

# Synthesis of phosphorus- and selenium-containing macrocycles and their complexation with Pd(II)Cl<sub>2</sub>

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A one-pot reaction was developed to synthesize phosphorus- and selenium-containing macrocycles starting from selenium *via* reduction with KBH<sub>4</sub>, treatment with bis[*o*-(bromomethyl)phenyl]phenylphosphine oxide **1** and reduction with KBH<sub>4</sub> followed by the addition of an appropriate dibromide. Thus, ten- to seventeen-membered macrocycles **3** having one phosphorus and two selenium atoms were synthesized. In this synthesis an eight-membered heterocycle **4** was also obtained. In addition, the condensation of compound **1** with selenium-containing diols **7** and **8** in the presence of sodium *tert*-butoxide gave macrocyclic ligands **9** and **10**, respectively. Reaction of these macrocycles with palladium(II) chloride gave 1 : 1 complexes, except **9** which gave a 2 : 1 complex. The molecular structures of the macrocycles **3c**, **3f** and **10** as well as the 2 : 1 palladium(II) complex **21** of related 2-(*p*-methylphenoxy)-2-oxo-1,3,6,2-dioxaselenaphosphocane **20** have been established by X-ray diffraction.

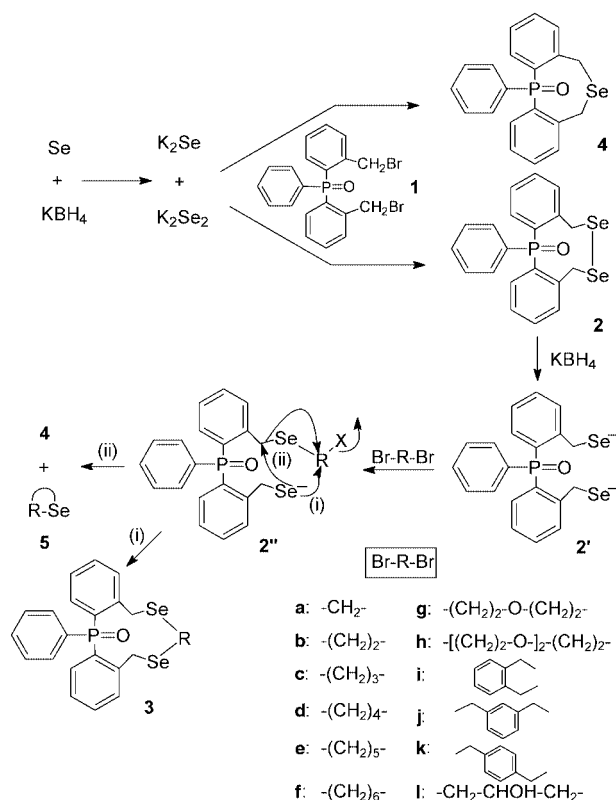
The chemistry of phosphorus-containing macrocycles as well as that of selenium-containing macrocycles has attracted great attention in recent years.<sup>1–4</sup> To the best of our knowledge, the simultaneous introduction of phosphorus and selenium atoms into the ring system of macrocycles has not been reported. Phosphine oxides have been demonstrated to serve as strong hydrogen-bond acceptors and good ligands for alkali,<sup>5</sup> alkaline-earth<sup>6</sup> and actinide<sup>7</sup> metal salts and selenium-containing macrocycles<sup>4</sup> exhibit excellent ligands for transition metals owing to the low electronegativity of selenium. Thus macrocycles incorporating a hard phosphine oxide group and soft selenium atoms into the ring system may act as potential heterodinucleating macrocyclic ligands, which will be used for future studies of bimetallic catalysis and formation of supramolecular systems.<sup>8,9</sup>

In our preliminary work, we have reported the synthesis of medium-sized heterocycles incorporating a phosphoryl group and a selenium atom in the ring.<sup>10</sup> Here, we report the synthesis of a series of macrocycles incorporating a phosphine oxide group and selenium atoms into the cycle. Complexation of these macrocycles with palladium chloride as well as the X-ray structure determination of macrocycles **3c**, **3f**, **10** and a related palladium complex **21** has also been investigated.

## Results and discussion

### Synthesis of the P- and Se-containing macrocycles

A facile synthetic method for a series of macrocycles containing a phosphine oxide group and selenium atoms was developed. Macrocycles **3a**, **3c**–**3l** were obtained by a one-pot reaction as shown in Scheme 1. Pulverized selenium metal was reduced with potassium borohydride in absolute alcohol to produce potassium diselenide which reacted with bis[*o*-(bromomethyl)phenyl]phenylphosphine oxide **1** to give an intermediate, 13-phenyl-7,13-dihydro-5*H*-13 $\lambda^5$ -dibenzo[*d,g*][1,2,6]diselenaphosphonin-13-one **2**. Without isolating **2**, the mixture was treated with potassium borohydride and sodium hydroxide to form a diselenide anion (**2'**), which was allowed to react with various  $\alpha,\omega$ -dibromides (Br–R–Br) to give macrocycles **3** *via* an intermediate **2''**. The yield of this one-pot reaction was moderate as shown in Table 1. In every case a side product, 12-phenyl-7,12-dihydro-5*H*-12 $\lambda^5$ -dibenzo[*c,f*][1,5]selenaphosphocin-12-one



Scheme 1

Table 1 Yields (%) of compounds **3a**–**k** and **4** <sup>a</sup>

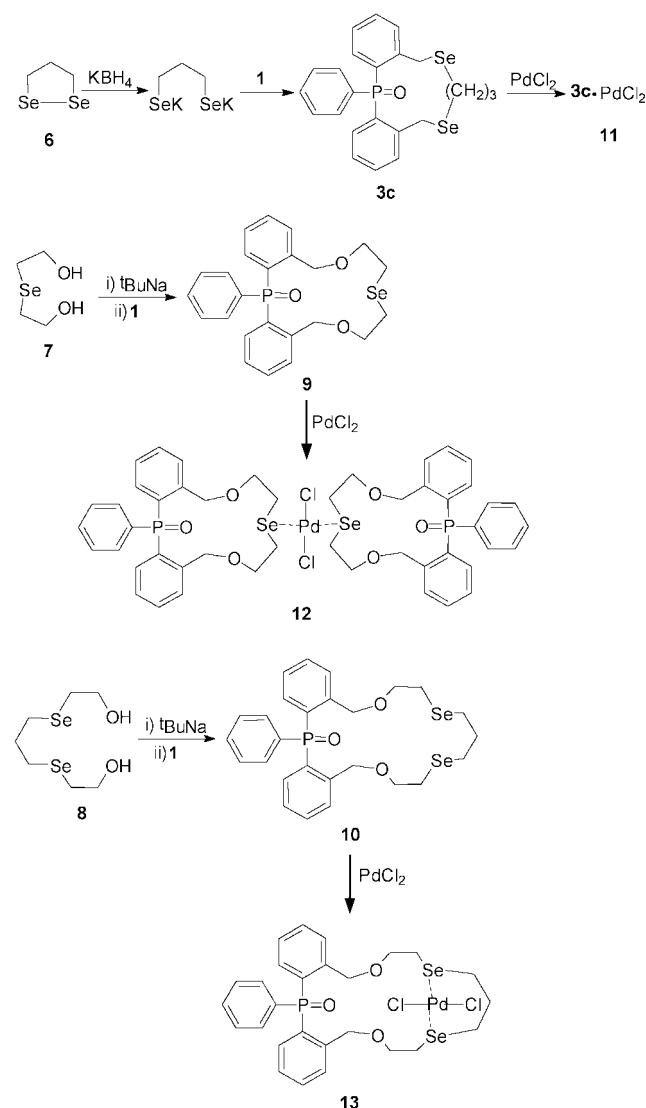
	a	b	c	d	e	f	g	h	i	j	k	l
<b>3</b>	24	0	22	25	12	19	30	21	25.6	16	35	15
<b>4</b>	nd	nd	nd	23	44	33	37	7.3	8.6	14	nd	nd

<sup>a</sup> nd: not determined.

