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Diorganodiselenides and zinc(II) organoselenolates containing (imino)aryl groups of type 2-(RN=CH)C₆H₄†‡

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Several new diorganodiselenides containing (imino)aryl groups, [2-(RN=CH)C₆H₄]₂Se₂ [R = Me₂NCH₂CH₂ (**4**), O(CH₂CH₂)₂NCH₂CH₂ (**5**), PhCH₂ (**6**), 2',6'-ⁱPr₂C₆H₃ (**7**)] were obtained by reacting [2-{(O)CH}C₆H₄]₂Se₂ (**3**) with RNH₂. Treatment of the diselenides **6** and **7** with stoichiometric amounts of K-selectride or Na resulted in isolation of the selenolates K[SeC₆H₄(CH=NCH₂Ph)-2] (**9**) and Na[SeC₆H₄(CH=NC₆H₃ⁱPr₂-2',6')-2] (**10**), respectively. The reaction of potassium selenolates with anhydrous ZnCl₂ (2 : 1 molar ratio) gave Zn[SeC₆H₄(CH=NCH₂Ph)-2]₂ (**11**) and Zn[SeC₆H₄(CH=NC₆H₃ⁱPr₂-2',6')-2]₂ (**12**). When the dark green solution obtained from diselenide **7** and an excess of Na (after removal of the unreacted metal) was reacted with anhydrous ZnCl₂ a carbon–carbon coupling reaction occurred and the 9,10-(2',6'-ⁱPr₂C₆H₃NH)₂C₁₄H₁₀ (**8**) species was obtained. The compounds were investigated in solution by multinuclear NMR (¹H, ¹³C, ⁷⁷Se, including 2D and variable temperature experiments) and by mass spectrometry. The molecular structures of **6**, **8**, **11** and **12** were established by single-crystal X-ray diffraction. All compounds are monomeric in the solid state. In the diselenide **6** the (imino)aryl group acts as a (*C*,*N*)-ligand resulting in a distorted T-shaped coordination geometry of type (*C*,*N*)SeX (X = Se). For the zinc complexes **11** and **12** the (Se,N) chelate pattern of the selenolato ligands results in tetrahedral Zn(Se,N)₂ cores.

Introduction

Organoselenium compounds containing an intramolecular $N \rightarrow Se$ interaction have attracted much interest in recent years mainly due to their increased stability as monomeric species and their applications in biology, asymmetric synthesis, catalysis or microelectronics.^{1–19} The presence of an organic group containing donor atoms available for intramolecular coordination provides increased stability of the monomeric Main Group metal selenolates.^{20–29} The Group 12 metal selenolates have raised considerable interest as single-source precursors for CVD processes.³⁰ Different strategies have been used in order to avoid polymerization, to stabilize monomeric species or, at least, to

reduce the degree of oligomerization for Group 12 metal selenolates, *i.e.* (i) the use of organoselenolato ligands with bulky substituents,³¹ (ii) the increase of the coordination number to the metal centre by additional neutral ligands,^{31d,32} or (iii) a combination of the advantages of both the above approaches by using organic groups containing donor atoms capable of intramolecular coordination.^{29,30d,e,33}

As part of our interest in hypervalent organoselenium compounds containing organic groups with pendant arms¹⁹ and their use as precursors for the preparation of metal selenolates, we have reported recently on the synthesis, solution behaviour and molecular structures of some new Group 12 metal complexes of $M[SeC_6H_4(CH_2NR_2)-2]_2$ (R = Me, Et; M = Zn, Cd).³⁴ As a continuation of these previous studies we report herein the synthesis and spectroscopic characterization of several new diorganodiselenides containing (imino)aryl groups, [2-(RN=CH)C₆H₄]₂Se₂ $[R = Me_2NCH_2CH_2$ (4), O(CH₂CH₂)₂NCH₂CH₂ (5), PhCH₂ (6), $2',6'-{}^{i}Pr_{2}C_{6}H_{3}$ (7)], as well as the alkali metal, $M[SeC_6H_4(CH=NR)-2]$ [M = K, R = PhCH₂ (9); M = Na, R = 2', 6'-¹ $Pr_2C_6H_3$ (10)], and the zinc(II) selenolates, $Zn[SeC_6H_4(CH=NR)-2]_2$ [R = PhCH₂ (11), 2',6'-Pr₂C₆H₃ (12)]. A serendipitous product, $9,10-(2',6'-iPr_2C_6H_3NH)_2C_{14}H_{10}$ (8), is also described. It was isolated following a carbon-carbon coupling process which occurred when the reaction of the dark green solution obtained from diselenide 7 and excess of Na (after removal of the unreacted metal) was reacted with anhydrous ZnCl₂. It should be noted here that C-C coupling reactions were previously described to occur when the reduction of

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[†] Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format for **6**, **8**, **11** and **12**; numbering schemes for NMR resonance assignments; selected molecular parameters for **8**; figures representing the optical isomers in the crystals of compounds **11** and **12**; figures representing the supramolecular architectures in the crystals of **6**, **8**, **11** and **12**; variable temperature NMR spectra for **12**. CCDC reference numbers 811932 (**6**), 811929 (**8**), 811930 (**11**) and 811931 (**12**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30098b

[‡]Dedicated to Professor Ionel Haiduc on the occasion of his 75th birthday.

transition metal complexes supported by Schiff-base ligands was carried out with elemental sodium. $^{35}\,$

Results and discussion

Synthesis and characterization of diselenides [2-(RN=CH) C_6H_4]₂Se₂ [R = Me₂NCH₂CH₂ (4), O(CH₂CH₂)₂NCH₂CH₂ (5), PhCH₂ (6), 2',6'-ⁱPr₂C₆H₃ (7)]

The diselenide **3**, already described in the literature, 10c,11h,36 is a useful starting material for the synthesis of diorgano diselenium (I) compounds supported by Schiff-base ligands^{11h} and it was obtained using an original, efficient procedure to deprotect the corresponding acetal 2 using aqueous HCl. The diselenides 4-7 were prepared by simple condensation between 3 and the corresponding amines (Scheme 1). When the reaction was carried out in CH₂Cl₂ in the presence of anhydrous Na₂SO₄ or in refluxing toluene with a Dean-Stark trap, with or without acid catalyst, no condensation product was observed and the unreacted starting materials were quantitatively recovered. The desired condensations were achieved in refluxing acetonitrile, in the absence of TosOH or anhydrous Na₂SO₄. It should also be noted that the attempts to prepare compound 7 using the treatment of the Grignard reagent with elemental selenium, followed by hydrolysis/oxidation, have failed. Similar condensation reactions were used to prepare mercury(II)³⁷ and antimony(III)³⁸ complexes supported by (imino)aryl ligands of the same type.

The new diselenides were obtained in good or moderate yields as orange oils (4 and 5) or pale yellow solids (6 and 7). They are soluble in common organic solvents, such as acetonitrile (hot, for 6 and 7) or chloroform. NMR data of 4-7 as well as elemental analytical data are consistent with the anticipated formulas.

The NMR spectra of the new compounds 4–7 were recorded in CDCl₃ solution, at room temperature. The assignment of resonances in the ¹H and ¹³C NMR spectra was made on the basis of 2D NMR (HSQC, HMBC and COSY) correlation spectra (for the numbering schemes, see ESI†). The room temperature NMR (¹H, ¹³C) spectra for compounds 4–7 provided no evidence for the presence of N→Se intramolecular interactions in solution. For all compounds only one set of resonances was observed, thus suggesting the equivalence of the organic groups in the molecule of the unique species, *i.e.* the diselenide, present in solution. The ¹H NMR spectra clearly show the formation of the -CH=N- double bond due to the upfield shift observed for the *CH* proton from δ 10.16 ppm for the starting material **3** (aldehyde derivative) to δ 8.57 (**4**), 8.53 (**5**), 8.67 (**6**) and 8.52 (**7**) ppm (imine derivatives). Therefore ¹H NMR spectroscopy is very useful to monitor the condensation reactions to yield diorganodiselenides supported by Schiff-base ligands (for details, see ESI[†]).

