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Synthesis and Structural Study of Novel Selenation Derivatives of *N, N*-Dialkylcyanamides

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The reaction of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide {[PhP(Se)(μ-Se)]$_2$, Woollins' reagent, **WR**} with *N, N*-dialkylcyanamides **1**–**3** in refluxing toluene solution led to the corresponding [2+3] cycloaddition products 4-dialkylamino-2,5-diphenyl-1,3,2,5-selenazadiphosphole 2,5-diselenides **4**–**6** in good yields, the latter were further treated with water resulting in the corresponding hydrolysis derivatives dialkyl-selenoureas **7**–**9**, and phosphinodiselenoates **10** and **11**. Selenourea **7** could be transferred into 1,3-selenazol-2-amines **12**–**15** in excellent yields by further cyclization with four different α-haloketones. All new compounds have been characterized by IR spectroscopy, multi-NMR (^{1}H, ^{13}C, ^{31}P, ^{77}Se) spectroscopy and accurate mass measurement. The single crystal X-ray structural features of nine new compounds are also discussed.

Introduction

The chemistry of selenium-containing heteroatom compounds has gained considerable attention in recent years, because of their interesting reactivity and potential pharmaceutical property,[1,2] new materials[3] as well as new reagents and catalysts for organic synthesis.[4] However, the synthesis of selenium-containing organic heteroatom compounds is not always easy due to the inconvenience of typical selenium reagents such as H_2Se, NaHSe, $(Me_3Si)_2Se$, potassium selenocyanate and tetraethylammonium tetraselenotungstate $[Et_4N]_2WSe_4$, each presenting its own problems including toxicity, solubility, difficulty in handling and poor reactivity. 2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide {[PhP(Se)(μ-Se)]$_2$, known as Woollins' reagent, **WR**} has been applied as a highly efficient selenation agent or synthetic precursor for the synthesis of a range of selenium-containing compounds from simple oxygen-selenium exchange to complex phosphorus-selenium heterocycles[5-21] as well as the surprising phosphorus-selenium-free products[22,23] by virtue of its less unpleasant chemical properties and ready preparation/handling in air.[6] In continuation of our investigation into the reactivity of Woollins' reagent towards different organic substrates, herein, we report the formation of a series of 4-(dialkylamino)-2,5-diphenyl-1,3,2,5-selenazadiphosphole 2,5-diselenides, 1,1-dialkylselenoureas and 1,3-selenazol-2-amines by the reactions of *N, N*-dialkylcyanamides with Woollins' reagent, followed by cyclisation with the corresponding α-haloketones and nine single crystal X-ray structures.

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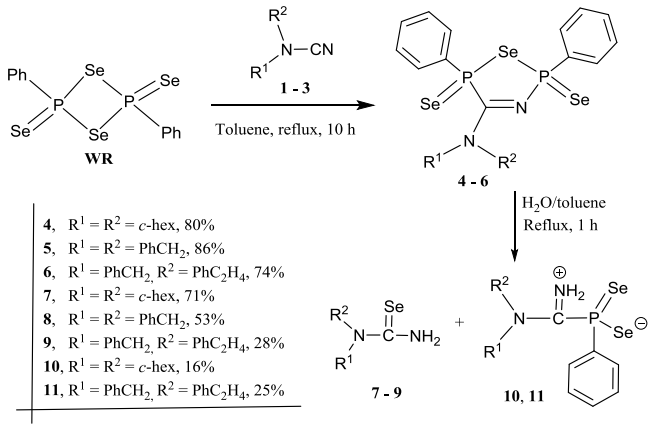
Results and Discussion

Synthesis and Characterisation

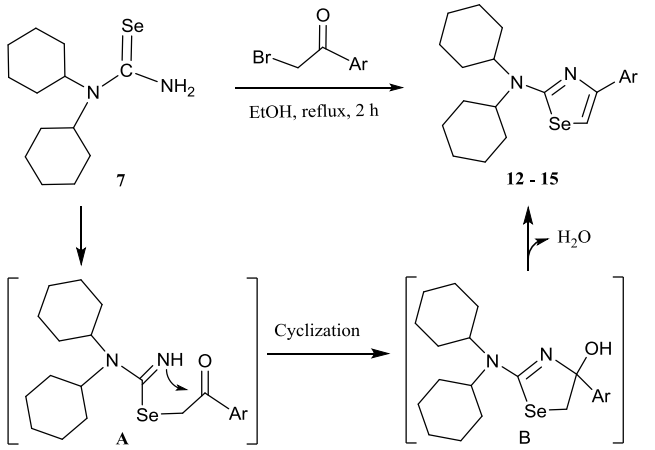
N, N-Dialkylcyanamides **1**–**3** were prepared by a modified literature method from cyanogen bromide with the corresponding secondary amines in dry methanol in the presence of excess of anhydrous CH_3COONa at room temperature in almost quantitative yields.[24] As shown in Scheme 1, heating a mixture of equal molar amount of Woollins' reagent and *N, N*-dialkylcyanamides **1**–**3** in toluene solution under anhydrous condition led to the formation of 4-(dialkylamino)-2,5-diphenyl-1,3,2,5-selenazadiphosphole 2,5-diselenides **4**–**6** in good yields (74–86%) after column chromatography purification (silica gel, 5 : 1 hexane/dichloromethane as eluent) in air and recrystallization by diffusion of n-hexane into a dichloromethane solution. Further hydrolysis of **4**–**6** in a mixture solvent of toluene/H_2O (19 : 1) afforded the corresponding selenoureas **7**–**9** (28 to 71% yields, respectively) and phosphinodiselenoates **10** and **11** (16% and 25% yields, respectively) after column chromatography purification (silica gel, dichloromethane as eluent). It is worth noting that in the case of *N, N*-dibenylcyanamide the expected phosphinodiselenoate was not obtained, indicating that the benzyl group ($C_6H_5CH_2$) is more favored than the cyclohexyl group (*c*-hex) for the generation of phosphinodiselenoates. The reaction mechanism for the formation of compounds **4**–**11** is similar to that reported in the literature.[25]

As shown in Scheme 2, the cyclization of selenourea **7** with an equivalent of the corresponding α-haloketones in refluxing ethanol solution led to the expected five-membered ring 4-substituted-1,3-selenazol-2-amines **12**–**15** in excellent yields (92–96%). The cyclisation reactions showed that electron-rich aryl rings enable cyclization reactions in good yields comparable to electron-deficient aromatic moieties. The highest yields were found for the formation of the 4-aryl-1,3-selenazoles **12** and **14** with electron-rich group (OMe or Br) on the aryl ring, the lowest yields were observed for the formation 4-aryl-1,3-selenazoles **13** and **15** with an electron-deficient group (NO_2) or two substituted groups on the aryl ring.