**4** was inevitably formed (Table 1). The formation of heterocycle **4** might occur along either of two routes (Scheme 1): one involving the reaction of **1** with potassium selenide which was formed

together with potassium diselenide, and the other involving the elimination reaction of a selenium atom from an intermediate monoanion **2'** with the simultaneous formation of cyclic selenide **5**. The former route is supported by the fact that **4** was isolated as one of the products when the reaction was interrupted before the  $\text{KBH}_4$  reduction of **2**. The proof for the latter is that, when 1,2-dibromoethane was used for the attempted synthesis of **3b** ( $\text{R} = -\text{CH}_2\text{CH}_2-$ ), no **3b** was obtained but instead the production of **4** was observed with the deposition of red selenium metal which resulted from the decomposition of unstable ethylene selenide. A similar phenomenon has been reported by Batchelor *et al.*<sup>11</sup>

An alternative synthesis of **3c** was carried out by the reduction of 1,2-diselenacyclopentane **6** with potassium borohydride followed by the condensation of the resulting potassium diselenide with **1** in 27% yield (Scheme 2). Two related macro-

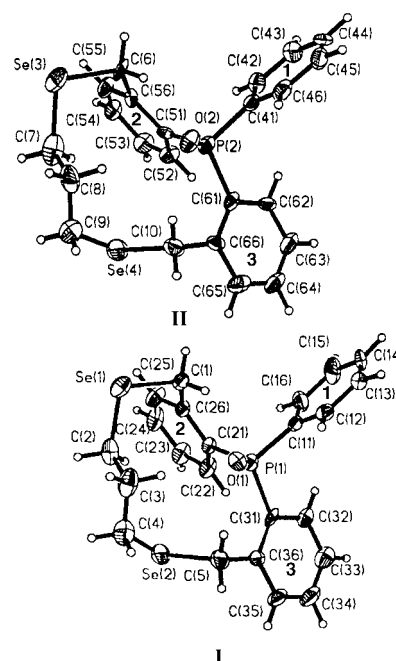


Scheme 2

cycles **9** and **10** containing two ethereal oxygen atoms in the cycle (Scheme 2) were also synthesized by the condensation of **1** with 3-selenapentane-1,5-diol **7** and 3,7-diselenanonan-1,9-diol **8** in the presence of sodium *tert*-butoxide in yields of 26% and 22%, respectively.

### Spectral properties of the macrocycles

All the macrolides **3a**, **3c–3l**, **4**, **9** and **10** were characterized by their elemental analyses and IR,  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR and mass spectral measurements. IR absorption bands appear at 1170–

Fig. 1 The ORTEP plot (30% probability level) for macrocycle **3c**.

1185  $\text{cm}^{-1}$  for  $\text{P}=\text{O}$ , 1431–1433  $\text{cm}^{-1}$  for  $\text{P}-\text{Ph}$  and at 570–580  $\text{cm}^{-1}$  and 529–541  $\text{cm}^{-1}$  for  $\text{C}-\text{Se}$ . The  $^1\text{H}$  NMR spectra exhibit two doublets characteristic of two equivalent  $\text{ArCH}_2$  groups at  $\delta$  3.50–5.50 ppm with  $\Delta\delta$  of about 1.0 ppm and the geminal coupling constant of about 12 Hz. The eight-membered compound **4** showed two AB quartets of two nonequivalent  $\text{ArCH}_2$  due to the restricted rotation of the three benzene rings on the phosphorus atom. A  $^{31}\text{P}$  NMR signal appears between  $\delta$  34.7 and 37.4 ppm as a singlet for macrocycles **3**, **9** and **10** except **3l** which has two singlets at 37.40 and 36.95 ppm due to the existence of a *cis-trans* equilibrium between the  $\text{P}=\text{O}$  and  $\text{CH}-\text{OH}$  group. On the other hand, the  $^{31}\text{P}$  NMR signal of **4** appears upfield at  $\delta$  27.54 ppm, which could be ascribed to the increase of ring strain. The electron impact mass spectra of these macrocycles **3**, **4**, **9** and **10** exhibited a molecular ion isotopic cluster as expected, among which the molecular ion peak calculated as  $^{80}\text{Se}$  was highest.

### X-Ray crystallographic analysis of macrolides **3c**, **3f** and **10**

The structures of **3c**, **3f** and **10** were finally established by X-ray crystallographic analyses (Table 2). Fig. 1 shows the molecular structure of **3c** in which the phosphoryl  $\text{P}=\text{O}$  bond is directed upwards to the inside of the macrocyclic ring. The unit cell contains four sets of two independent molecules (**I** and **II**) which cannot be transformed into one another by either a symmetrical or translational operation. There are no significant differences in the bonding parameters between **I** and **II**. The selected bond lengths and bond angles are listed in Table 3 and Table 4. The only difference between the two molecules is seen in the dihedral angles between the benzene ring planes, which are given in Table 5.

The molecular structures of **3f** and **10** are shown in Fig. 2 and Fig. 3, respectively. The geometrical arrangements of the triphenylphosphine oxide group in **3f** and **10** are similar to that of **3c**, so that the phosphoryl  $\text{P}=\text{O}$  bond is directed upwards to the inside of the macrocyclic ring. Table 5 also shows the dihedral angles between the three benzene ring planes in the crystals of **3f** and **10**.