⁷⁷Se NMR spectroscopy is a useful tool for the characterization of organoselenium compounds due to the high sensitivity of this nucleus. The ⁷⁷Se chemical shifts of the diselenides **4**–7 range from δ 467.9 to 471.1 ppm. The observed values are in good agreement with that found for the related [2-(PhMeCH=NCH)C₆H₄]₂Se₂ (δ 478 ppm).¹¹*h* The downfield shift for compounds **4**–7 compared to the related diselenides [2-{E(CH₂CH₂)₂NCH₂}C₆H₄]₂Se₂ (E = O, δ 424.0 ppm; E = MeN, δ 425.4 ppm),¹⁹*b* [2-(R₂NCH₂)C₆H₄]₂Se₂ (R = Me, δ 430 ppm;^{11*a*} R = Et, δ 427.4 ppm³⁴) or [2-(CyMeNCH₂) C₆H₄]₂Se₂ (δ 431.9 ppm),^{10*a*} might indicate that the sp² nitrogen atom is involved in a stronger intramolecular N→Se interaction.¹¹*h*

In the IR spectra of compounds containing Schiff-base ligands the stretching vibration of the carbon–nitrogen double bond is expected to be found in the 1650–1550 cm⁻¹ region. Broad bands of medium intensity, shifted to lower wave numbers, would be expected for the title compounds if intramolecular N→Se coordination is present and consequent delocalization of the π electrons in the –C=N– bond over the formed C₃NSe ring occurs. The $v_{C=N}$ stretching vibration was observed at 1642 and 1634 cm⁻¹ for compounds **6** and **7**, respectively. The sharp pattern of the bands is consistent with a considerable weakness of the intramolecular N→Se coordination, if present.

The solid state molecular structure of **6** was established by single-crystal X-ray diffraction and it is depicted in Fig. 1. Selected interatomic distances and angles are listed in Table 1. The crystal contains discrete molecules of diastereoisomer E regarding both -C==N- double bonds. The conformation of the



Scheme 1 Preparation of diselenides 4–7.



Fig. 1 ORTEP representation at 30% probability and atom numbering scheme for 6.

Table 1 Selected bond distances (Å) and angles (°) for compound $\mathbf{6}$

N(1)–Se(1)–Se(2)	166.21(5)	N(2)–Se(2)–Se(1)	176.49(5)
C(7)–N(1)–C(8)	118.5(2)	C(21)–N(2)–C(22)	119.2(3)
C(7)–N(1)–Se(1)	98.0(2)	C(21)–N(2)–Se(2)	101.5(2)
C(1)–Se(1)–Se(2)	102.34(8)	C(15)–Se(2)–Se(1)	103.01(8)
C(1)–Se(1)–N(1)	74.31(9)	C(15)–Se(2)–N(2)	75.51(9)
N(1)–C(7)	1.254(3)	N(2)–C(21)	1.249(3)
N(1)–C(8)	1.455(3)	N(2)–C(22)	1.459(3)
Se(1)–Se(2) Se(1)–C(1) Se(1)–N(1)	2.3585(4) 1.935(3) 2.795(2)	Se(2)–C(15) Se(2)–N(2)	1.932(3) 2.650(2)

C–Se–Se–C skeleton can be discussed in terms of "*cisoid*" (C–Se–Se–C torsion angle smaller than 90°) and "*transoid*" (C–Se–Se–C torsion angle larger than 90°) conformations. The torsion angle found for the C(1)–Se(1)–Se(2)–C(15) core in the molecule of **6** [77.8(1)°] is consistent with a "*cisoid*" conformation.

The intramolecular selenium–nitrogen interactions established in the diselenide **6** are not equivalent [Se(1)–N(1) 2.795(2) Å; Se(2)–N(2) 2.650(2) Å; *cf.* the sum of the corresponding van der Waals radii, $\sum r_{vdW}$ (Se,N) = 3.54 Å³⁹]. They are significantly shorter than in the related [2-(R₂NCH₂)C₆H₄]₂Se₂ [R = Me, 2.856(3)/2.863(4) Å;^{11*a*} R = Et, 2.713(5)/3.068(6) Å³⁴] or [2-{E (CH₂CH₂)₂NCH₂}C₆H₄]₂Se₂ [E = O, 2.813(2)/2.825(3) Å; E = MeN, 3.135(3)/2.7393(3) Å],^{19b} a behaviour consistent with the sp² nature of the donor nitrogen atoms. Consequently, the sum of the angles around each nitrogen atom [360.0(2)° for N(1) and 359.6(2)° for N(2)] is consistent with a trigonal planar geometry.

Due to the intramolecular N \rightarrow Se interactions a distorted T-shaped geometry is achieved around each selenium atom (hypervalent 10-Se-3 species).⁴⁰ The five-membered chelate rings thus formed are basically planar, with a deviation of 0.101(2) Å of N (1) and 0.061(2) Å of N(2) from the best residual Se(1)C₃ and Se(2)C₃ planes, respectively.

A closer check of the crystal packing of the diselenide **6** revealed C–H_{aryl}··· π (Ph_{centroid}) distances which suggest some π interaction between a hydrogen atom and an aromatic ring (*i.e.* H···Ph_{centroid} contacts shorter than 3.1 Å, with an angle γ between the normal to the phenyl ring and the line defined by the H atom and Ph_{centroid} smaller than 30°). These result in the formation of polymeric chains along the *b* axis [C(21)–H(21) ···Ph_{centroid}{C(9a)–C(14a)} 2.96 Å, $\gamma = 10.7^{\circ}$] (for details, see ESI†).

Synthesis and characterization of the serendipitous product, 9,10-(2',6'-ⁱPr₂C₆H₃NH)₂C₁₄H₁₀ (8), and of the metal organoselenolates, M[SeC₆H₄(CH=NR)-2] [M = K, R = PhCH₂ (9); M = Na, R = 2',6'-ⁱPr₂C₆H₃ (10)], and Zn [SeC₆H₄(CH=NR)-2]₂ [R = PhCH₂ (11), 2',6'-ⁱPr₂C₆H₃ (12)]

In an attempt to prepare a zinc(π) selenolate the dark green THF solution resulting from reducing the diorganodiselenide 7 with a large excess of sodium mirror was added to ZnCl₂, under argon. After working-up the reaction mixture, yellow crystals of **8** were isolated. Since no resonance was observed in the ⁷⁷Se NMR



Scheme 2 Preparation of compound 8.



Fig. 2 ORTEP representation at 30% probability and atom numbering scheme for 8. Hydrogen atoms [except those attached to C(13), C(14) and nitrogen atoms] are omitted for clarity.

spectrum we presumed that this product does not contain selenium. The MS studies were also consistent with the absence of selenium and any metal. Detailed NMR studies were used to elucidate the structure of this compound. The presence of a doublet ¹H resonance in the aliphatic region (δ 4.14 ppm) uncorrelated to a carbon atom in the HSQC spectrum suggests a reduction of the *imino* group to an *amino* group, *i.e.* from -N=CH- to -NH-CH- (also supported by the doublet resonance at δ 4.99 ppm assigned to the -CH- group). The formation of the serendipitous coupling product **8** (Scheme 2) was also supported by the ESI+ mass spectrum which contains peaks corresponding to the pseudo-molecular ion $[M + H^+]$ with the expected isotopic distribution.

