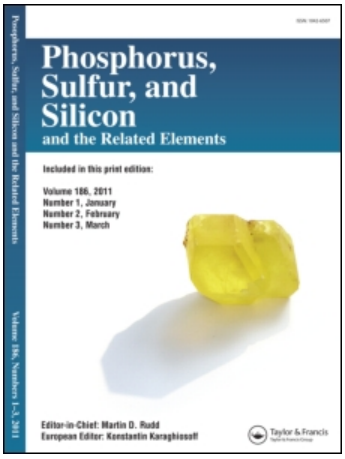

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Phosphorus-Selenium Heterocycles in the Quasi-Binary System RP/Se

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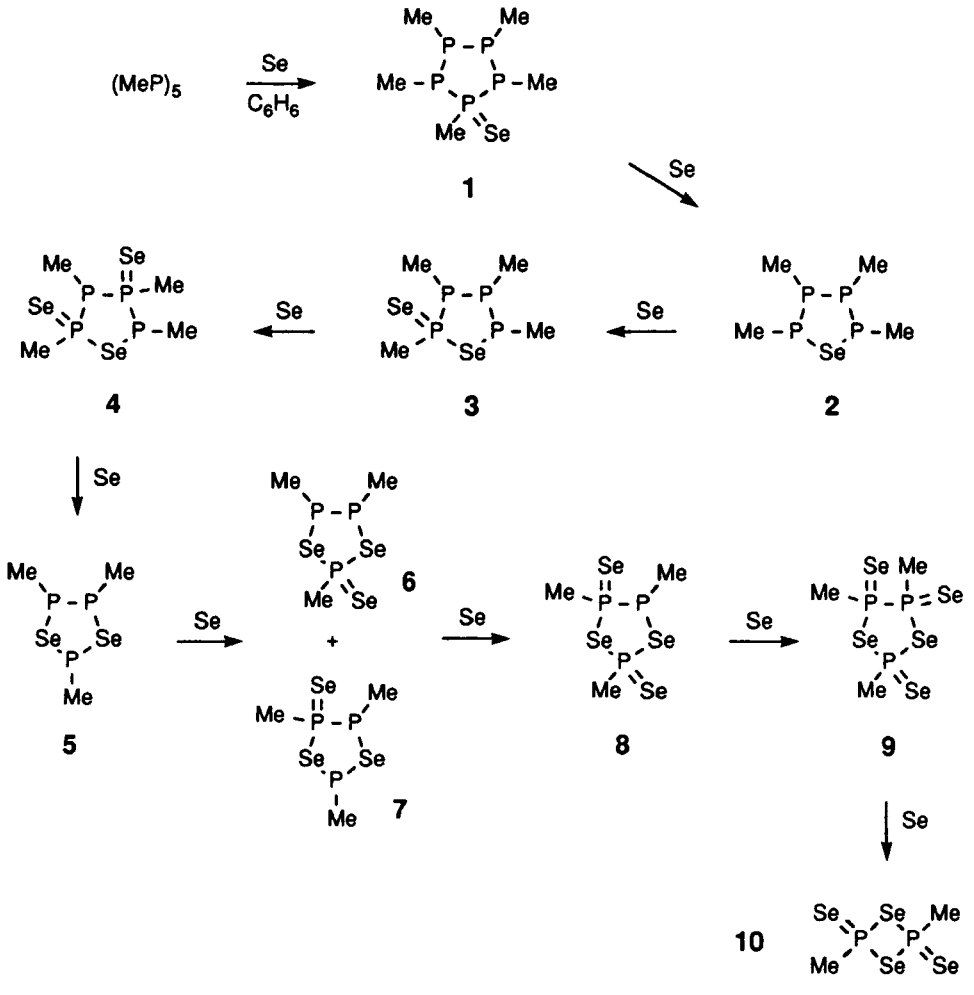
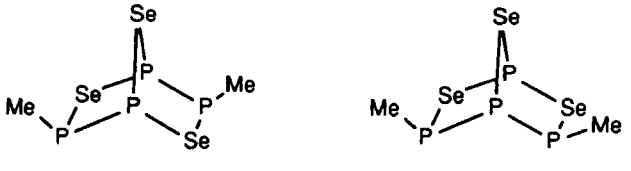
Heterocycles $(RP)_nSe_m$ formally derive from the combination of the isolobal six-electron units RP and Se. In this sense they can be prepared from a diphosphene[1] or a cyclophosphine[2–4] and elemental selenium.

