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Building blocks for phospha[*n*]pericyclynes

Sander G.A. van Assema [a], Petr B. Kraikivskii [b], Stanislav N. Zelinskii [b], Vitaly V. Saraev [b], G. Bas de Jong [a], Frans J.J. de Kanter [a], Marius Schakel [a], J. Chris Slootweg [a], Koop Lammertsma [a,*]

[a] *Department of Organic and Inorganic Chemistry, Faculty of Sciences, Vrije Universiteit, De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands*
[b] *Irkutsk State University, ul. Lermontova 126, Irkutsk 664033, Russia*

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Abstract

Reaction of *i*-Pr_2NPCl_2 with acetylenic Grignard reagents resulted in the formation of new acetylenic substituted phosphorus building blocks. These building blocks can be protected by forming the corresponding $W(CO)_5$ complex and the =O and =S derivatives for added stability as was demonstrated for aminophosphine (**11a**). From this building block, very sensitive product mixtures containing tetraphospha[4]pericyclynes (**16**) were obtained. In addition, the amino-substituent of phosphines (**11**) could be removed upon treatment with HCl to give chlorophosphine (**18**) from which novel trisethynylphosphines (**19**) bearing different substituted alkynes were obtained that may serve as building blocks for novel three-dimensional phospha-acetylenic scaffolds such as the (di)ethynyl-expanded phosphacubanes **8** and **25** that, according to DFT calculations, have a higher degree of cyclic electron delocalization and reduced HOMO–LUMO gaps compared to their carbon-analogues.

Keywords: Phosphor; Phosphines; Pericyclynes; Macrocycles

1. Introduction

Acetylene-based carbon frameworks are important molecules both as target and as tool in advanced molecular architectures and materials [1]. In particular, the synthesis of macrocyclic oligoacetylenes, like the buta-1,3-diynediyl-expanded molecules, are being pursued for use in molecular recognition, as molecular switches, and in electro-optical devices [2]. In this report, we focus on a special class of acetylenic scaffolds, the phospha[*n*]pericyclynes. The term [*n*]pericyclyne, coined by Scott [3], connotes a ring system of *n* acetylene functionalities with the numeral prefix [*n*] indicating the number of saturated corner units. The pericyclynes are with their rather simple and esthetically pleasing appearance a challenging and attractive research target from a synthetic [4] and theoretical [5] point of view. The incorporation of heteroatoms in such systems is still limited and has mainly focused on sulfur and silicon. Scott and Cooney reported the low yield (<15%) synthesis of dithia[4]pericyclyne (**1**) (Scheme 1) and related systems [6]. Attempts to synthesize tetrathia[4]pericyclynes have as of yet not succeeded [7].

Better accessible are the sila[*n*]pericyclynes ($n = 3$–6, 8, 10), bearing alkyl and aryl substituents, by treatment of double lithiated diethynylsilanes with dichlorosilanes (Scheme 2) [8]. The ring structures with alternating R_2Si and C≡C units are planar and twisted in the solid state depending on their substituents and ring size [8].

Few phosphorus containing pericyclynes are known, which is surprising considering the special P/C relationship [9]. In 1990, Scott and Unno [10] reported on the phosphamacrocycle (**5**) (11%; Scheme 3), obtained by double deprotonation of *tert*-butyldiethynylphosphine (**4**) using EtMgBr and subsequent reaction with *t*-$BuPCl_2$. The smaller

* Corresponding author. Tel.: +31 20 598 7474; fax: +31 20 598 7488.
E-mail address: K.Lammertsma@few.vu.nl (K. Lammertsma).

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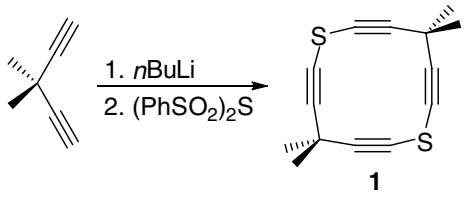


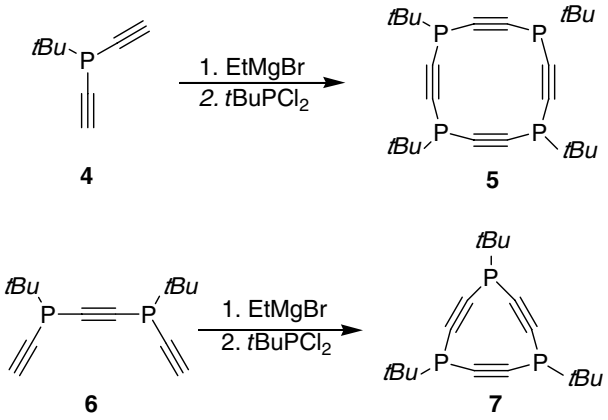
Scheme 1. Synthesis of dithia[4]pericyclyne (**1**).

triphospha[3]pericyclyne (**7**) (16%) was obtained similarly from **6** [6,10,11]. A mixed P,Si-pericyclyne was synthesized by condensation of $PhPCl_2$ with $Ph_2Si(C{\equiv}CH)_2$ following the same stategy [12]. In 2000, Märkl et al. [13] reported on the so-called "exploded" phospha[*n*]pericyclynes ($n = 3$–6, 8) bearing butadiyne spacers instead of single acetylenes, which were synthesized in low yields by oxidative Eglington coupling of diethynylphosphine building blocks.

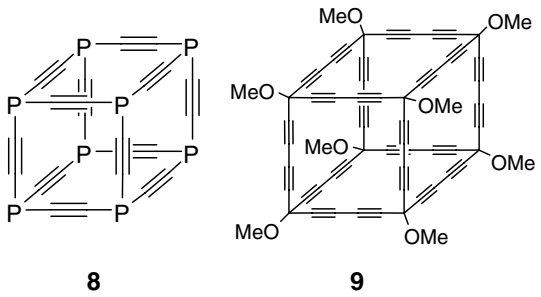
Typically, the acetylenic phosphine building blocks are synthesized by reacting chloro- or bromophosphines with metal acetylides, using Mg [14a,14b], Na [14c], Li [14c] or Ti [14d], as metal ion or with terminal alkynes using a Ni, Pd or Cu(I)-catalyzed coupling [15].

