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Letter

Synthesis of mono- and di-nuclear palladium diselenolenes from bis(cycloalkeno)-1,4-diselenins: X-ray crystal structure of $[Pd(C_7H_{10}Se_2)(PBu_3)_2]$

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The reaction between $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone), tributylphosphine, and a bis(cycloalkeno)-1,4-diselenin leads to either a mononuclear $[Pd\{SeC(R^1)=C(R^2)Se\}(PBu_3)_2]$, or a dinuclear $[Pd_2\{SeC(R^1)=C(R^2)Se\}_2(PBu_3)_2]$ diselenolene (R^1–R^2 = $(CH_2)_n$; n = 4, 5, 6) depending on the stoichiometry employed; the structure of the monomeric product with n = 5 has been determined by X-ray crystallography.

While organosulfur chemistry, and specifically that of dithiolene complexes, has been widely investigated, the field of organoselenium chemistry and diselenolenes had, until recent years remained relatively little studied. The current increase in research in this area is due to the greater accessibility and range of applications of these materials, *i.e.* the realisation that they may possess potentially useful properties for the electronics industry.[1]

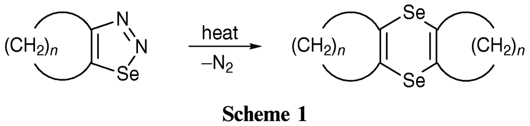
Despite their ready preparation from 1,2,3-selenadiazoles[2] (Scheme 1) little research into the chemistry of 1,4-diselenins has been documented.[3–5]

We previously reported that cycloalkeno-1,2,3-selenadiazoles react with the palladium(0) phosphine fragment '$Pd(PR_3)_2$' (R = Et, Bu^n) generated *in situ* from the reaction of $[Pd_2(dba)_3]$ with PR_3, to give the azo-complexes shown below (Scheme 2).[6]

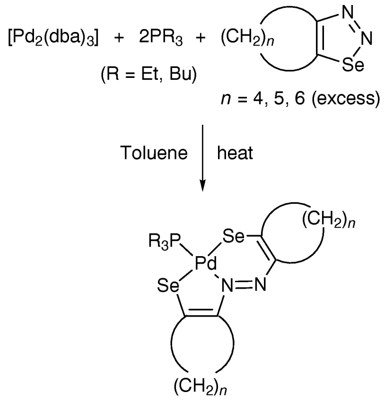
When the 1,2,3-selenadiazole (n = 5, 6) is replaced by the analogous 1,4-diselenin, a deep purple diselenolene is formed after heating the reaction mixture to reflux in toluene for 1 h. To obtain the corresponding product when n = 4 a higher temperature (reflux in xylene) and a longer reaction time are required. By manipulation of the stoichiometry the product obtained after column chromatography can be either the mononuclear (**1a**–**c**) or dinuclear (**2a**–**c**) complex (Scheme 3).†

The detailed mechanism of the reaction is not yet clear. However, based on previous research showing cleavage of the C–Se bond in 1,4-diselenins,[3] we postulate a first step of metal insertion into the heterocyclic ring system, followed by loss of the cycloalkyne (Scheme 4).

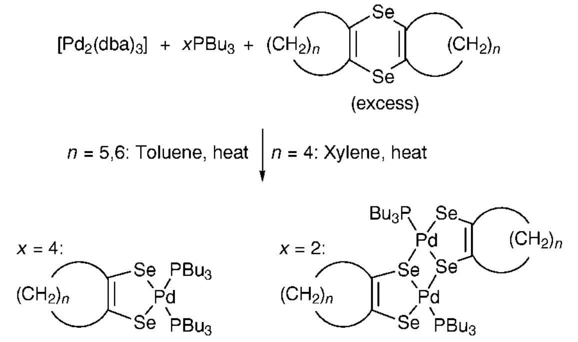
It is interesting to note the forcing conditions required to obtain a product when bis(cyclohexeno)-1,4-diselenin (n = 4) is employed. The dependence of product formation on ring size is not unusual for 1,4-diselenins.[5] Indeed this observation is in accordance with the proposed mechanism, as expulsion of a cycloalkyne fragment would be favourable for n = 6, cyclooctyne being an isolable species, but not for n = 4, the ring strain in cyclohexyne being significantly larger.



