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FULL PAPER

Dinuclear diselenolenes derived from cycloalkeno-1,2,3-selenadiazoles and tetrakis(triphenylphosphine)palladium

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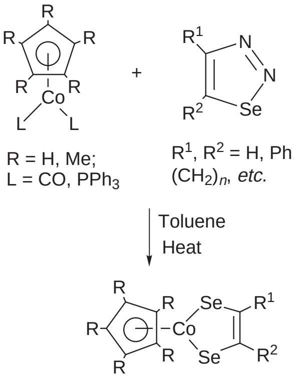
Reaction of [Pd(PPh$_3$)$_4$] with cycloalkeno-1,2,3-selenadiazoles or bis(cycloalkeno)-1,4-diselenines in toluene under reflux led in good yield to the dinuclear diselenolenes [Pd$_2${SeC(R^1)=C(R^2)Se}$_2$(PPh$_3$)$_2$] [R^1,R^2 = (CH$_2$)$_n$; n = 4, 5, 6] which have been characterised by microanalysis, multinuclear NMR, IR, and mass spectroscopy; the molecular structure of the compound with n = 6 has been determined by X-ray cystallography.

Transition metal dithiolenes have attracted considerable attention over the past thirty years, as a result of their potentially useful electrochemical and optical properties.[1] Possible areas of application include molecular electronics, infrared dyes, liquid crystals and catalysis.[2–4] By contrast, studies of the selenium analogues of dithiolenes (diselenolenes) have been rare.[5–9] This is largely because of the absence of generally applicable synthetic methods. Diselenolenes are, however, attractive synthetic targets since replacement of sulfur by selenium should lead to a decrease in the HOMO–LUMO gap, and the enhancement of intermolecular interactions in the solid state.

The reactions of 1,2,3-selenadiazoles with low-valent transition metal compounds have previously been used, by us[10] and others,[11] to prepare a wide variety of selenium-containing complexes. In particular we have shown that cyclopentadienylcobalt diselenolenes may be produced by this route [eqn. (1)].[12]



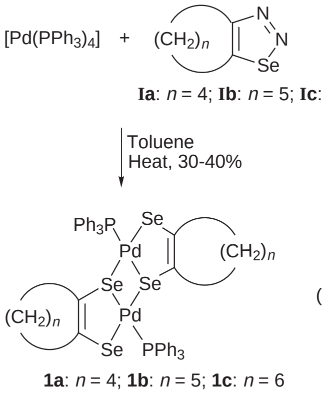
(1)

We now present the results of a study of the reactions of 1,2,3-selenadiazoles with the bis(triphenylphosphine)palladium(0) moiety, which is isolobal with cyclopentadienylcobalt(I).[13]

Results and discussion

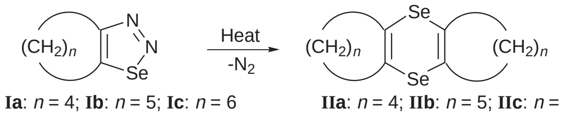
A toluene solution containing [Pd(PPh$_3$)$_4$] and an excess of one of the cycloalkeno-1,2,3-selenadiazoles **Ia**–**Ic** darkens rapidly on heating to reflux. Subsequent column chromatography leads to isolation of the air-stable dark green compounds **1a**–**1c** [eqn. (2)].

By following the course of the reaction by ^{31}P NMR spectroscopy, we have established that the only phosphorus-containing compounds present in significant concentration at any stage are the starting material, the final product and free triphenylphosphine: no long-lived intermediate appears to be formed.