### Complexation of the macrolides with palladium(II) chloride

Two solvent systems were used for the preparation of palladium chloride complexes of the macrolides. (1) Method A. Complexes **11**, **12**, **13** and **21** were prepared in 26, 48, 86 and 99%

**Table 2** X-Ray data collection parameters for compounds **3c**, **3f**, **10** and **21**

Macrocycle	<b>3c</b>	<b>3f</b>	<b>10<sup>a</sup></b>	<b>21</b>
Chemical formula	C <sub>23</sub> H <sub>23</sub> OPSe <sub>2</sub>	C <sub>26</sub> H <sub>26</sub> OPSe <sub>2</sub>	C <sub>27</sub> H <sub>31</sub> O <sub>3</sub> PSe <sub>2</sub>	C <sub>22</sub> H <sub>30</sub> Cl <sub>2</sub> O <sub>10</sub> P <sub>2</sub> PdSe <sub>2</sub>
Formula Weight	504.30	546.38	592.44	819.26
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 1̄ (No. 2)	<i>Pbca</i> (No. 61)	<i>P</i> 1̄ (No. 2)
$\mu/\text{mm}^{-1}$	3.600	3.153	2.9127	3.499
<i>R</i>	0.1628	0.1133	0.083	0.0838
<i>R<sub>w</sub></i>	0.1876	0.1913	0.088	0.1774
<i>a</i> /Å	13.524(3)	8.294(2)	16.012(3)	7.655(2)
<i>b</i> /Å	22.784(5)	8.305(2)	17.047(3)	15.047(3)
<i>c</i> /Å	14.838(3)	18.438(4)	18.176(4)	20.023(4)
<i>a</i> /deg	90.00(0)	100.38(3)	90.00(0)	72.73(3)
<i>β</i> /deg	112.98(3)	96.14(3)	90.00(0)	83.49(3)
<i>γ</i> /deg	90.00(0)	102.78(3)	90.00(0)	80.64(3)
<i>V</i> /Å <sup>3</sup>	4209(2)	1204(1)	4961(1)	2168(1)
<i>T</i> /K	293(2)	293(2)	298(1)	293(2)
<i>Z</i>	8	2	8	3
Measured/ independent reflections	5930/5680 [ <i>R</i> <sub>int</sub> = 0.0859]	4156/4015 [ <i>R</i> <sub>int</sub> = 0.0452]	4967/3516	6040/5836 [ <i>R</i> <sub>int</sub> = 0.0854]

<sup>a</sup> Refinement on *F*.**Table 3** The selected bond lengths of macrocycle **3c** (Å)

Se(1)–C(1)	2.002(16)	Se(3)–C(6)	1.983(15)
Se(1)–C(2)	1.929(17)	Se(3)–C(7)	1.967(19)
Se(2)–C(4)	1.930(19)	Se(4)–C(9)	1.941(24)
Se(2)–C(5)	1.941(14)	Se(4)–C(10)	1.934(14)
P(1)–O(1)	1.478(8)	P(2)–O(2)	1.452(9)
P(1)–C(11)	1.786(14)	P(2)–C(41)	1.803(14)
P(1)–C(21)	1.830(11)	P(2)–C(51)	1.795(12)
P(1)–C(31)	1.819(14)	P(2)–C(61)	1.823(14)

**Table 4** The selected bond angles of macrocycle **3c** (°)

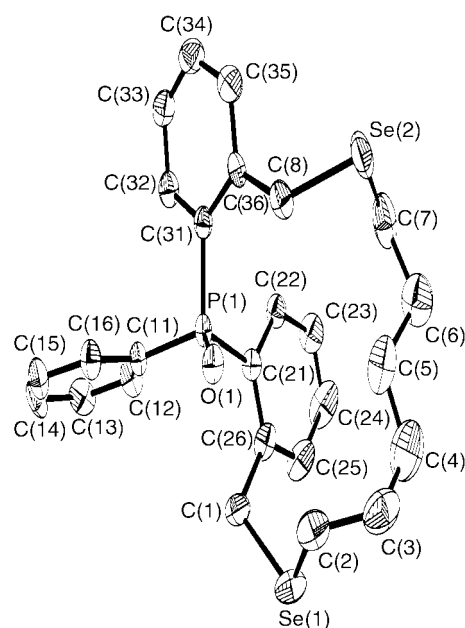
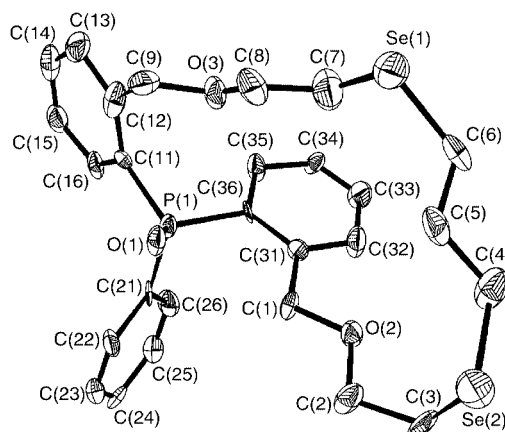
C(1)–Se(1)–C(2)	101.0(7)	C(6)–Se(3)–C(7)	100.2(7)
C(4)–Se(2)–C(5)	98.6(7)	C(9)–Se(4)–C(10)	98.3(8)
C(11)–P(1)–C(21)	103.7(6)	C(41)–P(2)–C(51)	103.6(6)
C(11)–P(1)–C(31)	107.2(7)	C(41)–P(2)–C(61)	105.8(7)
C(21)–P(1)–C(31)	108.9(5)	C(51)–P(2)–C(61)	107.2(5)

**Table 5** The dihedral angles between the benzene ring planes in the macrocycles **3c**, **3f** and **10** (°)

Molecule in crystal state	1 and 2	1 and 3	2 and 3
<b>3c(I)</b>	81.8	96.8	106.6
<b>3c(II)</b>	91.9	92.4	107.6
<b>3f</b>	79.0	85.0	92.3
<b>10</b>	107.1	91.6	84.5

yields, respectively, by heating a solution of palladium chloride and **3c**, **9**, **10** and **20** in 50 : 2 acetone–water for 26 h. (2) Method B. Complexes **14**, **15**, **16**, **17**, **18** and **19** were prepared in 83–95% yields by heating a solution of palladium chloride and **3d**, **3e**, **3f**, **3g**, **3j** and **3l**, respectively, in acetonitrile. Some properties of these palladium complexes are shown in Table 6. Except for **12** and **13**, the palladium complexes were so sparingly soluble in deuterated solvents that the NMR spectra were not measured. The elemental analyses indicated that the palladium complexes having two selenium atoms in the ring were 1 : 1 complexes, while complex **12** having one selenium atom was a 2 : 1 complex.

Although we were not successful in obtaining a single crystal for X-ray crystallography from any of these palladium complexes, we succeeded in obtaining a single crystal of the 2 : 1 palladium complex **21** of a related selenium-containing phosphocane **20** which was previously synthesized in our laboratory.<sup>10,12</sup> Fig. 4 shows (a) the molecular structure and (b) the crystal packing of complex **21**. In the unit cell, three

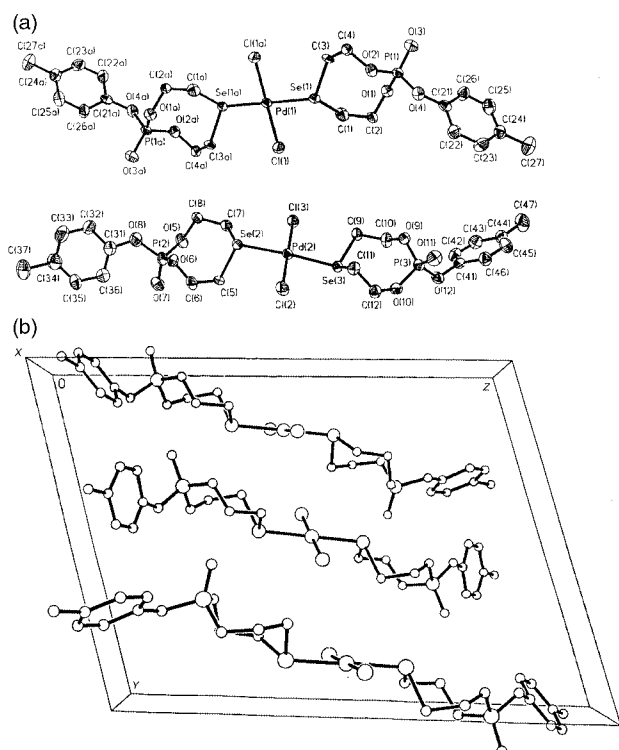
**Fig. 2** The ORTEP plot (30% probability level) for macrocycle **3f**.**Fig. 3** The ORTEP plot (30% probability level) for macrocycle **10**.