Scheme 1

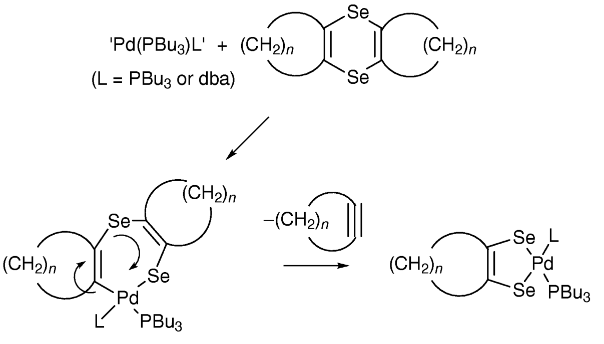


Scheme 2



1a: n = 4; **1b**: n = 5; **1c**: n = 6
2a: n = 4; **2b**: n = 5; **2c**: n = 6

Scheme 3



Scheme 4

We believe that this is the first example of a palladium diselenolene which has been isolated in both mononuclear and dinuclear forms. Monomeric palladium diselenolenes and even dithiolenes containing ancillary ligands such as phosphines appear to be unknown in the literature, although their platinum analogues are well established.[7] It is interesting here that no reaction was observed under a variety of conditions, when the corresponding platinum chemistry was examined. The colour of the reaction mixture remained unchanged and the starting material was recovered quantitatively by column chromatography. Perhaps the greater lability of palladium complexes is partly responsible for this difference in behaviour.

Very little has been documented regarding dinuclear diselenolenes, although we recently prepared an analogous complex containing triphenylphosphine.[8] A difference between these two reactions is that no mononuclear product containing triphenylphosphine could be isolated, despite an excess of phosphine being present in solution. Also, these complexes are dark green unlike their deep purple *n*-butyl analogues, although this appears to be due to intensity changes in the absorption spectra, rather than any significant differences in electronic structure.

The molecular structure of **1b** has been determined by X-ray crystallography‡ and is shown in Fig. 1. It consists of a distorted square-planar $PdSe_2P_2$ core, with only the outer atoms of the hydrocarbon ring and the butyl chains protruding significantly from this plane. The Se–Pd–Se bond angle (86.66°) is smaller than those previously reported in the related complexes $[NBu^n{}_4]_2[Pd(C_3Se_5)_2]$ **3** (91.5°)[9] and $[NMe_4][Pd(C_3S_3Se_2)_2]_2$ **4** (90.74, 91.18°).[10] This is presumably due to steric repulsion between the large adjacent trialkylphosphine ligands (P–Pd–P = 100.2°). The Pd–Se bond lengths in **1b** (2.402 and 2.419 Å) are similar to those in **3** and **4** [2.409 Å (av.) and 2.383 Å respectively].

The molecular formulae of **1a–c** and **2a–c** have been established by elemental analysis and mass spectrometry. The mass spectrum of each complex shows an intense cluster corresponding to the molecular ion, with the expected isotope distribution.

The NMR spectroscopic data are in accord with the proposed structures. For the mononuclear species analysis of the satellites in the ^{31}P NMR spectra allows evaluation of the coupling of the equivalent selenium atoms to the corresponding *cis*- ($J = 16$ Hz) and *trans*- ($J = 65$ Hz) phosphorus atoms. There is also coupling between the two phosphorus nuclei ($J = 44$ Hz) (*cf.* *cis*-$[PdCl_2(PMe_3)_2]$, $J = 8$ Hz; *cis*-$[PdCl_2\{P(OMe)_3\}_2]$, $J = 80$ Hz).[11] As expected in these symmetrical molecules there is only one ^{13}C resonance for the olefinic carbon atoms in the alicyclic ring, and only one signal in the ^{77}Se NMR spectrum.