So far the synthesis of hetero[*n*]pericyclynes has been limited to two-dimensional macrocycles, whereas the presence of phosphorus centers as corner units is ideally suited to construct cages like the ethynyl-expanded phosphacubane (**8**) (Scheme 4), in analogy to the diethynyl-expanded cubane (**9**) [16]. The use of ethynylphosphines as building blocks has been briefly explored [6]. The synthesis of three-dimensional phospha-acetylenic scaffolds would require a 'corner' molecule with either three differently protected acetylene groups, or two similar ones with an entirely different third protecting group that can be converted into an acetylenic unit after the (2-D) pericyclyne formation. Such phosphorus-based 'corner' molecules have to the best of our knowledge not yet been reported.

The focus of this paper is to explore the access to P-based building blocks for the construction of (exploded) phospha[*n*]pericyclynes. This report is an extension of recent work in which we examined the use of diethynylphosphine oxides toward 2-D pericyclyne formation [17]. In the present study, the amine substituent is addressed



Scheme 3. Phosphapericyclyne synthesis.

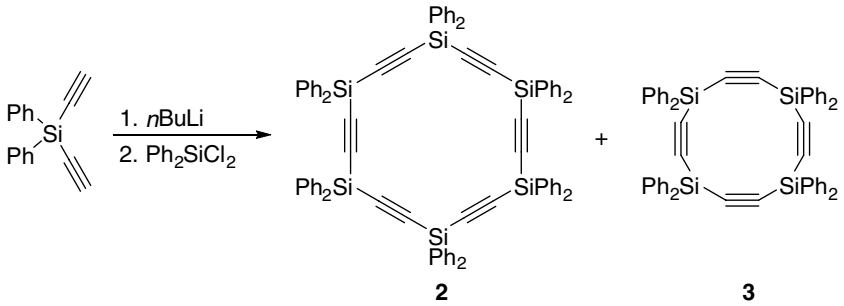


Scheme 4. (Di)ethynyl-expanded (phospha)cubanes.

for its suitability in the synthesis and its potential for further substitution/replacement toward 3-D structures.

2. Results and discussion

A potential corner unit for the synthesis of phospha[*n*]pericyclynes is *P*,*P*-diethynyl-*N*,*N*-diisopropylphosphinous amide (**11a**) and we briefly address the stabilization of this building block by protection of its phosphorus lone-pair. From **11a**, tetraphospha[4]pericyclcynes are synthesized as highly sensitive product mixtures. Furthermore, we focus on the synthesis of triethynylphosphines [18] by substitution of the amine functionality in **11** to give novel building blocks for three-dimensional structures. In the last section, we



Scheme 2. Example of silapericyclyne synthesis.

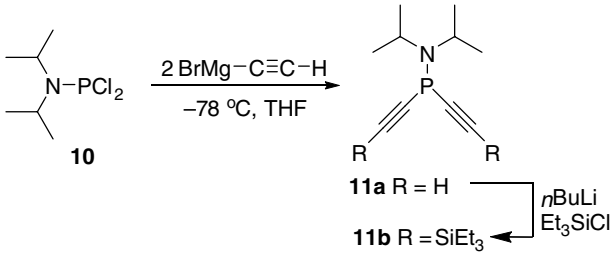
describe a brief computational analysis of (di)ethynyl expanded phosphacubanes to investigate the properties of these unusual 3-D structures.

2.1. Corner molecule

P,*P*-Diethynyl-*N*,*N*-diisopropylphosphinous amide (**11a**) ($\delta(^{31}P)$ −14.9) was prepared from diisopropylphosphoramidous dichloride (**10**) ($\delta(^{31}P)$ +172.0) and HC≡CMgBr and isolated by distillation as an air-sensitive, colorless liquid (60%; Scheme 5), which was stable at −20 °C but decomposed quickly above 80 °C to give a tar-like black solid. Double lithiation of **11a**, using *n*-BuLi, and quenching with Et_3SiCl (TES-Cl) yielded the silyl-protected derivative **11b** ($\delta(^{31}P)$ −15.5; 94%).

The diethynylphosphines (**11**) are more stable as the corresponding P(V) species, which was established for the =O and =S derivatives and for the $W(CO)_5$ and BH_3 adducts (Scheme 6). Oxidation of **11a** with *m*-CPBA in CH_2Cl_2 yielded phosphine oxide **12** ($\delta(^{31}P)$ −21.4) [17] after chromatography as a white crystalline solid (65%) that is stable for months when stored at −30 °C. Stable sulfur analogue **13** was generated by reacting **11a** with S_8 in CH_2Cl_2 at 40 °C and isolated as yellow crystals (53%) after chromatography. Metal-complexation was effected by heating **11a** with $W(CO)_5[CH_3CN]$ in THF at 40 °C to obtain $W(CO)_5$-complex **14** ($\delta(^{31}P)$ −2.4, $^1J(P,W) = 286.5$ Hz) in only 25% yield after chromatography due to decomposition of **11a** under the reaction conditions [19]. Protection of the phosphorus lone-pair with BH_3 can be attractive, because of the presumed ease of regenerating the phosphine [20]. Reaction of **11a** with $BH_3 \cdot SMe_2$ in THF at −10 °C gave indeed BH_3-adduct **15**, which is unfortunately not stable at room temperature as evidenced by the conversion of its $\delta(^{31}P)$ resonance at 19.0 ppm ($^1J(P,B) = 64$ Hz) into two very broad resonances at 40 and 50 ppm. We believe that the second reaction concerns the hydroboration of the terminal alkynes in **15** [21].

