DALTON

Synthesis of aryl selenides using arylmercurials. Cyclopalladation of Se(R)Ph [R = $C_6H_3(N{=}NC_6H_4Me\text{-}4')\text{-}2,Me\text{-}5$]. Crystal structures of Se_2R_2 and [$Pd\{C_6H_3[N{=}NC_6H_3(SePh)\text{-}2',Me\text{-}4']\text{-}2,Me\text{-}5\}Cl$]

Peter G. Jones * and M. Carmen Ramírez de Arellano *

Institut für Anorganische und Analytische Chemie der Technische Universität, Postfach 3329, D-38023 Braunschweig, Germany

The compound SePhCl reacted with HgR_2 or Hg(R)Cl [R = $C_6H_3(N{=}NC_6H_4Me\text{-}4')\text{-}2,Me\text{-}5$] to give Se(R)Ph **1**. Reaction between $SeCl_4$ and Hg(R)Cl or HgR_2 afforded Se(R)Cl, which reacts with HgR_2 affording SeR_2 **2** and is reduced with hydrazine hydrate to give RCl **3** and Se_2R_2 **4**. Palladium(II) chloride reacted with **1** to give [$Pd\{C_6H_3[N{=}NC_6H_3(SePh)\text{-}2',Me\text{-}4']\text{-}2,Me\text{-}5\}Cl$] **5** and with **2** or **4** to give Se(R)Cl. The crystal structures of compounds **4** and **5** were determined. The geometry of the diselenide **4** offers various possibilities for co-ordination and in the palladium complex **5** two chelate five-membered rings are formed by co-ordination through *o*-carbon, nitrogen and selenium.

The chemistry of organoselenium compounds has been the subject of increasing attention in recent years, because of their many synthetic applications.[1] Outlets for selenium materials include natural products synthesis, biological and medicinal applications, imaging systems, and new ion radical solids with metallic and superconducting properties.[2]

The general methods for the preparation of arylselanyl derivatives include the use of Grignard reagents,[3] copper areneselenolates,[4] photostimulated $S_{RN}1$ conditions[5] and alkali metals.[2] However, these methods often suffer from disadvantages such as the use of expensive reagents, incompatibility with the presence of certain functional groups, or laborious manipulation.

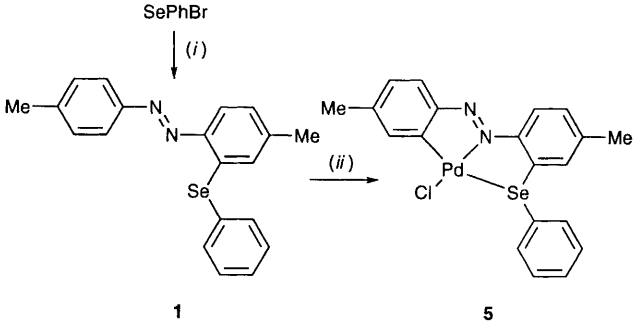
In a previous study we reported the synthesis of 2-(4-$MeC_6H_4N{=}N)C_6H_3$(Me-5)SeCl (RSeCl) using the corresponding diarylmercury compound.[6] It belongs to a class of derivatives that contain certain functionalised aryls and cannot be prepared by classical methods because of the unavailability or instability of the reagents. As the use of organomercurials in the synthesis of organoselenium derivatives is still very limited,[7] we have extended our study to the synthesis of other types of selenium derivatives.

There has been considerable recent interest in the chemistry of polydentate ligands with both hard and soft donor atoms, and the selenides we have prepared contain Se and N donor sets. We have studied the reactivity of the newly synthesised organoselenium derivatives toward palladium dichloride. Because of the simple procedure and high yields, our methods compare favourably with other syntheses described in the literature and represent a contribution to the growing interest in the ligand chemistry of organoselenium compounds.[8]

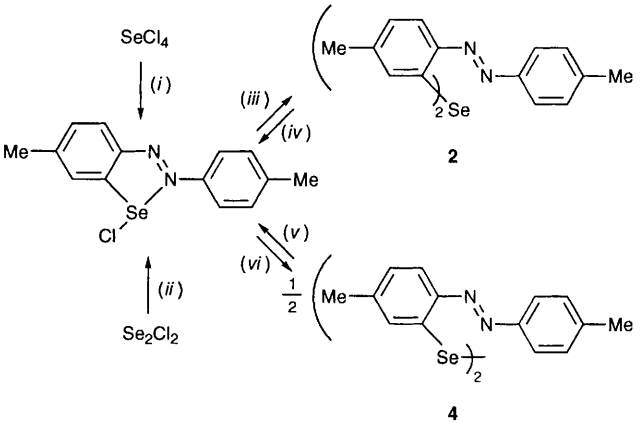
Results and Discussion

Synthesis of the diaryl selenides Se(R)Ph 1 and SeR_2 2

The selanyl halide SePhBr reacts with HgR_2 (1 : 1) in diethyl ether under mild conditions (room temperature, 18 h) whereby Hg(R)Cl precipitates and can be separated from the reaction product Se(R)Ph **1** (see Scheme 1). This mixed organoselenide can also be prepared by reaction of Hg(R)Cl and SePhBr in dichloromethane at room temperature (24 h); removal of the solvent and further addition of light petroleum precipitates the mercury halides, whereas compound **1** precipitates only after cooling the solution to 0 °C. The organoselanyl Se(R)Cl cannot



