Synthesis and properties of cyclic phosphadiynes

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Abstract

The first synthesis of medium-sized cyclic 1-arylphosphadiynes is reported. Details of the molecular structure of 1-phenylphosphacyclododeca-3,10-diyne sulfide (**9b**) and 1-(2′,4′,6′-tri-*tert*-butylphenyl)phosphacyclodeca-3,8-diyne sulfide (**9c**) are reported. © 2000 Elsevier Science Ltd. All rights reserved.

Amines with one or more prop-2-ynyl substituents are easily available by reacting the free amine with 2-propynyl halogenide.[1] Recently, cyclic derivatives such as 1,6-diazacyclodeca-3,8-diyne[2] and 1,6-diazabicyclo[4.4.4]tetradeca-3,8,12-triyne have also become available.[3]

Reports on phosphines with two prop-2-ynyl substituents are very sparse. To our knowledge only a few derivatives have been described in which the phosphorus is substituted with at least one bulky group as shown in **1**[4] and **2**[5] or the phosphorus atom was complexed as in **3**[6] (Fig. 1).
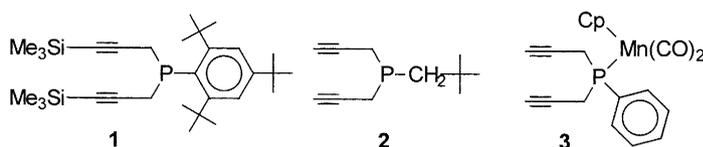

Fig. 1.

To investigate the properties of propargylic phosphines in which the triple bonds are in close proximity we started to synthesize cyclic phosphadiynes of medium ring size.

To establish a procedure to synthesize propargylic phosphines we treated 1-chlorohept-2-yne (**4**) with lithium metal in the presence of small amounts of biphenyl,[7] followed by reaction with *P,P*-dichlorophenylphosphine. This sequence yielded bis(hept-2-ynyl)phenylphosphine (**5**) (Scheme 1). To stabilize the phosphine for characterization we transferred **5**[8] into the corresponding sulfide **6**,[8] which could be isolated in a yield of 19%.

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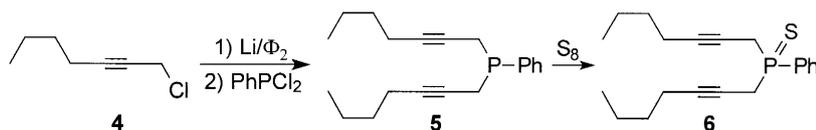
Scheme 1.

After having succeeded in preparing **5** and **6** we embarked in the synthesis of cyclic systems (Scheme 2). As starting materials we used 1,10-dichlorodeca-2,8-diyne (**7a**) and 1,11-dichloroundeca-2,9-diyne (**7b**), respectively, as starting materials and applied the same protocol as shown in Scheme 1. This afforded 1-phenylphosphacycloundeca-3,9-diyne (**8a**)[8] and 1-phenyl-phosphacyclododeca-3,10-diyne (**8b**),[8] respectively. Both compounds were transformed quantitatively to the corresponding sulfides **9a**[8] (0.6% yield) and **9b**[8] (9% yield). The reaction of 1,9-dichloronona-2,7-diyne (**7c**) with *P,P*-dichloro(2,4,6-tri-*tert*-butylphenyl)phosphine yielded 1-(2′,4′,6′-tri-*tert*-butylphenyl)phosphacyclodeca-3,8-diyne (**8c**)[8] which was oxidized to the sulfide **9c** (yield of 12%).[8] The latter could be reduced to **8c** with Si_2Cl_6.[9] In the case of **9b** and **9c** we were able to grow single crystals which allowed us to study the molecular structure of both compounds by means of the X-ray technique (Fig. 2).[10] It is interesting to note that both rings adopt a boat shape conformation. The bulky 2,4,6-tri-*tert*-butyl group adopts the axial position while the smaller phenyl group in **9b** prefers the equatorial position. The distances between the triple bonds are summarized in Table 1. Compound **9c** shows a distortion within the benzene ring which takes an envelope form comparable to known compounds (Fig. 3).[11] We ascribe this due to steric repulsion between the propargylic units of the cycle, the sulfur, and the *o-tert*-butyl groups.
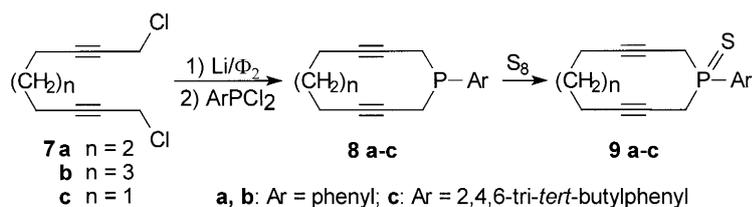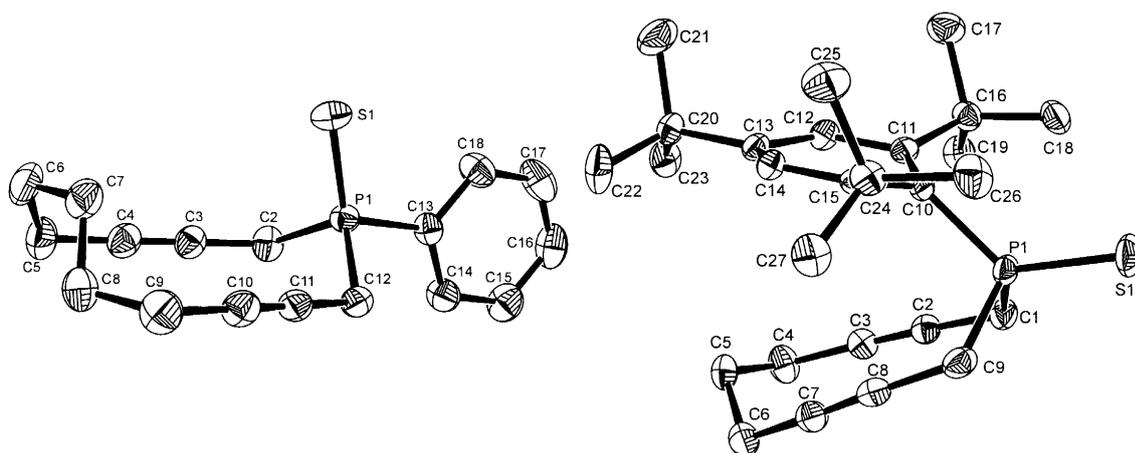

