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Reactivity of dihydrodiazaphosphinines towards unsaturated substrates: addition, [5 + 2] cycloaddition and rearrangement processes

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Abstract

Treatment of 4-amino-1-azadienes **1** with dichloro (diisopropylamino)phosphane gave 1,2-dihydro-1,3,2-diazaphosphinines **3**, which cycloadded in a [5 + 2] fashion to dimethyl acetylenedicarboxylate to furnish bicyclic iminophosphoranes **5**. The single addition compound **6** was formed by reaction of **3a** with $(CO)_5Cr{=}C(OMe)(C{\equiv}CPh)$. Compounds **5** underwent formal 1,7-rearrangement to **7** at room temperature. In turn, **5a** reacted with electrophiles (difluorochloroacetic acid and methyl iodide) through the valence isomer **5a'** to give polycyclic structures **13** and **14**, which led to **16** by fluoride-induced [4 + 2] cycloreversion. Other reactive electrophilic substrates, like diethyl azodicarboxylate and N-phenyltriazolinedione, led to the oxidized derivative **9** and to the addition product **12** respectively. The X-ray structures of **7a** and **12** are discussed.

Keywords: Diazaphosphinines; [5 + 2] Cycloaddition; Iminophosphoranes; Rearrangement; Heteropolycycles

1. Introduction

In the last years we have been involved in the synthesis of nitrogen heterocycles containing one heteroatom of the Groups 14–16 (Scheme 1) [1]. Thus, compounds **2**, like 1,2-dihydro-1,3,2-diazasilines (X = SiR_2) [2], -germines (X = GeR_2) [3] and -phosphinines {X = PR, P(O)R} [4], were prepared by condensation of 4-amino-1-azadienes **1** with the corresponding silicon, germanium and phosphorus chlorides. Interestingly, we discovered that the reactivity of the starting compounds **1** towards some electrophilic reagents changes dramatically when their silicon or germanium derivatives **2** are used. In fact, a number of medium ring heterocycles that cannot be made directly from **1** were efficiently synthesized by using their cyclic derivatives **2** [5].

Reactions involving the phosphorus lone pair and therewith converting λ^3- into λ^5-phosphorus compounds have been widely used in organic synthesis. The phosphanyl substituent has gained particular importance as a reactive peripheral functional group in cycloaddition reactions. Thus, it has been reported that *N*-phosphino imines [6] and *N*- and *C*-phosphino 1,3-dipoles [7,8] behave as 1,3- and 1,4-dipoles respectively, leading to five- and six-membered rings. The reaction is thought to occur by nucleophilic addition of phosphorus followed by 1,5- and 1,6-electrocyclic ring closure.

However, this methodology cannot be applied to the synthesis of seven-membered heterocycles. For instance, it was reported that the cycloaddition of *N*-phosphanyl nitrilimines and phenyl azide failed to give the desired [4 + 3] cycloadducts; instead the formation of the triazaphosphole derivative, resulting from the [4 + 1] cycloaddition, did take place [8].

It is remarkable that no reports regarding *N*-phosphino-1-azadienes (*N*-phosphino-α,β-unsaturated imines) have been released. Our interest in these compounds stems from two points. First, this structure seems amenable to accomplishing the synthesis of seven-membered heterocycles by a [5 + 2] cycloaddition strategy (1,5-dipolar cycloaddition). Second, the diazaphosphinines of type **2** actually contain the phosphorus-substituted azadiene unit. It should be noted that the synthesis of seven-membered heterocycles by 1,5-

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[1] X-ray crystal structures analyses.

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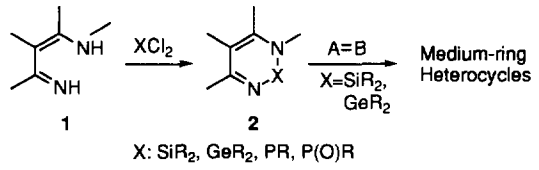


Scheme 1. Synthesis and reactivity of diazasilines, -germines and -phosphinine **2**.

dipolar cycloaddition reactions is unknown, as far as we are aware; to date only the intramolecular trapping of a vinylthiocarbonyl-*S*-sulfide (1,5-dipole) with an alkene has been reported [9] (for synthetic methods leading to seven-membered heterocycles, see Ref. [10]).

Accordingly, we report herein that 1,2-dihydro-1,3,2-diazaphosphinines **3** react with electron-poor substrates through the phosphorus atom leading to either [5 + 2] cycloadducts or open-chain derivatives, as well as on the reactivity of these products [11].