Scheme 1 (*i*) + HgR_2 − Hg(R)Cl or +Hg(R)Cl − HgX_2 (X = Cl or Br); (*ii*) +$PdCl_2$



Scheme 2 (*i*) + $3HgR_2$ − HgR_2 − 2Hg(R)Cl − RCl or +3Hg(R)Cl − Hg(R)Cl − $2HgCl_2$ − RCl; (*ii*) + HgR_2 − Se^0 − Hg(R)Cl or +Hg(R)Cl − Se^0 − $HgCl_2$; (*iii*) +HgR_2 − Hg(R)Cl; (*iv*) +$PdCl_2$ − Pd^0 − RH; (*v*) +$\frac{1}{2}$ $PdCl_2$ − $\frac{1}{2}$ Pd^0; (*vi*) +N_2H_4 (excess)

be arylated by reaction with Hg(R)Cl or HgR_2 in refluxing heptane, but reacts with the latter in refluxing xylene for 12 h producing the diorganoselenide SeR_2 **2** (see Scheme 2). The stronger conditions required for a further arylation of Se(R)Cl, compared to those for SePhBr, imply a significant negative influence of the N–Se bond in Se(R)Cl on the transmetallation reaction.[6]

Synthesis and reduction of Se(R)Cl

We have reported the synthesis of Se(R)Cl by the reaction of Se_2Cl_2 with HgR_2.[6] This compound can also be obtained in other ways. Thus, the reaction between Hg(R)Cl and Se_2Cl_2 in chloroform leads to Se(R)Cl in high yield and under very mild conditions (room temperature, 72 h). The by-products, Se^0 and $HgCl_2$, are insoluble. When HgR_2 was added to a solution of $SeCl_4$ (3:1) in tetrahydrofuran and the mixture stirred at room temperature for 21 h the reaction took place in 2:1 ratio, with precipitation of Hg(R)Cl after removal of the solvent and addition of diethyl ether. The remaining HgR_2 and the reaction products RCl **3** and Se(R)Cl (1:2:1) were separated by chromatography over silica gel. When Hg(R)Cl was added to a solution of $SeCl_4$ in tetrahydrofuran in 3:1 ratio no reaction was observed. However, when a 2:1 ratio was used in refluxing tetrahydrofuran for 9 h a reaction was observed: $HgCl_2$ precipitated on addition of hexane and the remaining solution was chromatographed over silica gel affording **3**, Hg(R)Cl and Se(R)Cl in 2:1:1 ratio. In contrast, it had earlier been found that HgR'_2 or Hg(R')Br (R' = Ph, *p*-tolyl, β-naphthyl or biphenyl) react with $SeBr_4$ in 3:1 ratio to give the corresponding diselenide SeR'_2, aryl bromide and Hg(R')Br or $HgBr_2$ respectively.[9]

Reduction of Se(R)Cl with an excess of hydrazine hydrate (1:8) in ethanol affords the symmetric diselenide Se_2R_2 **4** (Scheme 2) after stirring at room temperature for 1 h. The product was precipitated by cooling the reaction mixture to 0 °C. A similar method was used for the preparation of $Te_2(C_6H_4N{=}NPh\text{-}2)_2$.[10]

Reactions with $PdCl_2$

The compound Se(R)Cl does not react with $PdCl_2$ (1:1) on refluxing for 10 h in methanol. When Se(R)Ph **1** and $PdCl_2$ (1:1) were refluxed in methanol for 4 h a quantitative cyclometallation of the non-selenated azotoluene ring occurred, forming the palladium complex **5** and HCl (Scheme 1). However, reaction of the symmetric selenide SeR_2 with $PdCl_2$ in similar conditions, or even at room temperature, leads to reduction of the metal ion and the formation of free azotoluene and Se(R)Cl. No reaction occurs when a mixture of the diselenide Se_2R_2 **4** and palladium dichloride is refluxed in methanol for several hours, but in refluxing butan-1-ol reduction to metallic palladium and formation of Se(R)Cl was again observed. Therefore, cleavage of a selenium–selenium bond occurs in this reaction and the selenium goes from formal oxidation state $-$I to $+$II, whereas with SeR_2 **2**, cleavage of a selenium–carbon bond and oxidation from Se^{-II} to Se^{II} takes place.

