

# Novel palladium complexes of Se,N,Se tridentate ligands derived from cycloalkeno-1,2,3-selenadiazoles

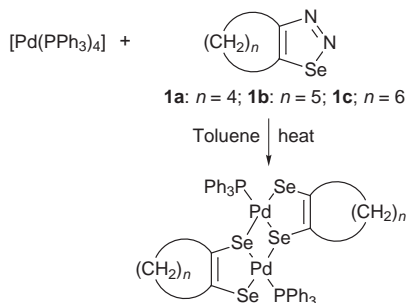
Susan Ford,<sup>a</sup> Christopher P. Morley<sup>\*a</sup> and Massimo Di Vaira<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Wales Swansea, Singleton Park, Swansea, UK SA2 8PP

<sup>b</sup> Dipartimento di Chimica, Università degli Studi di Firenze, Via Maragliano 75/77, 50144 Firenze, Italy

The reaction between  $[\text{Pd}_2(\text{dba})_3]$  (dba = dibenzylideneacetone), a trialkylphosphine, and a cycloalkeno-1,2,3-selenadiazole in toluene under reflux leads in good yield to the complexes  $[\text{PdL}(\text{PR}_3)]$  [L =  $\text{SeC}(\text{R}^1)=\text{C}(\text{R}^2)\text{N}=\text{NC}(\text{R}^1)=\text{C}(\text{R}^2)\text{Se}$ ;  $\text{R}^1-\text{R}^2 = (\text{CH}_2)_n$ ;  $\text{R} = \text{Et}, \text{Bu}^n$ ] containing a novel Se,N,Se tridentate ligand formed by the coupling of two 1,2,3-selenadiazole molecules; the structure of the product with  $\text{R} = \text{Bu}^n$  and  $n = 4$  has been determined by X-ray crystallography.

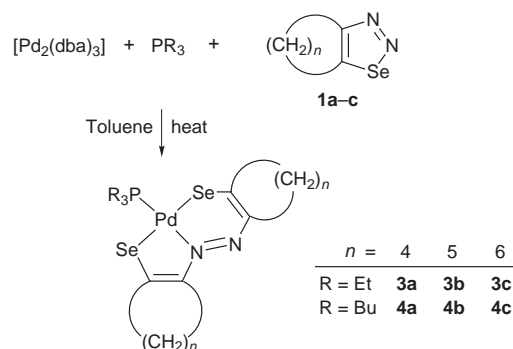
The chemistry of organoselenium ligands has attracted increased attention in the last few years, as a result of both their greater accessibility, and the realisation that they may display significantly different properties from their sulfur analogues.<sup>1</sup> We have previously demonstrated that 1,2,3-selenadiazoles may serve as the precursors to a range of selenium-containing ligands in cyclopentadienylcobalt complexes,<sup>2</sup> and recently reported on their reactions with  $[\text{Pt}(\text{PPh}_3)_4]$ .<sup>3</sup> The palladium compound  $[\text{Pd}(\text{PPh}_3)_4]$  behaves quite differently from its platinum analogue, yielding novel dinuclear diselenolenes (Scheme 1).<sup>4</sup> We have now studied the reactivity of a range of cycloalkeno-1,2,3-selenadiazoles (**1a-c**) towards other palladium(0) phosphine complexes, generated *in situ* from  $[\text{Pd}_2(\text{dba})_3]$  **2** (dba = dibenzylideneacetone).



Scheme 1

Heating a mixture of 2 equiv. of one of the 1,2,3-selenadiazoles **1a-c** with **2**, in the presence of triethylphosphine or tri-*n*-butylphosphine, leads to the formation of a deep purple solution, from which the product **3a-c** or **4a-c** may be isolated in good yield by column chromatography (Scheme 2).<sup>‡</sup> These intensely coloured compounds have the general formula  $[\text{PdL}(\text{PR}_3)]$  and contain the first examples of a new type of ligand L =  $\text{SeC}(\text{R}^1)=\text{C}(\text{R}^2)\text{N}=\text{NC}(\text{R}^1)=\text{C}(\text{R}^2)\text{Se}$ , which may be considered as an alicyclic analogue of an azo-dye.

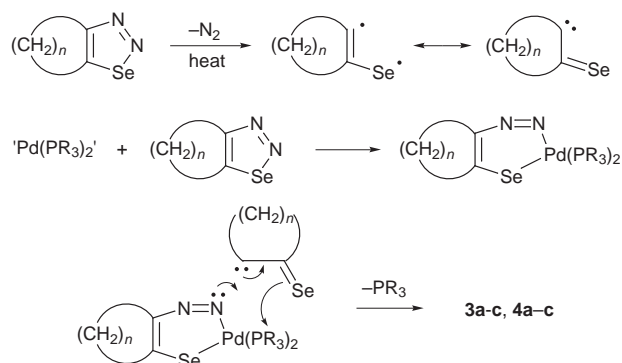
The detailed mechanism of the reaction remains unclear. In general, 1,2,3-selenadiazoles react *via* elimination of dinitrogen to yield a selenaketocarbene, the fate of which determines the outcome of the reaction.<sup>5</sup> Attack on another molecule of intact 1,2,3-selenadiazole is, to our knowledge, unprecedented. We therefore postulate initial insertion of palladium(0) into the selenium–nitrogen bond of a 1,2,3-selenadiazole molecule, followed by carbon–nitrogen bond formation by addition of a selenaketocarbene to this palladium(II) intermediate (Scheme