Single crystals of **8** were obtained by slow evaporation of an acetonitrile solution and an X-ray diffraction study has confirmed the proposed molecular structure. A molecule of **8** is depicted in Fig. 2 and reveals the presence of the -NH-CH- system as result of the *imino* group reduction and the C-C coupling reaction (the molecular parameters for **8** are available in the ESI†).

In the crystal of **8** dimer associations are formed through C–H_{aryl}····π (Ph_{centroid}) interactions [C(4)–H(4)····Ph_{centroid}{C(27)–C(32)} 2.86 Å, $\gamma = 12.6^{\circ}$]. Two intramolecular C–H_{alkyl}···π (Ph_{centroid}) interactions [C(23)–H(23B)····Ph_{centroid}{C(7)–C(12)} 2.86 Å, $\gamma = 2.5^{\circ}$; C(36)–H(36)····Ph_{centroid}{C(27)–C(32)} 3.00 Å, $\gamma = 28.3^{\circ}$] are also present. Such dimers are further associated through C–H_{methyl}···π (Ph_{centroid}) interactions [C(35)–H(35A) ····Ph_{centroid}{C(15a)–C(20a)} 2.84 Å, $\gamma = 11.5^{\circ}$] into ribbon-like chain polymers. Layers are built subsequently from parallel chains linked by C–H_{methyl}···π (Ph_{centroid}) interactions [C(34)–H (34A)····Ph_{centroid}{C(27)–C(32)} 2.84 Å, $\gamma = 14.9^{\circ}$] (for details, see ESI†).



Scheme 3 The proposed mechanism for the formation of 8 (R = 2',6'-ⁱPr₂C₆H₃).

A mechanism for the formation of 8 (Scheme 3) can be speculated based on (i) the deep green colour of the THF solution obtained from the diselenide 7 and a large excess of sodium, and (ii) the *cis*-9,10-bis(arylamino)-9,10-dihydroanthracene core of the finally isolated organic species 8. In a first step a radical intermediate (A) is considered to be formed through a THFassisted process, followed by its conversion to an organosodium species (**B**) in the presence of excess Na. Treatment with $ZnCl_2$ results in an organozinc(II) species which undergoes a rearrangement with C-C bond formation. The formation of the intermediate complex (D) might be decisive for the isolation of the cis-8 isomer. It should be mentioned here the recent report of the reaction of $2-(2',6'-{}^{1}Pr_{2}C_{6}H_{3}N=CH)C_{6}H_{4}Li$ with TiCl₄ (2:1 molar ratio) which resulted in isolation of the unexpected [cis-9,10- $PhenH_2(NR)_2TiCl_2$] species ($PhenH_2 = 9,10$ -dihydrophenanthrene; $R = 2', 6' - {}^{i}Pr_2C_6H_3$), which contains a related organic ligand obtained by sequential intramolecular C-C bond-forming reductive elimination and oxidative coupling reactions.41

Alkali metal selenolates are useful reagents for the preparation of other metal selenolates by metathesis reactions. Potassium selenolate 9 was prepared by reductive cleavage of the Se–Se bond in the diselenide 6 using potassium tri-sec-butyl hydroborate (K-selectride). Successful reduction of diselenide 7 was



Scheme 4 Preparation of compounds 11 and 12.

achieved using sodium sand (a stoichiometric amount of Na was used to avoid *over-reduction*) to yield the sodium selenolate **10**. The diselenides **4** and **5** were not used in this work to prepare new alkali metal selenolates or the corresponding zinc(II) complexes. The ¹H NMR spectra for the selenolates **9** and **10** were recorded in THF-d₈. A downfield shift of the resonance for the *imine* proton was observed for the potassium selenolate **9** (δ 9.58 ppm) compared to the corresponding diselenide **6** (δ 8.67 ppm). The reaction of **7** with sodium sand, in THF-d₈, was monitored for 15 days in an NMR tube. The resonance corresponding to the proton of the –CH==N– group was also significantly shifted downfield for the selenolate **10** (δ 9.15 ppm) with respect to the starting diselenide **7** (δ 8.52 ppm).

Zinc(II) selenolates 11 and 12 were prepared by salt metathesis reactions between anhydrous $ZnCl_2$ and two equivalents of the corresponding potassium selenolates (Scheme 4). The resulting greenish-yellow solids are moderately air-sensitive and they decompose to the corresponding diselenides in a few days. Spectroscopic studies, as well as elemental analytical data, are consistent with the anticipated formulas. Atmospheric pressure chemical ionization (APCI+) mass spectra showed for both zinc complexes significant peaks corresponding to the pseudo-molecular ion [M + H⁺].

The IR spectra indicated the presence of the -C==N- double bond for these Zn(II) complexes supported by Schiff-base ligands. The $v_{C==N}$ stretching vibration was observed at 1617 cm⁻¹ and 1604 cm⁻¹ for **11** and **12**, respectively, shifted to lower wavenumbers when compared to the corresponding diselenides ($v_{C==N}$ 1642 and 1634 cm⁻¹ for **6** and **7**, respectively). This is consistent with a strong intramolecular N \rightarrow Zn coordination and consequent partial electron delocalization within the six-membered ZnSeC₃N ring, assuming a solid state structure similar to that established for the related Zn-[SeC₆H₄(CH₂NMe₂)-2]₂.³⁴

The NMR spectra of complexes **11** and **12** were recorded in $CDCl_3$ solution. The assignment of resonances in the ¹H and ¹³C NMR spectra was based on 2D NMR (HSQC, HMBC and COSY) correlation spectra (for the numbering schemes see ESI†). The room-temperature ¹H NMR spectrum of **11** displays an AB spin system in the aliphatic region for the methylene protons of the benzyl moiety attached to nitrogen. In the



Fig. 3 1 H NMR spectra (CDCl₃, 300 MHz) of compound 12 at (a) -40 °C, and (b) +50 °C.

aromatic region the singlet resonance for the *imine* proton (δ 7.99 ppm) is shifted significantly upfield with respect to the related diselenide **6** (δ 8.67 ppm).

The ¹H NMR spectrum recorded at room temperature for **12** shows evidence of a dynamic process in solution which makes interpretation of the spectrum difficult (see ESI, Fig. S8b†). Therefore, variable temperature NMR experiments were carried out for this compound. The assignments of the chemical shifts in the spectra recorded at +50 °C and -40 °C were made according to the numbering schemes shown in Scheme 5 [(a) and (b) for +50 °C and -40 °C, respectively], and are based on 2D NMR experiments.

The two selenolato ligands in the molecular unit of 12 are equivalent since only one singlet resonance was observed in the aromatic region for the *imine* proton in the considered temperature range (+50 °C to -40 °C), e.g. δ 8.19 ppm at +50 °C, δ 8.20 ppm at +20 °C, and δ 8.24 ppm at -40 °C. In the ¹H (Fig. 3b) and ¹³C NMR (see ESI, Fig. S9a⁺) spectra recorded at +50 °C all isopropyl groups appear equivalent, thus suggesting a fast dynamic process in solution. However, the intramolecular $N \rightarrow Zn$ coordination induces restriction in the free rotation of the bulky 2,6-ⁱPr₂C₆H₃ groups and therefore non-equivalence of the two halves of this aromatic moiety. This behaviour was clearly revealed in the ¹H (Fig. 3a) and ¹³C NMR (see ESI, Fig. S9c⁺) spectra recorded at -40 °C, when the dynamic process was frozen and two sets of resonances were clearly observed for the two halves of a 2,6-¹Pr₂C₆H₃ group, including two doublet resonances in the aromatic region [δ 6.83 ppm (${}^{3}J_{\rm HH}$ 7.6 Hz), and 7.33 ppm (${}^{3}J_{\text{HH}}$ 7.7 Hz)] observed for the H-3'_a and H-3'_b protons (Scheme 5b).