Structure and spectroscopic properties of compounds 1–5

Repeated attempts to grow crystals of compounds Se(R)Ph **1** and SeR_2 **2** were unsuccessful, whereas compounds **3**–**5** have been characterised by X-ray diffraction (see below). The ^1H and ^{13}C NMR data for **1**–**5** are consistent with their formulation. The organoselenides **1** and **2** showed in their ^{77}Se NMR spectra [δ(SeMe$_2$) 0] singlets at δ 416.46 and 379.13, respectively, both shifts being within the region characteristic of diaryl selenides.[11] The palladium complex **5** exhibits a singlet at δ(Se) 367.39. The 49 ppm shift towards higher field from the free selenide Se(R)Ph **1** is probably due to σ-donation from the selenium to the palladium centre. For the diselenide Se_2R_2 **4** a singlet at δ(Se) 469.03 is in agreement with the magnetic equivalence of both selenium atoms, as found in other symmetric diaryl diselenides, and the shift is only 9 ppm to lower field than for Se_2Ph_2.[12] The electron impact (EI) mass spectra of compounds **1**–**5** exhibit peaks at *m*/*z* 165 ($C_{13}H_9^+$), 119 ($C_7H_7N_2^+$), 91 ($C_7H_5^+$), and 65 ($C_5H_5^+$) characteristic of the fragmentation of *ortho*-substituted azotoluene. The molecular peak was also observed in these spectra, except for Se_2R_2 **3** for which the largest observed fragment corresponded to the loss of one selenium atom (*m*/*z* 372, SeR_2^+).

Crystal structures

RCl 3. The structure has a chlorine atom at the *ortho* position of one ring, but disorder over an inversion centre (see Experimental section) rendered the structure unsatisfactory and quantitative aspects are not therefore discussed.

Se_2R_2 4. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation from an ethanol solution of the diselenide derivative. The structure (Fig. 1, Table 1) shows a selenium–selenium fragment with each selenium atom bonded to the *ortho* position of a different R group. The molecule has no internal symmetry. The Se–Se bond length of 2.380(2) Å and the C–Se–Se–C torsion angle of 83.2(3)° may be considered as normal values [*cf.* 2.343(1) Å, 84° in bis(1-naphthyl) diselenide].[13] All non-hydrogen atoms of the Se(1)-R[C(1)–C(17)] fragment are coplanar (mean deviation 0.021 Å), whereas this is not the case for the Se(2)-R[C(21)–C(37)] fragment; the N(4)–toluene plane (mean deviation 0.009 Å) is rotated by 20° with respect to the N(3)–toluene–Se(2) plane (mean deviation 0.021 Å). The observed distortion might be a consequence of the packing of these rather long molecules in the cell, but such assumptions are difficult to prove.

Palladium complex 5. Slow diffusion of methanol into a dichloromethane solution of complex **5** afforded crystals suitable for X-ray diffraction studies, which provided conclusive proof of its geometry. The structure (Fig. 2, Table 2) is revealed as an orthometallated monomer with the nitrogen and the selenium atoms co-ordinated to palladium. The palladium centre is four-co-ordinated in an approximately square-planar CNSeCl environment, all the non-hydrogen

