A Novel Type of Oligofunctional Macroheterocycle by Reaction of Silylidene-phosphanes and -arsanes with 1,6-Diisocyanohexane

Matthias Driess* and Hans Pritzkow

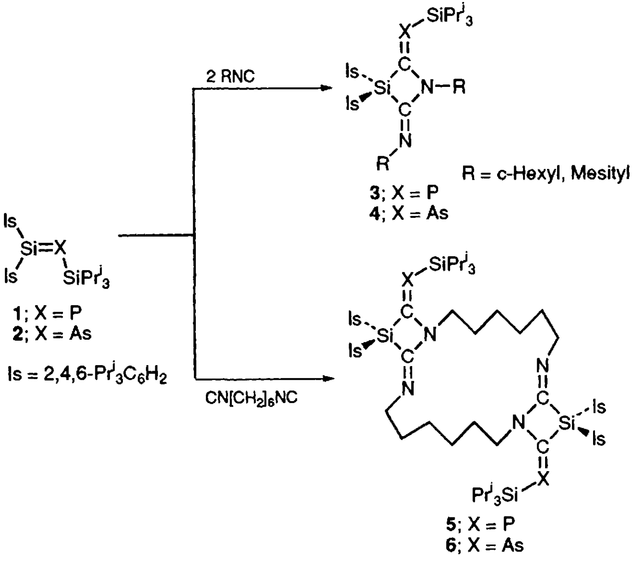
Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

The reaction of the 1,1-diisityl-3,3,3-triisopropyldisilaphosphene **1** (isityl = 2,4,6-triisopropylphenyl) and the analogous disilaarsene **2** with 1,6-diisocyanohexane results in the formation of the unusual tricyclic macroheterocycles **5** and **6**; the molecular structures of **5** and **6** have been established by X-ray crystallographic analysis.

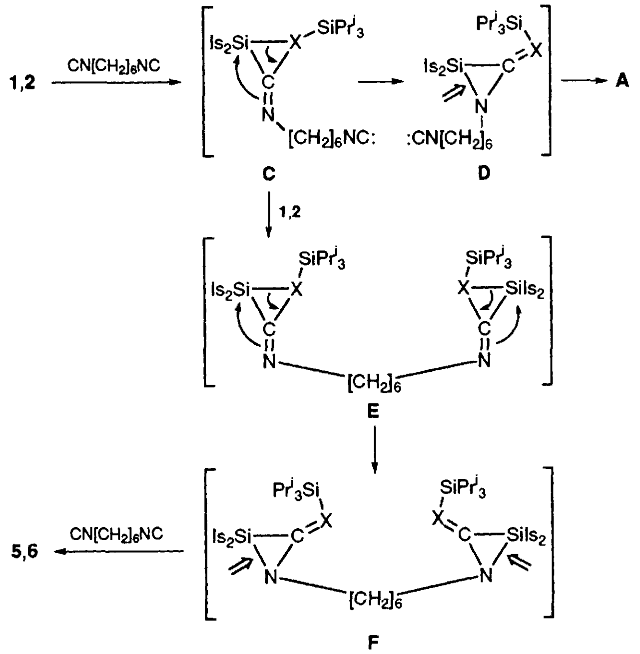
Unsaturated silicon compounds with λ^4,σ^3-coordinated silicon atoms and Si=X bonds (X = low-coordinated main group element) possess a high synthetic potential for the preparation of sila-heterocycles.[1] Whereas the chemistry of silanimines[2] has been extensively studied, until recently, only little was known about the reactivity of phosphasilenes (Si=P)[3] and nothing about the existence of an arsasilene derivative (Si=As). Recently we achieved a simple synthesis of the thermally stable 1,1-diisityl-3,3,3-triisopropylsilylidenephosphane **1**[3b] (isityl = 2,4,6-triisopropylphenyl) and of the first silylidenearsane derivative **2**.[4] Both compounds **1** and **2** react with different unsaturated organic compounds such as dienes, ketones, diazoalkanes and azides to give phospha(arsa)sila-heterocycles by [2 + *n*] cycloaddition reactions (*n* = 1–4).[4,5] The reactions of **1** and **2** with organic isocyanides lead surprisingly to the novel phosphaalkenes **3** and to the corresponding arsaalkene derivatives **4** (Scheme 1).[6]

These reactions are of particular interest because **1** and **2** react with isocyanides even at low temperature, independent of the chosen stochiometry, in the molar ratio 1 : 2. Therefore it was suggested to investigate whether **1**(**2**) reacts with the difunctional 1,6-diisocyanohexane in an intra- and/or an inter-molecular manner. An intramolecular cyclization would lead to **A** whereas an intermolecular pathway should give **B**.

