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-(Ph₂P)₂C₂H₄]

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=Se¹ and C=Se² 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 C₃S₅ unit^{4b,5} has been reported. We chose to investigate the selenium-containing salt (NBu₄)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 $\hat{\mathbf{6}}$ 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 PBu₃ in CH2Cl2 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 PBu₃ complex of 8) (Scheme 2). The use of PBu₃ 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



Scheme 1

contaminated with a variety of unidentified components. 1,2-Diselones are extremely rare species.² Electron diffraction experiments⁷ 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 CHCl₃ 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 NiCl₂(dppe) [dppe = 1,2-(Ph₂P)₂C₂H₄] 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 Rauchfuss³ and Bereman⁸ 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 2 Reagents and conditions: i, I_2 (2.1 equiv.), EtOH–acetone, -50 to 20 °C, 2 h; ii, PBu₃ (1 equiv.), DMAD (2 equiv.), CH₂Cl₂, 20 °C; iii, Hg(OAc)₂, CHCl₃–AcOH (3:1 v/v), 20 °C, 12 h; iv, NaOMe, MeOH, 30 min; v, NiCl₂ (dppe)

Chem. Commun., 1997 2293



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 NiS₂C₂ 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]diselenine¹⁰ (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; $\delta_{\rm H}$ (CDCl₃) 3.86 (6 H, s); $\delta_{\rm C}$ (CDCl₃) 53.72, 125.30, 136.15, 163.12 and 216.32; *m/z* (CI) 435 (⁸⁰Se, 25%), 58 (100); $v_{\rm max}$ (KBr)/cm⁻¹ 1723, 1703, 1574, 1248 and 1049. For **12**: mp > 250 °C; $\delta_{\rm H}$ ([²H₆]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); $v_{\rm max}$ (KBr)/cm⁻¹ 1721, 1566, 1434 and 1242.

§ *Crystal data* for **12**: C₃₄H₃₀NiO₄P₂S₂Se₂·C₂H₃N, *M* = 886.3, *T* = 150 K, monoclinic, space group *C*2/*c* (no. 15), *a* = 41.722(2), *b* = 9.199(1), *c* = 19.599(1) Å, β = 104.17(1)°, *V* = 7293(1) Å³, *Z* = 8, *D*_x = 1.61 g cm⁻³, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, μ = 27.7 cm⁻¹, crystal size 0.50 × 0.35 × 0.24 mm, 44429 reflections (10294 unique) with θ < 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*σ*(*I*), *R*(*F*) = 0.026; residual $\Delta\rho_{min,max}$ = 0.51, -0.47 e Å⁻³. CCDC 182/635.

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2294 Chem. Commun., 1997