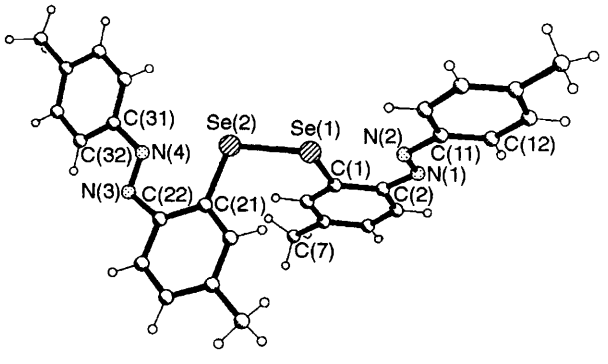


Fig. 1 Molecular structure of the diselenide Se_2R_2 **4**

Table 1 Selected bond lengths (Å) and angles (°) for compound **4**

Se(1)–C(1)	1.944(6)	Se(1)–Se(2)	2.380(2)
Se(2)–C(21)	1.906(7)	N(1)–N(2)	1.261(6)
N(1)–C(2)	1.385(7)	N(2)–C(11)	1.389(8)
N(3)–N(4)	1.230(8)	N(3)–C(22)	1.447(8)
N(4)–C(31)	1.499(10)		
C(1)–Se(1)–Se(2)	100.8(2)	C(21)–Se(2)–Se(1)	100.7(2)
N(2)–N(1)–C(2)	115.1(6)	N(1)–N(2)–C(11)	117.5(6)
N(4)–N(3)–C(22)	108.7(8)	N(3)–N(4)–C(31)	113.2(8)
C(6)–C(1)–C(2)	119.1(6)	C(6)–C(1)–Se(1)	122.2(5)
C(2)–C(1)–Se(1)	118.6(5)	N(1)–C(2)–C(3)	117.2(6)
N(1)–C(2)–C(1)	125.9(6)	C(3)–C(2)–C(1)	116.9(6)
C(16)–C(11)–N(2)	117.1(6)	C(16)–C(11)–C(12)	118.3(6)
N(2)–C(11)–C(12)	124.6(6)	C(26)–C(21)–C(22)	116.6(7)
C(26)–C(21)–Se(2)	123.6(6)	C(22)–C(21)–Se(2)	119.8(6)
C(23)–C(22)–C(21)	119.6(7)	C(23)–C(22)–N(3)	112.7(7)
C(21)–C(22)–N(3)	127.7(7)	C(36)–C(31)–C(32)	124.6(9)
C(36)–C(31)–N(4)	113.7(8)	C(32)–C(31)–N(4)	121.7(8)

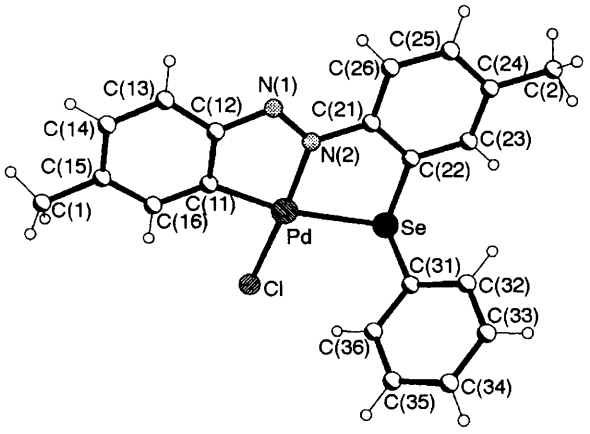


Fig. 2 Molecular structure of the palladium complex **5**

Table 2 Selected bond lengths (Å) and angles (°) for compound **5**

Pd–C(11)	1.987(3)	Pd–N(2)	1.989(2)
Pd–Cl	2.3116(7)	Pd–Se	2.4995(4)
Se–C(22)	1.929(3)	Se–C(31)	1.943(3)
N(1)–N(2)	1.279(3)	N(1)–C(12)	1.399(3)
N(2)–C(21)	1.429(3)	C(11)–C(12)	1.408(4)
C(21)–C(22)	1.398(4)		
C(11)–Pd–N(2)	79.42(10)	C(11)–Pd–Cl	96.68(9)
N(2)–Pd–Cl	176.07(6)	C(11)–Pd–Se	165.21(8)
N(2)–Pd–Se	85.96(6)	Cl–Pd–Se	97.96(2)
C(22)–Se–C(31)	99.81(11)	C(22)–Se–Pd	91.97(8)
C(31)–Se–Pd	100.47(8)	N(2)–N(1)–C(12)	110.6(2)
N(1)–N(2)–C(21)	116.6(2)	N(1)–N(2)–Pd	120.3(2)
C(21)–N(2)–Pd	123.1(2)	C(16)–C(11)–C(12)	118.3(3)
C(16)–C(11)–Pd	131.4(2)	C(12)–C(11)–Pd	110.3(2)
C(13)–C(12)–N(1)	119.0(3)	C(13)–C(12)–C(11)	121.6(3)
N(1)–C(12)–C(11)	119.4(2)	C(26)–C(21)–C(22)	119.5(2)
C(26)–C(21)–N(2)	122.2(2)	C(22)–C(21)–N(2)	118.3(2)
C(21)–C(22)–C(23)	119.4(2)	C(21)–C(22)–Se	120.5(2)
C(23)–C(22)–Se	119.9(2)		

atoms of the molecule except the phenyl group C(31)–C(36) being essentially coplanar (mean deviation 0.03 Å). At the palladium centre the chloride ligand is *trans* to the nitrogen atom. The Pd–Cl distance is 2.3116(7) Å, which is typical for Pd^{II}–Cl bonds; an analysis of the 224 Pd–Cl distances for four-co-ordinate palladium(II) complexes in the Cambridge Crystallographic Data Base yielded a mean distance of 2.326 Å.[14] The Pd–N(2) bond length [1.989(2)] is 0.05 Å smaller than the mean value found for 26 Pd–N distances, including those of bis(azobenzene)dichloropalladium(II) [2.023(9), 2.024(9) Å].[14,15] The remaining co-ordination sites of the palladium atom are occupied by mutually *trans* selenium and carbon atoms. The selenium donor is provided by the orthoselenated *p*-azotoluene and the carbon atom by the remaining *p*-azotoluene ring metallated at the *ortho* position. There is no precedent for azobenzene systems in which both rings are *ortho* substituted. The Pd–C(11) bond length [1.987(3) Å] is unremarkable and typical of palladium(II) organometallic compounds. In contrast, there are few examples of Pd–Se bond lengths; the Pd–Se distance [2.4995(4) Å] is 0.07 and 0.06 Å longer than the distances found in the complex $[Pd([16]aneSe_4)][PF_6]_2$ {[16]aneS_4 = 1,5,9,13-tetraselenacyclohexadecane}.[16]

