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First insights into the synthesis of *carbo*-phospholane and *carbo*-phospholene oxides

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Fifteen-membered ring *carbo*-mers of five-membered rings are considered in the heterocyclic series of the phosphole oxide and less unsaturated parents. The synthesis of the first *carbo*-phospholane oxides is achieved by a [14+1] two-step/one-pot macrocyclization route with 86 % yield. Reduction of the latter phosphora-[5]pericyclyne with $SnCl_2$ allowed consistent ^{1}H and ^{31}P NMR characterization of the corresponding *carbo*-phospholene, produced with 11 % yield. The ultimate *carbo*-phosphole oxide could not be isolated, but preliminary results on alternative strategies towards this 14 π_z-electron Hückel *carbo*-aromatic are reported.

Introduction

While *carbo*-mers [1] of six-membered carbon rings have been largely exemplified since 1995 [2], their five-membered counterparts have been much less studied. To the best of our knowledge, since the early reports by L. T. Scott *et al*. on the synthesis of peralkylated ring *carbo*-mers of cyclopentane, for which the term "[5]pericyclynes" was coined [3], only one experimental report on functional *carbo*-cyclopentane derivatives has been published [4]. Nevertheless, expanded [5]pericyclynes [5] and full hetero-[5]pericyclynes (pericyclynes of second generation, corresponding to the *carbo*$_2$-mer series), in particular sila- and germa-representatives **1**, have been described [2a,6] (**Figure 1**). Perphospha-[3], -[4], and -[6]pericyclynes of first and second generations were also exemplified [2a,7], but pentaphospha-[5]pericyclyne derivatives are still missing to the best of our knowledge. Mixed hetero/carbo-pericyclynes were also considered [2a,8], at both the experimental and theoretical levels in the case of the *carbo*-silolane **2** [9] which was envisaged as synthesis precursor of the

unknown *carbo*-silole **3a** (**Figure 1**). *Carbo*-mers of more or less aromatic heterocycles C_4H_4X with X = O, NH, S and PHX, are **3b-e**, of stoichiometry $C_{14}H_4X$, which are antiaromatic according to the Hückel rule (with a 16 π-electron count), were indeed calculated to exhibit positive Nucleus Independent Chemical Shift (NICS) values [8]. Only the *carbo*-phosphole oxide **3f** presents a negative NICS value of –4.9 ppm, which is comparable to that of phosphole (NICS = – 5.3 ppm): this is consistent with the Hückel rule for a strongly semipolar $P^+–O^-$ bond (*vs* P=O), giving a formal 14 π-electron count over the macrocycle. This makes **3f** a relevant *carbo*-aromatic target [2h].

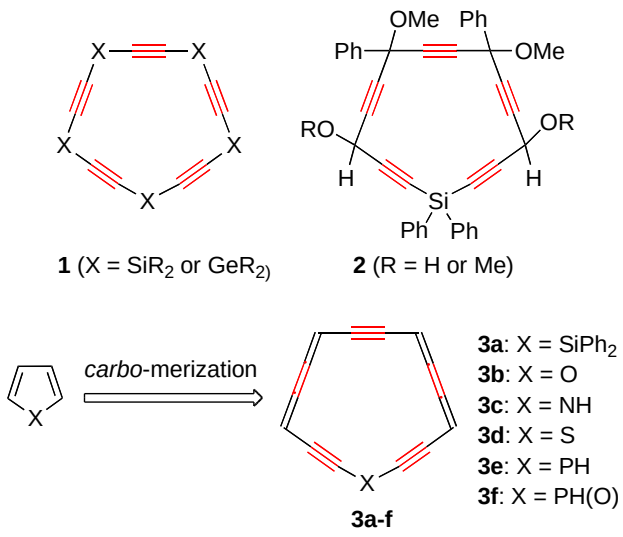


Figure 1. Full hetero-[5]pericyclynes **1** and mixed hetero/carbo-[5]pericyclynes **2** (*top*), and *carbo*-mers of cyclically π-conjugated five-membered heterocycles **3a-f** (*bottom*).