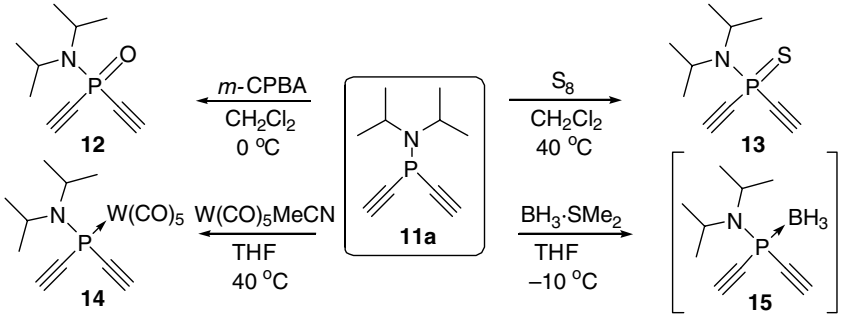
Thus, the diethynyl(amino)phosphine building blocks can be stabilized by both derivatization and complexation. This aspect is relevant for manipulation of the phospha[*n*]pericyclyne products. However, the added stability intrinsically reduces the reactivity of the building blocks. For example, the oxide hampers the conversion of the amino-substituent into the third acetylene function [17], and the sulfide was found sensitive toward reduction in the reaction of $P(S)Cl_3$ with acetylides [22].



Scheme 5. Synthesis of corner molecule **11**.

2.2. Pericyclyne synthesis

The synthesis of amino-substituted phospha[4]pericyclyne (**16**) can be pursued via the so-called 'shotgun' approach [13,23] and in a stepwise manner by combining double deprotonated **11a** with dichloro(amino)phosphine (**10**). In the 'shotgun' approach, the dianion of **11a**, obtained by reaction of **11a** with ethylmagnesium bromide in THF, was added slowly to a diluted solution of *i*-Pr_2NPCl_2 (**10**) in THF at −10 °C to give, after isolation and flash chromatography, a mixture of products as evidenced by the complex ^{31}P NMR that showed multiple resonances between −14 and −21 ppm (Fig. 1). This is not surprising as, in analogy with the reported synthesis of the *t*-Bu-derivative **5**, a mixture of four diastereomers can be expected (Scheme 7); the statistical ratio would be: **16a** (12.5%), **16b** (50%), **16c** (25%) and **16d** (12.5%) For symmetry reasons only single ^{31}P NMR resonances would be expected for each of the isomers **16a**, **c**, and **d**. Isolation of these isomers proved to be difficult, but their formation could be confirmed by their sharp singlet resonances at −17.8, −17.9 and −21.2 ppm in the ^{31}P NMR spectrum of the purified reaction mixture. The resonances at $\delta(^{31}P)$ −16.6 (t, $^3J(P,P)$ =17.6 Hz; 1P), −18.6 (dd, $^3J(P,P) = 9.5$ Hz, 17.6 Hz; 2P), and at −20.5 ppm (t, $^3J(P,P) = 9.5$ Hz; 1P) are assigned to isomer **16b** and its P,P-coupling pattern confirms formation of the desired tetraphospha[4]pericyclyne. The ratio of the four stereoisomers was found to be 11:58:24:7, which is close to the theoretical values



Scheme 6. Various protecting groups for P.

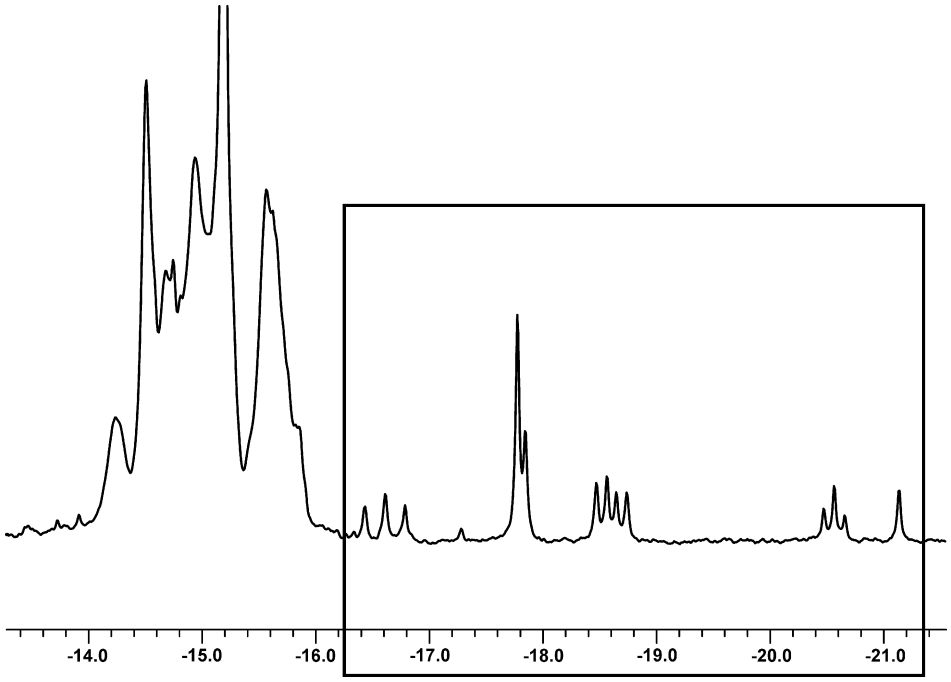
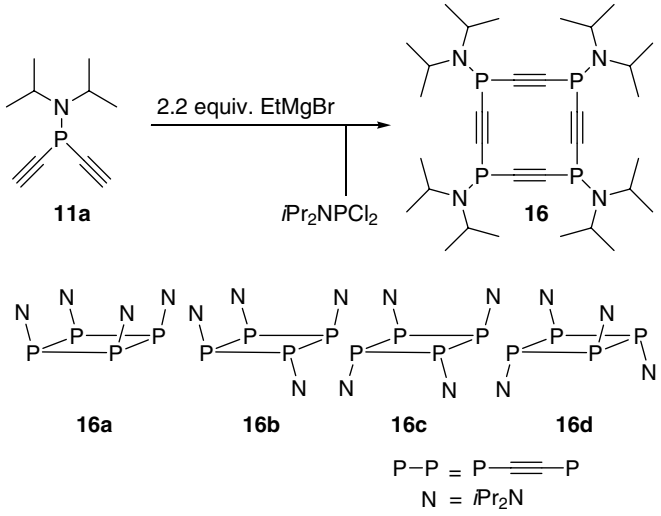


Fig. 1. ^{31}P NMR spectrum reaction mixture containing phospha[4]pericyclyne (**16**).