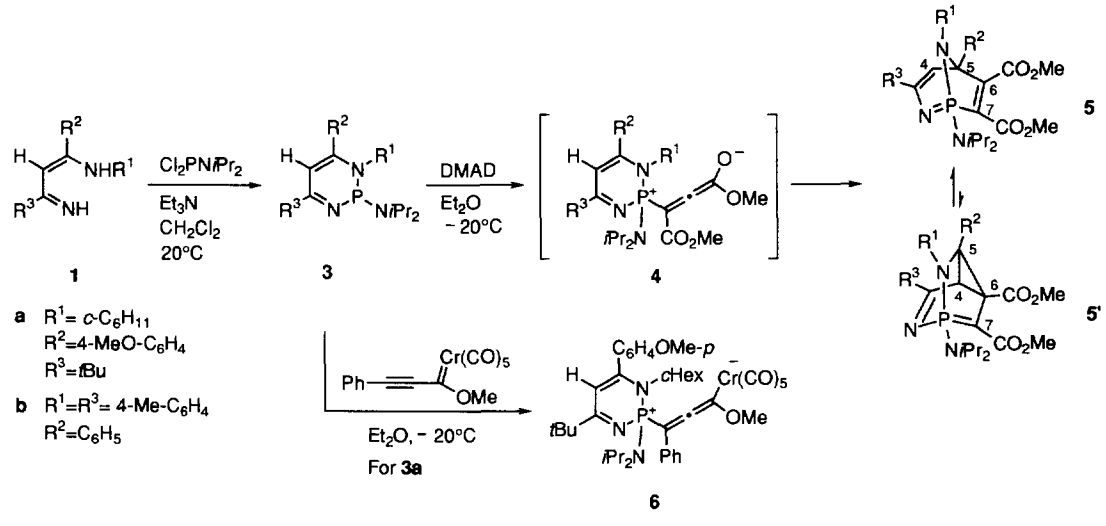
2. Results and discussion

2.1. Reaction of 1,3,2-diazaphosphinines (3) with activated alkynes

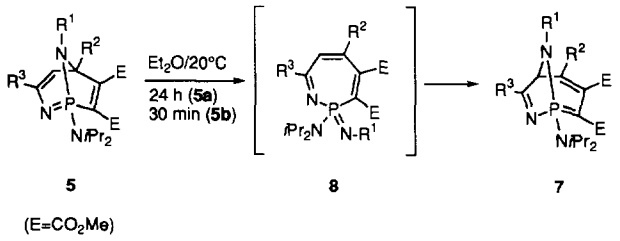
First, 1,2-dihydro-1,3,2-diazaphosphinines **3** (**3a**: R^1 = c-C_6H_{11}, R^2 = 4-MeO–C_6H_4, R^3 = CMe_3, ^{31}P NMR: 57.9 ppm; **3b**: R^1 = 4-Me–C_6H_4, R^2 = C_6H_5, R^3 = 4-Me–C_6H_4, ^{31}P NMR: 78.3 ppm) were formed by condensation of the corresponding 4-amino-1-azadienes **1** with dichloro(diisopropylamino)phosphane following a previously described procedure (Scheme 2) [4]. Then a solution of **3a** in ether was stirred with dimethyl acetylenedicarboxylate (DMAD) at −20 °C for 12 h; removal of the solvent at this temperature and crystallization from hexane afforded a single reaction product which was characterized as the bicyclo[3,2,1]-1-phospha-2,8-diaza-1,3,6-octatriene **5a** (80% yield from **3a**; ^{31}P NMR: 48.2 ppm), a new type of imino phosphorane structure. The diazaphosphinine **3b** also reacted with DMAD in ether at −20 °C to give the bicyclic derivative **5b** (^{31}P NMR: 41.9 ppm), which was not fully characterized as it rearranged rapidly at room temperature (see below).

The structure of **5a** was unambiguously established by an X-ray structure analysis [11]. The most significant features of this structure are the atomic distance C_4–C_6 (228.05 pm) and the C_4–C_5–C_6 angle (96.1°) as well as the pyramidalisation of C_7 (sum of angles 353.9°). These findings are not in total agreement with **5a**, but they suggest an equilibrium between the valence isomers **5a** and **5a'** in the solid state (see Scheme 2). (This phenomenon has been established for substituted semibullvalenes and barbaralanes, wherein Cope rearrangements take place. In these cases the non-bonding interatomic distances are generally in the range 220–230 pm; see Ref. [12]). In contrast, the ^{13}C NMR spectrum recorded in THF-d_8 reveals a structure very close to that of **5a** (C_4: 84.6 ppm; C_5: 67.2 ppm).