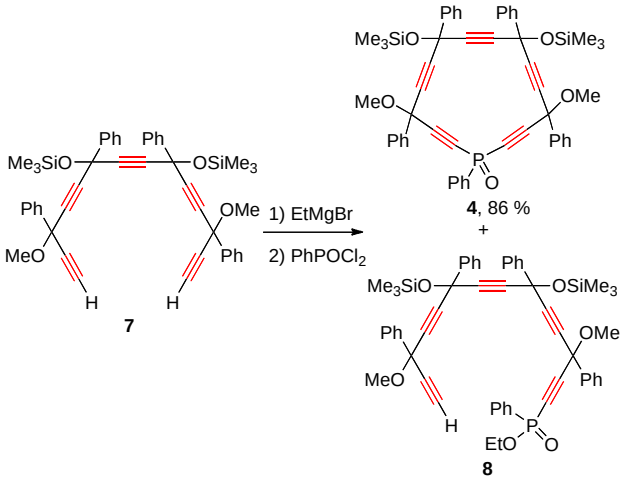
The *carbo*-phospholane oxide **4**, bearing a phenyl group at each vertex of the macrocycle, was thus envisaged as a precursor of the *carbo*-phosphole oxide **5**, a substituted version of **3f**. This target is the ring *carbo*-mer of pentaphenyl phosphole oxide that was recently described to exhibit intense solid state fluorescence properties [10]. Whereas the *carbo*-phosphole oxide **5** itself could not be obtained under the classical reductive aromatization conditions, the partly reduced *carbo*-phospholene oxide **6** could be evidenced. The preparation of the latter is described hereafter.

Results and discussion

The phosphora-[5]pericyclynic precursor **4** was readily obtained from the previously described pentayne **7** [11] by treatment of the dimagnesium salt of the latter with one equivalent of dichlorophenylphosphine oxide (**Scheme 1**). The two-step/one-pot [14+1] cyclization reaction occurred with a 86 % yield, a quite high yield for such a macrocyclization process in the absence of template. The formation of the side-product **8** however required a purification by silica gel chromatography. The ethyl alkynylphosphinate **8** likely resulted from a contamination of the commercial ethylmagnesium bromide solution used with ethoxymagnesium bromide.

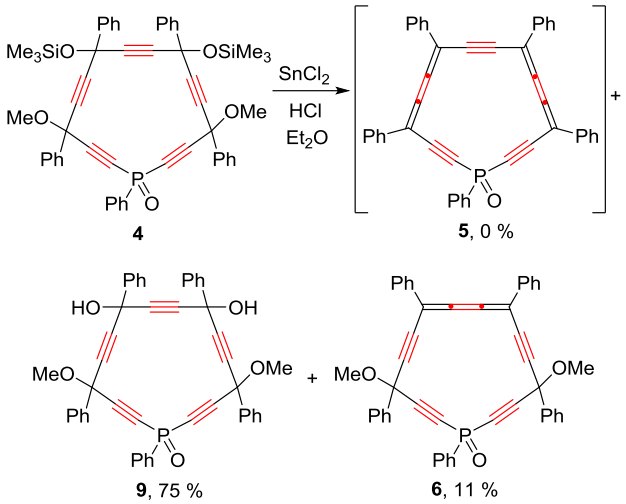
The *carbo*-phospholane oxide **4** was isolated as a mixture of its nine diastereoisomers, five of them being chiral. In ^{31}P NMR spectroscopy, the mixture of isomers gives a massif at -20 ppm, in the characteristic range for the ≡C-P(O)(Ph)-C≡ environment. The *carbo*-phosphole oxide **5** was then targeted

by reductive acidic treatment of **4** with $SnCl_2$/HCl, which is classically used for the synthesis of *carbo*-benzenes from hexapody-[6]pericyclynic precursors [2,12] (**Scheme 2**).



Scheme 1. Synthesis of the *carbo*-phospholane oxide **4**.