tetracoordinate palladium complexes are arranged in a centrosymmetric manner to form square planar structures. The central palladium atom is coordinated by two Pd–Se bonds and two Pd–Cl bonds with equal bond lengths of 2.442 and 2.289

**Table 6** Some properties of Pd(II)Cl<sub>2</sub> complexes

Parent macrocycle	Pd(II) complex	$\lambda_{\text{max}}$ /nm (solvent)	$\epsilon_{\text{max}}$ /dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup>	Ligand : Pd ratio
<b>3c</b>	<b>11</b>	325 (DMSO)	450	1 : 1
<b>9</b>	<b>12</b>	300 (CHCl <sub>3</sub> )	11 400	2 : 1
<b>10</b>	<b>13</b>	301 (CHCl <sub>3</sub> )	88 600	1 : 1
		405 (CHCl <sub>3</sub> )	16 300	
<b>3d</b>	<b>14</b>	nd <sup>a</sup>	nd <sup>a</sup>	1 : 1
<b>3e</b>	<b>15</b>	325 (CHCl <sub>3</sub> )	2470	1 : 1
<b>3f</b>	<b>16</b>	325 (DMSO)	2820	1 : 1
<b>3g</b>	<b>17</b>	327 (DMSO)	4720	1 : 1
<b>3k</b>	<b>18</b>	nd <sup>a</sup>	nd <sup>a</sup>	1 : 1
<b>3l</b>	<b>19</b>	327 (DMSO)	5300	1 : 1
<b>20</b>	<b>21</b>	325 (CHCl <sub>3</sub> )	10 100	2 : 1

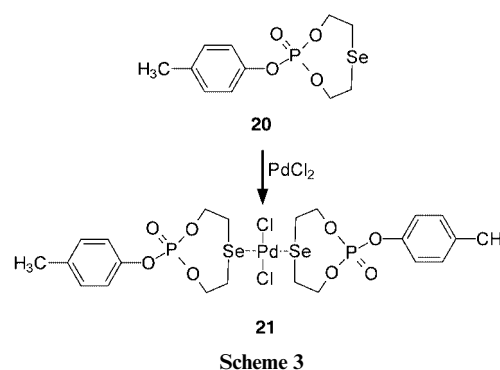
<sup>a</sup> nd: because of its low solubility, the UV spectrum of this compound was not determined.



**Fig. 4** (a) The ORTEP plot (30% probability level) for Pd complex **21** (b) The crystal packing of Pd complex **21**.

Å, respectively, and the Cl–Pd–Cl and Se–Pd–Se angles are both 180°. On the other hand, the outer two palladium atoms are coordinated by two Pd–Se bonds and two Pd–Cl bonds with different bond lengths of 2.434 and 2.429 Å (Pd–Se) and 2.291 and 2.284 Å (Pd–Cl), respectively, and the Cl–Pd–Cl and Se–Pd–Se angles are 179.5° and 174.9°, respectively.

We looked at the expected down-field shift of the resonance of the protons  $\alpha$  to the selenium atom occurring on the transformation of macrolides **20** and **9** into the 2 : 1 palladium complexes **21** and **12** (Scheme 3). The signals ( $\delta$  2.86 and 3.12 ppm) of the protons  $\alpha$  to the selenium atom for **20** are shifted 0.5–0.6 ppm to lower field ( $\delta$  3.50 and 3.60 ppm) for **21**, while those ( $\delta$  2.15 and 2.79 ppm) for **9** are shifted 0.6–0.7 ppm to lower field ( $\delta$  2.89 and 3.46 ppm) for **12**. This down-field shift resulted from the decrease of electron density on the selenium atom after complexation. It should be noted that only small down-field shifts (0–0.2 ppm) were observed for the protons  $\alpha$  to the oxygen atoms of **12** and **21**, indicating that no coordination of palladium(II) occurs on the oxygen atoms. Furthermore, complexes **12** and **21** had similar UV absorptions with  $\lambda_{\text{max}}$ /nm at 300 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 11 400) and 325 ( $\epsilon$  10 100), respectively. All the above facts indicate that the 2 : 1 palladium complex **12** has the same type of structure as **21**.



The same types of down-field shifts were observed in the cases of the 1 : 1 palladium complex **13**. Thus, the signals of the proton  $\alpha$  to the selenium atom in **10** ( $\delta$  2.45–2.27 ppm) are shifted 0.1–1.0 ppm to lower field ( $\delta$  3.49–2.37 ppm) for **13** suggesting the coordination of selenium atoms to palladium. On the other hand, the proton signals of Ar–CH<sub>2</sub>–O– at 4.50 and 5.30 ppm and of –O–CH<sub>2</sub>– at 3.68–3.61 ppm for **10** were shifted 0–0.2 ppm and 0.2–0.6 ppm, respectively, to lower field ( $\delta$  4.47–5.49 ppm and 3.75–4.25 ppm, respectively) for **13**. The down-field shift occurring with the –O–CH<sub>2</sub>– protons suggested that the partial coordination of palladium chloride to the ethereal oxygen atoms of **10** might occur. Further proof was obtained from the UV spectrum of **13** with  $\lambda_{\text{max}}$ /nm at 405 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 16 300) and 301 ( $\epsilon$  88 600), of which the former was absent in complex **12**. All other 1 : 1 palladium complexes **11**, **15**, **16**, **17** and **19** exhibit  $\lambda_{\text{max}}$  near 325 nm with relatively low  $\epsilon_{\text{max}}$  (Table 6), suggesting that they may have a similar type of structure.

## Experimental

All synthetic manipulations were carried out under a nitrogen atmosphere using the conventional Schlenk technique. Tetrahydrofuran (THF) was distilled from sodium–benzophenone immediately prior to use. Column chromatography and preparative TLC were carried out on silica gel (Qing Dao 300 and GF<sub>254</sub>, respectively). Melting points were measured with open capillaries and are uncorrected. IR spectra were recorded on a Bio-Rad FTS 3000 spectrometer. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker AC-P 200 spectrometer using SiMe<sub>4</sub> as internal standard and 85% phosphoric acid as external standard, respectively. Mass spectra were recorded at an ionizing voltage of 70 eV. Elemental analyses were performed on a Yanaco CHN CORDER MT-3 analyzer.