(2)

We believe the first step of the mechanism to be the decomposition of the 1,2,3-selenadiazole to form a 1,4-diselenine **IIa**–**IIc** [eqn. (3)]. This conversion is normally accomplished by heating the 1,2,3-selenadiazole to 140 °C under reduced pressure.[14] We therefore assume that it is catalysed by Pd^0 in this case. Support for our hypothesis comes from the observation that compounds **1a**–**1c** are formed in slightly higher yield, if, in place of the 1,2,3-selenadiazoles, the analogous 1,4-diselenines **IIa**–**IIc** are themselves treated with [Pd(PPh$_3$)$_4$] [eqn. (4)]. The detailed mechanism of this reaction remains unclear but we



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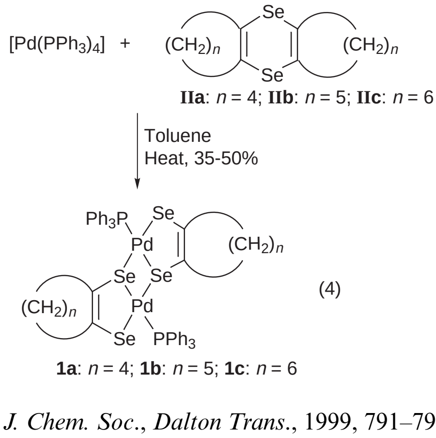


(4)

Table 1 Selected bond lengths (Å) and angles (°) in the structure of $[Pd_2\{SeC(R^1)=C(R^2)Se\}_2(PPh_3)_2]\cdot C_6H_5Me[R^1,R^2 = (CH_2)_6]$

Pd(1)–P(1)	2.293(8)	Pd(2)–P(2)	2.281(8)
Pd(1)–Se(2)	2.387(4)	Pd(2)–Se(4)	2.382(4)
Pd(1)–Se(1)	2.413(4)	Pd(2)–Se(3)	2.419(4)
Pd(1)–Se(3)	2.489(4)	Pd(2)–Se(1)	2.481(4)
Pd(1) · · · Pd(2)	3.078(3)		
Se(2)–Pd(1)–P(1)	93.6(2)	Se(4)–Pd(2)–P(2)	92.3(2)
P(1)–Pd(1)–Se(3)	101.3(2)	P(2)–Pd(2)–Se(1)	102.5(2)
Se(3)–Pd(1)–Se(1)	77.73(12)	Se(1)–Pd(2)–Se(3)	77.77(12)
Se(1)–Pd(1)–Se(2)	87.59(12)	Se(3)–Pd(1)–Se(4)	87.88(12)
Pd(1)–Se(1)–Pd(2)	77.92(12)	Pd(1)–Se(3)–Pd(2)	77.65(11)

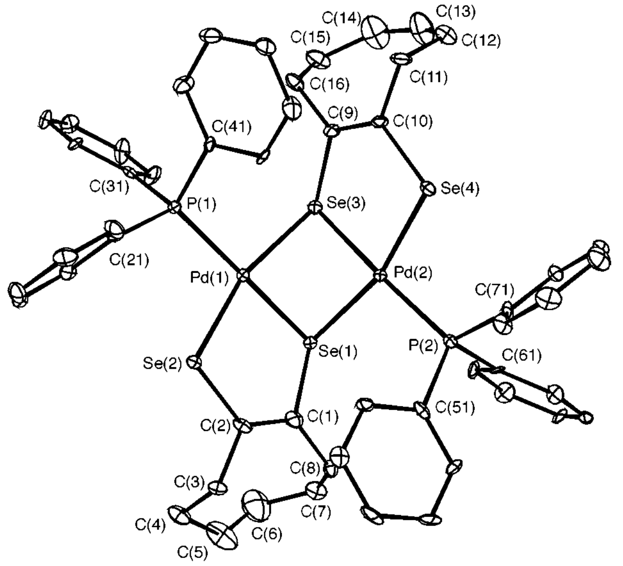
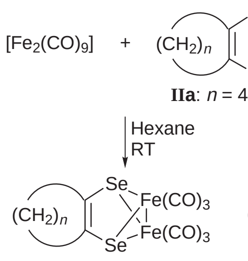