The procedure did not lead to the aromatic macrocycle **5**, but afforded the diol **9** as a main product, resulting from the cleavage of the two silylether groups of **4**. A side product was also identified as the *carbo*-phospholene oxide **6** resulting from a partial reduction of **4** (see below). The formation of another less polar side product was also revealed by a pink spot on silica gel TLC plates of the reaction mixture. The corresponding trace product can be tentatively assigned to the targeted *carbo*-phosphole oxide **5**, the strongly chromophoric nature of which being indeed consistent with a π-conjugation extent including a nearly planar dibutatrienylacetylene (DBA) moiety [12c,13]. Nevertheless, the very small amount formed prevented any characterization of the putative product **5**.



Scheme 2. Reductive treatment of the *carbo*-phospholane oxide **4**.

The *carbo*-phospholene oxide **6** was also obtained in small amount, but it could be isolated as a yellow solid and partly characterized. The ^{31}P and ^{1}H NMR spectra are fully consistent with the proposed structure. With respect to **4**, the simplification of the spectra of **6** is indeed in accordance with the reduction of the number of isomers. The two remaining asymmetric carbon atoms of **6** thus generate four stereoisomers (two of them containing a pseudo-asymmetric P atom) which are found to be formed in statistically equal amounts. This mixture gives rise to two ^{31}P NMR signals (at –19.89 and –20.32 ppm) and four ^{1}H NMR signals for the non-equivalent methoxy groups of **6** (**Figure 2**).

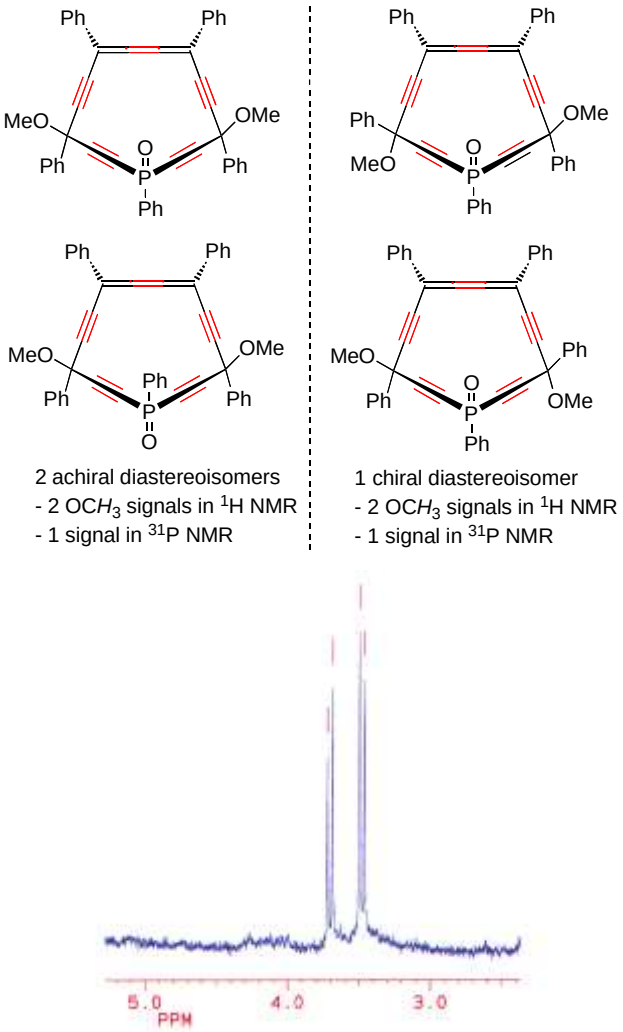
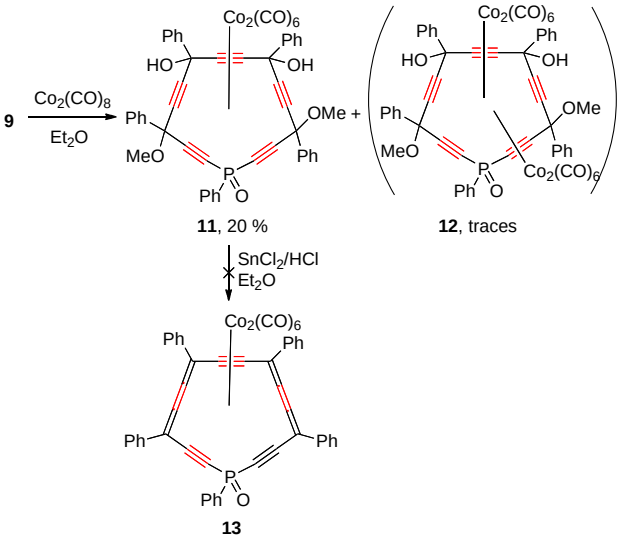