Bis[*o*-(bromomethyl)phenyl]phenylphosphine oxide **1**,<sup>13</sup> 1,2-diselenacyclopentane **6**,<sup>14</sup> 3-selenapentane-1,5-diol **7**,<sup>12</sup> 3,7-diselenanonanane-1,9-diol **8**<sup>15</sup> and 2-(*p*-methylphenoxy)-2-oxo-1,3,6,2λ<sup>5</sup>-dioxaselenaphosphocane **20**<sup>10,12</sup> were prepared according to the literature methods.



### General procedure for preparing macrocycles 3

A 250 mL three-necked flask was charged with selenium powder (0.49 g, 6.2 mmol), potassium borohydride (0.24 g, 4.4 mmol) and absolute ethanol (50 mL). Nitrogen gas was introduced with a glass inlet tube to the bottom of the flask. The mixture was stirred under reflux for 2 h. Then compound **1** (0.93 g, 2 mmol) dissolved in THF (60 mL) was added during a period of 1.5 h. After the mixture was stirred under reflux for another 4 h, sodium hydroxide (0.24 g, 6.0 mmol) and potassium borohydride (0.32 g, 6.0 mmol) were added. When the mixture turned clear and colourless, a solution of an appropriate dihaloalkane (2 mmol) in THF (60 mL) was added dropwise over 3 h. After the mixture was refluxed for another 12 h, the reaction mixture was cooled and solid materials removed by filtration and the evaporation of the filtrate gave a white solid, which was mixed with chloroform (50 mL) and water (50 mL) under shaking. The organic phase was separated and washed to neutral with water (2 × 20 mL), dried with anhydrous magnesium sulfate and evaporated. The residue was purified by preparative TLC to give macrocycles **3a**, **3c–3l** and the eight-membered heterocycle **4**. The yields of **3** and **4** are given in Table 1.

**5-Phenyl-5,14-dihydro-10H-5 $\lambda^5$ -dibenzo[e,h][1,3,7]diselenaphosphecin-5-one 3a.** Colourless crystals (from dichloromethane and petroleum ether), 24% yield; mp 176–178 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.53–7.20(13H, m), 5.31(2H, d, *J* 12.2), 4.50(1H, d, *J* 11.5), 4.03(1H, d, *J* 11.5), 3.94(2H, d, *J* 12.2);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 34.70; *m/z*(EI) 478 (M<sup>+</sup>, 2%), 384 (17), 303 (60), 213 (16), 179 (96), 165 (100), 91 (46);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3060(ArH), 2940(CH<sub>2</sub>), 1433(P–Ph), 1179(P=O), 571, 539(C–Se); Anal. C<sub>21</sub>H<sub>19</sub>OPSe<sub>2</sub> (MW 476.25): Calcd. C, 52.96; H, 4.02. Found, C, 53.03; H, 4.06%.

**5-Phenyl-5,13,14,16-tetrahydro-10H,12H-5 $\lambda^5$ -dibenzo[g,j][1,5,9]diselenaphosphacyclododecin-5-one 3c.** Colourless crystals (from dichloromethane and petroleum ether), 22% yield; mp 206–208 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.80–6.80(13H, m), 5.50(2H, d, *J* 10.8), 3.90(2H, d, *J* 10.8), 2.92–1.80(6H, m);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 36.53; *m/z*(EI) 506 (M<sup>+</sup>, 2%), 304 (100), 202 (5);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3050(ArH), 2920(CH<sub>2</sub>), 1433(P–Ph), 1181(P=O), 571, 533(C–Se); Anal. C<sub>23</sub>H<sub>23</sub>OPSe<sub>2</sub> (504.31): Calcd. C, 54.77; H, 4.60. Found, C, 54.50; H, 4.63%.

**5-Phenyl-5,12,13,14,15,17-hexahydro-10H-5 $\lambda^5$ -dibenzo[c,f][1,9,5]diselenaphosphacyclotridecin-5-one 3d.** Colourless crystals (from dichloromethane and petroleum ether), 25% yield; mp 171–173 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.57–6.75(13H, m), 5.12(2H, d, *J* 11.2), 3.69(2H, d, *J* 11.2), 3.23–3.12(2H, m), 2.49–2.36(2H, m), 1.58(4H, m);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 37.36; *m/z*(EI) 520 (M<sup>+</sup>, 1%), 385 (8), 304 (100), 178 (54), 165 (55);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3050(ArH), 2920(CH<sub>2</sub>), 1433(P–Ph), 1179(P=O), 570, 532(C–Se); Anal. C<sub>24</sub>H<sub>25</sub>OPSe<sub>2</sub> (MW 518.33): Calcd. C, 55.61; H, 4.86. Found, C, 55.80; H, 4.94%.

**5-Phenyl-5,13,14,15,16,18-hexahydro-10H,12H-5 $\lambda^5$ -dibenzo[c,f][1,9,5]diselenaphosphacyclotetradecin-5-one 3e.** Colourless crystals (from dichloromethane and petroleum ether), 12% yield; mp 147–148 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.66–6.79(13H, m), 4.84(2H, d, *J* 12.6), 3.77(2H, d, *J* 12.6), 2.88–2.74(2H, m), 2.47–2.33(2H, m), 1.87–1.76(4H, m), 1.54–1.18(2H, m);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 36.45; *m/z*(EI) 534 (M<sup>+</sup>, 1%), 385 (10), 304 (100), 178 (55), 165 (60);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3060(ArH), 2908(CH<sub>2</sub>), 1433(P–Ph), 1180(P=O), 570, 537(C–Se); Anal. C<sub>25</sub>H<sub>27</sub>OPSe<sub>2</sub> (532.36): Calcd. C, 56.40; H, 5.11. Found, C, 56.41; H, 5.14%.

**5-Phenyl-5,12,13,14,15,16,17,19-octahydro-10H-5 $\lambda^5$ -dibenzo[c,f][1,9,5]diselenaphosphacyclopentadecin-5-one 3f.** Colourless crystals (from dichloromethane and petroleum ether), 19%

yield; mp 135–136 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.75–6.77(13H, m), 4.75(2H, d, *J* 11.8), 3.78(2H, d, *J* 11.8), 2.78–2.48(4H, m), 1.88–1.29(8H, m);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 36.02; *m/z*(EI) 548 (M<sup>+</sup>, 2%), 385 (22), 304 (100), 178 (76), 165 (80);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3050(ArH), 2905(ws, CH<sub>2</sub>), 1433(P–Ph), 1170(P=O), 570, 530(C–Se); Anal. C<sub>26</sub>H<sub>29</sub>OPSe<sub>2</sub> (MW 546.38): Calcd. C, 57.15; H, 5.35. Found, C, 57.23; H, 5.45%.

**5-Phenyl-5,12,13,15,16,18-hexahydro-10H-5 $\lambda^5$ -dibenzo[f,i][1,4,12,8]oxadiselenaphosphacyclotetradecin-5-one 3g.** Colourless crystals (from dichloromethane and petroleum ether), 30% yield; mp 176–180 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.74–6.82(13H, m), 4.93(2H, d, *J* 12.4), 3.81(2H, d, *J* 12.4), 3.89–3.78(2H, m), 3.39–3.26(2H, m), 3.20–3.06(2H, m), 2.60–2.46(2H, m);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 36.43; *m/z*(EI) 536 (M<sup>+</sup>, 1%), 385 (14), 303 (100), 179 (73), 165 (77), 91 (36);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3050(ArH), 2920, 2840, 2820(CH<sub>2</sub>), 1433(P–Ph), 1179(P=O), 570, 538(C–Se); Anal. C<sub>24</sub>H<sub>25</sub>O<sub>2</sub>PSe<sub>2</sub> (MW 534.33): Calcd. C, 53.94; H, 4.72. Found, C, 54.06; H, 5.06%.

