, according to the literature procedure employing the more reactive red form of selenium.[6a] Oxidation of **6** with I_2 in EtOH–acetone at −50 °C afforded a highly insoluble, air-stable† compound $(C_3S_3Se_2)_n$, assumed to be polymer **7**, in excellent yield. Treatment of **7** with PBu_3 in CH_2Cl_2 at 20 °C in the presence of excess dimethyl acetylenedicarboxylate (DMAD) afforded the bicyclic 1,4-diselenine derivative **9** in 57% yield, presumably *via* the intermediacy of the highly-reactive 1,2-diselone **8** (or a PBu_3 complex of **8**) (Scheme 2). The use of PBu_3 to depolymerise **7** was more successful than the usual method employed for the sulfur analogue $(C_3S_5)_n$ **5**, which is heated in a solvent such as benzene, toluene, dioxane or chlorobenzene.[4] The use of these conditions with **7** led to poor yields of adduct **9**, which was contaminated with a variety of unidentified components. 1,2-Diselones are extremely rare species.[2c] Electron diffraction experiments[7] clearly revealed that a cyclic 1,2-diselenete structure (*cf.* structure **2′**) is favoured over the acyclic diselone structure $F_3CC(Se)–C(Se)–CCF_3$. However, this is less likely to be the situation for intermediate **8**, which is the first exocyclic 1,2-diselone: the diselenete tautomer of **8** would be a very strained bicyclic system.

Conversion of the thione functionality in **9** into the oxo derivative **10** proceeded almost quantitatively on reaction with mercuric acetate in a mixture of $CHCl_3$ and AcOH. Opening of the 1,3-dithiole ring of **10** was achieved by reaction with MeONa in anhydrous MeOH: the disodium salt of 5,6-dimethoxycarbonyl-1,4-diselenine-2,3-dithiolate **11** thereby formed reacted *in situ* with $NiCl_2$(dppe) [dppe = 1,2-$(Ph_2P)_2C_2H_4$] to afford the dark green dithiolene complex (5,6-dimethoxycarbonyl-1,4-diselenine-2,3-dithiolate)Ni(dppe) **12**. Complexation of 1,4-dithiine-2,3-dithiolate units with nickel species has been previously reported both by Rauchfuss[3] and Bereman[8] but, to the best of our knowledge, this is the first time the 1,4-diselenine-2,3-dithiolate system has been prepared. X-Ray analysis of crystals of complex **12**, grown from MeCN, unambiguously proved the structure of the complex (Fig. 1).‡

In complex **12**, the nickel atom adopts a square planar coordination, distorted by a slight (6.5°) tetrahedral twist. The



Scheme 1



Scheme 2 *Reagents and conditions*: i, I_2 (2.1 equiv.), EtOH–acetone, −50 to 20 °C, 2 h; ii, PBu_3 (1 equiv.), DMAD (2 equiv.), CH_2Cl_2, 20 °C; iii, $Hg(OAc)_2$, $CHCl_3$–AcOH (3 : 1 v/v), 20 °C, 12 h; iv, NaOMe, MeOH, 30 min; v, $NiCl_2$ (dppe)

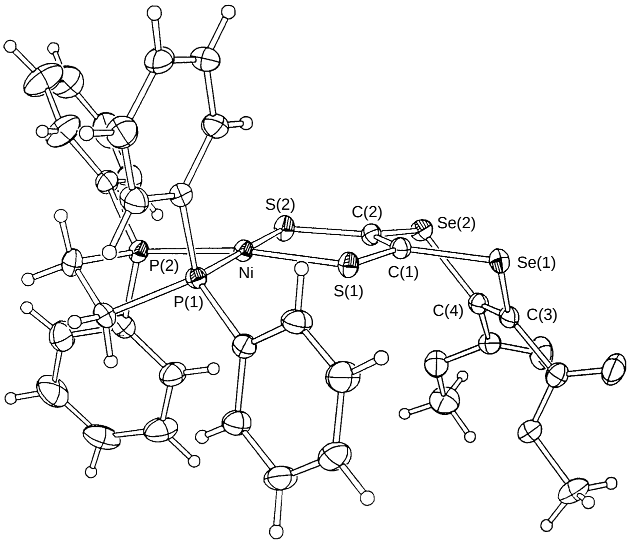


Fig. 1 Molecular structure of **12**. Bond distances (Å): Ni–S(1) 2.168(1), Ni–S(2) 2.173(1), Ni–P(1) 2.175(1), Ni–P(2) 2.191(1), S(1)–C(1) 1.750(2), S(2)–C(2) 1.755(2), C(1)–Se(1) 1.917(2), C(2)–Se(2) 1.917(2), C(1)–C(2) 1.343(2), C(3)–Se(1) 1.918(2), C(4)–Se(2) 1.922(2), C(3)–C(4) 1.338(2).