Figure 2. Stereoisomers of the *carbo*-phospholene oxide **6** (*top*) and ^{1}H NMR signature of the OCH_3 groups of the mixture (*bottom*).

These first results tend to indicate that the regiochemistry of the first reduction step prevents the formation of the second butatriene motif that should lead to the target *carbo*-phosphole oxide **5**. As exemplified for the synthesis of a hexaalkynyl-*carbo*-benzene [14], organometallic assistance was thus envisaged through the coordination of one butyne edge of **9** with dicobaltoctacarbonyl (**Scheme 3**). Reaction of **9** with one equivalent of $Co_2(CO)_8$, mainly afforded the expected complex **11** which could be separated from traces of the double adduct **12** by silica gel chromatography. However, all attempts at reductive aromatization of **11** by treatment with $SnCl_2$ and HCl failed to produce the *carbo*-phosphole oxide complex **13**. Analysis of the reaction medium by infrared spectroscopy indicated the removal of the $Co_2(CO)_6$ unit, and only the formation of undetermined polymeric materials could be evidenced.



Scheme 3. Attempts at organometallic assistance for the synthesis of the *carbo*-phosphole oxide **13**.

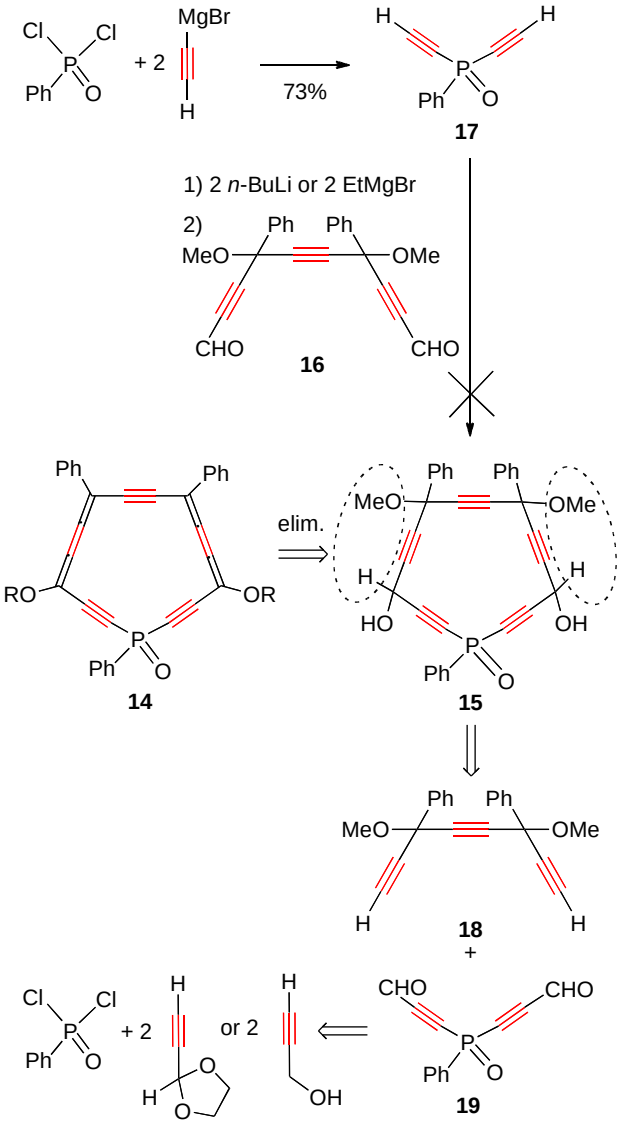
Prospects and conclusions

The first examples of *carbo*-phospholane oxides have been described, and a *carbo*-phospholene oxide has also been identified. The target *carbo*-phosphole oxide **5** could however not be isolated by the classical reductive elimination process. An alternative isohypsic elimination process could thus be envisaged for the synthesis of *carbo*-phosphole oxides **14** from the tetraoxy-*carbo*-phospholane **15** containing two secondary carbinol vertices