**5-Phenyl-5,12,13,15,16,18,19,21-octahydro-10H-5 $\lambda^5$ -dibenzo[i,l][1,4,7,15,11]dioxadiselenaphosphacycloheptadecin-5-one 3h.** Colourless crystals (from dichloromethane and petroleum ether), 21% yield; mp 119–120 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.74–6.89(13H, m), 4.60(2H, d, *J* 12.6), 3.97(2H, d, *J* 12.6), 3.75–3.55(8H, m), 2.80(4H, m);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 35.57; *m/z*(EI) 580 (M<sup>+</sup>, 2%), 383 (28), 303 (100), 178 (62), 165 (66);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3053(ArH), 2926, 2854(CH<sub>2</sub>), 1439(P–Ph), 1178(P=O), 1114(C–O), 578, 547(C–Se); Anal. C<sub>26</sub>H<sub>29</sub>O<sub>3</sub>PSe<sub>2</sub> (MW 578.38): Calcd. C, 53.79; H, 5.05. Found, C, 54.04; H, 4.96%.

**12-Phenyl-5,12,17,19-tetrahydro-7H-12 $\lambda^5$ -tribenzo[c,h,k]-[1,9,5]diselenaphosphacyclotridecin-12-one 3i.** White powder, 25.6% yield; mp 186–187 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.50–6.90(17H, m), 4.97(2H, d, *J* 11.4), 4.23(2H, d, *J* 11.9), 4.05(2H, d, *J* 11.4), 3.84(2H, d, *J* 11.9);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 35.27; *m/z*(EI) 568 (M<sup>+</sup>, 3%), 487 (3), 385 (21), 303 (48), 178 (62), 104 (100);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3050(ArH), 2920(CH<sub>2</sub>), 1433(P–Ph), 1181(P=O), 571, 545, 535(C–Se); Anal. C<sub>28</sub>H<sub>25</sub>OPSe<sub>2</sub> (MW 566.37): Calcd. C, 59.37; H, 4.45. Found, C, 59.44; H, 4.40%.

**11-Phenyl-11,16-dihydro-4H,6H,18H-11 $\lambda^5$ -tribenzo[c,f,k,l]-[1,9,5]diselenaphosphacyclotetradecin-11-one 3j.** White powder, 16% yield; mp 169–170 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.76–6.66(17H, m), 4.75(2H, d, *J* 13.5), 3.87(2H, d, *J* 12.9), 3.71(2H, d, *J* 13.5), 3.63(2H, d, *J* 12.9);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 36.32; *m/z*(EI) 568 (M<sup>+</sup>, 1%), 385 (12), 303 (60), 179 (100), 104 (45);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3050(ArH), 2930(CH<sub>2</sub>), 1439, 1431(P–Ph), 1170(P=O), 575, 536(C–Se); Anal. C<sub>28</sub>H<sub>25</sub>OPSe<sub>2</sub> (MW 566.37): Calcd. C, 59.37; H, 4.45. Found, C, 59.74; H, 4.31%.

**10-Phenyl-3,10,15,17-tetrahydro-5H-tribenzo[c,f,k,l,m][1,9,5]diselenaphosphacyclopentadecin-10-one 3k.** White powder, 35% yield; mp 209–212 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.85–6.56(17H, m), 4.44(2H, d, *J* 13.7), 3.81(4H, ABq, *J* 11.5), 3.53(2H, d, *J* 13.7);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 35.66; *m/z*(EI) 568 (M<sup>+</sup>, 2%), 464 (1), 383 (11), 304 (67), 179 (50), 165 (47), 104 (100);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3040(ArH), 2910(CH<sub>2</sub>), 1433(P–Ph), 1174(P=O), 570, 529(C–Se); Anal. C<sub>28</sub>H<sub>25</sub>OPSe<sub>2</sub> (MW 566.37): Calcd. C, 59.37; H, 4.45. Found, C, 59.71; H, 4.61%.

**5-Phenyl-13-hydroxy-5,13,14,16-tetrahydro-10H,12H-5 $\lambda^5$ -dibenzo[g,j][1,5,9]diselenaphosphacyclododecin-5-one 3l.** Colourless crystals (from dichloromethane and petroleum ether), 15% yield; mp 210–2 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.60–6.91(13H, m), 5.35(2H, d, *J* 10.5), 4.33(1H, br s, OH), 3.80(2H, d, *J* 10.5), 3.67(1H, br s, CH), 3.12(2H, dd, <sup>3</sup>*J* 4.2, <sup>2</sup>*J* 13.8), 2.72(2H, dd, <sup>3</sup>*J* 6.9, <sup>2</sup>*J* 13.8);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 37.40, 36.95; *m/z*(EI) 522 (M<sup>+</sup>, 0.3%), 464 (0.6), 384 (10), 303 (40), 213 (15), 179 (84), 165 (58), 58 (100);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3350(ws, O–H), 3050(ArH), 2910(CH<sub>2</sub>),

1433(P–Ph), 1170(P=O), 575, 535(C–Se); Anal. C<sub>23</sub>H<sub>23</sub>O<sub>2</sub>PSe<sub>2</sub> (MW 520.30): Calcd. C, 53.09; H, 4.45. Found, C, 53.14; H, 4.40%.

**12-Phenyl-7,12-dihydro-5H-12 $\lambda^5$ -dibenzo[*c,f*][1,5]selenaphosphocin-12-one 4.** White powder, mp 195–6 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 8.12–7.02(13H, m), 3.98(2H, ABq, *J* 13.6), 3.63(2H, ABq, *J* 12.5); *m/z*(EI) 384 (M<sup>+</sup>, 18%), 303 (33), 213 (11), 179 (100), 165 (65), 137 (13);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 27.54;  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 1433(P–Ph), 1185(P=O), 580, 541, 517(C–Se); Anal. C<sub>20</sub>H<sub>17</sub>OPSe (MW 383.27): Calcd. C, 62.67; H, 4.47; Found, C, 62.97; H, 4.50%.

**Alternative synthesis of 5-phenyl-5,13,14,16-tetrahydro-10H, 12H-5 $\lambda^5$ -dibenzo[*g,j*][1,5,9]diselenaphosphacyclododecin-5-one 3c**

A stirred mixture of 1,2-diselenacyclopentane **6** (1.0 g, 5 mmol), sodium hydroxide (0.6 g, 15 mmol), potassium borohydride (0.81 g, 15 mmol) and absolute ethanol (100 mL) was heated under reflux until the solution became clear and colourless. To this solution was slowly added over 8.5 h a solution of bis[*o*-(bromomethyl)phenyl]phenylphosphine oxide **1** (2.32 g, 5 mmol) in absolute ethanol (50 mL). The mixture was refluxed for another 12 h. The solid deposited was removed by filtration. After removal of the solvent, the residue was distributed between methylene chloride (100 mL) and water (100 mL). The aqueous layer was extracted with methylene chloride (2 × 50 mL). The organic phases were combined, washed with brine, dried over MgSO<sub>4</sub>, and evaporated *in vacuo*. The crude product was purified by chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> and recrystallized from absolute ethanol to give 0.67 g (27%) of pure **3c** as pale yellow crystals.