The ⁷⁷Se NMR spectra also indicated an increase in the strength of the N \rightarrow Zn intramolecular coordination as the observed resonance was shifted from δ –2.5 ppm to δ –22.1 ppm when decreasing the temperature from +50 °C to



Scheme 5 Numbering scheme for NMR assignments for compound 12.

-40 °C. The significant upfield shift of the ⁷⁷Se resonance of complex **12** compared to that of the diselenide **7** is due to the filled d orbitals (d¹⁰) of the metal, which thus cannot accept electron density from the selenolato RSe⁻ ligand.^{33*a*} At lower temperature (-40 °C) the molecular structure is frozen closer to that observed in the solid state (see subsequent discussion) and the stronger N→Zn intramolecular interaction results in more polar metal–selenium bond and, consequently, in a further increased upfield shift of the ⁷⁷Se resonance of complex **12**.

Single crystals of **11** and **12** were obtained from a CH_2Cl_2 -n-hexane mixture (1 : 5, v/v), in inert atmosphere. The solid state molecular structures of both compounds were established by X-ray diffraction and are depicted in Fig. 4 and 5. Selected interatomic distances and angles are listed in Table 2.

The crystals of the zinc(II) complexes **11** and **12** consist of discrete molecules separated by normal van der Waals distances between heavy atoms. In both cases the organoselenolato groups behave as monometallic biconnective moieties, being attached to the metal centre covalently by selenium and secondarily by the *iminic* nitrogen of the pendant arms. The length of the zinc–selenium bonds [Zn(1)–Se(1) 2.3523(11)/Zn(1)–Se(2) 2.3659(12)]



Fig. 4 ORTEP representation at 30% probability and atom numbering scheme for the Δ_{Zn} -($S_{Zn(N1)}$, $S_{Zn(N2)}$)-11 isomer. Hydrogen atoms have been omitted for clarity.



Fig. 5 ORTEP representation at 30% probability and atom numbering scheme for the Δ_{Zn} -($S_{Zn(N1)}$, $S_{Zn(N1a)}$)-12 isomer. Hydrogen atoms have been omitted for clarity.

Å in **11**; Zn(1)–Se(1) 2.3562(7) Å in **12**] is similar to that observed in the related Zn[SeC₆H₄(CH₂NMe₂)-2]₂ [Zn(1)–Se(1) 2.390(2) Å].³⁴ Consistent with the sp² nature of the donor nitrogen atoms, the intramolecular metal–nitrogen interactions in **11** [Zn(1)–N(1) 2.018(5)/Zn(1)–N(2) 2.063(5) Å] and **12** [Zn(1)–N(1) 2.078(4) Å] are slightly stronger [*cf.* the sum of the corresponding van der Waals radii, $\sum r_{vdW}(Zn,N) = 2.94$ Å³⁹] than in Zn[SeC₆H₄(CH₂NMe₂)-2]₂ [Zn(1)–N(1) 2.124(5) Å].³⁴

The tetrahedral geometry achieved around the zinc centre is distorted, with dihedral angle of 83.4° (for 11) and 81.6° (for 12) between the two ZnSeN planes. A distorted tetrahedral complex with unsymmetrical chelate ligands has a C_2 -symmetry and its molecule is helical. The corresponding enantiomeric configurations at the metal can be given as Δ_M (or P_M) and Λ_M (or M_M) with respect to the right-handed or left-handed helicity of the two chelate rings along the C_2 -axis⁴² passing through the centre of the Se...Se edge, the metal ion and the centre of the

Table 2	Selected bond	distances (Å) and	angles (°) for	compounds 11
and 12				

11		12 ^{<i>a</i>}	
Zn(1)-Se(1)	2.3523(11)	Zn(1)-Se(1)	2.3562(7)
Zn(1) - Se(2) Zn(1) = N(1)	2.3659(12)	$7_{n}(1)$ N(1)	2.078(4)
$Z_{n(1)} = N(1)$ $Z_{n(1)} = N(2)$	2.018(5)	$\Sigma \Pi(1) = \mathbb{N}(1)$	2.078(4)
2n(1) n(2)	2.005(5)		
Se(1)-C(1)	1.910(6)	Se(1)-C(1)	1.894(6)
N(1)-C(7)	1.284(7)	N(1)-C(7)	1.277(6)
N(1)-C(8)	1.472(7)	N(1)–C(8)	1.451(6)
Se(2) - C(15)	1.908(6)		
N(2)-C(21)	1.271(7)		
N(2)–C(22)	1.485(7)		
$S_{2}(1) = T_{2}(1) = S_{2}(2)$	119.02(4)	$S_{2}(1) = 7\pi(1) = S_{2}(1_{2})$	125 22(5)
Se(1) - Zii(1) - Se(2) Se(1) - Zii(1) - N(1)	110.92(4) 102.36(12)	Se(1) - Zii(1) - Se(1a) Se(1) - Zii(1) - N(1)	123.22(3) 07.03(12)
Se(2) - Zn(1) - N(2)	98 18(12)	SC(1) = ZII(1) = IV(1)	97.95(12)
Se(1) - Zn(1) - N(2)	118.66(14)	Se(1) - Zn(1) - N(1a)	110.06(12)
Se(2)-Zn(1)-N(1)	116.21(12)	~~(-) =-(-) - ()	
N(1) - Zn(1) - N(2)	101.98(18)	N(1)-Zn(1)-N(1a)	117.0(2)
$C(1)$ $S_{2}(1)$ $T_{2}(1)$	101.05(18)	$C(1)$ $S_{2}(1)$ $T_{2}(1)$	00.26(17)
C(1) = Se(1) = ZII(1) C(15) = Se(2) = Zn(1)	101.93(18) 100.38(18)	C(1)-Se(1)-ZII(1)	99.20(17)
C(13) - 3C(2) - ZII(1)	100.38(18)		
C(7)-N(1)-Zn(1)	126.7(4)	C(7)-N(1)-Zn(1)	125.0(4)
C(8) - N(1) - Zn(1)	115.6(3)	C(8) - N(1) - Zn(1)	117.5(3)
C(7) - N(1) - C(8)	117.3(5)	C(7) - N(1) - C(8)	116.1(4)
C(21) = N(2) = Zn(1)	126 8(4)		
C(22) - N(2) - Zn(1)	117.3(4)		
C(21)-N(1)-C(22)	115.9(5)		

Symmetry equivalent atoms (-x, y, 0.5 - z) are given by "a".

N…N edge. Zinc complexes containing a Schiff base ligand⁴³ or a reduced Schiff base ligand⁴⁴ were previously reported to crystallize as Λ_{Zn} and Δ_{Zn} isomers, respectively.

The ZnSeC₃N metallacycles exhibit different conformations. In the molecule of **11** one six-membered chelate ring is almost planar [deviations from the best SeC₃: Zn(1) 0.162 Å, N(1) -0.007 Å], while the other one exhibits a boat conformation with selenium and C_{imine} atoms at the apices. By contrast, for **12** both six-membered chelate rings have a boat conformation with selenium and C_{imine} atoms at the apices.