Fig. 1 Molecular structure of $[Pd_2\{SeC(R^1)=C(R^2)Se\}_2(PPh_3)_2]$ $[R^1,R^2 = (CH_2)_6]$ **1c**.

have observed C–Se bond cleavage in the reactions of 1,4-diselenines before.[15] The formation of diiron diselenolates from 1,4-diselenines and $[Fe_2(CO)_9]$ has also been previously reported [eqn. (5)].[16] By comparison, the reaction of $[Pt(PPh_3)_4]$ with 1,2,3-selenadiazoles takes a different course, to yield in at least one case a selenaketocarbene complex [eqn. (6)].[17]



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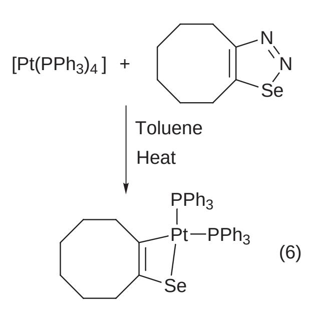


(6)

The crystal structure of the toluene solvate of complex **1c** has been determined by X-ray diffraction (Fig. 1). Selected bond lengths and angles are listed in Table 1. The data are not good enough to justify detailed discussion of the molecular parameters, but the positions of the heavy atoms are relatively well defined. Each palladium atom is approximately square planar co-ordinated; the maximum deviation from the least squares plane passing through the palladium atom and its four nearest neighbours is *ca.* 0.2 Å. In contrast to the situation in $[Pd_2(\eta^3\text{-}C_3H_5)_2\{Ph_2P(O)NP(Se)Ph_2\text{-}Se\}_2]$, where the Pd_2Se_2 core is planar,[18] there is a relatively acute angle between the two square planes [75.6(1)°]. This brings the two palladium atoms closer (3.078 Å) than the sum of the van der Waals radii (3.26 Å[19]). There is, however, no evidence for any significant interaction between them. Similar instances of short non-bonding Pd–Pd contacts have recently been noted.[20] There is also considerable distortion of the co-ordination geometry, imposed by the geometric constraints of the bridging ligands. The Pd–Se bond lengths in the Pd_2Se_2 unit are not equal (average: 2.485, 2.416 Å), each selenium being closer to the palladium to which it is chelating. Both distances are, however, within the range of previous observed values: *cf.* 2.409 Å (average) in $[NMe_4][Pd(C_3S_3Se_2)_2]_2$[6c] and 2.401, 2.419 Å in $[Pd\{SeC(R^1)=C(R^2)Se\}(PBu_3)_2]$ $[R^1,R^2 = (CH_2)_5]$.[21] The Se–Pd–Se angles in the bridge are also far less than 90° (average: 77.7°).

Table 2 NMR Spectroscopic data[a] (δ) for complexes **1a**–**1c**

		1a	**1b**	**1c**
^1H	*m*-H of C_6H_5	7.65–7.60	7.64–7.59	7.61–7.56
	o-, *p*- 2H of C_6H_5	7.37–7.34	7.39–7.29	7.33–7.26
	$(CH_2)_n$	1.86–0.58	1.94–0.67	1.76–0.82
^{13}C	$(CH_2)_n$	21.52	26.43	25.75
		21.95	26.79	26.40
		34.64	32.83	29.55
		37.03	38.89	30.41
			42.63	35.14
				39.69
	C=C	119.91	123.93	122.10
		144.36	150.13	148.55[b]
	C_6H_5	127.99	128.18	127.89
		130.35	130.44	130.19
		131.67[c]	131.71[c]	131.30[c]
		134.93	135.12	134.91
^{31}P	$P(C_6H_5)_3$	30.4	30.7	30.4
^{77}Se	terminal	559.8[d]	576.1[d]	575.7[d]
	bridging	408.8[e]	422.2[e]	386.5[e]

[a] In $CDCl_3$ solution. [b] $J(^{13}C\text{-}^{31}P) = 13.7$ Hz (resolved for **1c** only). [c] $J(^{13}C\text{-}^{31}P) = 45.7$ (**1a**), 45.2 (**1b**), 45.5 Hz (**1c**). [d] $J(^{77}Se\text{-}^{31}P) = 30$ Hz (**1a**, **1b** and **1c**). [e] $J(^{77}Se\text{-}^{31}P) = 110, \approx 11$ (**1a**); 107, 15 (**1b**); 111, 15 Hz (**1c**).