Scheme 1. Formation of phosphorus-selenium heteroatom compounds **4**–**11**

The formation of 4-substituted-1,3-selenazol-2-amines **12**–**15** can be explained considering the mechanism depicted in Scheme 2. The intermediate A, the addition product of selenourea **7** and α-halohekones, further carried on the cyclization reaction resulting in another intermediate B, which subsequently lost one molecule of H_2O leading to the formation of compounds **12**–**15**.



Scheme 2. Synthesis of 4-substituted-1,3-selenazol-2-amines **12**–**15**

The characterisation of compounds **4**–**15** is based on ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra, IR spectroscopy and mass spectrometry. All compounds showed the anticipated $[M+H]^+$ peak in their CI^+ mass spectra as well as satisfactory accurate mass measurements and appropriate isotopic distribution. Strong ν(C-N) vibrations in the range 1548–1558 cm^{-1} for 4-dialkylamino-2,5-diphenyl-1,3,2,5-selenazadiphosphole 2,5-diselenides **4**–**6** and in the range 1543–1550 cm^{-1} for selenoureas **7**–**9** were observed, while the range 520–552 cm^{-1} shows the presence of the intense ν(P-Se) vibrations for selenoureas **7**–**9**; these values are comparable with the similar 2,5-diselenides[26] or selenoureas.[27] The phosphorus atoms in compounds **4**–**6** are potentially stereogenic centers, in fact, a pair of diastereomers with 2 : 1 intensity ratio was identified in compound **6**. The ^{31}P NMR of **4**–**6** exhibit two sets of double resonances with two sets of satellites in the range of 310– 65 Hz and 786–822 Hz for the endocyclic and exocyclic selenium atoms, respectively. The different chemical shifts {82.3 and 59.1 ppm for compound **4**, 76.6 and 60.5 ppm for compound **5**, and 77.2[76.1] and 61.8[61.3] ppm for compound **6**} indicate the presence of two different single P-Se and two different double P-Se bonds in each compound due to the two different phosphorus atoms. The difference is further substantiated by the ^{77}Se NMR spectra, which exhibit a doublet of doublets in each case. The chemical shifts and coupling constants are comparable to the similar structures in the literature.[27,28] Detailed NMR spectroscopic analysis and iterative simulation reveal the coupling constant between two phosphorus atoms (^{2}J(P,P) 9.4–16.4 Hz) in **4**–**6**. Similar chemical shifts were observed in ^{77}Se NMR spectra of **7**–**9** [251.7 ppm for compound **7**, 238.9 ppm for compound **8** and 236.7 ppm for compound **9**], however, these values are significantly lower than that in the *N*-benzyl aromatic selenoamides [δ_{Se} 517.0–638.0 ppm][28] and the primary aryl substituted selenoamides [δ_{Se} 529.0–715.8 ppm].[27,30] ^{31}P NMR spectra of compounds **10** and **11** display sharp singlets at 32.5 and 29.0/28.2 ppm, respectively, in each singlet is flanked by selenium satellites with ^{31}P-^{77}Se coupling constants of 695 and 685/685 Hz, indicating a single P-Se bond order of approximately 1.5, however, the values are comparable to that in the similar structures[25] and slightly bigger than that in phosphonodiselenoate salts [*ca*. 657–680 Hz],[31] confirming the presence of the zwitterionic structures for both compounds. In contrast to compound **10**, a pair of isomers with 2 : 1 intensity ratio was found in compound **11**, attributed to the steric effect of benzyl(phenethyl)amino leading to the co-existence of one non-zwitterionic structure and one zwitterionic structure.

In the IR spectra of five-membered ring 4-substituted-1,3-selenazol-2-amines **12**–**15**, strong bands in the range 1545–1540 cm^{-1} from the ν(C=N) vibration were observed together with intense vibrations in the range 853–815 cm^{-1} being characteristic of the ν (C-Se).[32] In the ^{13}C NMR spectra of 4-substituted-1,3-selenazol-2-amines **12**–**15**, the chemical shifts for the selenazole ring backbone carbon atoms fall in the range 167.3 to 169.3, 150.7 to 158.7, 100.6 to 108.7 ppm, respectively, these value are slightly lower than that in 4-aryl-1,3-selenazoles [170.7 to 190.1, 153.7 to 159.6 and 109.4 to 127.1 ppm].[25] More interestingly, ^{77}Se NMR chemical shifts in 4-substituted-1,3-selenazol-2-amines **12**–**15** range from 582.1 to 604.4 ppm, which are significantly lower than that in 2,4-diaryl-1,3-selenazoles [705.5 to 798.8 ppm][25] and 5-aminoselenazoles [629.0–707.0 ppm].[28] The results indicated the high influence by the basic skeletons of selenazoles and the substituents close to the selenium atom.[33] It is worth noting that the 4-substituted-1,3-selenazol-2-amine **13** bearing one electron-withdrawing group (NO_2) on the aryl ring shows the highest chemical shift, compared to the others with one or two electron-releasing groups on aryl ring.