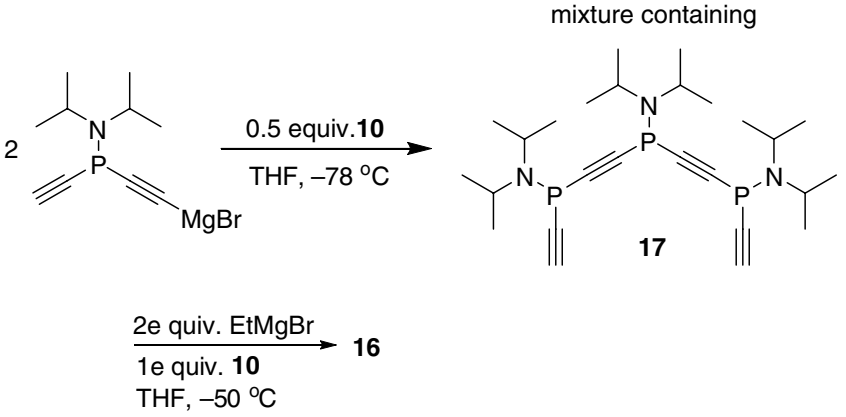
Scheme 7. One step 'shotgun' synthesis to tetraphospha[4]pericyclyne (**16**).

(12.5:50:25:12.5) and the total yield of phospha[4]pericyclynes (**16**) is ca. 9% (Fig. 1). The formation of **16** was confirmed by the parent mass ([M+H] 621.4) observed in the MS spectrum. Finally, we attribute the broad ^{31}P resonances that are observed in the range −14 to −16 ppm to differently sized oligomers. Due to the experimental conditions inherent to the 'shotgun' approach, the cyclic products have to compete with the favored formation of linear products.

The stepwise approach to tetraphospha[4]pericyclyne (**16**) was pursued in the hope to limit the undesired formation of byproducts and to increase the yield and possibly the selectivity [24]. Thus, phosphine (**11a**) was deprotonated with 1 equiv. of EtMgBr and subsequently reacted with 0.5 equiv. of *i*-Pr_2NPCl_2 (**10**) to form triphosphine (**17**), confirmed by MS ([M+H] *m/z* 492.2; Scheme 8). The product mixture was shown to be very sensitive toward oxygen and silica gel and therefore not further purified. Treatment of the crude reaction mixture with 2 equiv. of EtMgBr followed by slow addition to a dilute solution of *i*-Pr_2NPCl_2 (**10**) in THF resulted in the same mixture of products that was obtained by the 'shotgun' approach, be it with a slightly better ratio of **16a–d** to byproducts, according to ^{31}P NMR. Purification of macrocycle **16** was pursued by conversion to the corresponding sulfides but this led to complete decomposition.

2.3. Amino acetylene exchange

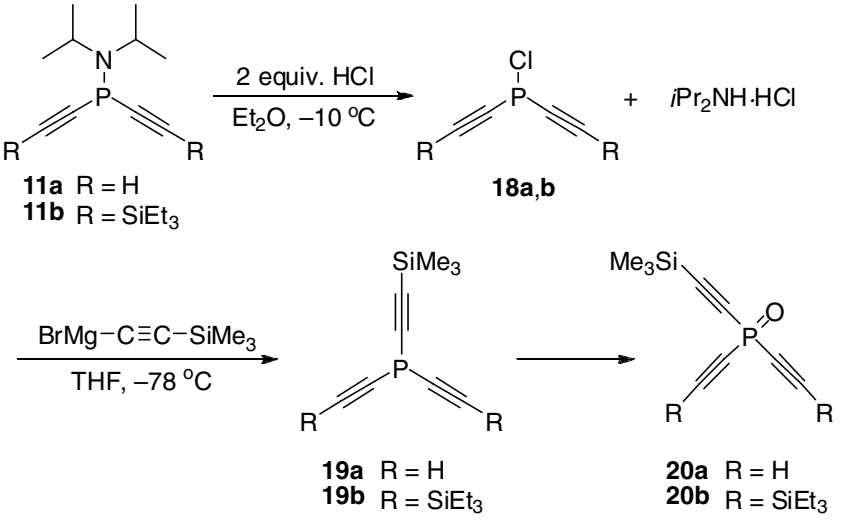
Conversion of the amino-phospha[*n*]pericyclynes to e.g. triethynylphosphine building blocks is plausible, but only practical starting from the free phosphines. The potential of the amino-group on phosphorus to serve as a handle for further functionalization is known and reaction with HCl (g) leads to the formation of ammonium salts and chlorophosphines [25], which we tested for model substrate **11**. Reaction of *i*-$Pr_2NP(C{\equiv}CH)_2$ (**11a**) with HCl (0.1 M in Et_2O) in diethyl ether at −10 °C gave indeed immediate precipitation of *i*-$Pr_2NH \cdot HCl$ and ^{31}P NMR spectroscopy confirmed the quantitative formation of the desired chlorophosphine (**18**) ($\delta(^{31}P)$ 18.5), which was moderately stable below 0 °C. For the related phosphine oxide **12**, this facile substitution of the amino-group does not occur [17]. Chlorophosphine (**18**) is an attractive building block for the synthesis of functionalized triethynylphosphines and we reacted **18** with $BrMg–C{\equiv}CSiMe_3$ to give phosphine



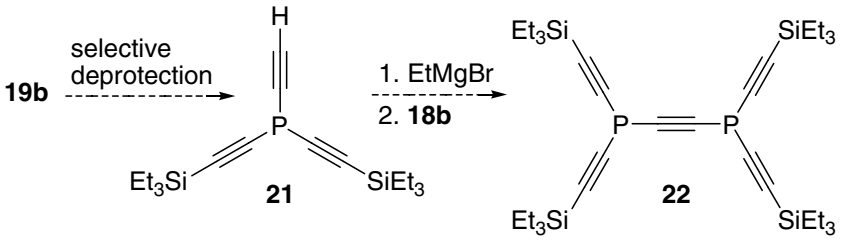
Scheme 8. Stepwise synthesis toward tetraphospha[4]pericyclyne.