That the dimeric structure demonstrated in the solid state for complex **1c** is retained in solution by all of **1a**–**1c** has been confirmed by multinuclear NMR spectroscopy (Table 2). The ^{77}Se NMR spectra contain two resonances, corresponding to the bridging and terminal selenium environments. The first of these shows coupling to two magnetically inequivalent phosphorus nuclei: a large coupling of *ca.* 110 Hz to the *trans*-phosphorus, and a small coupling of *ca.* 15 Hz to the phosphorus in the *cis* position. The second ^{77}Se resonance shows only a *cis* coupling ($^2J \approx 30$ Hz). Analogous features are present in the satellite structure of the single ^{31}P resonance (Fig. 2), analysis of which yields $^4J(^{31}P\text{–}^{31}P) = 7.7$ Hz. The ^{13}C NMR spectra contain resonances for each carbon atom in the alicyclic ring, confirming that the diselenolate ligands are asymmetrically bound to the $Pd_2(PPh_3)_2$ unit.

The microanalytical and mass spectroscopic data are in accord with the proposed formulations (Table 3). In the mass spectra the stability of the dimeric structure is apparent from the intensity of the molecular ion, and of the fragments derived from it by loss of triphenylphosphine. To our knowledge **1a**–**1c** are the first dinuclear diselenolenes to be described. Complexes

Table 3 Microanalytical, infrared and mass spectroscopic data for complexes **1a**–**1c**

	1a	**1b**	**1c**
Yield[a] (%)	44.9	33.1	46.2
Mp/°C	183–184	202–203	285–287
Microanalysis			
C (%)	46.57 (47.51)	49.10 (48.37)	51.37 (52.04)[b]
H (%)	3.65 (3.82)	4.33 (4.06)	4.84 (4.59)[b]
Mass spectrum[c] *m/z* (%)			
M^+	1216 (100)	1244 (76)	1272 (78)
$M^+ - PPh_3$	954 (52)	982 (100)	1010 (100)
Infrared[d]			
(cm^{-1})	3048m	3048m	3052m
	2932vs	2924vs	2918vs
	2850s	2856s	2844s
	1597m	1598m	1586m
	1478m	1478m	1480m
	1433s	1434s	1435s
	1094s	1093s	1095s
	747, 731s	746s	744s
	694vs	692vs	693vs
	527vs	524vs	527vs
	514s	513s	512s
	496m	496m	495m

[a] From diselenine. [b] Calculated figures are for toluene solvate. [c] Recorded using FAB; figures are for isotopomers containing ^{80}Se, ^{106}Pd. [d] Recorded as KBr disks; selected bands only.