X-ray Structure Analysis

Molecular structures of compounds **4**, **5**, **7**, **8**, **9**, **10**, **13**, **14** and **15** were also confirmed by single crystal X-ray analysis and perspective views with selected parameters are shown in Figures 1–16. Crystal data and details of the structure determination are given in Tables S1 and S2 (see Supporting Information). The structure of **5** as shown in Figure 2 contains one independent molecules, meanwhile, the structure of **4** in Figure 1 contains two independent molecules within the unit cell, the differences in metric parameters in the two molecules results from the rotation of *c*-hexyl – *c*-hexyl group leading to some steric interactions in the second independent molecule. The frameworks of two 4-dialkylamino-2,5-diphenyl-1,3,2,5-selenazadiphosphole 2,5-diselenides **4** and **5** contain a five-membered P_2SeCN ring bearing a P(Se)-Se-P(Se) linkage with the exocyclic P=Se groups orientated *trans* to each other. The P=Se bond lengths and angles are normal and comparable with those found in the literature.[34-37] The distorted tetrahedral geometries around P(1) and around P(3) are considerably different [Se(1)-P(1)-Se(2) and Se(2)-P(3)-Se(3): 113.09(8)[113.86(9)]° and 112.84(8)[111.91(9)]° for **4** and 115.27(8)° and 115.34(7)° for **5**] due to the different effects of the steric hindrance from two benzyl groups and two *c*-hexyl groups. The trans-annular P···P bond distances are 3.216[3.241] Å for **4** and 3.214 Å for **5**, respectively, being comparable with that in the similar structures[25], however, marginally longer than those observed in the four-membered P_2Se_2

ring system [3.1 Å] and considerably shorter than those measured in six-membered ring system P_2Se_4 ring system [4.3 Å].[38] Interestingly, strong intramolecular $C_{c\text{-}hex}$-H···Se=P hydrogen bonding interactions can be observed in the solid state in the structure of **4** with the H(6)···Se(1) distance of 2.8832(9)[2.8049(10)] Å, which are significantly shorter than the sum of van der Waals radii of the hydrogen and selenium atoms [3.1 Å], along with the C(6)-H(6)···Se(1) angle of 138.92[137.37]° (Figure 3). There are no intramolecular interactions present in the structure of **5**.

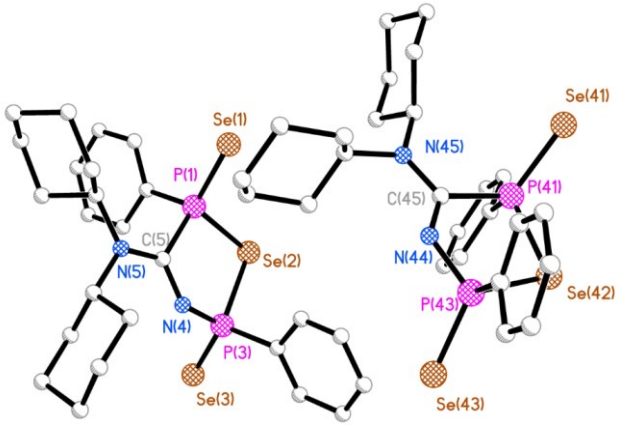


Figure 1. Single crystal X-ray structure of compound **4**. (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): (dimensions for second independent molecule in square parentheses): P(1)-Se(1) 2.1005(18)[2.0877(19)], P(1)-Se(2) 2.220(2)[2.218(2)], P(1)-C(5) 1.891(7)[1.905(7)], C(5)-N(4) 1.284(10)[1.300(9)], P(3)-Se(2) 2.2925(19)[2.294(2)], P(3)-Se(3) 2.0839(18)[2.082(2)], P(3)-N(4) 1.618(6)[1.623(7)], P(1)-C(13) 1.816(7)[1.821(7)], P(3)-C(19) 1.787(8)[1.796(7)]; Se(1)-P(1)-Se(2) 113.09(8)[113.86(9)], Se(1)-P(1)-C(13) 116.3(2)[116.5(2)], Se(2)-P(1)-C(5) 99.8(2)[98.8(2)], Se(1)-P(1)-C(5) 115.8(2)[116.5(2)], Se(2)-P(3)-C(19) 103.9(2)[105.0(2)], Se(2)-P(3)-Se(3) 112.84(8)[111.91(9)], Se(2)-P(3)-N(4) 102.1(2)[102.6(2)], P(3)-N(4)-C(5) 127.3(5)[126.6(5)], N(4)-C(5)-P(1) 118.4(5)[120.0(5)], N(4)-C(5)-N(5) 120.6(6)[121.7(6)], P(1)-C(5)-N(5) 120.9(6)[118.3(5)].

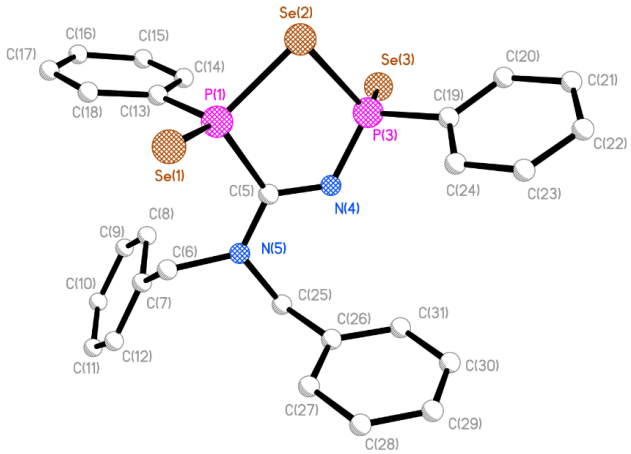


Figure 2. Single crystal X-ray structure of compound **5**. (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): P(1)-Se(1) 2.0983(18), P(1)-Se(2) 2.2336(18), P(1)-C(5) 1.912(6), C(5)-N(4) 1.280(8), P(3)-Se(2) 2.2806(18), P(3)-Se(3) 2.0917(18), P(3)-N(4) 1.640(5), P(1)-C(13) 1.816(6), P(3)-C(19) 1.814(6); Se(1)-P(1)-Se(2) 115.27(8), Se(1)-P(1)-C(13) 115.3(2), Se(2)-P(1)-C(5) 98.7(2), Se(1)-P(1)-C(5) 114.57(19), Se(2)-P(3)-C(19) 103.3(2), Se(2)-P(3)-Se(3) 115.34(7), Se(2)-P(3)-N(4) 102.85(19), P(3)-N(4)-C(5) 124.6(4), N(4)-C(5)-P(1) 119.9(4), N(4)-C(5)-N(5) 120.4(5), P(1)-C(5)-N(5) 119.5(4).