Se(1)C(1)C(2)Se(2) moiety forms dihedral angles of 6.5° with the planar NiS_2C_2 ring and of 52.8° with the Se(1)C(3)C(4)Se(2) plane. The ester substituents at C(3) and C(4) are inclined to the latter plane by 48.5 and 55.3°, respectively.§ The folding of the diselenine ring in **12** is similar to that observed in [1,4]diselenino[2,3-*b* : 5,6-*b*′]di[1]benzoselenole (54°) and 1,2,3,4,5,6,8,9,10,11,12,13-dodecahydrodicycloocta[1,4]diselenine[10] (49°), but larger than in nickel complexes with isoelectronic 2,3-dithiolato-1,4-dithiine ligands (28–43°).[3,11]

In summary, we have devised a short and expedient route to the 1,2-diselone **8** which has been converted to the 1,4-diselenine derivative **9** and hence the nickel complex **12**. This methodology affords a new and efficient approach to the synthesis of highly-functionalised derivatives of the rare 1,4-diselenine ring system. Further research into the Diels–Alder trapping of 1,2-diselone intermediate **8**, and the downstream organic and organometallic reactions of the products derived therefrom, will be reported in due course.

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Footnotes and References

* E-mail: m.r.bryce@durham.ac.uk

† The analysis and reactivity of this material were unchanged by storage in a sealed container on the bench for at least three months.

‡ Satisfactory elemental analysis were obtained for **7**, **9**, **10** and **12**. *Selected data* for **9**: mp 215–217 °C; δ_H ($CDCl_3$) 3.86 (6 H, s); δ_C ($CDCl_3$) 53.72, 125.30, 136.15, 163.12 and 216.32; *m/z* (CI) 435 (^{80}Se, 25%), 58 (100); ν_{max} (KBr)/cm^{-1} 1723, 1703, 1574, 1248 and 1049. For **12**: mp > 250 °C; δ_H ([$^2H_6$]DMSO) 3.56 (4 H, t, *J* 7.8), 3.66 (6 H, s), 7.55 (12 H, m) and 7.69 (8 H, m); ν_{max} (KBr)/cm^{-1} 1721, 1566, 1434 and 1242.

§ *Crystal data* for **12**: $C_{34}H_{30}NiO_4P_2S_2Se_2\cdot C_2H_3N$, $M = 886.3$, $T = 150$ K, monoclinic, space group $C2/c$ (no. 15), $a = 41.722(2)$, $b = 9.199(1)$, $c = 19.599(1)$ Å, $\beta = 104.17(1)°$, $V = 7293(1)$ Å^3, $Z = 8$, $D_x = 1.61$ g cm^{-3}, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 27.7$ cm^{-1}, crystal size 0.50 × 0.35 × 0.24 mm, 44429 reflections (10294 unique) with $\theta < 61.5°$ measured using a Siemens SMART CCD area detector; $R_{int} = 0.078$ before, 0.047 after face-indexing (integration) absorption correction ($T_{min,max} = 0.310, 0.573$), full-matrix least-squares refinement using SHELXTL software, on F^2 of all data to $wR = 0.067$ (non-H atoms anisotropic, H isotropic; MeCN molecule disordered over two positions with occupancies of 78.3 and 21.7(5)%; total of 562 variables); for 9030 observed data with $I > 2\sigma(I)$, $R(F) = 0.026$; residual $\Delta\rho_{min,max} = 0.51, -0.47$ e Å^{-3}. CCDC 182/635.

1 M. R. Bryce and A. Chesney, *J. Chem. Soc., Chem. Commun.*, 1995, 195.

2 (*a*) H. Fischer, K. Treier, C. Troll and R. Stumpf, *J. Chem. Soc., Chem. Commun.*, 1995, 2461; (*b*) N. Takeda, N. Tokitoh and R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 660; (*c*) S. Yoshida, M. R. Bryce and A. Chesney, *Chem. Commun.*, 1996, 2375.

3 X. Yang, T. B. Rauchfuss and S. Wilson, *J. Chem. Soc., Chem. Commun.*, 1990, 34.

4 (*a*) O. Y. Neiland, Y. Y. Katsens and Y. N. Kreitsberga, *Z. Org. Chim.*, 1989, **25**, 592; (*b*) N. Svenstrup and J. Becher, *Synthesis*, 1995, 215.

5 G. Steimecke, H.-J. Sieler, R. Kirmse and E. Hoyer, *Phosphorus Sulfur*, 1979, **7**, 49.

6 (*a*) R. M. Olk, A. Röhr, B. Olk and E. Hoyer, *Z. Chem.*, 1988, **28**, 304; (*b*) H. Poleschner, R. Radeglia and J. Fuchs, *J. Organomet. Chem.*, 1992, **427**, 213; (*c*) J. Garín, J.Orduna, M. Savirón, M. R. Bryce, A. J. Moore and V. Morisson, *Tetrahedron*, 1996, **52**, 11063.

7 A. B. Borisenko, M. Broschag, I. Hargittai, T. M. Klapötke, D. Schröder, A. Schulz, H. Schwartz, I. C. Tornieporth-Oetting and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1994, 2705.

8 J. H. Welch, R. D. Bereman, J. Bordner, W. Hatfield and J. H. Helms, *Inorg. Chem.*, 1985, **24**, 2905.

9 V. P. Litvinov, I. A. Dzhumaev, G. V. Gridunova, V. E. Shklover, Yu. T. Struchkov and B. M. Zolotarev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 782.

10 M. R. J. Dorrity, A. Lavery, J. F. Malone, C. P. Morley and R. R. Vaughan, *Heteroatom Chem.*, 1992, **3**, 87; F. R. Fronczek, H. E. Folsom and P. W. Rabideau, private communication to CCDC, 1995, ref. code PAPKUM01.

11 H. Kim, A. Kobayashi, Y. Sasaki, R. Kato, H. Kobayashi, T. Nakamura, T. Nogami and Y. Shirota, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2559.

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