(**19a**) ($\delta(^{31}P)$ −89.7) as the sole product (27%) after rapid filtration over silica gel. Its ^{31}P resonance is in close agreement to that of the C_3-symmetrical phosphines P–(C≡C–$CH_3)_3$ ($\delta(^{31}P)$ −87 ppm) and P–(C≡CH)$_3$ ($\delta(^{31}P)$ −91 ppm) [26]. The volatile P(C≡CH)$_2$(C≡C–TMS) **19a** undergoes rapid oxidation by air, silica gel or other oxidants to yield the more stable phosphine oxide **20a** ($\delta(^{31}P) = -58.3$ ppm). In analogy, silylated derivative **11b** ($\delta(^{31}P)$ −15.5) also showed clean conversion into the mixed triethynylphosphine (**19b**) ($\delta(^{31}P)$ −88.2), via chlorophosphine (**18b**) ($\delta(^{31}P)$16.1), and oxidation of **19b** by air to give **20b** ($\delta(^{31}P)$ −57.4) (see Scheme 9).

The triethynylphosphines (**19**), bearing differently protected acetylenes, are promising building blocks for the selective synthesis of larger phospha[*n*]pericyclynes, like bis(diethynylphosphino)ethyne (**22**) (Scheme 10) that can lead to three-dimensional acetylenic phosphines, such as the ethynyl-expanded phosphacubane (**8**) [27].



Scheme 9. Synthesis of triethynylphosphines.



Scheme 10. Synthetic approach towards larger phospha[*n*]pericyclynes.

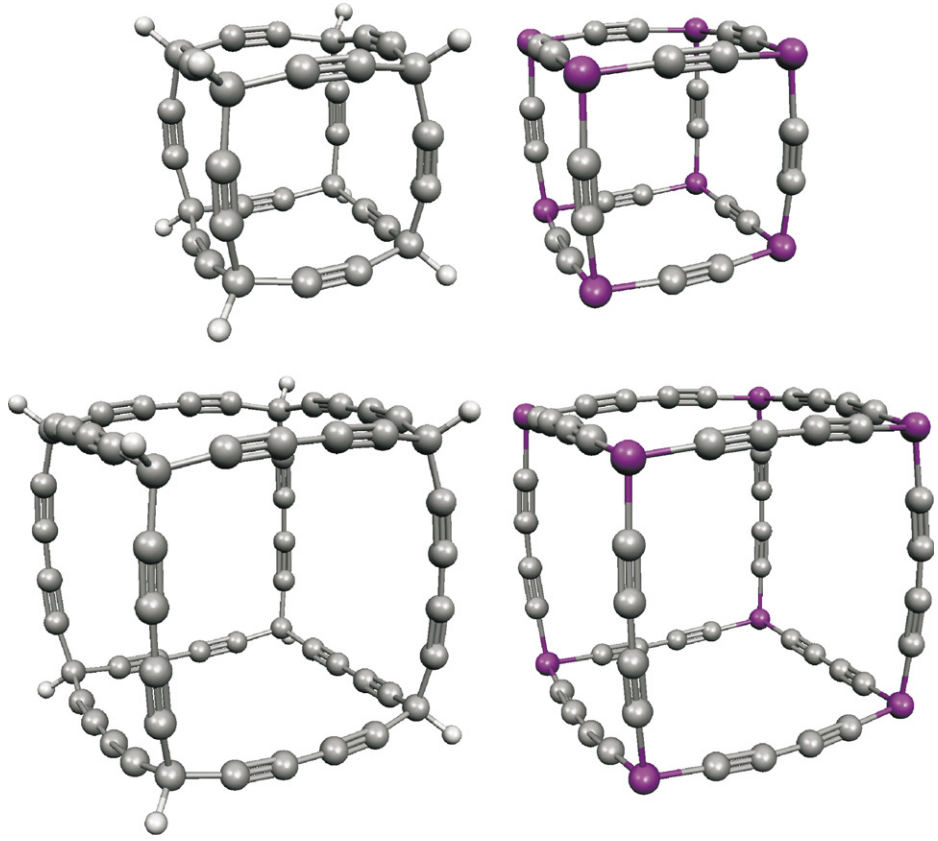


Fig. 2. Calculated structures of (di)ethynyl-expanded (phospha)cubane **8**, **23**–**25** (all *Oh* symmetry) at the B3PW91/6-31G(d) level of theory. Selected bond lengths (Å) and angles (°). Ethynyl-expanded cubane **23**: HC–C 1.480, C≡C 1.208; C–CH–C 107.0, HC–C≡C 166.6. Ethynyl-expanded phosphacubane **8**: P–C 1.783, C≡C 1.218; C–P–C 96.6, P–C≡C 175.2. Diethynyl-expanded cubane **24**: HC–C 1.475, C≡C 1.215, C–C 1.363; C–CH–C 108.5, HC–C≡C 169.4, C≡C–C 175.7. Diethynyl-expanded phosphacubane **25**: P–C 1.770, C≡C 1.222, C–C 1.359; C–P–C 98.5, P–C≡C 178.8, C≡C–C 174.9.

To investigate the properties of these aesthetically pleasing molecules, we resorted to DFT calculations on phosphacubane (**8**), its diethynyl-expanded derivative **25**, and their carbon analogues **23** and **24** (Fig. 2), of which **24** [28] is the parent structure of the octamethoxy-substituted cubane (**9**) [16]. Geometry optimizations (all *Oh* symmetry), performed at the B3PW91/6-31G(d) level of theory [29], show that the phosphacubanes **8** and **25** enjoy a substantial degree of cyclic electron delocalization [6,28a] as their C≡C bonds are elongated (**23**: 1.208 vs. **8**: 1.218 and **24**: 1.215 vs. **25**: 1.222 Å) and their internal C–C bonds shortened (**24**: 1.363 vs. **25**: 1.359 Å) compared to their carbon analogues. In addition, phosphacubanes **8** and **25** show reduced HOMO–LUMO gaps, calculated at HF/6-311+G(2df,p)//B3PW91/6-31G(d) [29], compared to their C-analogues (**23**: 11.27 vs. **8**: 10.56 and **24**: [28a] 10.56 vs. **25**: 9.65 eV) [29], which makes the phosphacubanes interesting synthetic targets and therefore further studies on these remarkable phosphines (or their P(V) counterparts) and their (opto-electronic)properties are needed.