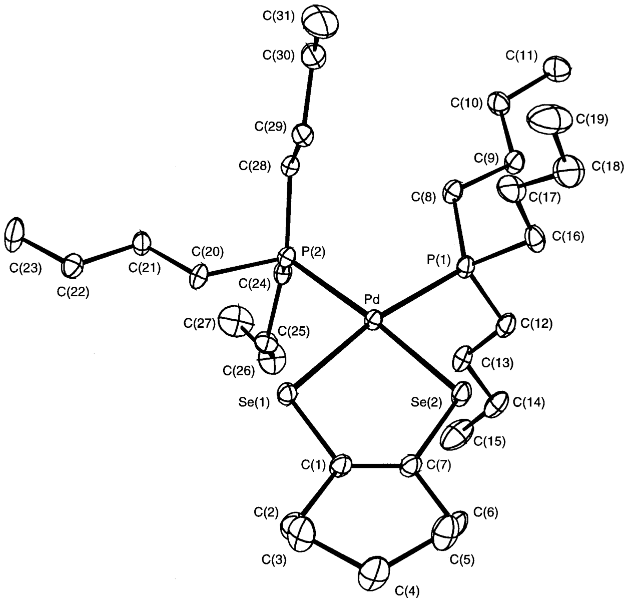


Fig. 1 Structure of **1b** with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–P(1) 2.318(3), Pd–P(2) 2.326(3), Pd–Se(1) 2.402(1), Pd–Se(2) 2.419(1), P(1)–Pd–Se(2) 84.3(1), Se(2)–Pd–Se(1) 86.66(4), Se(1)–Pd–P(2) 88.8(1), P(2)–Pd–P(1) 100.2(1).

For the dinuclear species the selenium NMR spectra contain two signals corresponding to the terminal and bridging selenium atoms. The resonance due to the bridging selenium atoms is a doublet of doublets, due to coupling to the *cis*- ($J = 9$ Hz) and *trans*- ($J = 111$ Hz) phosphorus atoms. These are similar coupling constants to those observed in the analogous triphenylphosphine complexes.[8] The signal corresponding to the terminal selenium atoms is an apparent singlet, as the expected small coupling to the neighbouring *cis*-phosphorus atoms is not resolved.

Owing to the delocalisation of the electrons present in the metal ligand bonding system, diselenolenes, like their sulfur analogues, are expected to display rich and varied chemical behaviour. The properties and reactivity of **1a–c** and **2a–c** are currently being investigated.

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Notes and references

† Synthesis of palladium diselenolenes **1b** and **2b**: PBu_3 [0.16 g, 0.8 mmol (**1b**) or 0.08 g, 0.4 mmol (**2b**)] was added to a toluene solution (100 cm^3) of $[Pd_2(dba)_3]\cdot dba$ (0.23 g, 0.2 mmol). After stirring at room temperature for a short time, bis(cyclohepteno)-1,4-diselenin (0.14 g, 0.4 mmol) was added and the mixture heated to reflux for 1 h. Removal of the solvent under reduced pressure left a dark coloured oil, which was purified by column chromatography on an alumina column, with toluene as the eluent. Collection of the deep purple band and recrystallisation from hexane gave **1b** or **2b** as an analytically pure solid.

1b: yield: 0.042 g (14%); mp 119 °C. ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$), δ 2.47 (m, 4H), 1.73 (m, 12H), 1.56 (m, 4H), 1.40 (m, 14H), 1.34 (m, 12H), 0.85 (t, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$), δ 131.4 [average $J(^{13}C-^{31}P)$ 7 Hz], 39.9, 29.7, 27.3, 26.2 [average $J(^{13}C-^{31}P)$ 12 Hz], 24.9 [average $J(^{13}C-^{31}P)$ 7 Hz], 24.4, 13.7; ^{31}P NMR (101 MHz, $CDCl_3$, external 85% H_3PO_4), δ 0.80; ^{77}Se NMR (47.7 MHz, $CDCl_3$, external $SeMe_2$), δ 533 [$J(^{77}Se-^{31}P)$ 65, 16 Hz]; UV-VIS (hexane): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 560 (140), 410 (420), 322sh (4600), 285 (24000), 225 (29000) nm; MS (FAB): *m*/*z* (%) 764 (15) [M^+], 203 (100) [$PBu_3{}^+$].

2b: yield: 0.12 g (54%); mp 112 °C. ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$), δ 2.53 (m, 8H), 1.65 (m, 12H), 1.54 (m, 12H), 1.41 (m, 24H), 0.93 (t, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$), δ 151.1, 120.7, 43.6, 40.6, 33.0, 31.0, 26.4, 24.4, 24.2, 24.0, 13.8; ^{31}P NMR (101 MHz, $CDCl_3$, external 85% H_3PO_4), δ 11.2; ^{77}Se NMR (47.7 MHz, $CDCl_3$, external $SeMe_2$), δ 498, 434 [$J(^{77}Se-^{31}P)$ 111, 9 Hz]; UV-VIS (hexane): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 565 (2100), 405 (8700), 325 (16000), 285 (24000), 270 (25000), 240 (49000) nm; MS (FAB): *m*/*z* (%) 1122 (5) [M^+], 203 (100) [$PBu_3{}^+$].