The intramolecular N \rightarrow Zn coordination resulting in nonplanar chelate rings induces planar chirality (with the aromatic ring and the metal atom as chiral plane and pilot atom, respectively; isomers are given as $S_{Zn(N)}$ and $R_{Zn(N)}$.⁴⁵ Therefore both compounds crystallize as a 1:1 mixture of Δ_{Zn} -($S_{Zn(N)}$, $S_{Zn(N)}$)/ Λ_{Zn} -($R_{Zn(N)}$, $R_{Zn(N)}$) isomers (with respect to the metal centre and the two chelate rings *per* molecular unit, respectively).

In contrast to the Zn[SeC₆H₄(CH₂NMe₂)-2]₂ analogue,³⁴ in **11** and **12** the two C₆H₄ rings of the molecular unit are placed on opposite sides of the best plane described by the nitrogen and the *imino* carbon atoms with respect to the selenium and the zinc atoms. In the case of the centrosymmetric molecule of **12** this brings the aromatic C₆H₄ rings closer to the methyl groups of the 2,6-ⁱPr₂C₆H₃ moieties and weak C–H_{methyl}···π (Ph_{centroid}) interactions [C(19)–H(19C)····Ph_{centroid}{C(1a)–C(6a)} 2.93 Å, $\gamma = 8.0^{\circ}$] are established.

A closer inspection of the crystal structure of the zinc(II) selenolates revealed supramolecular associations built through

C–H··· π (Ph_{centroid}) interactions. Thus, in the crystal of **11** intermolecular C–H_{ary1}··· π (Ph_{centroid}) interactions [C(5)–H(5)···Ph_{centroid} {C(23b)–C(28b)} 2.73 Å, $\gamma = 0.8^{\circ}$] are established between neighbouring molecules resulting in *zig-zag* chain polymers of either Λ_{Zn} -($R_{Zn(N1)}$, $R_{Zn(N2)}$) or Δ_{Zn} -($S_{Zn(N1)}$, $S_{Zn(N2)}$) isomers, respectively. By contrast, the crystal of **12** contains chain polymers of alternating Λ_{Zn} -($R_{Zn(N1)}$, $R_{Zn(N1a)}$) and Δ_{Zn} -($S_{Zn(N1)}$, $S_{Zn(N1a)}$) isomers doubly bridged through C–H_{methy1}··· π (Ph_{centroid}) interactions [C(15)–H(15C)···Ph_{centroid}{C(8a)–C(13a)} 2.92 Å, $\gamma =$ 4.0°] (for details, see ESI†). Apparently, in both cases no contacts are established between parallel polymeric chains.

Conclusions

New diorganodiselenides supported by Schiff-base ligands, $[2-(RN=CH)C_6H_4]_2Se_2$ [R = Me₂NCH₂CH₂ (4), O(CH₂CH₂)₂- NCH_2CH_2 (5), PhCH₂ (6), 2', 6'-ⁱPr₂C₆H₃ (7)] were prepared and characterized in solution and in the solid state. When anhydrous ZnCl₂ was treated with the dark green solution obtained from diselenide 7 and an excess of Na (after removal of the unreacted metal) a C-C coupling reaction occurred and the 9,10- $(2',6'-{}^{1}Pr_{2}C_{6}H_{3}NH)_{2}C_{14}H_{10}$ (8) species was obtained. Treatment of anhydrous ZnCl₂ with potassium selenolates gave Zn $[SeC_6H_4(CH=NCH_2Ph)-2]_2$ (11) and $Zn[SeC_6H_4(CH=NC_6H_3 {}^{1}Pr_{2}-2',6'-2]_{2}$ (12). For 12 a dynamic behaviour in solution was evidenced by variable temperature NMR studies. The solid-state monomeric structure of both complexes is stabilized by intramolecular $N \rightarrow Zn$ interactions. The unsymmetrical (Se,N) chelate pattern of the selenolato ligands resulted in distorted tetrahedral Zn(Se,N)₂ cores with non-planar ZnSeC₃N metallacycles. This induces both helical chirality at the metal centre and planar chirality and therefore the complexes were found to crystallize as a 1:1 mixture of Δ_{Zn} - $(S_{Zn(N)}, S_{Zn(N)})/\Lambda_{Zn}$ - $(R_{Zn(N)}, R_{Zn(N)})$ isomers. Supramolecular associations built through C-H··· π (Ph_{centroid}) interactions were found in the crystals of the diselenide 6, and species 8 resulting from a C-C coupling reaction, as well as the zinc(II) organoselenolates 11 and 12.

Experimental section

General procedures

Multinuclear NMR spectra were recorded at room temperature on BRUKER 200, 300, 400 and 500 instruments. Variable temperature studies were recorded on BRUKER 500 (for 11) and 300 (for 12) instruments. The ¹H and ¹³C chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. CHCl₃: ¹H 7.26, ¹³C 77.0 ppm; THF: ¹H 3.58, 1.73 ppm). ¹H and ¹³C resonances were assigned generally using 2D NMR experiments (COSY, HMQC and HMBC). The ⁷⁷Se spectra were obtained using diphenyl diselenide as an external standard. Chemical shifts are reported relative to dimethyl selenide (δ 0 ppm) by assuming that the resonance of the standard is at δ 461 ppm.⁴⁶ The NMR spectra were processed using the MestReC and MestReNova software.47 Mass spectra (ESI and APCI) were recorded on an Agilent 6320 Ion Trap instrument. Infrared spectra were recorded on a Jasco FTIR 615 machine, as KBr pellets. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. Elemental analyses were

performed on a VarioEL analyser. For the alkali metal organoselenolates **9** and **10** elemental analyses were not performed due to their high sensitivity to hydrolysis. All manipulations were carried out under an inert atmosphere of argon using Schlenk techniques. Solvents were dried and freshly distilled under argon prior to use. The acetal $2-[(CH_2O)_2CH]C_6H_4Br^{48}$ was obtained according to a reported literature method. All other reagents were obtained from Aldrich or Merck, and were used as received.

Synthesis of [2-{(CH₂O)₂CH}C₆H₄]Li (1). The compound was prepared according to a reported method^{11e} from a solution of n-BuLi in hexane (13.0 mL, 1.6 M, 20.8 mmol) and 2-bromobenzaldehyde acetal (4.696 g, 20.5 mmol) in diethyl ether (100 mL). The resulting white precipitate was left to deposit, washed with diethyl ether (2 × 50 mL) and dried in vacuum to give 1.952 g (61%) of compound 1.

Synthesis of $[2-{(CH_2O)_2CH}C_6H_4]_2Se_2$ (2). The diselenide was obtained according to a slightly modified published procedure.^{11e} Selenium powder (0.987 g, 12.50 mmol) was added under argon to a solution of 1 (1.951 g, 12.50 mmol) in dry THF (100 mL). The reaction mixture was stirred for 2 h and then it was poured into water (100 mL). Stirring was continued for one hour, then the resulting mixture was filtered to remove unreacted selenium powder and extracted with diethyl ether and CH₂Cl₂. The combined organic extracts were dried over anhydrous Na₂SO₄, concentrated to ca. 10 mL and hexane (50 mL) was added. The resulting precipitate was collected by filtration and dried in vacuum to afford 2 as a yellowish solid (1.539 g, 54%). ¹H NMR (300 MHz, CDCl₃): δ 4.13 (8 H, m, H-8, C₂H₄O₂), 6.04 (2 H, s, H-7, O₂CH), 7.27 (4 H, m, H-4,5, C₆H₄), 7.50 (2 H, m, H-3 or H-6, C₆H₄), 7.81 (2 H, m, H-3 or H-6, C_6H_4). ⁷⁷Se NMR (57.3 MHz, CDCl₃): δ 411.6.