3. Conclusions

Several building blocks for phospha[*n*]pericyclynes were synthesized. Phosphine (**11a**) is readily available from simple starting materials and its sensitivity can be controlled by $W(CO)_5$ complexation or conversion to the =O and =S derivatives. The formation of tetraphospha[4]pericyclynes (**16**) from **11a** is demonstrated, but their sensitivity towards oxidation hampers their isolation and further use. Chlorophosphines (**18**), obtained from phosphines (**11**) and HCl, gives access to triethynylphosphines (**19**) with various substituents on the acetylene. With these molecules now accessible, we believe the synthesis of three-dimensional structures such as the ethynyl-expanded phosphacubanes **8** and **25** is one step closer. According to DFT calculations, these aesthetically pleasing phosphacubanes have, when compared to their carbon-analogues, a higher degree of cyclic electron delocalization and reduced HOMO–LUMO gaps.

4. Experimental

4.1. Computations

Geometry optimizations (B3PW91/6-31G(d)) and single-point energy computations (HF/6-311+G(2df,p)//B3PW91/6-31G(d)) were carried out with density functional theory (DFT) using the GAUSSIAN-03 suite of pro-

grams [29]. Vibrational analyses were performed at the B3PW91/6-31G(d) level of theory to verify whether minima were obtained on the potential energy surface.

4.2. General

BrMg–C≡C–$SiMe_3$ [30], BrMg–C≡C–H [30] and *i*-Pr_2NPCl_2 (**10**) [31] were prepared according to the literature procedures. All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 300 K on Bruker Avance 250 (respectively, 250.13, 62.90 and 101.25 MHz) or MSL 400 (respectively, 400.13, 100.64 and 162.06 MHz) spectrometers. ^1H and ^{13}C NMR spectra were internally referenced to residual solvent resonances and ^{31}P NMR spectra externally to 85% H_3PO_4. Low-resolution mass spectroscopy was performed by direct infusion analysis of a methanol solution containing the phosphine into an ion trap mass spectrometer (LCQ-deca, Thermo Electron). High-resolution mass spectra (HRMS) were recorded on a Finnigan Mat 900 (EI, 70 eV). IR spectra were recorded on a Mattson 6030 Galaxy spectrophotometer. Melting points were measured on samples in unsealed capillaries and are uncorrected.

4.3. *i*-Pr_2N–P[C≡CH]$_2$ (**11a**)

A solution of freshly prepared HC≡C–MgBr (ca. 0.5M in THF) was added to a solution of *i*-Pr_2N–PCl_2 (11.9 g, 58.9 mmol) in THF (100 mL) at −78 °C. The reaction was monitored by ^{31}P NMR to stop the addition of the Grignard reagent (120 mL added) after complete conversion of *i*-Pr_2NPCl_2 was observed. After quenching of the reaction mixture with a few drops of water, solvent evaporation under reduced pressure, and extraction with diethyl ether (2 × 100 mL), a brown solid remained. Distillation at 60 °C/7 mm Hg yielded **11a** as a colorless liquid (6.48 g, 60%), which solidified upon cooling and that can be stored at −20 °C for months without any signs of decomposition. Storage at room temperature caused a color change to brown. ^{31}P NMR ($CDCl_3$) $\delta = -14.9$ (s); ^{13}C NMR ($CDCl_3$) $\delta = 23.4$ (d, $^3J(C,P) = 7.6$ Hz; CH_3), 49.7 (d, $^2J(C,P) = 8.9$ Hz; N–CH), 83.8 (d, $^1J(C,P) = 10.9$ Hz; P–C≡), 91.3 (d, $^2J(C,P) = 6.6$ Hz; ≡CH); ^1H NMR ($CDCl_3$) $\delta = 1.15$ (d, $^3J(H,H) = 6.7$ Hz, 12H; CH_3), 2.98 (d, $^3J(H,P) = 1.4$ Hz, 2H; ≡C–H), 3.60 (sp, $^3J(H,H) = 6.7$ Hz, 2H; N–CH).

4.4. *i*-Pr_2NP(C≡C–TES)$_2$ (**11b**)

n-BuLi (18.8 mmol, 1.6 M in hexanes) was added dropwise to a solution of phosphine (**11a**) (1.70 g, 9.4 mmol) in THF (200 mL) at −78 °C. The resulting solution was stirred for 3 h and quenched with freshly distilled Et_3SiCl (TES-Cl; 2.83 g, 18.8 mmol). The light yellow solution was evaporated under reduced pressure to yield a yellow oil that was filtered over Al_2O_3 with hexane to yield **11b** (3.61 g, 94%) as a light yellow oil. ^{31}P NMR ($CDCl_3$) $\delta = -15.5$ (s); ^{13}C NMR ($CDCl_3$) $\delta = 4.5$ (d, $^4J(C,P) = 6.8$ Hz; $SiCH_2$), 7.5 (d, $^5J(C,P) = 2.6$ Hz; $SiCH_2CH_3$), 23.3 (d, $^3J(C,P) = 7.5$ Hz; $CH(CH_3)_2$), 49.4 (s, CH), 107.5 (d, $^1J(C,P) = 39.7$ Hz; P–C≡), 112.7 (s, ≡C–Si); ^1H NMR ($CDCl_3$) $\delta = 0.61$ (q, $^3J(H,H) = 7.8$ Hz, 12H; $SiCH_2$), 1.00 (t, $^3J(H,H) = 7.8$ Hz, 18H; $SiCH_2CH_3$), 1.16 (d, $^3J(H,H) = 6.8$ Hz, 12H; $CH(CH_3)_2$), 3.65 (sp, $^3J(H,H) = 6.8$ Hz, 2H; CH).