(**Scheme 4**). As summarized in Scheme 4, a [5+10] cyclization route from the triyne **16** and the diyne **17** was envisaged but failed to produce **15** [15]. The same target could however be envisaged through an alternative [8+7] strategy from the triyne **18** [2h,11,17] and the unknown C_7P bisynal **19** (**Scheme 4**). Advances in this sense for the synthesis of *carbo*-phosphole oxides will be communicated in due course.

Experimental section

General. All reagents were used as commercially available from Acros Organics, Avocado, Aldrich, Lancaster, Strem. THF and diethylether were dried and distilled on sodium/benzophenone, pentane and dichloromethane on P_2O_5. Commercial solutions of EtMgBr were 3 M in diethylether. Commercial solutions of *n*-BuLi were 1.6 or 2.5 M in hexane. The HCl solutions were 2M in diethylether. Previously described procedures were used for the preparation of **7** [11, 15]. All the reactions were carried out under nitrogen or argon atmosphere, using Schlenk tubes and vacuum line techniques. Column chromatographies were carried out with SDS silicagel (60 Å C.C. 70–200 mm). Thin layer chromatography (TLC) plates were purchased from SDS (60F254, 0.25 mm) and revealed by treatment with an ethanolic solution of phosphomolybdic acid (20 %). The following analytical instruments were used. IR: 0.1 mm CaF_2 cell, Perkin-Elmer GX FT-IR. ^1H and ^{13}C NMR: Brucker AC 200, WM 250, DPX 300 or AMX 400. Mass spectrometry: Quadrupolar Nermag R10-10H. All IR and NMR spectra were recorded in $CDCl_3$ solutions. IR absorption frequencies ν are in cm^{-1}. NMR chemical shifts δ are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants *J* are in Hz.



Scheme 4. Explored and proposed routes to *carbo*-phosphole oxides **14** through an isohypsic elimination process.

4,13-Dimethoxy-1,4,7,10,13-pentaphenyl-7,10-bis[(trimethylsilyl)oxy]-1-λ^5-phosphacyclopentadeca-2,5,8,11,14-pentayn-1-one (**4**)**.** EtMgBr (0.093 mL, 0.28 mmol) was added dropwise to a stirred solution of **7** (0.100 g, 0.14 mmol) in THF (5 mL) at 0 °C. The resulting mixture was stirred for 15 min at the same temperature before addition of dichlorophenylphosphine oxide (0.027 mL, 0.14 mmol). The temperature was allowed to warm up slowly, and the reaction mixture was stirred for 3 h at rt. The solution was diluted with diethylether (15 mL) and washed with a saturated aqueous NH_4Cl solution (2 x 25 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by silica gel chromatography (heptane/acetone 8:2) to give **4** as a pale yellow oil in 86 % yield (100 mg, 0.12 mmol).

TLC: R_f (heptane/acetone 8/2) = 0.24.

MS (DCI/NH_3): *m/z* = 858 $[M+NH_4]^+$, 751 $[M-OSiMe_3]^+$

^{1}H NMR ($CDCl_3$): δ = -0.07 – 0.35 (m, 18 H, -OSi(C*H*$_3$)$_3$), 3.28 – 3.70 (m, 6 H, -OC*H*$_3$), 7.29 – 7.43 and 7.59 – 7.76 (m, 23 H, *o*-, *m*-, *p*-C$_6$*H*$_5$ and *m*-, *p*-C$_6$*H*$_5$-PO), 7.76 – 8.09 (m, 2 H, *o*-C$_6$*H*$_5$-PO).