When a toluene solution of **1**(**2**) was treated with 1,6-diisocyanohexane at −80 °C the colour of the reaction solution changed immediately from orange to yellow. Surprisingly, the only product which could be isolated in 74% (70%) yield was the tricyclic macroheterocycle **5**(**6**) so that the major product corresponds to **B** (Scheme 1). **5** and **6** were isolated from hexane as pale-yellow crystals. Both reaction solutions contain approximately 10–20% of the corresponding cyclization product **A** which has been proven by means of NMR spectroscopy.† However, the latter compounds could not be isolated. The reaction mechanism for the formation of **5** and **6** is, as yet, unknown. No intermediate can be proven by NMR spectroscopy. It is proposed as given in Scheme 2 that **5** and **6** (**B**) are formed *via* **C**, **E** and **F** whereas the formation of **A** is most reasonably explained by the intermediates **C** and **D**. A similar mechanism was previously discussed for **3** and **4**.[6]



Scheme 1

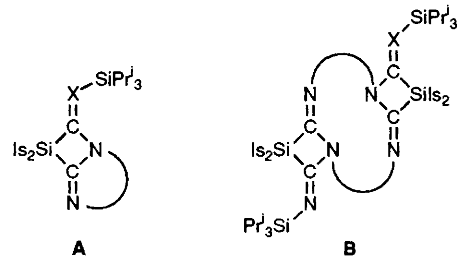


Scheme 2

Two equiv. of the compound **1**(**2**) probably react with the two isocyano groups of the 1,6-diisocyanohexane in terms of [2 + 1] cycloaddition reactions to give the bis(cyclopropanimine) **E** which further isomerizes to **F**. The insertion of a second molecule of 1,6-diisocyanohexane into the Si–N bonds of **E** could then finally give **5**(**6**, **B**).

The constitution and composition of **5** and **6** was confirmed by NMR and IR spectroscopic data as well as FD mass spectrometry.‡ The final molecular structures were unequivocally determined by X-ray crystallography as shown in Fig. 1.§

Both molecules **5** and **6** have a inversion centre of symmetry and are isotypic. The puckered $C_{14}N_4$ 18-membered ring is condensed with two planar SiC_2N four-membered rings and the SiC_2N rings each possess an exocyclic C=P(As) bond with λ^3,σ^2-coordinated P(As)-atoms as well as an exocyclic imino group; the C=P and C=As bond lengths were found to be typical for non-conjugated phosphaalkenes[7] and arsaalkenes.[6] The reaction of **1** and **2** with 1,6-diisocyanohexane poses the question of whether it is possible to synthesize more functionalized azaheteromacrocycles (*e.g.* azahetero crown ethers) by employing appropriate modified diisocyanides; this is currently under investigation.



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† *Selected NMR data* of the **A**-type compounds: (*a*) corresponding to **5**: ^{31}P (81 MHz, C_6D_6): δ 42.8; ^{13}C (50 MHz, C_6D_6): δ 170.40 (d, C=N, $^3J_{PC}$ 17.9 Hz) and 217.1 (d, P=C, $^1J_{PC}$ 114.1 Hz); ^{29}Si (39.7 MHz): δ −8.0 (d, Is$_2$Si, $^2J_{Si,P}$ 49.1 Hz) and 11.4 (d, SiPr$^i_3$, $^1J_{Si,P}$ 96.4 Hz); (*b*) corresponding to **6**: ^{13}C (50 MHz, C_6D_6): δ 156.10 (s, C=N) and 256.0 (s, As=C); ^{29}Si (39.7 MHz): δ −6.0 (s, Is$_2$Si) and 11.0 (s, SiPr$^i_3$).