4.5. *i*-Pr_2N–P(O)[C≡CH]$_2$ (**12**)

A solution of dried *m*-CPBA in CH_2Cl_2 (2.0 mL, ~1 M) was added dropwise to a solution of phosphine (**11a**) (181 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C and the reaction mixture was stirred at 0 °C for 1 h. ^{31}P NMR indicated a clean conversion to phosphine oxide (**12**). The CH_2Cl_2 solution was washed with H_2O (2 × 5 mL), dried over $MgSO_4$, and purified by column chromatography (silica gel, ethyl acetate/hexane 1:3) to yield **12** (130 mg, 65%) as a pale white solid. M.p. 134–135 °C; ^{31}P NMR ($CDCl_3$) $\delta = -21.4$ (s); ^{13}C NMR ($CDCl_3$) $\delta = 22.5$ (d, $^3J(C,P) = 2.1$ Hz; CH_3), 46.9 (d, $^2J(C,P) = 6.9$ Hz; NCH), 81.1 (d, $^1J(C,P) = 224.7$ Hz; PC≡), 88.3 (d, $^2J(C,P) = 41.5$ Hz; ≡CH); ^1H NMR ($CDCl_3$) $\delta = 1.31$ (d, $^3J(H,H) = 6.8$ Hz, 12H; CH_3), 3.05 (d, $^3J(H,P) = 11.6$ Hz, 2H; ≡CH), 3.60–3.74 (m, $^3J(H,P) = 21.2$ Hz, $^3J(H,H) = 6.8$ Hz, 2H; NCH); MS (70 eV): *m*/*z* (%): 197.1 (8) $[M]^+$, 182.1 (70) $[M-CH_3]^+$, 140.0 (100) $[M-NCH(CH_3)_2]^+$; HRMS: calcd. for $C_{10}H_{16}NOP$ 197.0970, found 197.09719.

4.6. *i*-Pr_2N–P(S)[C≡CH]$_2$ (**13**)

A solution of phosphine (**11a**) (680 mg, 3.75 mmol) and S_8 (721 mg, 2.81 mmol) in dichloromethane (40 mL) was heated at reflux for 24 h during which the solution slowly turned black. The solution was filtered and evaporation of dichloromethane at reduced pressure followed by column chromatography (silica gel, DCM/pentane 1:1) gave **13** (410 mg, 53%) as a yellow solid. M.p. 99–100 °C; ^{31}P NMR ($CDCl_3$) $\delta = 0.3$ (s); ^{13}C NMR ($CDCl_3$) $\delta = 22.7$ (d, $^3J(C,P) = 2.7$ Hz; CH_3), 48.7 (d, $^2J(C,P) = 6.1$ Hz; NCH), 81.7 (d, $^1J(C,P) = 192.4$ Hz; PC≡), 88.9 (d, $^2J(C,P) = 36.1$ Hz; ≡CH); ^1H NMR ($CDCl_3$) $\delta = 1.37$ (d, $^3J(H,H) = 6.9$ Hz, 12H; CH_3), 3.24 (d, $^3J(H,P) = 11.4$ Hz, 2H; ≡CH), 3.84–3.99 (m, $^3J(H,P) = 21.2$ Hz, $^3J(H,H) = 6.9$ Hz, 2H; NCH); MS (70 eV): *m*/*z* (%): 213.1 (6) $[M]^+$, 198.1 (8) $[M-CH_3]^+$, 180.1 (50) $[M-HS]^+$, 156.0 (16) $[M-CH(CH_3)_2-CH_3]^+$; HRMS: calcd. for $C_{10}H_{16}NPS$ 213.0741, found 213.07466.

4.7. *i*-Pr_2N–P[W(CO)$_5$][C≡CH]$_2$ (**14**)

To a solution of phosphine (**11a**) (1.25 g, 6.90 mmol) in dry THF (10 mL) was added at once $W(CO)_5$[MeCN] (2.52 g, 6.90 mmol) and the reaction mixture was heated at

50 °C for 8 h. The resulting black solution was concentrated under reduced pressure and the residue was purified by column chromatography (silica gel, pentane/dichloromethane 4:1) to yield **14** (870 mg, 25%) as colorless crystals. M.p. 80–81 °C; ^{31}P NMR ($CDCl_3$) $\delta = -2.4$ (s, ^1J(P,W) = 286.5 Hz); ^{13}C NMR ($CDCl_3$) $\delta = 23.2$ (d, ^3J(C,P) = 4.8 Hz; CH_3), 52.1 (d, ^2J(C,P) = 9.5 Hz; NCH), 83.3 (d, ^1J(C,P) = 83.0 Hz; PC≡), 93.1 (d, ^2J(C,P) = 18.1 Hz; ≡CH), 196.9 (d, ^2J(C,P) = 8.2 Hz, ^1J(C,W) = 127.3 Hz; *cis*-CO), 199.7 (d, ^2J(C,P) = 26.7 Hz; *trans*-CO); ^{1}H NMR ($CDCl_3$) δ = 1.38 (d, ^3J(H,H) = 6.9 Hz, 12H; CH_3), 3.42 (d, ^3J(H,P) = 6.4 Hz, 2H; ≡CH), 3.92–4.10 (m, ^3J(H,H) = 6.9 Hz, 2H; NCH); IR (CH_2Cl_2) ν(CO) = 2077 (w, CO_{ax}), 1945 (vs, CO_{eq}) cm^{-1}; MS (70 eV): *m*/*z* (%): 505.1 (26) $[M]^+$, 449.1 (24) $[M-2CO]^+$, 421.1 (14) $[M-3CO]^+$, 365.1 (87) $[M-5CO]^+$; HRMS: calcd. for $C_{15}H_{16}NO_5P^{186}W$ 507.0309, found 507.02640; calcd. for [M−2CO] 449.0378, found 449.03696.

4.8. Reaction of *i*-Pr_2N–P[C≡CH]$_2$ (**11a**) with $BH_3 \cdot SMe_2$

To a cooled solution of phosphine (**11a**) (320 mg, 1.75 mmol) in THF (25 mL) was dropwise added $BH_3 \cdot SMe_2$ (1.0 mL, 2.0 mmol; 2 M in THF) at 0 °C. After 30 min at 0 °C, the ^{31}P NMR spectrum showed complete conversion of the starting material and a broad resonance appeared at $\delta = 19.0$ ppm (^1J(P,B) = 64 Hz), indicating the formation of *i*-Pr_2N–P(BH_3)[C≡CH]$_2$ (**15**). Upon warming to room temperature, the reaction mixture slowly turned from yellow to orange and the signal at δ(^{31}P) 19.0 converted into very broad resonances at δ^{31}P 40 and 50 ppm that we presume to be polymeric material. The desired borane-adduct *i*-Pr_2N–P(BH_3)[C≡CH]$_2$ (**15**) could not be isolated.