^{13}C{^{1}H} NMR ($CDCl_3$) : δ = 0.95, 1.26 and 1.47 (OSi(*C*H$_3$)$_3$), 53.43 – 54.15 (-O*C*H$_3$), 65.75 (≡C-*C*(OSiMe$_3$)Ph-C≡), 72.23 (≡C-*C*(OMe)Ph-C≡), 79.74 – 88.72 (*C*≡C), 99.95 (d, $^1J_{P-C}$ = 37 Hz, ≡*C*-PO), 125.93 – 129.84 (*o*-, *m*-, *p*-*C*$_6$H$_5$ and *m*-*C*$_6$H$_5$-PO), 130.52 (d, $^2J_{P-C}$ = 13 Hz, *o*-*C*$_6$H$_5$-PO), 133.12 (*p*-*C*$_6$H$_5$-PO), 137.84 (d, $^1J_{P-C}$ = 39 Hz, *ipso*-*C*$_6$H$_5$-PO), 141.75 (*ipso*-*C*$_6$H$_5$-C-OMe), 142.12 (*ipso*-*C*$_6$H$_5$-C-OSiMe$_3$)

^{31}P{^{1}H} NMR ($CDCl_3$) : δ = -20.6 – -19.8

IR ($CDCl_3$) : ν = 3066 – 2935 (s, Csp^3-H), 2829 (m, OCH_3), 2246 and 2196 (s, C≡C-P), 1955 (w, C≡C), 1591, 1490 and 1450 (m, C=C Ph), 1439 (m, P-C$_6$H$_5$), 1253 (s, C-Si), 1178 (m, P=O), 1116 (s, Si-O-C), 1069 (s, C-O).

Ethyl {3,12-dimethoxy-3,6,9,12-tetraphenyl-6,9-bis[(trimethylsilyl)oxy]tetradeca-1,4,7,10,13-pentayn-1-yl}(phenyl)phosphinate (**8**)**.** Side-product isolated by silica gel chromatography from the reaction mixture obtained during the synthesis of **4**.

TLC: R_f (heptane/acetone 8/2) = 0.19.

MS (DCI/NH_3): *m/z* = 904 $[M+NH_4]^+$, 888 $[M+H]^+$, 797 $[M-OSiMe_3]^+$.

^{1}H NMR ($CDCl_3$): δ = -0.09 – 0.32 (m, 18 H, -OSi(C*H*$_3$)$_3$), 1.35 (q, 3 H, -OCH$_2$C*H*$_3$), 2.76 (s, 1 H, ≡C-*H*), 3.32 – 3.59 (m, 6 H, -OC*H*$_3$), 4.12 – 4.21 (m, 2 H, -OC*H*$_2$CH$_3$), 7.29 – 7.45 and 7.52 – 8.09 (m, 25 H, *o*-, *m*-, *p*-C$_6$*H*$_5$ and *o*-, *m*-, *p*-C$_6$*H*$_5$-PO).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 1.32 (OSi(*C*H$_3$)$_3$), 16.31 (-OCH$_2$*C*H$_3$), 53.23 – 53.94 (-O*C*H$_3$), 62.35 (-O*C*H$_2$CH$_3$), 65.74 (≡C-*C*(OSiMe$_3$)Ph-C≡), 71.62 (≡C-*C*(OMe)Ph-C≡), 75.43 (≡*C*-H), 80.54 – 89.12 (*C*≡C), 100.94 (d, $^1J_{P-C}$ = 33 Hz, ≡*C*-PO), 125.92 – 129.82 (*o*-, *m*-, *p*-*C*$_6$H$_5$ and *m*-*C*$_6$H$_5$-PO), 130.54 (d, $^2J_{P-C}$ = 13 Hz, *o*-*C*$_6$H$_5$-PO), 133.12 (*p*-*C*$_6$H$_5$-PO), 137.84 (d, $^1J_{P-C}$ = 40

Hz, *ipso*-C_6H_5-PO), 141.72 (*ipso*-C_6H_5-C-OMe), 142.14 (*ipso*-C_6H_5-C-$OSiMe_3$)).