**Synthesis of 5-phenyl-5,12,13,15,16,18-hexahydro-10H-5 $\lambda^5$ -dibenzo[*i,l*][1,7,4,11]dioxaselenaphosphacyclotetradecin-5-one 9**

To a 250 mL three-necked flask was added sodium (0.10 g, 4.34 mmol) and <sup>t</sup>BuOH (20 mL). The mixture was refluxed until the sodium disappeared. To the mixture was added a solution of 3-selenapentane-1,5-diol **7** (0.34 g, 2 mmol) in THF (50 mL). After the addition was completed, the reaction mixture was refluxed for 1 h. Then a solution of bis[*o*-(bromomethyl)phenyl]phenylphosphine oxide **1** in THF (50 mL) was added slowly over 8 h. The reaction mixture was refluxed for another 24 h. The solid deposited was filtered off and the solvent was evaporated from the filtrate to leave a solid material which was dissolved in chloroform (50 mL). The chloroform solution was washed to neutral with water, dried over MgSO<sub>4</sub> and evaporated *in vacuo*. The crude product was purified by chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O 10 : 1 and recrystallized from Et<sub>2</sub>O to give 0.25 g (26%) of pure **9** as colourless crystals, mp 115–116 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.59–6.69(13H, m), 5.42(2H, d, *J* 11.5), 4.39(2H, d, *J* 11.5), 4.12–3.97(2H, m), 3.80–3.63(2H, m), 2.90–2.68(2H, m), 2.24–2.05(2H, m);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 34.98; *m/z*(EI) 472 (M<sup>+</sup>, 12%), 365 (21), 335 (79), 319 (95), 165 (100), 134 (45), 107 (29).  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 1438(P–Ph), 1188(P=O), 545(C–Se). Anal. C<sub>24</sub>H<sub>25</sub>O<sub>3</sub>PSe: Calcd. C, 61.15; H, 5.35. Found, C, 60.95; H, 5.48%.

**Synthesis of 5-phenyl-5,12,13,16,17,19,20,22-octahydro-10H, 15H-5 $\lambda^5$ -dibenzo[*m,p*][1,11,4,8,15]dioxadiselenaphosphacyclooctadecin-5-one 10**

Following the method for preparing macrocycle **9**, macrocycle **10** was synthesized from 3,7-diselenanonane-1,9-diol **8** (0.58 g, 2 mmol), bis[*o*-(bromomethyl)phenyl]phenylphosphine oxide **1** (0.93 g, 2 mmol). The crude product was purified by chromatography over silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O 10 : 1 and recrystallized from Et<sub>2</sub>O to give 0.26 g (22%) of pure **10** as colourless prismatic crystals, mp 131–132 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.71–6.96(13H, m), 5.30(2H, d, *J* 12.8), 4.50(2H, d, *J* 12.8), 3.68–

3.61(4H, m), 2.45–2.27(8H, m), 2.01–1.79(2H, m);  $\delta_{\text{P}}$ NMR-(CDCl<sub>3</sub>) 35.13; *m/z*(EI) 594 (M<sup>+</sup>, 6%), 335 (62), 319 (100), 289 (43), 134 (14), 107 (11);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 1441(P–Ph), 1189(P=O), 545(C–Se). Anal. C<sub>27</sub>H<sub>31</sub>O<sub>3</sub>PSe<sub>2</sub>: Calcd. C, 54.74; H, 5.28. Found, C, 54.48; H, 5.24%.

**Synthesis of palladium(n) complexes**

**Method A:** A solution of the macrocycle **3c** (0.10 mmol), **9** (0.20 mmol), **10** (0.20 mmol) or **20**<sup>10,12</sup> (0.20 mmol) and palladium chloride (0.10 mmol) in acetone (50 mL) and water (2 mL) was stirred under reflux for 36 h. The solvent was removed and a yellow powder was obtained which was washed thoroughly with acetone to give complexes **11**, **12**, **13** or **21** respectively.

*Dichloro(5-phenyl-5,13,14,16-tetrahydro-10H,12H-5 $\lambda^5$ -dibenzo[*g,j*][1,5,9]diselenaphosphacyclododecin-5-one- $\kappa^2$ Se, Se')palladium 11.* Yellow powder, 26% yield; mp 240 °C dec.;  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3150, 1433, 1181, 1174, 571, 535;  $\lambda_{\text{max}}$ (DMSO)/nm 325 ( $\epsilon$ /dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup> 450); Anal. C<sub>23</sub>H<sub>23</sub>OPSe<sub>2</sub>·PdCl<sub>2</sub>: Calcd. C, 40.53; H, 3.40. Found, C, 40.86; H, 3.60%.

*Dichlorobis(5-phenyl-5,12,13,15,16,18-hexahydro-10H-5 $\lambda^5$ -dibenzo[*i,l*][1,7,4,11]dioxaselenaphosphacyclotetradecin-5-one)-palladium 12.* Yellow powder, 48% yield; mp 238 °C dec.;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.69–6.92(13H, m), 5.17(2H, br s), 4.58(2H, d, *J* 11.1), 4.13–3.75(4H, br d), 3.55–3.37(2H, br d), 3.13–2.64(2H, br d);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 1435, 1191, 545;  $\lambda_{\text{max}}$ (CHCl<sub>3</sub>)/nm 300 ( $\epsilon$ /dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup> 11 400); Anal. (C<sub>24</sub>H<sub>25</sub>O<sub>3</sub>PSe<sub>2</sub>)<sub>2</sub>·PdCl<sub>2</sub>: Calcd. C, 51.47; H, 4.50. Found, C, 51.41; H, 4.55%.

*Dichloro(5-phenyl-5,12,13,16,17,19,20,22-octahydro-10H, 15H-5 $\lambda^5$ -dibenzo[*m,p*][1,11,4,8,15]dioxadiselenaphosphacyclooctadecin-5-one- $\kappa^2$ Se, Se')palladium 13.* Yellow powder, 89% yield; mp 259 °C dec.;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.90–6.67(m, 13H), 5.49(1H, d, *J* 11.4), 5.28(1H, d, *J* 11.5), 4.56(1H, d, *J* 11.5), 4.47(1H, d, *J* 11.5), 4.25–4.10(1H, m), 4.05–3.86(1H, m), 3.82–3.75(2H, m), 3.49–3.24(1H, m), 3.17–2.95(1H, m), 2.85–2.37(6H, m), 2.25–1.66(2H, m);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 3058, 2923, 1439, 1183, 1092 and 547;  $\lambda_{\text{max}}$ (CHCl<sub>3</sub>)/nm 301 ( $\epsilon$ /dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup> 88 600) and 405 (16 300); Anal. C<sub>27</sub>H<sub>31</sub>O<sub>3</sub>PSe<sub>2</sub>·PdCl<sub>2</sub>: Calcd. C, 42.13; H, 4.05. Found, C, 41.99; H, 4.32%.