We have found no precedents for C,N,Se ligands in the literature, but one other complex with the same donor atoms (but involving two ligands) at palladium is known; the ligands are 4-*tert*-butylpyridine and *N*,*N*-dimethylthiophene-2-carboselenoamide, with bond lengths Pd–Cl 2.362(2), Pd–Se 2.359(1), Pd–N 2.138(6) and Pd–C 1.986(6) Å.[17] It is noteworthy that in **5** the Pd–Se bond is much longer and the Pd–N bond much shorter than in ref. 17, presumably because the chemical nature of the ligands is quite different.

The main deviations from ideal sp^2 geometry in the C, N chelate system of compound **5** are the angles C(12)–C(11)–Pd and N(2)–N(1)–C(12) [110.3(2), 110.6(2)°]; the small 'bite' of the ligand [C(11)–Pd–N(2) 79.42(10)°], as was also observed for Se(R)Cl, could explain these features. In the N, Se chelate ring the N(2)–Pd–Se angle [85.96(6)°] is close to the expected value for a palladium square-planar environment and no significant deviation from ideal sp^2 geometry was found for the nitrogen and carbon atoms. However, the Pd–Se–C(22) angle [91.97(8)°] is strongly distorted from an ideal tetrahedral geometry, compared to the C(22)–Se–C(31) and Pd–Se–C(31) angles [99.81(11), 100.47(8)°]. The repulsion from the non-bonding pair on the selenium atom and the tension imposed by the five-membered ring would account for these facts. The N(2)–Pd–Cl axis is almost linear [176.07(6) Å] whereas C(11)–Pd–Se is more distorted at 165.21(8)°, probably as a consequence of chelate ring strain.

Experimental

All experimental procedures were performed under dry nitrogen using standard Schlenk techniques. Solvents were dried by refluxing with the appropriate drying agent and distilled before use. The NMR spectra were recorded at ambient temperatures on a Bruker AM 400 (^1H and ^{13}C) and AC 200 (^{77}Se) spectrometers, mass spectra on a Finnigann MAT 8430 instrument.

Preparations

Se(R)Cl. The compound Hg(R)Cl (194.6 mg, 0.44 mmol) was added to a solution of Se_2Cl_2 (100 mg, 0.44 mmol) in chloroform (20 cm^3) and stirred at room temperature for 7 d. The remaining suspension was filtered and the filtrate concentrated to dryness affording Se(R)Cl (138 mg, 97%).

Se(R)Ph 1. (*a*) The compound HgR_2 (1.312 mg, 2.12 mmol) was added to a solution of SeBrPh (500 mg, 2.12 mmol) in diethyl ether (70 cm^3). A suspension formed and was stirred at room temperature for 4 h; it was then filtered and the filtrate concentrated to dryness affording compound **1** (731 mg; 94%).

(*b*) The compound Hg(R)Ph (1 g, 2.25 mmol) was added to a solution of SeBrPh (529.9 mg, 2.25 mmol) in dichloromethane (50 cm^3). A suspension formed and was stirred at room temperature for 2 d; it was then filtered, the mother-liquor concentrated to dryness and the residue eluted over silica gel with dichloromethane–hexane (1 : 10). Removal of the solvent under vacuum afforded the organoselenide **1** (430 mg; 81%) (Found: C, 65.15; H, 4.80; N, 7.40. Calc. for $C_{20}H_{18}N_2Se$: C, 65.75; H, 4.95; N, 7.65%), mp 82 °C. EI mass spectrum: *m*/*z* 366 (M^+), 314 ($M^+ - C_4H_4^+$), 289 ($M^+ - C_6H_5^+$), 234 ($C_{12}H_{10}$), 165 ($C_{13}H_9^+$), 157 ($C_6H_5Se^+$), 119 ($C_7H_7N_2^+$), 91 ($C_7H_5^+$), 77 ($C_6H_5^+$), 65 ($C_5H_5^+$) and 50 ($C_4H_2^+$). NMR: ^1H, ($CDCl_3$), δ 7.88 (d, 2 H, C_6H_4, ^3J = 8.32), 7.79 (d, 1 H, C_6H_3, ^3J = 8.16), 7.75–7.71 (m, 2 H, Ph), 7.43–7.40 (m, 3 H, Ph), 7.31 (d, 2 H, C_6H_4), 7.06 (dd, 1 H, C_6H_3, ^4J = 1.4 Hz), 6.79 (d, 1 H, C_6H_3), 2.44 (s, 3 H, Me) and 2.21 (s, 3 H, Me); ^{13}C ($CDCl_3$), δ 150.31 (s, C, CN), 147.71 (s, C, CN), 141.40 (s, C, *C*Me), 141.35 (s, C, *C*Me), 136.75 (s, 2 CH, Ph), 134.69 (s, C, CSe), 129.74 (s, 2 CH, C_6H_4), 129.68 (s, CH, C_6H_3), 129.55 (s, 2 CH, Ph), 129.23 (s, C, CSe), 128.71 (s, CH, Ph), 126.93 (s, CH, C_6H_3), 122.82 (s, 2 CH, C_6H_4), 122.38 (s, CH, C_6H_3) and 21.49 (s, 2 Me); ^{77}Se ($SeMe_2$, δ 0); δ 416.46 (s).