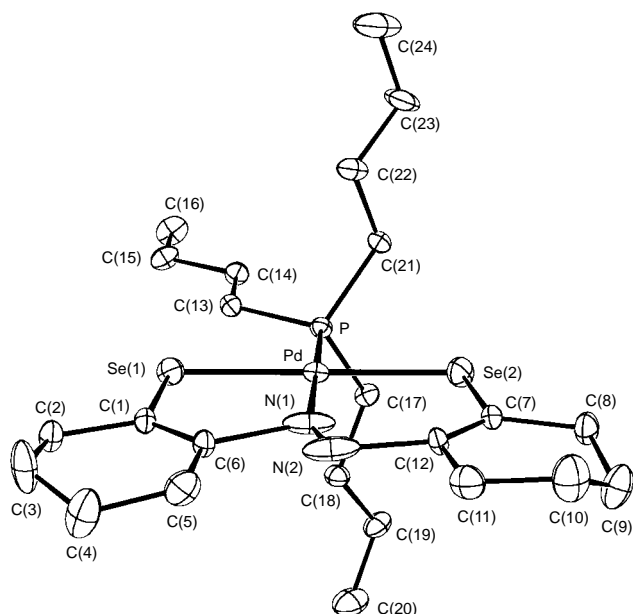
Scheme 2

3). It is interesting that behaviour analogous to that of  $[\text{Pd}(\text{PPh}_3)_4]$  is not observed. This we ascribe to the greater basicity of the phosphines used in this study, when compared with that of triphenylphosphine.

The molecular structure of **4a** has been determined by X-ray crystallography<sup>§</sup> and is shown in Fig. 1. The palladium atom is square-planar coordinated, with the phosphine *trans* to a nitrogen atom of the novel tridentate Se,N,Se ligand. The twelve atoms associated with the  $\pi$ -system of the ligand [ $\text{Se}-\text{C}(\text{C})=\text{C}(\text{C})-\text{N}=\text{N}-\text{C}(\text{C})=\text{C}(\text{C})-\text{Se}$ ] are also coplanar, so that overall this part of the molecule is virtually flat. Only the three *n*-butyl groups on the phosphine protrude significantly from the coordination plane. There are relatively few examples of Pd–Se distances in the literature. The bond lengths in **4a** [2.370(1), 2.371(1) Å] are comparable with the shortest thus far reported. In the related complexes  $[\text{Pd}\{\text{PhSeNC}(4\text{-MeC}_6\text{H}_4)\text{NNC}(4\text{-MeC}_6\text{H}_4)\text{NSePh}\}(\text{PPh}_3)]$ <sup>6</sup> **5** and  $[\text{PdCl}\{5\text{-MeC}_6\text{H}_3\text{-2}-(\text{N}=\text{N}-4'\text{-MeC}_6\text{H}_3\text{-2}'\text{-SePh})\}]$ <sup>7</sup> **6** the Pd–Se distances are 2.375(1) and 2.4495(4) Å, respectively. The Pd–P distance is typical for  $\text{PBu}_3$  derivatives, and similar to that in  $[\text{Pd}\{2\text{-OC}_8\text{H}_8\text{N}=\text{N}(-5'\text{-NO}_2\text{C}_6\text{H}_3\text{-2}'\text{-O})\}(\text{PBu}_3)]$  **7**<sup>8</sup> [**4a**, 2.264(2); **7**, 2.289(2) Å]. The Pd–N distance of 2.081(8) is rather long [*cf.* 2.024(2),



Scheme 3



**Fig. 1** Structure of **4a** with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–N(1) 2.081(8), Pd–P 2.264(2), Pd–Se(1) 2.370(2), Pd–Se(2) 2.371(1); P–Pd–Se(1) 91.72(6), Se(1)–Pd–N(1) 88.0(3), N(1)–Pd–Se(2) 93.1(3), Se(2)–Pd–P 87.23(6).

1.989(2) and 1.997(4) Å in **5**, **6** and **7**, respectively]. There is also considerable thermal motion associated with the nitrogen atoms, implying that the N(1)–Pd interaction is rather weak, and not strongly directional. Detailed discussion of bond angles and bond lengths in the azo-group is therefore not appropriate. The molecular formula is confirmed by the mass spectrum, where there is an intense cluster around  $m/z = 656$  corresponding to the molecular ion, with the expected isotope distribution.