Scheme 2.

Fig. 2. Molecular structures of **9b** (left) and **9c** (right)[10]

Table 1
Transannular distances (pm) and angles (degrees) at the *sp* centers of **9b** and **9c**

	transannular distance		deformation from 180° at the sp centers	
	a	b	a	b
9b	353	405	0.9	5.2
9c	306	300	6.7	7.4

For the definition of **a** and **b** see Figure 3.
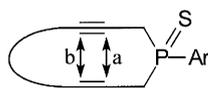
Fig. 3.

Acknowledgements

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8. Compound **5**: $C_{20}H_{27}P$ [M(cation$^+$)], calcd: 298.1850; found: 298.1846. Compound **6**: $C_{20}H_{27}PS$ [M(cation$^+$)], calcd: 330.1571; found: 330.1568. ^{1}H NMR (300 MHz, CDCl$_3$): δ=8.03 (m, 2H, *o*-Ar*H*), 7.48 (m, 3H, *p*-Ar*H*/*m*-Ar*H*), 3.21 (m, 4H, P–C*H*$_2$), 2.16 (m, 4H, $\equiv$C–C*H*$_2$CH$_2$), 1.37 (m, 8H, $\equiv$C–CH$_2$C*H*$_2$ and $\equiv$C–CH$_2$CH$_2$C*H*$_2$), 0.86 (t, 6H, C*H*$_3$). ^{31}P NMR (121 MHz, CDCl$_3$): δ=+41.76. Compound **8a**: $C_{16}H_{17}P$ [M(cation$^+$)], calcd: 240.1068; found: 240.1092. Compound **8b**: $C_{17}H_{19}P$ [M(cation$^+$)], calcd: 254.1225; found: 254.1221. Compound **8c**: $C_{27}H_{39}P$ [M(cation$^+$)], calcd: 394.2789; found: 394.2782. ^{1}H NMR (300 MHz, C_6D_6): δ=7.20 (d, $^4J_{H,P}$=1.5 Hz, 2H, *m*-Ar*H*), 2.79 (m, 4H, P–C*H*$_2$), 1.45 (m, 4H, $\equiv$C–C*H*$_2$CH$_2$), 1.33 (s, 18H, P–*o*-C(C*H*$_3$)$_3$), 1.26 (s, 9H, P–*p*-C(C*H*$_3$)$_3$), 1.05 (m, 2H, $\equiv$C–CH$_2$C*H*$_2$). ^{31}P NMR (121 MHz, C_6D_6): δ=−25.49. Compound **9a**: $C_{16}H_{17}PS$ [M(cation$^+$)], calcd: 272.0789; found: 272.0781. ^{1}H NMR (500 MHz, CDCl$_3$): δ=8.18 (m, 2H, *o*-Ar*H*), 7.55 (m, 1H, *p*-Ar*H*), 7.50 (m, 2H, *m*-Ar*H*), 3.25 (m, 4H, P–C*H*$_2$), 2.13 (m, 4H, $\equiv$C–C*H*$_2$CH$_2$), 1.67 (m, 4H, $\equiv$C–CH$_2$C*H*$_2$). ^{31}P NMR (121 MHz, CDCl$_3$): δ=+36.89. Compound **9b**: $C_{17}H_{19}PS$ [M(cation$^+$)], calcd: 286.0945; found: 286.0939. ^{1}H NMR (500 MHz, CDCl$_3$): δ=8.08 (m, 2H, *o*-Ar*H*), 7.56 (m, 1H, *p*-Ar*H*), 7.51 (m, 2H, *m*-Ar*H*), 3.26 (m, 4H, P–C*H*$_2$), 2.23 (m, 4H, $\equiv$C–C*H*$_2$CH$_2$), 1.67 (m, 2H, $\equiv$C–CH$_2$CH$_2$C*H*$_2$), 1.44 (m, 4H, $\equiv$C–CH$_2$C*H*$_2$). ^{31}P NMR (121 MHz, CDCl$_3$): δ=+38.87. Compound **9c**: $C_{27}H_{39}PS$ [M+H(cation$^+$)], calcd: 427.2588; found: 427.2596. ^{1}H NMR (500 MHz, CDCl$_3$): δ=7.39 (d, $^4J_{H,P}$=4.3 Hz, 2H, *m*-Ar*H*), 3.29 (m, 4H, P–C*H*$_2$), 1.96 (m, $\equiv$C–CH$_2$C*H*$_2$). ^{31}P NMR (202 MHz, CDCl$_3$): δ=+34.46.