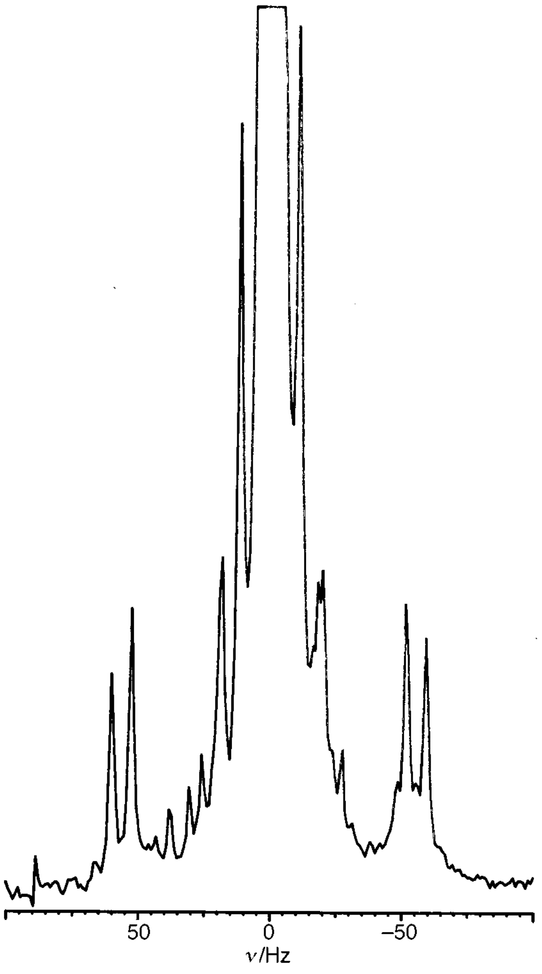
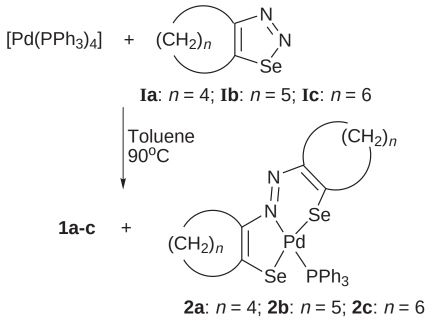


Fig. 2 Satellite structure of the ^{31}P NMR resonance for complex **1c**. Analysis of the data gives $^2J(^{31}P–^{77}Se) = 111.3$, 15.2; $^4J(^{31}P–^{31}P) = 7.7$ Hz. The lines at ±11.2 Hz have enhanced intensity due to coincidence between satellites arising from coupling to ^{77}Se and ^{13}C.

with bridging unsaturated dithiolate ligands are known,[22] but here too examples containing palladium do not appear to have been reported.

It is interesting that complexes **1a**–**1c** are formed in preference to mononuclear diselenolenes containing two molecules of triphenylphosphine, despite the presence of free phosphine in solution. Palladium dithiolenes and diselenolenes with monodentate ancillary ligands appear to be unknown in the literature, although we have recently prepared the complexes $[Pd\{SeC(R^1)=C(R^2)Se\}(PBu_3)_2]$ $[R^1,R^2 = (CH_2)_n;\ n = 4, 5, 6.]$[21] The corresponding platinum species are well established,[8,23] so it would appear that the greater lability of palladium(II) complexes is partly responsible for this behaviour.

If the reaction between $[Pd(PPh_3)_4]$ and one of the 1,2,3-selenadiazoles **Ia**–**Ic** is carried out at slightly lower temperatures, traces of the azo-compounds **2a**–**2c** are produced [eqn. (7)]. One of these (**2a**) has been obtained in sufficient quantity and purity to be characterised by NMR and mass spectroscopy. Compounds **2a**–**2c** are analogous to the products formed when trialkylphosphinepalladium(0) complexes are used in place of $[Pd(PPh_3)_4]$.[24] It should be noted, however, that in this case no dinuclear diselenolenes are formed from **Ia**–**Ic**. This we ascribe to the greater basicity of the trialkylphosphine, allowing oxidative addition to the Se–N bond to compete successfully with loss of N_2 from the 1,2,3-selenadiazole.



(7)

Experimental

All reactions were performed using standard Schlenk techniques and pre-dried solvents under an atmosphere of dinitrogen. ^1H and ^{13}C NMR spectra: Bruker AC400; tetramethylsilane as internal standard. ^{31}P and ^{77}Se NMR spectra: Bruker WM250; 85% phosphoric acid or dimethyl selenide as external standard. IR spectra: Perkin-Elmer 1725X. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using fast atom bombardment (FAB).

Cycloalkeno-1,2,3-selenadiazoles **Ia**–**Ic**,[14] tetrakis(triphenylphosphine)palladium[25] and bis(cycloalkeno)-1,4-diselenines **IIa**–**IIc**[14] were prepared by literature methods.