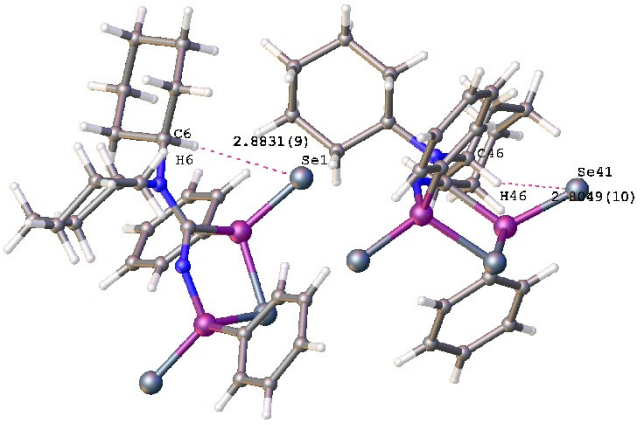


Figure 3. The intramolecular $C_{c\text{-}hex}$-H···Se=P hydrogen bonding interactions (red dashed line) in **4**

The X-ray crystal structures of selenoureas **7**–**9** are shown in Figures 4–6. The structure of **7** contains three molecules of the compound and one molecule of solvent dichloromethane within the unit cell; meanwhile, the structures of **8** and **9** have two independent molecules within the unit cell. The C-Se bond lengths in **7**–**9** are 1.864(9)[1.862(9) and 1.882(9)] Å in **7**, 1.876(5)[1.863(5)] Å in **8** and 1.874(7)[1.859(7)] Å in **9** are comparable with that in the similar structures [1.850(4)–1.877(7) Å],[25] these values are marginally longer than that in aryselenoamides [1.820(4)–1.848(2) Å].[29] Compared to the normal C-N bond distances [N(2)-C(2) and N(2)–C*: 1.486(11)[1.486(12) and 1.467(13)] Å and 1.479(11) [1.480(12) and 1.481(12)] Å in **7**, 1.47(6)[1.475(6)] Å and 1.471(6) [1.472(6)] Å in **8**, 1.460(9)[1.456(9)] Å and 1.472(10)[1.467(9)] Å in **9**], the shortness of the C-N bond lengths in which the C-N bonds are adjacent to the C=Se double bond {C(1)-N(1) and C(1)-N(2): 1.350(11)[1.307(11) and 1.335(12)] Å and 1.321(11)[1.346(11) and 1.341(12)] Å in **7**, 1.315(6)[1.323(7)] Å and 1.330(6)[1.334(6)] Å in **8**, 1.335(10)[1.354(10)] Å and 1.338(9)[1.335(10)] Å in **9**] reveals some multiple bonding character. In the structures of **7**–**9**, N(1)-N(2)-C(1)-Se(1) is nearly planar with Se(1) lying 0.02 Å [0.03 Å for molecule 2 and 0.01 Å for molecule 3] for **7**, 0.02 Å [0.00 Å for molecule 2] for **8** and 0.01 Å [0.02 Å for molecule 2] for **9** out of this mean plane. There are strong intramolecular $C_{c\text{-}hex}$-H···Se=P hydrogen bonding interactions in **7** (Figure 7). The hydrogen bonding Se(1)···H(2), Se(21)···H(22) and Se(41)···H(42) distances are 2.4682(9), 2.4674(9) and 2.4343(9) Å, respectively, along with C(2)-H(2)···Se(1), N(1)-H(1B)···Se(11) and N(11)-H(11A)···Se(11) angles of 121.73, 123.06, and 124.49°. However, the weak intramolecular $C_{c\text{-}hex}$-H···Se=P and intermolecular $C_{methene}$-H···Se=P hydrogen bonding interactions are observed in **8** [Se(1)···H(11), Se(1)···H(22B) and Se(1)···H(24) distances are 3.0512(14), 3.0385(12) and 3.1886(5) Å, respectively, with the corresponding C(11)-H(11)···Se(1), C(22)-H(22B)···Se(1) and C(24)-H(24)···Se(1) angles of 131.67, 171.13 and 158.34°] (Figure 8). Interestingly, there are only weak intermolecular N-H···Se=P and $C_{methene}$-H···Se=P hydrogen bonding interactions present in **9** [N(1)-H(1A)···Se(21) and C(2)-H(2B)···Se(21) distances of 3.0680(9) and 2.9377(8) Å along with N(1)-H(1A)···Se(21) and C(2)-H(2B)···Se(21) angles of 137.07 and 174.44° (Figure 9).

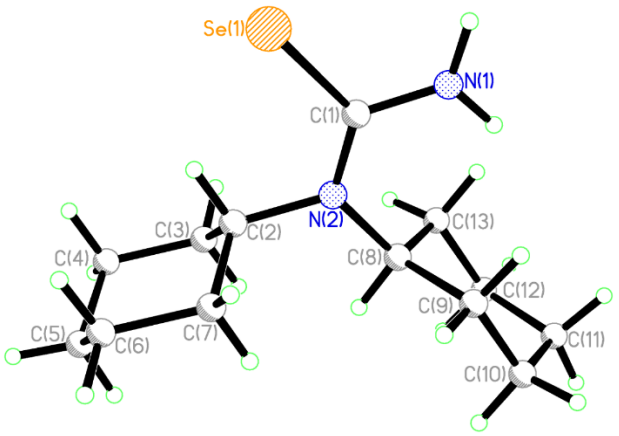


Figure 4. Single crystal X-ray structure of compound **7**. Selected bond lengths (Å) and angles (˚) (dimensions for second and third independent molecules in square parentheses): Se(1)-C(1) 1.864(9) [1.862(9), 1.882(9)], C(1)-N(1) 1.350(11) [1.307(11), 1.335(12)], C(1)-N(2) 1.321(11) [1.346(11), 1.341(12)]; N(2)-C(2) 1.486(11) [1.486(12), 1.467(13)], N(2)-C(8) 1.479(11) [1.480(12), 1.481(12)]; N(1)-C(1)-Se(1) 115.7(6) [117.2(7), 115.4(7)], N(2)-C(1)-Se(1) 125.0(6) [123.5(6), 122.7(7)], N(1)-C(1)-N(2) 119.2(8) [119.3(8), 121.9(8)].