Synthesis of $[2-{(O)CH}C_6H_4]_2Se_2$ (3). A solution of HCl (3.5 mL, 1 M) was added to a stirred solution of 2 (0.808 g, 1.77 mmol) in acetone (30 mL). The reaction mixture was refluxed for 1 h and then it was concentrated until precipitation started. Water (10 mL) was added and the solid product was filtered, washed with water and dried in vacuum to give compound **3** as a yellow solid (0.620 g, 95%). ¹H NMR (300 MHz, CDCl₃): δ 7.41 (4 H, m, H-4,5, C₆H₄), 7.83 (4 H, m, H-3,6, C₆H₄), 10.16 (2 H, s, H-7, CH=O). ⁷⁷Se NMR (57.3 MHz, CDCl₃): δ 457.4.

Synthesis of [2-(Me₂NCH₂CH₂N=CH)C₆H₄]₂Se₂ (4). 2-(Dimetilamino)ethylamine (0.100 g, 1.13 mmol) was added to a stirred solution of 3 (0.208 g, 0.54 mmol) in acetonitrile (30 mL), at reflux temperature. The reaction mixture was refluxed for one hour after which the solvent was removed. The remaining residue was extracted with hexane (2 × 20 mL) and the evaporation of the solvent yielded **4** as an orange oil (0.184 g, 67%). Anal. Calcd for C₂₂H₃₀N₄Se₂ (508.43): C, 51.97; H, 5.95; N 11.02; Found: C, 51.68; H, 5.76; N 10.86%. ¹H NMR (300 MHz, CDCl₃): δ 2.33 (12 H, s, H-10, N(CH₃)₂), 2.74 (4 H, t, H-9, CH₂, ³J_{HH} 7.0 Hz), 3.86 (4 H, t, H-8,=NCH₂, ³J_{HH} 6.9 Hz), 7.21 (4 H, m, H-4,5, C₆H₄), 7.53 (2 H, dd, H-3, C₆H₄, ³J_{HH} 7.1, ⁴J_{HH} 1.5 Hz), 7.85 (2 H, d, H-6, C₆H₄, ³J_{HH} 7.4 Hz), 8.57 (2 H, s, H-7, CH=N). ¹³C NMR (75.5 MHz, CDCl₃): δ 45.90 [s, C-10, N(CH₃)₂], 58.69 (s, C-8,=NCH₂), 60.31 (s, C-9, CH₂), 125.65 (s, C-5), 130.26 (s, C-4), 131.31 (s, C-3 or C-6), 131.36 (s, C-3 or C-6), 133.39 (s, C-2), 134.75 (s, C-1), 161.63 (s, C-7, CH=N). ⁷⁷Se NMR (57.3 MHz, CDCl₃): δ 467.9.

Synthesis of [2-{O(CH₂CH₂)₂NCH₂CH₂N=CH}C₆H₄]₂Se₂ (5). 4'-(2-Aminoethyl)morfoline (0.141 g, 1.08 mmol) was added to a stirred solution of 3 (0.199 g, 0.54 mmol) in acetonitrile (30 mL), at reflux temperature. The reaction mixture was refluxed for one hour and then the solvent was removed. The remaining residue was extracted with hexane $(2 \times 20 \text{ mL})$ and the evaporation of the solvent yielded 5 as an orange oil (0.240 g, 75%). Anal. Calcd for C₂₆H₃₄N₄O₂Se₂ (592.50): C, 52.71; H, 5.78; N 9.46; Found: C, 52.46; H, 5.86; N 9.33%. ¹H NMR (300 MHz, CDCl₃): δ 2.54 (8 H, t, H-10, NCH₂, ³J_{HH} 4.5 Hz), 2.76 (4 H, t, H-9, CH₂N, ³J_{HH} 6.9 Hz), 3.69 (8 H, t, H-11, CH₂O, ³*J*_{HH} 4.6 Hz), 3.85 (4 H, t, H-8,=NCH₂, ³*J*_{HH} 6.7 Hz), 7.19 (4 H, m, H-4,5, C_6H_4), 7.50 (2 H, dd, H-3, C_6H_4 , ${}^{3}J_{HH}$ 7.3, ⁴J_{HH} 1.6 Hz), 7.83 (2 H, d, H-6, C₆H₄, ³J_{HH} 7.5 Hz), 8.53 (2 H, s, H-7, CH=N). ¹³C NMR (75.5 MHz, CDCl₃): δ 53.77 (s, C-10, NCH₂), 57.55 (s, C-8,=NCH₂), 59.25 (s, C-9, CH₂N), 66.78 (s, C-11, CH₂O), 125.59 (s, C-5), 130.18 (s, C-4), 131.16 (s, C-3 or C-6), 131.23 (s, C-3 or C-6), 133.19 (s, C-2), 134.55 (s, C-1), 161.66 (s, C-7, CH=N). ⁷⁷Se NMR (57.3 MHz, CDCl₃): *δ* 467.9.

Synthesis of [2-(PhCH₂N=CH)C₆H₄]₂Se₂ (6). Benzyl amine (0.231 g, 2.16 mmol) was added to a stirred solution of 3 (0.398 g, 1.08 mmol) in acetonitrile (100 mL), at reflux temperature. The reaction mixture was refluxed for one hour. Cooling of the reaction mixture yielded compound 6 as a pale yellow solid (0.555 g, 94%) which was filtered off and dried in vacuum, mp 134-135 °C. Anal. Calcd for C₂₈H₂₄N₂Se₂ (546.41): C, 61.55; H, 4.43; N 5.13; Found: C, 61.26; H, 4.56; N 5.26%. ¹H NMR (300 MHz, CDCl₃): δ 5.01 (4 H, s, H-8, NCH₂), 7.28 (6 H, m, H-4,5, C_6H_4 + H-4', C_6H_5), 7.42 (4 H, t, H-3', C_6H_5 , ${}^{3}J_{HH}$ 7.5 Hz), 7.52 (4 H, d, H-2', C₆H₅, ³J_{HH} 7.5 Hz), 7.60 (2 H, d, H-3, C₆H₄, ³J_{HH} 7.1 Hz), 7.95 (2 H, d, H-6, C₆H₄, ³J_{HH} 7.7 Hz), 8.67 (2 H, s, H-7, CH=N). ¹³C NMR (75.5 MHz, CDCl₃): δ 63.97 (s, C-8,=NCH₂), 125.68 (s, C-4 or C-5), 126.94 (s, C-4'), 127.92 (s, C-2'), 128.46 (s, C-3'), 130.43 (s, C-4 or C-5), 131.44 (s, C-6), 131.74 (s, C-3), 133.45 (s, C-1), 134.63 (s, C-2), 138.92 (s, C-1'), 161.94 (s, C-7, CH=N). ⁷⁷Se NMR (57.3 MHz, CDCl₃): δ 470.3. IR (KBr): ν(-CH=N-) 1642(s) cm^{-1} .