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10. Compound **9b**: $C_{17}H_{19}PS$, *M*=286.35, crystal dimensions 0.56×0.14×0.13 mm^3, crystal system orthorhombic, space group $P2_12_12_1$, Z=4, *a*=9.0875(1) Å, *b*=10.3108(1) Å, *c*=16.9438(2) Å, *V*=1587.62(3) Å^3, *F*(000)=608, ρ_{calcd}=1.20 g/cm^3, 2Θ_{max}=50.9°. Radiation MoK$_a$, λ=0.71073 Å, 0.3° ω-scans with CCD detector, *T*=200(2) K, 11 436 reflections collected, 2743 unique, 2634 observed (*I*>2σ(*I*)), an empirical absorption was applied using SADABS^{12} based on the Laue symmetry of the reciprocal space, μ=0.29 mm^{-1}, T_{min}=0.61, T_{max}=0.97, structure solved by direct methods and refined against F^2 with a full matrix least square algorithm using the SHELXTL (5.10) software package,^{13} 248 parameters refined.

Final residual values R_F=0.024, wR_{F2}=0.061, residual electron density 0.20 and -0.20 e$\mathrm{\mathring{A}}^{-3}$. Compound **9c**: $C_{27}H_{39}PS$, M=426.61, crystal dimensions $0.27 \times 0.12 \times 0.12$ mm^3, crystal system triclinic, space group $P\bar{1}$, Z=2, a=10.0391(2) $\mathrm{\mathring{A}}$, b=10.3061(2) $\mathrm{\mathring{A}}$, c=14.6797(1) $\mathrm{\mathring{A}}$, V=253.56(4) $\mathrm{\mathring{A}}^3$, F(000)=464, ρ_{calcd} 1.13 $\mathrm{g/cm}^3$, $2\Theta_{max}$=55.0°. Radiation MoK$_a$, λ=0.71073 $\mathrm{\mathring{A}}$, 0.3° ω-scans with CCD area detector, T=200(2) K, 12 981 reflections collected, 5727 unique, 3995 observed ($I > 2\sigma(I)$), an empirical absorption was applied using SADABS[12] based on the Laue symmetry of the reciprocal space, μ=0.20 mm^{-1}, T_{min}=0.79, T_{max}=0.97, structure solved by direct methods and refined against F^2 with a full matrix least square algorithm using the SHELXTL (5.10) software package,[13] 271 parameters refined. Final residual values R_F=0.046, wR_{F2}=0.101, residual electron density 0.28 and -0.31 e$\mathrm{\mathring{A}}^{-3}$. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 141828 (**9b**) and CCDC 141829 (**9c**), respectively.

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