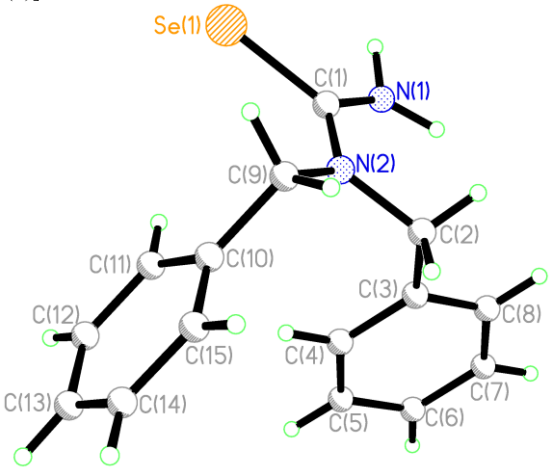


Figure 5. Single crystal X-ray structure of compound **8**. Selected bond lengths (Å) and angles (˚) (dimensions for second independent molecule in square parentheses): C(1)-Se(1) 1.876(5) [1.863(5)], N(1)-C(1) 1.315(6) [1.323(7)], C(1)-N(2) 1.330(6) [1.334(6)], N(2)-C(2) 1.4796) [1.475(6)], N(2)-C(9) 1.471(6) [1.472(6)]; Se(1)-C(1)-N(1) 118.7(4) [118.5(4)], Se(1)-C(1)-N(2) 122.3(4) [123.2(4)], N(1)-C(1)-N(2) 119.0(4) [118.2(4)], C(1)-N(2)-C(2) 120.2(4) [120.7(4)], C(1)-N(2)-C(9) 122.6(4) [122.8(4)]; Se(1)-C(1)-N(2)-C(2) 179.6(3) [-176.0(4)], Se(1)-C(1)-N(2)-C(9) -10.7(6) [-6.8(7)], N(1)-C(1)-N(2)-C(2) 1.3(6) 4.3(7)], N(1)-C(1)-N(2)-C(9) 171.0(4) [173.4(4)].

The structure of **10** crystallises in the monoclinic space group $P2_12_12_1$ with two crystallographically independent molecules of compound and dichloromethane in the asymmetric unit (Figure 10). The structure adopts a skewed '*T*' shape conformation and reveals that the molecule of compound is in a zwitterionic structure. The statistically invariant two P-Se bonds [P(1)-Se(1) 2.127(3) Å and P(1)-Se(2) 2.140(3) Å] are comparable with that in the similar structures [2.0142(2)–2.1492(19) Å].[39] These values are marginally longer than those in other double bond P=Se systems [2.08–2.12 Å], but are still considerably shorter than those in single bonded P-Se systems [2.2–2.3 Å],[40] indicating the more or less extent of resonance delocalisation within PSe_2 group. The two C-N bonds are also essentially equal [C(2)-N(2) 1.320(14) Å and C(2)-N(3) 1.315(14) Å]. The Se-P-Se angle of 117.29(15)° is considerably smaller than the idealized tetrahedron. There are the strong intramolecular N-H···Se=P and $C_{c\text{-}hexyl}$-H···Se-P hydrogen bonding interactions present in **10** with Se(2)···H(2B) and Se(1)···H(18) distances of 2.5453(12) and 2.6995(13) Å with the corresponding N(2)-H(2B)···Se(2) and C(18)-H(18)···Se(1) angles of 129.08 and 137.75° as shown in Figure 11.

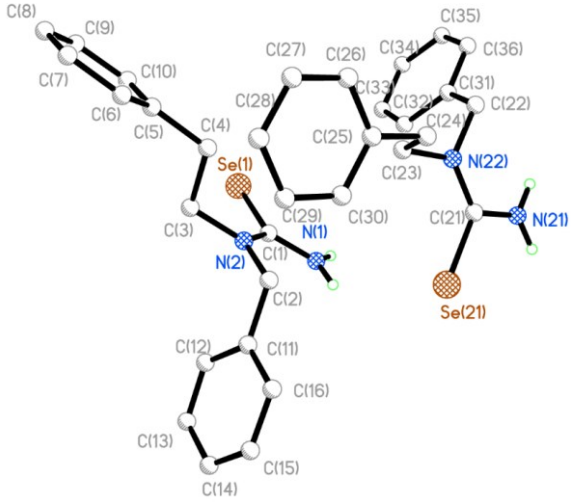


Figure 6. Single crystal X-ray structure of compound **9** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (˚) (dimensions for second independent molecule in square parentheses): C(1)-Se(1) 1.874(7)[1.859(7)], N(1)-C(1) 1.335(10)[1.354(10)], C(1)-N(2) 1.338(9)[1.335(10)], N(2)-C(2) 1.460(9)[1.456(9)], N(2)-C(3) 1.472(10)[1.467(9)]; Se(1)-C(1)-N(1) 117.6(5)[117.7(6)], Se(1)-C(1)-N(2) 122.8(6)[124.7(5)], N(1)-C(1)-N(2) 119.6(6)[117.5(7)], C(1)-N(2)-C(2) 123.7(6)[123.8(6)], C(1)-N(2)-C(3) 122.6(6)[121.2(6)].