‡ *Selected NMR data* of **5**: ^{31}P (81 MHz, C_6D_6): δ 58.4; ^{13}C (50 MHz, C_6D_6): δ 167.20 (d, C=N, $^3J_{PC}$ 17.4 Hz) and 214.2 (d, P=C, $^1J_{PC}$ 113 Hz); ^{29}Si (39.7 MHz): δ −8.2 (d, Is$_2$Si, $^2J_{Si,P}$ 49.5 Hz) and 11.0 (d, SiPr$^i_3$, $^1J_{Si,P}$ 98.7 Hz); FD (field desorption) mass spectrum: *m*/*z*(%) 1517 (M$^+$, 100); IR (KBr): ν/cm^{-1} 1684 (C=N) and 1231 (C=P). Selected NMR data of **6**: ^{13}C (50 MHz): δ 155.07 (br, C=N) and 255.37 (s, As=C); ^{29}Si (39.7 MHz): δ −6.3 (s, Is$_2$Si) and 10.7 0 (s, SiPr$^i_3$); FD MS: *m*/*z*(%) 1605 (M$^+$, 100); IR (KBr): ν/cm^{-1} 1698 (C=N) and 1101 (C=As).

§ *Crystal data*: compound **5** with two benzene solvate molecules, triclinic, space group $P\bar{1}$, a = 12.204(6), b = 13.207(7), c = 18.666(9) Å, α = 97.08(4), β = 92.74(4), γ = 112.31(4)°, V = 2747 Å Z = 1, D_c = 1.01 g cm^{-3}. 8603 Reflections [5116 observed $I > 2\sigma(I)$] were collected up to 2θ = 48° on a four-circle diffractometer [Mo-Kα radiation (λ = 0.71069 Å), ω-scan]. Refinement based on F^2, non-hydrogen atoms anisotropic, solvate benzene and methyl groups as rigid bodies and other hydrogen atoms in calculated positions, wR^2 = 0.207 for all reflections, R = 0.067 for observed reflections, benzene molecule disordered. Compound **6** with two benzene solvate molecules, triclinic, space group $P\bar{1}$, a = 12.188(10), b = 13.327(10), c = 18.685(10) Å, α = 97.98(6), β = 92.31(7), γ = 112.69(6)°, V = 2758 Å^3, Z = 1, D_c = 1.06 g cm^{-3}. 9211 Reflections [3981 observed $I > 2\sigma(I)$] were collected up to 2θ = 49° on a four-circle diffractometer [Mo-Kα radiation (λ = 0.71069 Å), ω-scan]. Refinement based on F^2, non-hydrogen atoms anisotropic, phenyl (isityl and solvate benzene) and methyl groups as rigid bodies and other hdyrogen atoms in calculated positions, wR^2 = 0.201 for all reflections, R = 0.073 for observed reflections, benzene molecule disordered. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

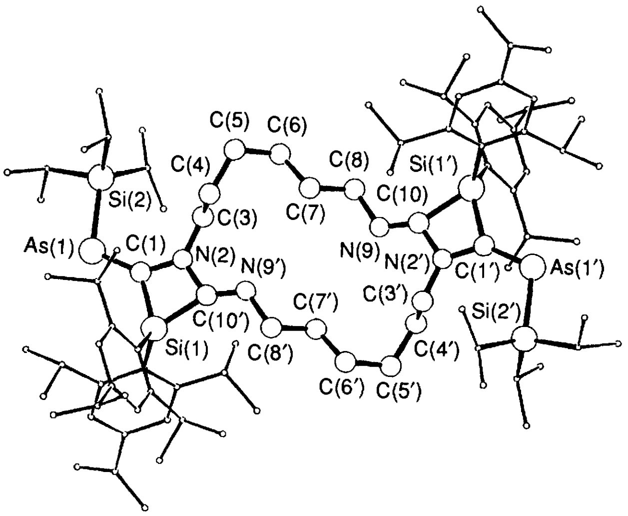

Fig. 1 Molecular structure of **6** which is isotypic to **5**. Selected bond lengths (Å) and angles (°) of **5**: P(1)–Si(2) 2.273(2), P(1)–C(1) 1.698(4), C(1)–N(2) 1.384(4), C(10′)–N(2) 1.423(4), C(10)–N(9) 1.266(4), Si(1)–C(1) 1.925(4), Si(1)–C(10′) 1.934(4); Si(2)–P(1)–C(1) 115.9(1), Si(1)–C(1)–N(2) 91.1(2), C(1)–N(2)–C(10′) 107.5(3). Selected bond lengths (Å) and angles (°) of **6**: As(1)–Si(2) 2.379(3), As(1)–C(1) 1.816(6), C(1)–N(2) 1.386(7), C(10′)–N(2) 1.423(7), C(10)–N(9) 1.250(7), Si(1)–C(1) 1.929(6), Si(1)–C(10′) 1.942(7); Si(2)–As(1)–C(1) 113.4(2), Si(1)–C(1)–N(2) 90.8(4), C(1)–N(2)–C(10′) 108.1(5).

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