The NMR spectroscopic data show that this structure is maintained in solution for **4a**, and that the structures of **3a–c** and **4b,c** are similar. The selenium atoms are inequivalent and give rise to two signals in the  $^{77}\text{Se}$  NMR spectrum, each of which shows a small splitting ( $J = 9$  Hz) due to coupling to the phosphorus atom in the *cis* position. As expected, each atom in the two alicyclic rings gives a separate  $^{13}\text{C}$  resonance.

The complexes **3a–c** and **4a–c** may be expected to resemble diselenolenes and dithiolenes in having delocalised metal–ligand bonding. We therefore anticipate rich and varied chemical and physical behaviour for these compounds and their derivatives.

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## Notes and References

† E-mail: c.p.morley@swan.ac.uk

‡ **Synthesis of 4b**: a mixture of **1b** (0.19 g, 1.01 mmol), **2-dba** (0.28 g, 0.24 mmol) and  $\text{PBu}^n_3$  (0.10 g, 0.50 mmol) in toluene (100 cm<sup>3</sup>) was heated under reflux for 1 h under an N<sub>2</sub> atmosphere. The solvent was removed by evaporation under reduced pressure and the residue chromatographed on alumina. The product was eluted with a mixture of hexane and toluene (1 : 2) as a bright purple band. It was purified by recrystallization from hexane. Yield: 0.17 g (53%). Mp 146 °C.  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>),  $\delta$  3.13 (m, 2 H), 3.05 (m, 2 H), 2.88 (m, 2 H), 2.71 (m, 2 H), 1.93 (m, 8 H), 1.84 (m, 2 H), 1.72 (m, 4 H), 1.50 (m, 8 H), 1.43 (m, 6 H), 0.91 (t, 9 H);  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>),  $\delta$  157.3, 144.1, 141.9, 131.3, 36.9, 35.9, 34.7, 30.4, 26.3, 25.6, 25.2 [ $J(^{13}\text{C}-^{31}\text{P})$  29 Hz], 24.8, 24.2 [ $J(^{13}\text{C}-^{31}\text{P})$  14 Hz], 24.0, 22.7, 13.7;  $^{31}\text{P}$  NMR (101 MHz, CDCl<sub>3</sub>, external 85% H<sub>3</sub>PO<sub>4</sub>),  $\delta$  13.70;  $^{77}\text{Se}$  NMR (47.7 MHz, CDCl<sub>3</sub>, external SeMe<sub>2</sub>),  $\delta$  548 [ $J(^{77}\text{Se}-^{31}\text{P})$  9 Hz], 366 [ $J(^{77}\text{Se}-^{31}\text{P})$  9 Hz]; IR (KBr disk), 2929vs, 2857s, 1578m, 1479m, 1450m, 1405m, 1359m, 1307w, 1262m, 1091vs, 1050s, 904m, 802s, 720w cm<sup>-1</sup>; UV–VIS (hexane):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 570 (6000), 480 (5000), 295 (13 000), 250 (29 000), 220 (12 000); MS (FAB):  $m/z$  (%) 656 (74) [M<sup>+</sup>], 203 (100) [PBu<sup>n</sup><sub>3</sub>].

§ **Crystal data for 4b**: C<sub>24</sub>H<sub>43</sub>N<sub>2</sub>PPdSe<sub>2</sub>;  $M = 654.90$ ; crystal size 0.05 × 0.50 × 0.70 mm, triclinic, space group  $P\bar{1}$  (no. 2);  $a = 9.930(2)$ ,  $b = 12.044(3)$ ,  $c = 13.277(3)$  Å,  $\alpha = 63.43(2)$ ,  $\beta = 83.55(2)$ ,  $\gamma = 81.16(2)^\circ$ ,  $U = 1401.6(6)$  Å<sup>3</sup> (by least squares refinement on setting angles of 24 reflections,  $Z = 2$ ),  $F(000) = 660$ ,  $D_c = 1.552 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 3.33 \text{ mm}^{-1}$ . Data collection (Enraf-Nonius CAD4, graphite-monochromated Mo-K $\alpha$  radiation,  $\lambda = 0.71069$  Å,  $T = 295$  K),  $\omega$ - $2\theta$  scans,  $2.5 < \theta < 25^\circ$ . 4956 measured reflections ( $\pm h, \pm k, +l$ ), 4923 unique. Structure solution by direct methods, with SIR,<sup>9</sup> and heavy atom procedures with SHELXL-93.<sup>10</sup> Empirical absorption correction ( $\psi$  scan; min., max. correction factors 0.66, 1.00). Final refinement cycles performed against  $F^2$  with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions. Refinement on 274 variables converged at  $R_1 = 0.052$  (based on 2936 reflections with  $F_o > 4\sigma F_o$ ),  $R_1 = 0.110$  (on all reflections),  $wR_2 = 0.139$ , GOF = 1.021. Max., min. peaks in the final difference map = 0.54,  $-0.53 \text{ e} \text{ \AA}^{-3}$ . CCDC 182/872.

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