The oxidation of $(MeP)_5$ with gray selenium yields intermediately the fivemembered heterocycles **1** - **9** and finally the triseleno-methylphosphonic acid anhydride **10**[4] (red crystalline solid) with a fourmembered alternating P_2Se_2 ring. The first oxidation product is the cyclopentaphosphine monoselenide **1** (pale yellow oil), in which the P_5-ring is retained. On further oxidation the ring system changes and a first and subsequently a second selenium atom is incorporated in place of MeP in the fivemembered ring to give **2** - **4** with a selenatetraphospholane and **5** - **9** with a 1,3-diselena-2,4,5-triphospholane ring. **7** and **8** are obtained each as a mixture of two isomers. In the crystal the fivemembered ring of **8** and **9** (yellow and orange red crystals, respectively) adopt a distorted envelope conformation with trans orientation of 4-Me and 5-Me.

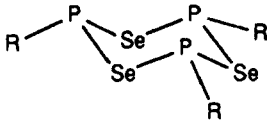


Alternatively **4** - **8** are obtained from the condensation of $MePCl_2$ with $Se(SiMe_3)_2$ or Na_2Se. An unexpected side product of this reaction are the bicyclic compounds α- and β-$P_4Se_3Me_2$, which represent the first derivatives of this type with organic substituents at phosphorus.



$\alpha : \beta = 4 : 1$

With increasing steric demand of the phosphorus substituent in addition to fivemembered heterocycles also derivatives with smaller and larger P,Se-rings are formed. Thus the six- and eightmembered heterocycles **11** and **12** (R = *t*Bu) were identified as products from the reaction of tBuPCl$_2$ with Se(SiMe$_3$)$_2$ and characterized by ^{31}P- and ^{77}Se-NMR. For R = Mes or Tmp they are obtained as the only reaction products. As shown by ^{31}P-NMR, **11** is formed at first and changes slowly into the thermodynamically more stable **12** (pale yellow crystals). The large $^2J_{PP}$ values (~ 200 Hz) indicate a chair conformation for **11** and a crown conformation for **12** with R in equatorial position. This is confirmed by the result of X-Ray structure determinations for **12**, R = Mes, Tmp.



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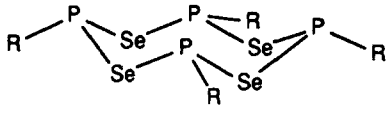

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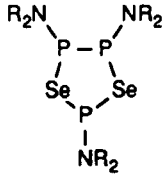
R = *t*Bu, Mes, Tmp

The condensation of R$_2$NPCl$_2$ with Na$_2$Se (R = *i*Pr, C$_6$H$_{11}$, Ph) yields the heterocycles **13** - **15** together with α-P$_4$Se$_3$(NR$_2$)$_2$ and [(R$_2$N)$_2$PSe]$_2$. **14** is obtained more conveniently from R$_2$NPCl$_2$ and Na$_2$Se$_2$ as the only reaction product. Remarkably it contains a diselenide moiety bonded to a tervalent amino substituted phosphorus. According to the result of an X-Ray crystal structure determination the P$_3$Se-ring in **15**, R = *i*Pr$_2$N, is bent with an all-trans orientation of the amino substituents.



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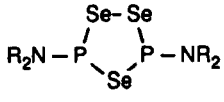

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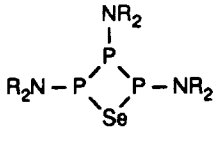
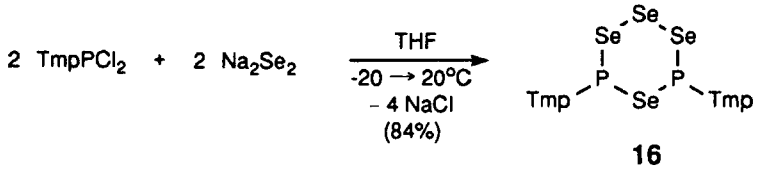


15

R = *i*Pr, C$_6$H$_{11}$, Ph

Surprisingly the condensation of $TmpPCl_2$ with Na_2Se_2 yields the sixmembered heterocycle **16** with a mono- and a triselenide unit bridging the two phosphorus atoms. The large value of $^2J_{PP}$ (193 Hz) indicates a chair conformation with the bulky Tmp-substituents in equatorial position. Thus **16** may be regarded as derived from cyclohexaselene, in which two selenium atoms in 1,3-position are substituted by RP units.



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