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 8.7 – 8.8

IR ($CDCl_3$): ν = 3306 (w, ≡C-H), 3064 – 2905 (m, Csp^3-H), 2826 (w, OCH_3), 2248 and 2167 (s, C≡C-P), 1952 (w, C≡C), 1600, 1490 and 1450 (m, C=C), 1253 (vs, C-Si), 1176 (m, P=O), 1069 (s, C-O).

7,10-Dihydroxy-4,13-dimethoxy-1,4,7,10,13-pentaphenyl-1-λ^5-phosphacyclopentadeca-2,5,8,11,14-pentayn-1-one (**9**)**.** To a solution of **4** (0.070 g, 0.08 mmol) in diethylether (3 mL) under stirring at -50 °C were added $SnCl_2$ (0.180 g, 0.80 mmol) and HCl (6 mL, 12 mmol). The resulting mixture was stirred 5 h between -50 °C and -10 °C before dilution with diethylether (15 mL). The solution was washed with a saturated aqueous NH_4Cl solution (2 x 10 mL) and the combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (heptane/acetone 7:3) to give the diol **9** as a pale yellow oil in 75 % yield (0.042 g, 0.06 mmol).

TLC: R_f (heptane/acetone 8/2) = 0.17.

MS (DCI/NH_3): *m/z* = 714 $[M+NH_4]^+$, 697 $[M+H]^+$, 679 $[MH-H_2O]^+$.

^1H NMR ($CDCl_3$): δ = 3.27 – 3.65 (m, 6 H, OCH_3), 7.30 – 8.09 (m, 25 H, *o*-, *m*-, *p*-C_6H_5 and *o*-, *m*-, *p*-C_6H_5-PO).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 53.81 – 54.45 (-OCH_3), 65.33 – 65.45 (≡C-*C*(OH)Ph-C≡), 72.42 (≡C-*C*(OMe)Ph-C≡), 79.85 – 83.83 (*C*≡C), 100.11 (d, $^1J_{P-C}$ = 33 Hz, ≡*C*-PO), 125.89 – 129,83 (*o*-, *m*-, *p*-C_6H_5 and *m*-C_6H_5-PO), 130.52 (d, $^2J_{P-C}$ = 13 Hz, *o*-C_6H_5-PO), 133.54 (*p*-C_6H_5-PO), 137.86 (d, $^1J_{P-C}$ = 40 Hz, *ipso*-C_6H_5-PO), 140.58 (*ipso*-C_6H_5-C-OMe), 140.62 (*ipso*-C_6H_5-C-OH).

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = -20.7 – -19.8.

4,13-Dimethoxy-1,4,7,10,13-pentaphenyl-1-λ^5-phosphacyclopentadeca-7,8,9-trien-2,5,11,14-tetrayn-1-one (**10**)**.** Isolated by silica gel chromatography from the reaction mixture of the reductive elimination from **4**, in 11% yield (5 mg)

TLC: R_f (heptane/acetone 7/3) = 0.38.

^1H NMR ($CDCl_3$): δ = 3.46, 3.50, 3.69 and 3.72 (4s, 6 H, -OCH_3), 7.36 – 8.12 (m, 25 H, *o*-, *m*-, *p*-C_6H_5 and *o*-, *m*-, *p*-C_6H_5-PO).

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = -20.3, -19.9 (2s).

{η^2-(7,10-dihydroxy-4,13-dimethoxy-1,4,7,10,13-pentaphenyl-1-λ^5-phosphacyclopentadeca-2,5,8,11,14-pentayn-1-one)}dicobalthexacarbonyl (**11**)**.** Dicobaltoctacarbonyl (0.038 g, 0.11 mmol) were added to a degassed solution of **9** (0.070 g, 0.10 mmol) in diethylether (5 mL) under stirring at 0 °C. After 1.5 h, the solvent was removed under reduced pressure and the red residue was purified by silica gel chromatography (heptane/acetone 8/2) to give **11** as a red oil in 20 % yield (0.016 g, 0.02 mmol).

TLC: R_f (heptane/acetone 8/2) ≈ 0.29.