‡ Crystal data for **1b**: $C_{31}H_{64}P_2PdSe_2$; $M = 763.08$; crystal size 0.30 × 0.40 × 0.60 mm, monoclinic, space group $P2_1/c$ (no. 14); $a = 10.447(2)$, $b = 22.124(4)$, $c = 16.772(2)$ Å, $\beta = 94.80(1)°$, $U = 3863(1)$ Å^3 (by least squares refinement on setting angles of 24 reflections, $Z = 4$), $F(000) = 1576$, $D_c = 1.312$ g cm^{-3}, μ(Mo-Kα) = 2.46 mm^{-1}. Data collection (Enraf-Nonius CAD4, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $T = 295$ K), ω–2θ scans, $2.5 < \theta < 25°$. 5924 measured reflections ($\pm h$, $+k$, $+l$), 5458 unique ($R_{int} = 0.047$). Structure solution by direct methods, with SIR,[12] and heavy-atom procedures with SHELXL-93.[13] Empirical absorption correction (ψ scans; min., max. correction factors 0.71, 1.00). Final refinement cycles performed against F^2 with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions. Refinement on 331 variables converged at $R_1 = 0.054$ (based on 2858 reflections with $F_o > 4\sigma F_o$), $R_1 = 0.154$ (on all reflections), $wR_2 = 0.150$, GOF = 1.021. Max., min. peaks in the final difference map 0.47, −0.42 e Å^{-3}.

CCDC reference number 440/126.

1 J. Arnold, *Prog. Inorg. Chem.*, 1995, **43**, 353; M. L. Steigerwald and C. R. Sprinkle, *J. Am. Chem. Soc.*, 1987, **109**, 7200; P. O'Brien, *Chemtronics*, 1991, **5**, 61.

2 H. Meier and E. Voigt, *Tetrahedron*, 1972, **28**, 187.

3 C. M. Bates, P. K.Khanna, C. P. Morley and M. Di Vaira, *Chem. Commun.*, 1997, 913.

4 M. R. J. Dorrity, A. Lavery, J. F. Malone, C. P. Morley and R. R. Vaughan, *Heteroatom Chem.*, 1992, **3**, 87; A. Chesney, M. R. Bryce, A. S. Batsanov and J. A. K. Howard, *Chem. Commun.*, 1997, 2293.

5 A. J. Mayr, H.-S. Lien, K. H. Pannell and L. Parkanyi, *Organometallics*, 1985, **4**, 1580.

6 S. Ford, C. P. Morley and M. Di Vaira, *Chem. Commun.*, 1998, 1305.

7 C. E. Johnson, R. Eisenberg, T. R. Evans and M. S. Burbery, *J. Am. Chem. Soc.*, 1983, **105**, 1795; C. M. Bollinger and T. B. Rauchfuss, *Inorg. Chem.*, 1982, **21**, 3947; R. D. McCullough, J. A. Belot, J. Seth, A. L. Rheingold, G. P. A. Yap and D. O. Cowan, *J. Mater. Chem.*, 1995, **5**, 1581: D. M. Giolando, T. B. Rauchfuss and A. L.Rheingold, *Inorg. Chem.*, 1987, **26**, 1636.

8 S. Ford, P. K. Khanna, C. P. Morley and M. Di Vaira, *J. Chem. Soc., Dalton Trans.*, 1999, 791.

9 C. Faulmann, J. P. Legros, P. Cassoux, J. Cornelissen, L. Brossard, M. Inokuchi, H. Tajima and M. Tokumoto *J. Chem. Soc., Dalton Trans.*, 1994, 249.

10 G. Matsubayashi, S. Tanaka and A. Yokozawa, *J. Chem. Soc., Dalton Trans.*, 1992, 1827.

11 S. Berger, S. Braun and H. O. Kalinowski, *NMR Spectroscopy of the Non-metallic Elements*, Wiley, London, p. 954.

12 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.

13 G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

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