SeR_2 2. The compound HgR_2 (191.3 mg, 0.31 mmol) was added to a solution of Se(R)Cl (100 mg, 0.31 mmol) in xylene (20 cm^3). A solution formed after refluxing for 12 h; the solvent was then removed under vacuum, light petroleum (b.p. 60–

Table 3 Summary of crystal data, data collection and structure refinement for compounds **3–5***

	3	**4**	**5**
Empirical formula	$C_{14}H_{13}ClN_2$	$C_{28}H_{26}N_4Se_2$	$C_{20}H_{17}ClN_2PdSe$
Colour, habit	Orange prism	Orange needle	Red rhomb
Size/mm	0.48 × 0.44 × 0.18	0.45 × 0.10 × 0.05	0.40 × 0.40 × 0.20
M	244.72	576.45	506.17
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	7.845(2)	6.759(2)	9.5136(10)
b/Å	5.6650(10)	8.273(3)	9.9006(10)
c/Å	14.375(3)	23.341(7)	10.3389(8)
α/°		98.19(2)	81.731(6)
β/°	100.01(2)	94.91(2)	67.264(6)
γ/°		93.33(3)	88.627(8)
U/Å^3	629.2(3)	1283.7(7)	888.3(2)
Z	2	2	2
D_c/Mg m^{-3}	1.292	1.491	1.892
μ/mm^{-1}	0.28	2.90	3.25
$F(000)$	256	580	496
$2\theta_{max}$/°		50	55
Reflections collected		6210	4285
Unique reflections R_{int}		4452, 0.074	4051, 0.011
Transmissions		0.71–0.95	0.55–0.99
$wR2$ (all reflections)		0.069	0.068
$R1[I > 2\sigma(I)]$		0.049	0.025
Parameters, restraints		311, 313	229, 0
S		0.71	1.05
Maximum $\Delta\rho$/e Å^{-3}		0.46	1.16

* All data collections were carried out at 173 K on a Siemens P4 diffractometer equipped with an LT-2 low-temperature attachment; λ(Mo-Kα) = 0.710 73 Å. Absorption corrections were based on ψ scans. Structures **4** and **5** were solved by the heavy-atom method and refined anisotropically on all F^2 data (using SHELXL 93).[18] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included using a riding model or as rigid methyl groups; weighting schemes of the form $w^{-1} = [\sigma^2(F_o^2) + aP^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a, b are constants optimised by the program.[18]

70 °C) added (20 cm^3) and the resulting suspension filtered off. The filtrate was concentrated to dryness affording compound **2**, which was recrystallised from dichloromethane–methanol (139.3 mg, 90%) (Found: C, 67.05; H, 5.10; N, 10.5. Calc. for $C_{28}H_{26}N_4Se$: C, 67.60; H, 5.25; N, 11.25%). EI mass spectrum: m/z 498 (M^+), 289 (SeR^+), 246 ($C_{13}H_{10}Se^+$), 194 ($C_{13}H_{10}N_2^+$), 165 ($C_{13}H_9^+$), 91 ($C_7H_5^+$) and 65 ($C_5H_5^+$). NMR: ^{1}H ($CDCl_3$), δ 7.75 (d, 4 H, C_6H_4, ^3J = 8.36), 7.74 (d, 2 H, C_6H_3, ^3J = 8.07), 7.29 (d, 2 H, C_6H_3, ^4J = 1.06 Hz), 7.23 (d, 4 H, C_6H_4), 7.15 (dd, 2 H, C_6H_3), 2.38 (s, 6 H, Me) and 2.27 (s, 6 H, Me); ^{13}C ($CDCl_3$), δ 150.57 (s, 2 C, CN), 149.95 (s, 2 C, CN), 141.40 (s, 2 C, *C*Me), 141.36 (s, 2 C, *C*Me) 134.42 (s, 2 CH, C_6H_3), 132.96 (s, 2 C, CSe), 129.67 (s, 4 CH, C_6H_4), 128.69 (s, 2 CH, C_6H_3), 122.96 (s, 4 CH, C_6H_4), 120.22 (s, 2 CH, C_6H_3), 21.50 (s, 2 Me) and 21.35 (s, 2 Me); ^{77}Se δ 379.135 (s).