Synthesis of [2-(2',6'-ⁱPr₂C₆H₃N=CH)C₆H₄]₂Se₂ (7). 2,6-Diisopropylaniline (0.365 g, 2.06 mmol) was added to a stirred solution of **3** (0.379 g, 1.03 mmol) in acetonitrile (30 mL), at reflux temperature. The reaction mixture was refluxed for one hour to give compound **7** as a pale yellow solid (0.403 g, 57%) which was filtered off and dried in vacuum, mp 148–149 °C. Anal. Calcd for C₃₈H₄₄N₂Se₂ (686.70): C, 66.47; H, 6.46; N 4.08; Found: C, 66.23; H, 6.25; N 4.26%. ¹H NMR (300 MHz, CDCl₃): δ 1.23 (24 H, d, H-8', CH₃, ³J_{HH} 6.9 Hz), 3.11 (4 H, hept, H-7', CH, ³J_{HH} 6.8 Hz), 7.19 (6 H, m, H-3',4', C₆H₃), 7.35 (4 H, m, H-4,5, C₆H₄), 7.70 (2 H, m, H-3, C₆H₄), 8.05 (2 H, m, H-6, C₆H₄), 8.52 (2 H, s, H-7, CH==N). ¹³C NMR (75.5 MHz, CDCl₃): δ 23.79 (s, C-8', CH₃), 28.06 (s, C-7', CH), 123.01 (s, C-3'), 124.62 (s, C-4'), 125.80 (s, C-5), 131.15 (s, C-4), 131.66 (s, C-6), 132.57 (s, C-3), 134.39 (s, C-1 or C-2), 134.61 (s, C-1 or C-2), 137.92 (s, C-2'), 147.33 (s, C-1'), 162.34 (s, C-7, CH=N). ⁷⁷Se NMR (57.3 MHz, CDCl₃): δ 471.1. IR (KBr): ν (-CH=N-) 1634(s) cm⁻¹.

Synthesis of 9,10-(2',6'-ⁱPr₂C₆H₃NH)₂C₁₄H₁₀ (8). A solution of 7 (0.40 g, 0.58 mmol) in anhydrous THF (50 mL) was added to a sodium mirror (large excess), under argon atmosphere. The reaction mixture was stirred overnight, then filtered to remove unreacted Na. The resulting dark green solution was added via canula to ZnCl₂ (0.079 g, 0.58 mmol) in anhydrous THF (10 mL). The reaction was left overnight to complete, then the THF was removed under vacuum and the remaining crude product was treated with acetonitrile in open atmosphere. The insoluble solid was filtered off and slow evaporation of the solvent from the clear solution yielded 8 as yellow, needleshaped, crystals (0.121 g, 38%), mp 187-188 °C. Anal. Calcd for C₃₈H₄₆N₂ (530.77): C, 85.99; H, 8.74; N 5.28; Found: C, 85.77; H, 8.62; N 5.26%. ¹H NMR (300 MHz, CDCl₃): δ 1.12 (24 H, d, H-8', CH₃, ³J_{HH} 6.8 Hz), 3.36 (4 H, hept, H-7', CH, ³*J*_{HH} 6.8 Hz), 4.14 (2 H, d, NH, ³*J*_{HH} 6.5 Hz), 4.99 (2 H, d, H-9, CH, ${}^{3}J_{HH}$ 6.5 Hz), 7.19 (14 H, m, H-3',4', C₆H₃ + H-1,2). ${}^{13}C$ NMR (75.5 MHz, CDCl₃): δ 23.98 (s, C-8', CH₃), 27.99 (s, C-7', CH), 64.23 (s, C-9, NHCH), 123.40 (s, C-3'), 124.75 (s, C-4'), 127.35 (s, C-2), 128.53 (s, C-1), 139.22 (s, C-1a), 141.34 (s C-1'), 144.81 (s, C-2'). MS (ESI+), m/z (%): 531 (100) $[M + H^+].$

Synthesis of K[SeC₆H₄(CH=NCH₂Ph)-2] (9). KB[CH(CH₃) C₂H₅]₃H (K-selectride) (1 mL of 1 M solution in THF) was added dropwise to a stirred solution of 6 (0.27 g, 0.5 mmol) in anhydrous THF (30 mL) at -78 °C, under argon atmosphere. Stirring was continued until the reaction mixture warmed up to room temperature. The solvent was removed under vacuum and the crude product was washed with anhydrous toluene and pentane to yield an orange solid. ¹H NMR (200 MHz, THF-d₈): δ 4.72 (2 H, s, H-8, NCH₂), 6.66 (2 H, m, aryl), 7.25 (5 H, m, aryl), 7.71 (2 H, m, aryl), 9.58 (1 H, s, H-7, CH=N).

Synthesis of Na[SeC₆H₄(CH=NC₆H₃ⁱPr₂-2',6')-2] (10). Sodium (6 mg, 0.26 mmol) was mixed with 7 (89.4 mg, 0.13 mmol) in an NMR tube with a Young tap and THF-d₈ (*ca.* 0.6 mL) was condensed over the mixture. The yellow reaction mixture was monitored for several days until the NMR spectrum of the mixture remained unchanged. ¹H NMR (200 MHz, THF-d₈): δ 1.18 (12 H, d, H-8', CH₃, ³J_{HH} 6.6 Hz), 3.13 (2 H, hept, H-7', CH, ³J_{HH} 6.8 Hz), 6.96 (5 H, m, H-3',4', C₆H₃ + H-4,5, C₆H₄), 7.86 (2 H, m, H-3,6, C₆H₄), 9.15 (1 H, s, H-7, CH=N).

Synthesis of $Zn[SeC_6H_4(CH=NCH_2Ph)-2]_2$ (11). A solution of 10 [prepared as above from K-selectride (1 mL of 1 M solution in THF) and 6 (0.273 g, 0.50 mmol) in anhydrous THF (30 mL)] was added *via* canula to $ZnCl_2$ (0.068 g, 0.50 mmol) in anhydrous THF (10 mL). The reaction was left overnight to complete. The THF was removed in vacuum, the crude product was treated with anhydrous CH_2Cl_2 and the KCl was filtered off. The solvent was evaporated from the clear solution, the remaining solid was washed several times with anhydrous diethyl ether and then dried in vacuum to give 11 as a greenish-yellow solid

Table 3	Crystallographic	data for	compounds	6, 8,	11	and 12	
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	6	8	11	12
Empirical formula	C ₂₈ H ₂₄ N ₂ Se ₂	C ₃₈ H ₄₆ N ₂	C ₂₈ H ₂₄ N ₂ Se ₂ Zn	C ₃₈ H ₄₄ N ₂ Se ₂ Zn
M	546.41	530.77	611.78	752.04
Т	297(2)	297(2)	297(2)	297(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\overline{1}$	$P2_1/n$	C2/c
a (Å)	10.8520(8)	10.6487(10)	13.398(5)	15.0512(16)
$b(\mathbf{A})$	22.7903(18)	11.7585(11)	14.424(6)	13.1067(14)
$c(\dot{A})$	9.6203(7)	13.4318(12)	13.532(5)	18.4747(19)
α (°)	90.00	90.607(2)	90.00	90.00
β (°)	90.1520(10)	93.675(2)	110.608(7)	101.281(2)
γ (°)	90.00	106.769(2)	90.00	90.00
$V(Å^3)$	2379.3(3)	1606.3(3)	2447.7(17)	3574.1(7)
Z	4	2	4	4
No. of reflections collected	22 703	15 517	11 492	12 649
No. of independent reflections	$4190 (R_{int} = 0.0476)$	5617 ($R_{int} = 0.0557$)	$4214 (R_{int} = 0.0953)$	$3143 (R_{int} = 0.0582)$
Absorption correction	Multi-scan ⁵⁰	Multi-scan ⁵⁰	Multi-scan ⁵⁰	Multi-scan ⁵⁰
μ (Mo-K α) (mm ⁻¹)	3.126	0.063	3.997	2.751
$R_1 \left[I > 2\sigma(I) \right]$	0.0291	0.0799	0.0584	0.0660
wR_2	0.0681	0.1532	0.1490	0.1187
GOF on F^2	1.053	1.196	0.978	1.211