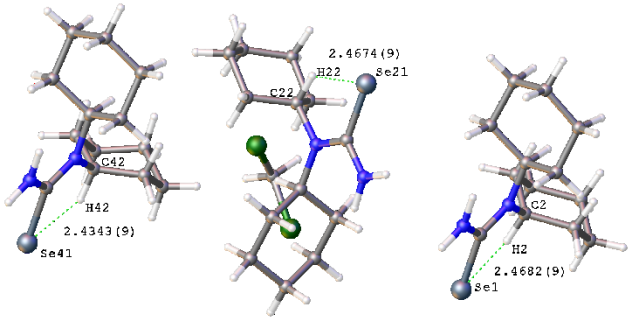


Figure 7. The intramolecular $C_{c\text{-}hex}$-H···Se=P hydrogen bonding interactions (green dashed line) in **7**

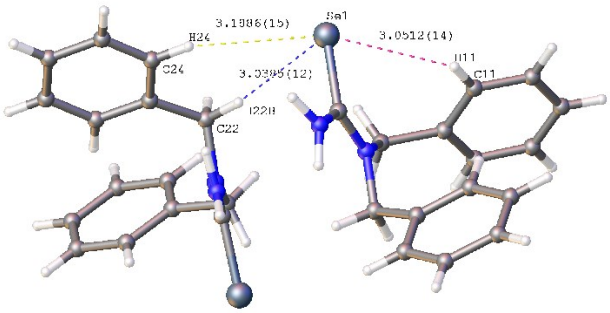


Figure 8. The intramolecular $C_{c\text{-}hex}$-H···Se=P (red dashed line), and intermolecular $C_{methene}$-H···Se=P (blue dashed line) and C_{phenyl}-H···Se=P (yellow dashed line) hydrogen bonding interactions in **8**

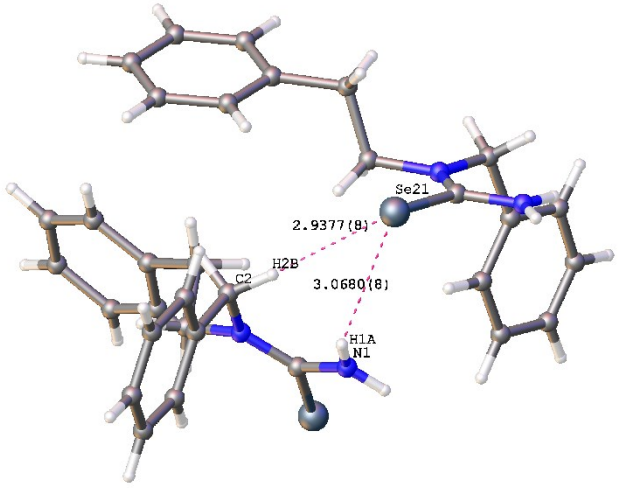


Figure 9. The intermolecular N-H···Se=P and $C_{methene}$-H···Se=P hydrogen bonding interactions (red dashed line) in **9**

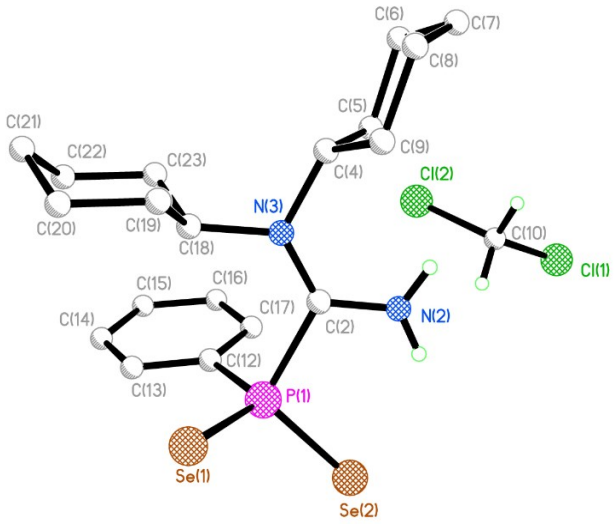


Figure 10. Single crystal X-ray structure of compound **10** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): P(1)-Se(1) 2.127(3), P(1)-Se(2) 2.140(3), P(1)-C(2) 1.916(11), C(2)-N(2) 1.320(14), C(2)-N(3) 1.315(14); Se(1)-P(1)-Se(2) 117.29(15), Se(1)-P(1)-C(12) 115.7(4), Se(2)-P(1)-C(12) 108.0(4), Se(1)-P(1)-C(2) 108.2(3), Se(2)-P(1)-C(2) 106.8(4), C(2)-P(1)-C(12) 99.0(5), P(1)-C(2)-N(3) 123.3(8), P(1)-C(2)-N(2) 113.3(8), N(2)-C(2)-N(3) 123.3(9).

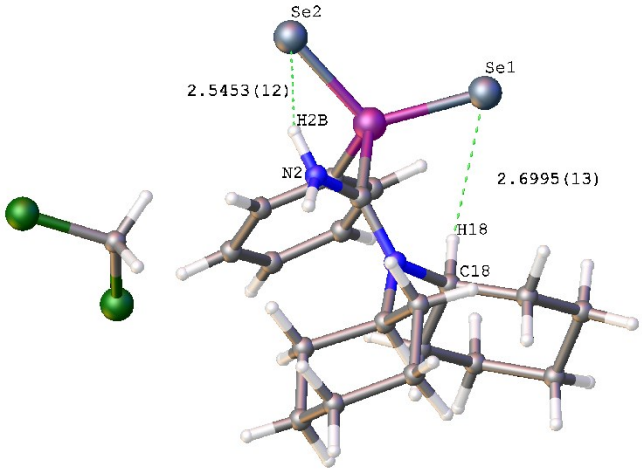


Figure 11. The intramolecular N-H···Se=P and $C_{c\text{-}hexyl}$-H···Se-P hydrogen bonding interactions (green dashed line) in structure of **10**