RCl 3. The compound Hg(R)Cl (1.23 mg, 2.72 mmol) was added to a solution of $SeCl_4$ (200 mg, 0.91 mmol) in tetrahydrofuran (40 cm^3) and the reaction mixture refluxed for 12 h and filtered. The filtrate was then dried and hexane added to the residue; the resulting solution was then eluted with hexane over silica gel, affording pure RCl (138 mg, 62%) (Found: C, 68.15; H, 5.10; N, 11.00. Calc. for $C_{14}H_{13}ClN_2$: C, 68.70; H, 5.35; N, 11.45%). EI mass spectrum: m/z 244 (M^+), 165 ($C_{13}H_9^+$), 91 ($C_7H_5^+$) and 65 ($C_5H_5^+$). NMR ($CDCl_3$): ^{1}H, δ 7.86 (d, 2 H, C_6H_4, ^3J = 8.31), 7.62 (d, ^{1}H, C_6H_3, ^3J = 8.19), 7.36 (d, 1 H, C_6H_3, ^4J = 1.35 Hz), 7.30 (d, 2 H, C_6H_4), 7.12 (dd, 1 H, C_6H_3), 2.43 (s, 3 H, Me) and 2.40 (s, 3 H, Me); ^{13}C ($CDCl_3$), δ 151.01 (s, C, CN), 146.69 (s, C, CN), 142.31 (s, C, *C*Me), 141.90 (s, C, CMe), 135.14 (s, C, CCl), 130.96 (s, CH, C_6H_3), 129.78 (s, 2 CH, C_6H_4), 128.11 (s, CH, C_6H_3), 123.24 (s, 2 CH, C_6H_4), 117.25 (s, CH, C_6H_3), 21.55 (s, Me) and 21.20 (s, Me).

Se_2R_2 4. A solution of $N_2H_4{\cdot}H_2O$ (224 mg, 4.47 mmol) in EtOH (10 cm^3) was added to a suspension of Se(R)Cl (175 mg, 0.54 mmol) in EtOH (25 cm^3). A dark red suspension formed after stirring for 3 h at room temperature; it was then cooled to 0 °C, filtered off and air-dried to give compound **4** (130 mg, 83%) (Found: C, 57.95; H, 4.35; N, 9.50. Calc. for $C_{28}H_{26}N_4Se_2$: C, 58.35; H, 4.55; N, 9.70%). EI mass spectrum: m/z 372 (M^+ − Se), 289 (M^+ − SeR), 245 ($C_{13}H_9Se^+$), 186, 165 ($C_{13}H_9^+$), 106, 91 ($C_7H_5^+$), 79 (Se^+), 73, 65 ($C_5H_5^+$). NMR: ^{1}H ($CDCl_3$); δ 7.92 (d, 4 H, C_6H_4, ^3J = 8.30), 7.88 (d, 2 H, C_6H_3, ^3J = 8.03), 7.69 (d, 2 H, C_6H_3, ^4J = 1.17 Hz), 7.32 (d, 4 H, C_6H_4), 7.17 (dd, 2 H, C_6H_3), 2.44 (s, 6 H, Me) and 2.30 (s, 6 H, Me); ^{13}C ($CDCl_3$), δ 149.39 (s, 4 C, CN), 141.68 (s, 4 C, *C*Me), 131.84 (s, 2 CH, C_6H_3), 129.91 (s, 4 CH, C_6H_4), 129.18 (s, 2 C, CSe), 127.72 (s, 2 CH, C_6H_3), 126.26 (s, 2 CH, C_6H_3), 122.80 (s, 4 CH, C_6H_4), 21.68 (s, 2 Me) and 21.58 (s, 2 Me); ^{77}Se, δ 469.03 (s).