(0.142 g, 46%), mp 215–216 °C. Anal. Calcd for $C_{28}H_{24}N_2Se_2Zn$ (611.78): C, 54.97; H, 3.95; N 4.58; Found: C, 54.76; H, 3.85; N 4.36%. ¹H NMR (500 MHz, CDCl₃): δ AB spin system with A at 4.63 and B at 4.74 ppm (4 H, H-8, NCH₂, ²J_{HH} 13.8 Hz), 6.89 (4 H, d, H-2', C₆H₅, ³J_{HH} = 7.5 Hz), 7.12 (12 H, m, H-3,4,5, C₆H₄ + H-3',4', C₆H₅), 7.95 (2 H, d, H-6, C₆H₄, ³J_{HH} 7.4 Hz), 7.99 (2 H, s, H-7, CH=N). ¹³C NMR (125.8 MHz, CDCl₃): δ 64.34 (s, C-8,=NCH₂), 123.31 (s, C-4), 127.76 (s, C-4'), 128.44 (s, C-3'), 128.86 (s, C-2'), 130.88 (s, C-5), 131.54 (s, C-1), 135.33 (s, C-1'), 138.70 (s, C-3), 139.10 (s, C-6), 139.33 (s, C-2), 172.00 (s, C-7, CH=N). ⁷⁷Se NMR (76.3 MHz, CDCl₃): δ 20.2. MS (APCI+), *m/z* (%): 654 (15) [M + CH₃CN + H⁺]. 613 (100) [M + H⁺]. IR (KBr): *v*(-CH=N–) 1617(s) cm⁻¹.

Synthesis of Zn[SeC₆H₄(CH=NC₆H₃ⁱPr₂-2',6')-2]₂ (12). KB [CH(CH₃)C₂H₅]₃H (K-selectride) (1 mL of 1 M solution in THF) was added dropwise to a stirred solution of 7 (0.343 g, 0.50 mmol) in anhydrous THF (30 mL) at -78 °C, under argon atmosphere. Stirring was continued until the reaction mixture warmed up to room temperature. The resulting solution was added via canula to ZnCl₂ (0.068 g, 0.50 mmol) in anhydrous THF (10 mL). The reaction was left overnight to complete. The THF was removed in vacuum, the crude product was treated with anhydrous CH2Cl2 and the KCl was filtered off. The solvent was evaporated from the clear solution, the remaining solid was washed with anhydrous diethyl ether (20 mL) and then dried in vacuum to give 12 as a greenish-yellow solid (0.213 g, 56%), mp 236-237 °C. Anal. Calcd for C₃₈H₄₄N₂Se₂Zn (752.04): C, 60.69; H, 5.90; N 3.72; Found: C, 60.36; H, 5.85; N 3.58%. ¹H NMR (300 MHz, CDCl₃, -40 °C): δ 0.41 (6 H, d, H-8'_{a1}, CH₃, ³J_{HH} 6.1 Hz), 0.98 (6 H, d, H-8'_{a2}, CH₃, ³J_{HH} 6.3 Hz), 1.05 (6 H, d, H-8'_{b1}, CH₃, ³J_{HH} 6.6 Hz), 1.39 (6 H, d, H-8'_{b2}, CH₃, ${}^{3}J_{HH}$ 6.5 Hz), 2.54 (2 H, hept, H-7'_a, CH, ${}^{3}J_{HH}$ 6.2 Hz), 3.24 (2 H, hept, H-7'_b, CH, ³J_{HH} 6.5 Hz), 6.83 (2 H, d, H-3'_a, C₆H₃, ³J_{HH} 7.6 Hz), 6.99 (2 H, t, H-5, C₆H₄, ³J_{HH} 7.3 Hz), 7.08 (2 H, t, H-4, C₆H₄, ³J_{HH} 7.3 Hz), 7.16 (2 H, d, H-3, C₆H₄, ³J_{HH} 7.6 Hz), 7.22 (2 H, t, H-4', C₆H₃, ³J_{HH} 7.7 Hz), 7.33

³J_{HH} 7.8 Hz), 8.24 (2 H, s, H-7, CH=N). ¹H NMR (300 MHz, CDCl₃, +50 °C): δ 1.02 (24 H, s, br, H-8, CH₃), 3.03 (4 H, s, br, H-7, CH), 6.92 (2 H, t, H-5, C₆H₄, ³J_{HH} 7.5 Hz), 7.06 (8 H, m, H-3', C_6H_3 + H-3,4, C_6H_4), 7.18 (2 H, t, H-4', C_6H_3 , ${}^{3}J_{HH}$ 7.6 Hz), 7.53 (2 H, d, H-6, C₆H₄, ³J_{HH} 7.8 Hz), 8.19 (2 H, s, H-7, CH=N). ¹³C NMR (75.5 MHz, CDCl₃, -40 °C): δ 20.69 (s, C-8'_{a1}, CH₃), 23.56 (s, C-8'_{b2}, CH₃), 25.22 (s, C-8'_{a2}, CH₃), 25.71 (s, C-8'b1, CH3), 28.52 (s, C-7'b, CH), 29.37 (s, C-7'a, CH), 122.28 (s, C-3'a), 123.72 (s, C-4), 124.07 (s, C-3'b), 126.71 (s, C-4'), 131.38 (s, C-5), 131.84 (s, C-2), 137.20 (s, C-3), 137.77 (s, C-1), 138.58 (s, C-2'a), 138.64 (s, C-6), 141.30 (s, C-2'_b), 146.63 (s, C-1'), 173.37 (s, C-7, CH=N). ¹³C NMR (75.5 MHz, CDCl₃, +50 °C): δ 23.94 (s, br, C-8', CH₃), 29.12 (s, C-7', CH), 123.47 (s, C-3', C-4), 126.90 (s, C-4'), 131.06 (s, C-5), 132.48 (s, C-2), 137.04 (s, C-3), 139.21 (s, C-6), 139.46 (s, C-1), 140.55 (s, C-2'), 147.02 (s, C-1'), 173.92 (s, C-7, CH=N). ⁷⁷Se NMR (76.3 MHz, CDCl₃, -40 °C): $\delta -22.1$. ⁷⁷Se NMR (76.3 MHz, CDCl₃, +20 °C): δ -9.4. ⁷⁷Se NMR (76.3 MHz, CDCl₃, +50 °C): δ –2.5. MS (APCI+), *m/z* (%): 753 (100) [M + H⁺]. IR (KBr): v(-CH=N-) 1604 (s) cm⁻¹.

(2 H, d, H-3'_b, C₆H₃, ³J_{HH} 7.7 Hz), 7.50 (2 H, d, H-6, C₆H₄,

Crystal structures

Yellow crystals of **6** were obtained by slow diffusion, using a CH₂Cl₂–CH₃CN system (1 : 4 by volume). Colourless crystals of **8** were grown by slow evaporation of an acetonitrile solution. Yellow crystals of **11** (at room temperature) and **12** (at -20 °C) were grown by slow diffusion using a CH₂Cl₂-n-hexane system (1 : 4 by volume), under argon. The details of the crystal structure determination and refinement are given in Table 3. The crystals were mounted with epoxy glue on cryoloops and the data were collected at room temperature on a Bruker SMART APEX diffractometer, using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were refined with anisotropic thermal parameters. The hydrogen atoms attached to nitrogens in **8** were located from the difference map. The other hydrogen

atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.⁴⁹ The drawings were created with the Diamond program.⁵¹

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