The structures of **13**–**15** have a single molecule of the compound in the asymmetric unit, except for **15** in which the asymmetric unit contains two independent molecules. All structures confirmed the formation of five-membered ring (Figures 12-14). The newly formed five-membered N(1)-C(2)-Se(3)-C(4)-C(5) rings in **13**–**15** are approximately planar with Se atom deviating 0.006 Å in **13**, 0.001 Å in **14** and 0.002[0.002] Å in **15** from the selenazole mean planes. There are some differences in the dihedral angles between peripheral ring plane and the selenazole ring mean plane [6.99° in **13**, 25.56° in **14** and 8.48° in **15**]. The C-Se bond distances in **13**–**15** vary from 1.857(4)–1.922(4) Å, being marginally longer that in 2,4-diaryl-1,3-selenazoles [1.803(13)–1.909(3) Å].[36] These values cover the range of C-Se bond lengths observed in the five-membered ring 1,3,4-selenadiazoles [1.87 to 1.89 Å][8,14,30,41] and in 2,5-diarylselenophenes [*ca*. 1.86–1.89 Å],[7] and are marginally shorter than that would be expected from the typical C-Se single bond lengths [*ca*. 1.92–1.94 Å].[42-44] The C=N double bond distances {1.291(8) in **13**, 1.292(6) in **14**, and 1.298(5) [1.290(5)] in **15**} are comparable with that in 2,4-diaryl-1,3-selenazoles [1.285(14) to 1.309(11) Å] and the C-N single bond distances {1.394(7) and 1.358(7) Å in **13**, 1.395(5) and 1.357(6) Å in **14**, 1.403(5) [1.392(5)] and 1.360(5) [1.360(5)] Å in **15**} are similar to that in 2,4-diaryl-1,3-selenazoles [1.377(13) to 1.403(11) Å],[40] which are significantly shorter than the usual C-N single bond length of 1.47 Å,[45-47] indicating clearly that some degree of delocalization occurring in these newly formed selenazole rings. The C-Se-C angles in **13**–**15** are similar [84.1(3)° in **13**, 84.22(19)° in **14** and 84.33(16)[83.87(17)]° in **15**], and wider than that in 1,3,4-selenadiazoles [81.9(4)–82.7(2)°],[8,14,30,41] and smaller than that in the 2,5-diarylselenophenes [87.8(8)°].[7]

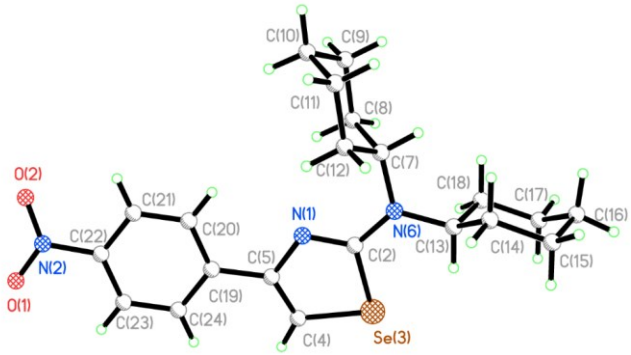


Figure 12. Single crystal X-ray structure of compound **13**. Selected bond lengths (Å) and angles (°): N(1)-C(2) 1.291(8), C(2)-Se(3) 1.910(6), Se(3)-C(4) 1.882(7), C(4)-C(5) 1.336(9), N(1)-C(5) 1.394(7), C(2)-N(6) 1.358(7); N(1)-C(2)-N(6) 124.8(5), N(1)-C(2)-Se(3) 113.7(4), C(2)-Se(3)-C(4) 84.1(3), C(4)-C(5)-N(1) 118.1(6), C(5)-N(1)-C(2) 113.6(5).

Despite the similarities in compounds **13**–**15** in term of their chemical constitution and their overall molecular shape, the intramolecular or intermolecular interaction are different. There is a strong intramolecular $C_{c\text{-}hex}$-H···Se hydrogen bonding interaction present with Se(3)···H(13) distance being 2.4921(5) Å along with C(13)-H(13)···Se(3) of 121.11° in structure of **13** as shown in Figure 14. Interestingly, no intramolecular interaction is observed in **14** and **15**, however, there are three types of intermolecular interactions present in the structure of **15**: $C_{c\text{-}hex}$-H···O hydrogen bonding interactions with O(32)···H(8A) distance of 2.866(3) Å along with C(8)-H(8A)···O(32) angle of 136.3°; $C_{c\text{-}hex}$-H···Se hydrogen bonding interactions with Se(33)···H(10B) distance of 3.3057(6) Å along with C(10)-H(10B)···Se(33) angle of 141.60° and $C_{c\text{-}hex}$-H···N hydrogen bonding interactions with N(31)···H(9B) distance of 2.740(3) Å along with C(9)-H(9B)···N(31) angle of 152.81° (Figure 16).

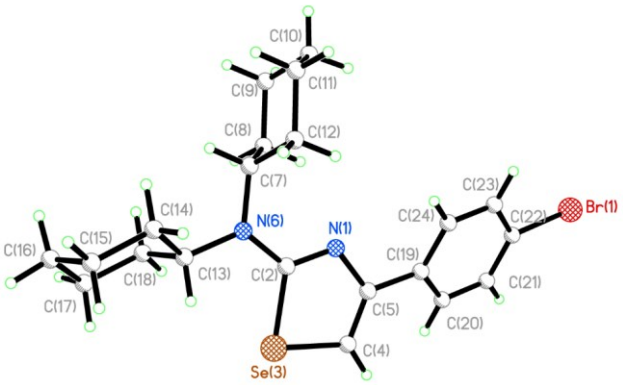


Figure 13. Single crystal X-ray structure of compound **14**. Selected bond lengths (Å) and angles (˚): N(1)-C(2) 1.292(6), C(2)-Se(3) 1.922(4), Se(3)-C(4) 1.873(5), C(4)-C(5) 1.352(6), N(1)-C(5) 1.395(5), C(2)-N(6) 1.357(6); N(1)-C(2)-N(6) 124.4(4), N(1)-C(2)-Se(3) 113.7(3), C(2)-Se(3)-C(4) 84.22(19), C(4)-C(5)-N(1) 117.9(4), C(5)-N(1)-C(2) 113.6(3).