Synthesis of palladium diselenolenes (1a–1c)

In a typical experiment a solution containing tetrakis(triphenylphosphine)palladium (0.30 g, 0.26 mmol) and cyclohexeno-1,2,3-selenadiazole, **Ia** (0.20 g, 1.06 mmol) in toluene (100 cm^3) was heated under reflux for 1 h. After this time the solution had darkened considerably. Removal of the solvent under reduced pressure left an intensely coloured oily solid, which was purified by column chromatography on alumina using a 2:1 mixture of toluene and hexane. Collection of the dark green band and recrystallisation from hexane gave **1a** as an analytically pure solid.

The same product was obtained in slightly higher yield by the use of bis(cyclohexeno)-1,4-diselenine, **IIa**, in place of **Ia**. Compounds **1b** and **1c** were prepared by an analogous procedure using the corresponding 1,2,3-selenadiazole or

1,4-diselenine. Yields, spectroscopic and analytical data are summarised in Tables 2 and 3.

By conducting the reaction of $[Pd(PPh_3)_4]$ with **Ia** at a lower temperature (*ca.* 90 °C) the by-product **2a** could be isolated. This eluted as a deep purple band just before the dark green band corresponding to **1a**. **4a**: mp 196–197 °C; ^{1}H NMR δ 7.69 (m, 6 H), 7.48–7.40 (m, 9 H), 3.07 (m, 2 H), 2.98 (m, 2 H), 2.75 (m, 4 H), 1.93 (m, 2 H) and 1.78–1.70 (m, 6 H); ^{13}C NMR δ 164.2, 157.8, 143.9, 143.0 [$J(^{13}\mathrm{C}–^{31}\mathrm{P})$ 6], 134.9 [$J(^{13}\mathrm{C}–^{31}\mathrm{P})$ 12], 130.9, 130.8 [$J(^{13}\mathrm{C}–^{31}\mathrm{P})$ 51] and 128.0 [$J(^{13}\mathrm{C}–^{31}\mathrm{P})$ 11 Hz]; ^{31}P NMR δ 30.4; ^{77}Se NMR δ 604 [$J(^{77}\mathrm{Se}–^{31}\mathrm{P})$ 25] and 432 [$J(^{77}\mathrm{Se}–^{31}\mathrm{P})$ 24]; MS *m*/*z* 715 (M^+).

X-Ray crystallography

Crystal data. $C_{59}H_{62}P_2Pd_2Se_4$ **1c**, $M = 1361.66$, crystal size $0.15 \times 0.30 \times 0.50$ mm, monoclinic, space group $P2_1/n$ (alternative setting of no. 14), $a = 12.614(4)$, $b = 22.037(15)$, $c = 21.567(4)$ Å, $\beta = 92.79(2)°$, $U = 5988(5)$ Å^3 (by least squares refinement on setting angles of 24 reflections, $Z = 4$), $F(000) = 2696$, $D_c = 1.510$ g cm^{-3}, μ(Mo-Kα) = 3.12 mm^{-1}. Data collection (Enraf-Nonius CAD4, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $T = 295$ K), ω–2θ scans, $2.5 < \theta < 22°$, 6784 measured reflections ($\pm h$, $+k$, $+l$), 6334 unique. Structure solution by direct methods, with SIR,[26] and heavy-atom procedures with SHELXL 93.[27] Empirical absorption correction (ψ scan; minimum, maximum correction factors 0.84, 1.00). Final refinement cycles performed against F^2 with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions. Refinement on 521 variables converged at $R1 = 0.082$ (based on 2978 reflections with $F_o > 4(F_o)$, $R1 = 0.221$ (on all reflections), $wR2 = 0.399$, goodness of fit = 1.415. Maximum, minimum peaks in the final difference map = 1.23, −0.99 e Å^{-3}.

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