*Dichlorobis[2-(*p*-methylphenoxy)-2-oxo-1,3,6,2-dioxaselenaphosphocane]palladium 21.* Reddish brown crystals, 99% yield; mp 192–4 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 7.10(s, 4H, ArH), 4.72(br t, 2H, OCH<sub>2</sub>), 4.42(br m, 2H, OCH<sub>2</sub>), 3.60(br s, 2H, SeCH<sub>2</sub>), 3.50(br s, 2H, SeCH<sub>2</sub>), 2.30(s, 3H, ArCH<sub>3</sub>); *m/z*(EI). 322 (20<sup>+</sup>, 4%), 215 (12), 134 (100);  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 1276(s, P=O),  $\lambda_{\text{max}}$ (CHCl<sub>3</sub>)/nm 325 ( $\epsilon$ /dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup> 10 100); Anal. C<sub>22</sub>H<sub>30</sub>Cl<sub>2</sub>O<sub>10</sub>P<sub>2</sub>Se<sub>2</sub> (819.63). Calcd.: C, 32.24; H, 3.69. Found, C, 31.86; H, 3.86%.

**Method B:** 50 mg of macrocycles **3d**, **3e**, **3f**, **3g**, **3k** or **3l** and an equimolar amount of palladium chloride in deoxygenated acetonitrile (20 mL) were stirred under reflux for 2 h to give a yellow powder, which was collected by filtration and washed sufficiently with ether to give complexes **14**, **15**, **16**, **17**, **18** or **19** respectively.

*Dichloro(5-phenyl-5,12,13,14,15,17-hexahydro-10H-5 $\lambda^5$ -dibenzo[*c,f*][1,9,5]diselenaphosphacyclotridecin-5-one- $\kappa^2$ Se, Se')palladium 14.* Yellow powder, 85% yield; mp >230 °C dec.;  $\nu_{\text{max}}$ (KBr)/cm<sup>−1</sup> 1432, 1181, 1179, 1119, 1111, 540; Anal. C<sub>24</sub>H<sub>25</sub>OPSe<sub>2</sub>·PdCl<sub>2</sub> (MW 695.64) Calcd. C, 41.13; H, 3.62. Found, C, 41.50; H, 3.86%.

*Dichloro(5-phenyl-5,13,14,15,16,18-hexahydro-10H,12H-5 $\lambda^5$ -dibenzo[*c,f*][1,9,5]diselenaphosphacyclotetradecin-5-one- $\kappa^2$ Se, Se')palladium 15.* Yellow powder, 90% yield; mp 219–220 °C dec.;  $\nu_{\text{max}}$ (KBr)/ 1433, 1178, 1115, 535 cm<sup>−1</sup>;  $\lambda_{\text{max}}$ (DMSO)/nm 325 ( $\epsilon$ /dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup> 2470); Anal. C<sub>25</sub>H<sub>27</sub>OPSe<sub>2</sub>·PdCl<sub>2</sub> (MW 709.674) Calcd. C, 42.31; H, 3.84. Found, C, 41.92; H, 3.67%.

*Dichloro(5-phenyl-5,12,13,14,15,16,17,19-octahydro-10H-5 $\lambda^5$ -dibenzo[*c,f*][1,9,5]diselenaphosphacyclopentadecin-5-one- $\kappa^2$ Se, Se')palladium 16.* Yellow powder, 83% yield; mp >230 °C

dec.;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1433, 1185, 1181, 1175, 1119, 1111, 540;  $\lambda_{\max}(\text{DMSO})/\text{nm}$  325 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  2820); Anal.  $\text{C}_{26}\text{H}_{29}\text{OPSe}_2 \cdot \text{PdCl}_2$  (MW 723.69) Calcd. C, 43.14; H, 3.52. Found, C, 43.05; H, 3.80%.

*Dichloro(5-phenyl-5,12,13,15,16,18-hexahydro-10H-5 $\lambda^5$ -dibenzo[*f,i*][1,4,12,8]oxadiselenaphosphacyclotetradecin-5-one- $\kappa^2\text{Se},\text{Se}'$ )palladium 17.* Yellow powder, 85% yield; mp >221 °C dec.;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1435, 1180, 1175, 1119, 1111, 539;  $\lambda_{\max}(\text{DMSO})/\text{nm}$  327 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4720); Anal.  $\text{C}_{24}\text{H}_{25}\text{O}_2\text{PSe}_2 \cdot \text{PdCl}_2$  (MW 711.64) Calcd. C, 40.50; H, 3.54. Found, C, 40.47; H, 3.52%.

*Dichloro(10-phenyl-3,10,15,17-tetrahydro-5H-tribenzo[*c,f,klm*][1,9,5]diselenaphosphacyclopentadecin-10-one- $\kappa^2\text{Se},\text{Se}'$ )palladium 18.* Yellow powder, 95% yield; mp 239.5 °C dec.;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1433, 1191, 1179, 1118, 539; Anal.  $\text{C}_{24}\text{H}_{25}\text{O}_2\text{PSe}_2 \cdot \text{PdCl}_2$  (MW 743.68) Calcd. C, 45.22; H, 3.39. Found, C, 45.00; H, 3.39%.

*Dichloro(5-phenyl-13-hydroxy-5,13,14,16-tetrahydro-10H,12H-5 $\lambda^5$ -dibenzo[*g,i*][1,5,9]diselenaphosphacyclododecin-5-one- $\kappa^2\text{Se},\text{Se}'$ )palladium 19.* Yellow powder, 83% yield; mp >208 °C dec.;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1435, 1180, 1175, 1115, 539;  $\lambda_{\max}(\text{DMSO})/\text{nm}$  327 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  5300); Anal.  $\text{C}_{23}\text{H}_{23}\text{O}_2\text{PSe}_2 \cdot \text{PdCl}_2$  (MW 697.61) Calcd. C, 39.60; H, 3.32. Found, C, 39.92; H, 3.43%.

#### X-Ray analysis of macrocycles **3c**, **3f**, **10** and **21** †

The measurements were carried out on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ),  $\omega$ - $2\theta$  scans. X-Ray quality crystals of **3c**, **3f** and **10** were obtained by evaporation of the methylene chloride solution. A single crystal of **21** was obtained by recrystallization from acetonitrile. No significant crystal decay or movement was observed. The weighting scheme employed was  $w = 1/(\sigma^2(F) + 0.0001F^2)$ . The selected crystals were mounted onto glass fibers and coated with epoxy resin to inhibit desolvation and crystal decomposition during data collection. The

† CCDC reference numbers 159814–159816. See <http://www.rsc.org/suppdata/pl/b0/b005045h/> for crystallographic data in CIF or other electronic format.

structures were solved by direct method and developed by using full-matrix least-squares refinement. The raw data were corrected for absorption using DIFABS. All non-H atoms were refined anisotropically, while H atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. A summary of the crystallographic data and data collection and refinement parameters are given in Table 2.

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