^{1}H NMR ($CDCl_3$): δ = 3.05 – 3.62 (m, 6 H, -OC*H*$_3$), 6.88 – 8.15 (m, 25 H, *o*-, *m*-, *p*-C_6H_5).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 52.52 – 53.94 (-O*C*H$_3$), 65.36 (≡C-*C*(OH)Ph-C≡), 72.44 (≡C-*C*(OMe)Ph-C≡), 79.83 – 83.84 (*C*≡C), 100.13 – 102.42 (coordinated ≡*C*-PO and *C*≡C), 125.95 – 132.55 (*o*-, *m*-, *p*-C_6H_5 and *o*-, *m*-, *p*-C_6H_5-PO), 140.04 – 140.99 (*ipso*-C_6H_5-C-OMe and *ipso*-C_6H_5-C-OH), 197.42 – 197.84 (*C*≡O).

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = -20.8 – -20.4

IR ($CDCl_3$): ν = 3572 (w, OH), 3065 – 2935 (w, Csp^3-H), 2826 (w, OCH_3), 2104, 2070 and 2041 (vs, C≡O), 1601 (m), 1490 (m) and 1450 (s, C=C), 1438 (m, P-C_6H_5), 1207 (m, P=O), 1069 (s, C-O).

Diethynylphenylphosphine oxide (**17**, **diethynylphosphoryl)benzene**). In a Schlenk tube at -50°C, a solution of ethynylmagnésium bromide (30 mL, 0.015 mol) is added dropwise to $PhP(O)Cl_2$ (426 µL ; 0,003 mol). After stirring for 15 min at -50°C, then for 17 h at 0°C, the mixture is terated with a saturated aqueous solution of NH_4Cl. The aqueous layer is separated and extracted twice with Et_2O. The combined organic layers are washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was submitted to silica gel chromatography (heptane/EtOAc 5/5) to give **17** in 73% yield as a white solid (380 mg).

TLC (heptane/EtOAc 5/5): $R_f \approx 0{,}21$.

MS (DCI/NH_3): *m/z* = 192 $[M+NH_4]^+$, 175 $[M+H]^+$.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.38 (d, $^3J_{P-H}$ = 11 Hz, 2 H, ≡C-*H*), 7.45-7.56 (m, 3 H, *m*-, *p*-C_6H_5), 7.82-7.93 (m, 2 H, *o*-C_6H_5).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = -20,38 (s, *P*=O).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 63 MHz): δ = 78.20 (d, $^1J_{C-P}$ = 194 Hz, *C*≡CH), 93.42 (d, $^2J_{C-P}$ = 35 Hz, C≡*C*-H), 128.79-130.39 (*o*- and *m*-C_6H_5), 131.92 (*ipso*-C_6H_5), 133.34 (*p*-C_6H_5).

IR ($CDCl_3$: ν = 3288 (vs, C_{sp}–H), 3064 (w, C_{sp2}–H), 2066 (vs, C≡C), 1591 (m), 1486 (vw, endocyclic C=C), 1440 (vs, P–Ph), 1214 (vs, P=O).

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[15] The envisaged [10+5] cyclization to **15** consists in the reaction of the known triyndial **16** [11,16] with diethynylphosphine oxide **17** [17]. The latter has been actually been prepared in 73 % yield directly from $PhP(O)Cl_2$ (avoiding the oxidation step of the original report claiming a 44 % overall yield only [17]). Double deprotonation of **17** in THF solution however resulted in the precipitation of the corresponding dilithium or dimagnesium salt, and no reaction with **16** took place after 2 h at r. t., while polymerization of **16** occurred after heating with the dimagnesium dibromide salt of **17** in refluxing THF. Facing this insolubility problem of the salts of **17** (likely promoted by intermolecular $[-C{\equiv}C–M\cdots O{=}P-]_n$ aggregation, M = Li, MgBr] the reaction of **16** with the P(III) counterpart of **17**, $(HC{\equiv}C)_2PhP$:, could be explored. Ultimate efforts should however focus on the reverse [8+7] cyclization strategy involving the challenging dialdehyde **19** (**Scheme 4**).

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