4.9. Phosphapericyclynes (**16**)

(A) Shotgun synthesis: Freshly prepared EtMgBr in THF (9 mL, ca. 1.0M) was added to a solution of **11a** (740 mg, 4.1 mmol) in THF (150 mL) at −50 °C. The resulting light brown, cloudy solution was stirred for 30 min., warmed to room temperature, and added slowly to a diluted (∼0.03 M) solution of *i*-Pr_2NPCl_2 (**10**) (909 mg, 4.5 mmol) in THF at −10 °C, after which the black reaction mixture was stirred at room temperature for an additional 2 h. After removal of the solvent and multiple extractions with hexane, the dark brown oily product mixture was subjected to flash chromatography (silica gel, hexane) during which extensive product decomposition occurred. Low-resolution mass spectroscopy and ^{31}P NMR indicated the presence of the desired phospha[4]pericyclyne (**16**). The product mixture was kept at −20 °C to prevent further decomposition. ^{31}P NMR ($CDCl_3$) δ = −17.8, −17.9 and −21.2 (**16a**, **c**, **d**); **16b**: ^{31}P NMR ($CDCl_3$) $\delta = -20.5$ (t, ^3J(P,P) = 9.5 Hz), −18.6 (dd, ^3J(P,P) = 9.5 Hz, ^3J(P,P) = 17.6 Hz), −16.6 (t, ^3J(P,P) = 17.6 Hz); low-resolution mass spectroscopy of mixture: *m*/*z* 621.4 (M+H).

*(B) Stepwise synthesis via **17***: To a solution of **11a** (3.0 g, 16.6 mmol) in THF (300 mL) was added dropwise freshly prepared EtMgBr (85 mL, 0.2 M in THF, 1.1 equiv.) at −50 °C. After warming up to room temperature, this reaction mixture was slowly added together with a solution of **10** (1.67 g, 8.3 mmol) in THF (300 mL) to 200 mL of THF at −50 °C and stirred for and additional 1 h. After evaporation of the solvent at room temperature under reduced pressure the dark brown residue was extracted with hexane, filtered and kept at −70 °C to prevent product decomposition. ^{31}P NMR ($CDCl_3$) δ = −15.4 to −14.2 (multiple resonances); low-resolution mass spectroscopy of mixture: *m*/*z* 492.2 (M+H).

*Ring closure of **17** to **16***: To the hexane solution of triphosphine (**17**) at −50 °C was added 300 mL THF and then slowly a freshly prepared solution of EtMgBr (2 equiv. based on first step, 85 mL, 0.2 M). The resulting di-anion solution of **17** and a THF solution (300 mL) of **10** (1.67 g, 8.3 mmol) were simultaneously added in a dropwise manner to 200 mL of THF cooled to −50 °C. The product mixture containing **16** was obtained after solvent removal and extraction of the residue with hexane. The NMR spectroscopic data are similar to those obtained from the shotgun approach.

4.10. P(C≡CH)$_2$(C≡C–TMS) (**19a**)

A solution of phosphine (**11a**) (543 mg, 3.00 mmol) in diethyl ether (10 mL) was cooled in an ice-salt bath at −10 °C. To this solution was added a freshly prepared solution of HCl (∼0.1 M) in diethyl ether. The reaction was followed by ^{31}P NMR and addition of HCl/Et_2O was stopped (31 mL added) when full conversion of **11a** to chlorophosphine (**18a**) (δ^{31}P 18.5) was observed. Filtration of the salts yielded a clear colorless solution. The ethereal solution was concentrated to about 10% of its initial volume, while keeping the temperature below 0 °C. THF (10 mL) was added and the colorless solution was cooled to −78 °C. Subsequently, a freshly prepared solution of BrMg–C≡C–TMS (6 mL, 0.5 M in THF) was added dropwise and the reaction mixture was slowly warmed up to room temperature. The solvent was evaporated under reduced pressure. The product was extracted with diethyl ether and the magnesium salts were washed with diethyl ether. The solution was filtered and evaporated and the remaining oil was purified by fast filtration (silica gel, hexane) to yield **19a** as a colorless oil (140 mg, 27%). Phosphine (**19a**) is highly sensitive and quickly oxidizes in air to the corresponding oxide **20a** (δ^{31}P − 58.3). **19a**: ^{31}P NMR ($CDCl_3$) $\delta = -89.7$ (s); ^{13}C NMR ($CDCl_3$) δ = −0.5 (s, CH_3), 75.3 (d, ^1J(C,P) = 1.4 Hz; P–C≡CH), 94.1 (s, P–C≡C–Si), 94.6 (d, ^2J(C,P) = 9.1 Hz; ≡CH), 116.8 (d, ^2J(C,P) = 2.1 Hz; ≡C–Si); ^{1}H NMR ($CDCl_3$) $\delta = 0.21$ (s, 9H; CH_3), 3.09 (s, 2H; ≡CH).

4.11. $P(C{\equiv}C{-}TES)_2(C{\equiv}C{-}TMS)$ (**19b**)

Phosphine (**11b**) (0.1 mmol) was reacted with HCl(g)/Et_2O and BrMg–C≡C–TMS to give trisethynylphosphine (**19b**) in analogy to the procedure described above for **19a**. The reaction was followed by ^{31}P NMR and showed that chlorophosphine (**18b**) ($\delta^{31}P$ 16.1) is cleanly converted to **19b**. Rapid filtration over silica gel resulted in partial conversion to the phosphine oxide **20b** ($\delta^{31}P$ (hexane) −57.4). Filtration of the mixture (**19b** and **20b**) over Al_2O_3 enabled the isolation of **19b**. ^{31}P NMR ($CDCl_3$) $\delta = -88.5$ (s); ^1H NMR ($CDCl_3$) $\delta = 0.2$ (s, 9H; $Si(CH_3)_3$), 0.64 (q, $^3J(H,H) = 7.8$ Hz; $SiCH_2CH_3$), 1.02 (t, $^3J(H,H) = 7.8$ Hz; $SiCH_2CH_3$).

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Appendix A. Supplementary material

Cartesian coordinates (Å) and energies (a.u.) of all stationary points and NMR spectral data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.02.017.

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