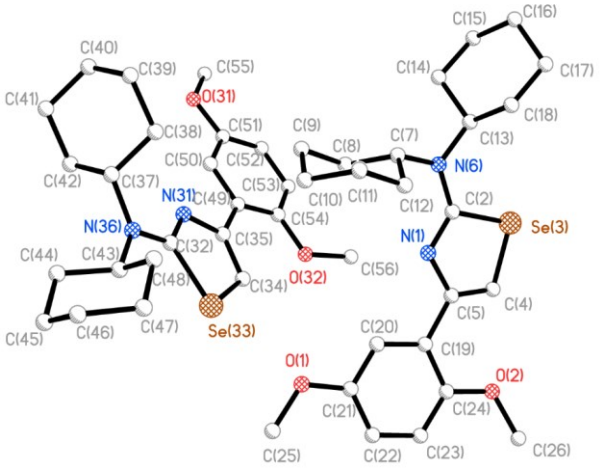


Figure 14. Single crystal X-ray structure of compound **15** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (˚) (dimensions for second independent molecule in square parentheses): N(1)-C(2) 1.298(5)[1.290(5)], C(2)-Se(3) 1.915(4)[1.913(4)], Se(3)-C(4) 1.863(4)[1.857(4)], C(4)-C(5) 1.337(6)[1.357(5)], N(1)-C(5) 1.403(5)[1.392(5)], C(2)-N(6) 1.360(5)[1.360(5)]; N(1)-C(2)-N(6) 125.0(3)[125.0(3)], N(1)-C(2)-Se(3) 113.6(3)[114.2(3)], C(2)-Se(3)-C(4) 84.33(16)[83.87(17)], C(4)-C(5)-N(1) 117.8(3)[116.9(3)], C(5)-N(1)-C(2) 113.1(3)[113.5(3)].

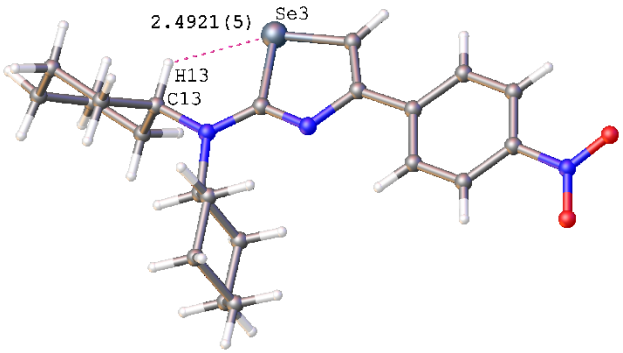


Figure 15. The intramolecular $C_{c\text{-}hex}$-H···Se hydrogen bonding interaction (red dashed line) in **13**

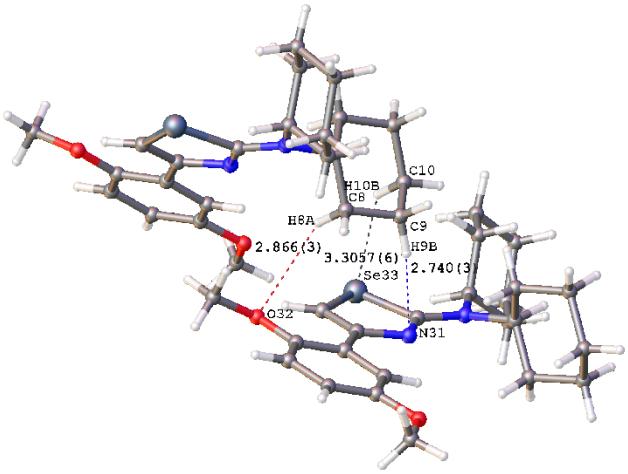


Figure 16. The intermolecular $C_{c\text{-}hex}$-H···O (red dashed line), $C_{c\text{-}hex}$-H···Se (green dashed line) and $C_{c\text{-}hex}$-H···N (blue dashed line) hydrogen bonding interactions in **15**

Conclusions

In summary, Woollins' reagent reacts with *N, N*-dialkylcyanamides **1**–**3** leading to the corresponding [2+3] cycloaddition products 2,5-diphenyl-1,3,2,5-selenazadiphosphole 2,5-diselenides **4**–**6**, the latter can be further hydrolyzed leading to the corresponding dialkyl-selenoureas **7**–**9**, and ((dialkylamino)(iminio)methyl)(phenyl)phosphinodiselenoates **10** and **11**. The selenourea **7** was converted into 1,3-selenazol-2-amines **12**–**15** by further treating with different *α*-haloketones. The structures of all new compounds have been elucidated by using ^{1}H, ^{13}C, ^{77}Se NMR spectroscopy and accurate mass measurement. Nine single crystal X-ray structures were studied to reveal different the molecular structure profiles.

Supporting Information (see footnote on the first page of this article): Copies of the synthesis, full characterisation, and NMR (^{1}H and ^{13}C) spectra of the compounds **4**–**15**; X-ray data collections and refinements details for compounds **4**, **5**, **7**, **8**, **9**, **10**, **13**, **14**, **15**.

Acknowledgements

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Keywords: Cyanamides · Phosphorus-selenium heteroatom compounds · 1,3-Selenazol-2-amines · Selenoureas · Woollins' reagent

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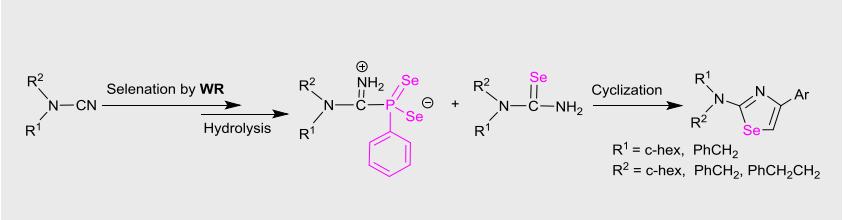

Treating Woollins' reagent [**WR**] with *N, N*-dialkylcyanamides gave the corresponding [2+3] cycloaddition products 4-(dicyclohexylamino)-2,5-diphenyl-1,3,2,5-selenazadiphosphole 2,5-diselenides, the latter were hydrolyzed leading to dialkyl-selenoureas and phosphinodiselenoates. The dialkyl-selenoureas can be further transferred into 1,3-selenazol-2-amines via a cyclization with *α*-haloketones. Nine single crystal X-ray structures were discussed and reveal different molecular structural profiles.

Organo Phosphorus-Selenium Chemistry

Guoxiong Hua, Junyi Du, Alexandra M. Z. Slawin and J. Derek Woollins*…….. Page No. … Page No.

Synthesis and Structural Study of Novel Selenation Derivatives of *N, N*-Dialkylcyanamides