[Pd{C_6H_3[N=NC_6H_3(SePh)-2′,Me-4′]-2,Me-5}Cl] 5. Compound **1** (210 mg, 0.57 mmol) was added to a suspension of $PdCl_2$ (100 mg, 0.56 mmol) in methanol (20 cm^3). A dark red suspension formed after refluxing for 4 h; it was then filtered off and air-dried to give **5** (261 mg, 92%) (Found: C, 47.30; H, 3.25; N, 5.25. Calc. for $C_{20}H_{17}ClN_2PdSe$: C, 47.45; H, 3.40; N, 5.55%). EI mass spectrum: m/z 506 (M^+), 365 (M^+ − PdCl), 351 (M^+ − SePh), 180 ($C_{14}H_{12}^+$), 165 ($C_{13}H_9^+$), 152, 125, 89 ($C_7H_5^+$), 77 ($C_6H_5^+$) and 50 ($C_4H_2^+$). NMR: ^{1}H ($CDCl_3$), δ 8.08 (d, 1 H, C_6H_3, ^3J = 8.50), 7.78 (d, 1 H, C_6H_3, ^3J = 7.90), 7.67 (m, 2 H, Ph), 7.61 (s, 1 H, C_6H_3), 7.59 (s, 1 H, C_6H_3), 7.35 (d, 1 H, C_6H_3, ^3J = 8.50), 7.29 (m, 3 H, Ph), 7.05 (d, 1 H, C_6H_3, ^3J = 7.90 Hz), 2.40 (s, 3 H, Me) and 2.31 (s, 3 H, Me); ^{13}C ($CDCl_3$), δ 163.76 (s, C, CN or CPd), 163.66 (s, C, CN or CPd), 150.28 (s, C, CN or CPd), 145.06 (s, C, *C*Me), 147.95 (s, C, *C*Me), 137.30 (s, CH, C_6H_3), 135.08 (s, CH, C_6H_3), 132.13 (s, CH, C_6H_3), 131.73 (s, 2 CH, Ph), 129.95 (s, 2 CH, Ph), 129.82 (s, C, CSe), 129.51 (s, CH, C_6H_3), 129.12 (s, CH, Ph), 127.53 (s, CH, C_6H_3), 126.82 (s, C, CSe), 120.16 (s, CH, C_6H_3), 22.63 (s, Me) and 21.29 (s, Me); ^{77}Se, δ 367.39 (s).

Crystallography

Full details of the data collection and structure determination appear in Table 3. The crystal structure for RCl **3** was not fully determined because the molecule is disordered over an inversion centre.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/77.

Acknowledgements

We thank Professor J. Vicente for his continuing interest and encouragement, the Alexander von Humboldt-Stiftung for a fellowship to (M. C. R. de A.) and the Fonds der Chemischen Industrie for a materials grant.

References

1 H. J. Reich, *Acc. Chem. Res.*, 1979, **12**, 22.
2 D. J. Sandman, J. C. Stark, L. A. Acampora and P. Gagne, *Organometallics*, 1983, **2**, 549.
3 A. N. Nedugov, N. N. Pavlova and I. I. Lapkin, *Zh. Org. Khim.*, 1991, **27**, 2068.
4 A. Osuka, N. Ohmasa and H. Suzuki, *Synthesis*, 1982, 857.
5 R. A. Rossi and A. B. Peñéñory, *J. Org. Chem.*, 1981, **46**, 4580.
6 P. G. Jones and M. C. Ramírez de Arellano, *Chem. Ber.*, 1995, **128**, 741.
7 H. M. Leicester, *J. Am. Chem. Soc.*, 1935, **57**, 1901; Y. Okamoto and T. Yano, *J. Organomet. Chem.*, 1971, **29**, 99; S. A. Mbogo, T. S. Lobana, W. R. McWhinnie and M. R. Graves, *J. Organomet. Chem.*, 1990, **395**, 167.
8 H. J. Gysling, in *The Chemistry of Organic Selenium and Tellurium Compounds*, eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1986, vol. 1.
9 H. M. Leicester, *J. Am. Chem. Soc.*, 1938, **60**, 619.
10 M. A. K. Ahmed and W. R. McWhinnie, *J. Organomet. Chem.*, 1985, **281**, 205.
11 L. Christiaens, J. L. Piette, L. Laitem, M. Baiwir, J. Denoel and G. Llabres, *Org. Magn. Reson.*, 1976, **8**, 354.
12 S. Gronowitz, A. Konar and A. B. Hörnfeldt, *Org. Magn. Reson.*, 1977, **9**, 213.
13 P. G. Jones, C. Kienitz and C. Thöne, *Z. Kristallogr.*, 1994, **209**, 83.
14 A. G. Orpen, L. Bramner, F. H. Allen, O. Kennnard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
15 G. P. Khare, R. G. Little, J. T. Veal and R. J. Doedens, *Inorg. Chem.*, 1975, **14**, 2475.
16 N. R. Champness, P. F. Kelly, W. Levason, G. Reid, A. M. Z. Slawin and D. J. Williams, *Inorg. Chem.*, 1995, **34**, 651.
17 H. Mizuno, M. Kita, J. Fujita and M. Nonoyama, *Inorg. Chim. Acta*, 1992, **202**, 183.
18 G. M. Sheldrick, SHELXL 93, a program for refining crystal structures, University of Göttingen, 1983.

Received 25*th January* 1996; *Paper* 6/00584E