This unprecedented 1,5-dipolar cycloaddition most probably involves phosphorus nucleophilic attack on the electrophilic alkyne leading to the zwitterionic intermediate **4a** followed by 1,7-electrocyclization. This type of intermediate might be isolable if negative charge is more efficiently stabilized. In this way, we found that the diazaphosphinine **3a** added in CH_2Cl_2 at room temperature to phenylethynyl(methoxy)pentacarbonyl chromium carbene complex to afford the zwitterionic phosphonium structure **6** in good yield. Compound **6** contains a stereogenic phosphorus center and a chiral axis and was obtained as a 9:1 mixture of diastereoisomers (for the addition of phosphines to alkynyl(methoxy)carbene complexes, see Ref. [13]).



Scheme 2. Formation of phosphorus ylide **5** and phosphonium salt **6** from diazaphosphinines **3**.



Scheme 3. Rearrangement of compounds **5** into compounds **7**.

The cycloadducts **5** were found to rearrange smoothly at room temperature in ether or dichloromethane (24 h for **5a** and 30 min for **5b**) to give the bicyclo[3,2,1]-1-phospha-7,8-diaza-1,3,6-octatriene **7** in quantitative yield [^{31}P NMR: 56.5 (**7a**) and 56.8 ppm (**7b**)] (Scheme 3). This formal 1,7-sigmatropic shift probably initiates by a retro-Michael ring opening of **5**, leading to the 1,2-azaphosphepine structure **8**, which would then afford **7** by a Michael ring re-closing reaction.

The structure of these new cyclic phosphorus ylides **7** was confirmed by an X-ray determination performed on compound **7a** (Fig. 1).

Crystal data of **7a**: $C_{32}H_{48}N_3O_5P_1$, $M_r = 585.70$, monoclinic, space group $P2_1/n$, $a = 13.468(5)$ Å, $b = 17.328(8)$ Å, $c = 14.360(6)$ Å, $\beta = 92.49(3)°$, $V = 3348(3)$ Å^3, $Z = 4$, $D_x = 1.162$ Mg m^{-3}, Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å), $\mu = 0.123$ mm^{-1}, $F(000) = 1264$, $T = 293(2)$ K. Final conventional $R = 0.049$ and $wR_2 = 0.123$ for 3413 'observed' reflections and 488 variables.

In the structure of **7a** some details should be noted. At 1.439(3) Å the carbon–carbon bond length between the phosphorus-bonded carbon C_7 and the carbonyl

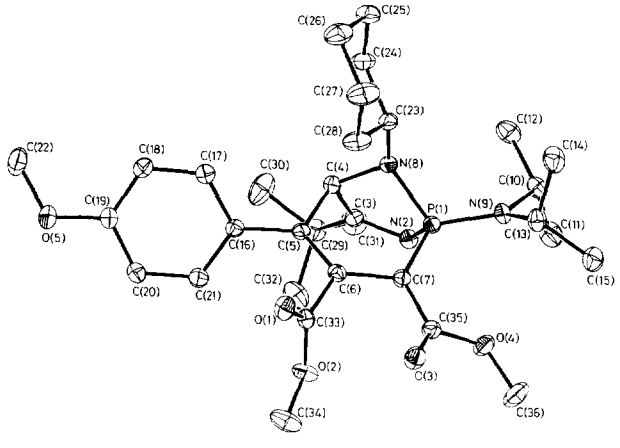


Fig. 1. Crystal structure of **7a**. Selected bond lengths (pm) and bond angles (°): P1–N2 168.4(2), P1–N8 167.0(2), P1–N9 161.3(2), P1–C7 172.3(2), N2–C3 129.8(3), C3–C4 153.3(3), C4–C5 153.2(3), C5–C6 137.6(3), C6–C7 145.5(3), C4–N8 147.3(3), C7–C35 143.9(3), C35–O3 121.6(3), C35–O4 136.0(3), C6–C33 150.4(3), C33–O1 119.7(3), C33–O2 134.1(3); N2–P1–N8 94.7(1), N8–P1–C7 106.2(1), N2–P1–C7 106.8(1), C3–N2–P1 106.2(2), N2–C3–C4 114.9(2), C3–C4–C5 104.9(2), C4–C5–C6 118.2(2), C5–C6–C7 126.3(2), C6–C7–P1 112.1(2), C4–N8–P1 101.0(2).

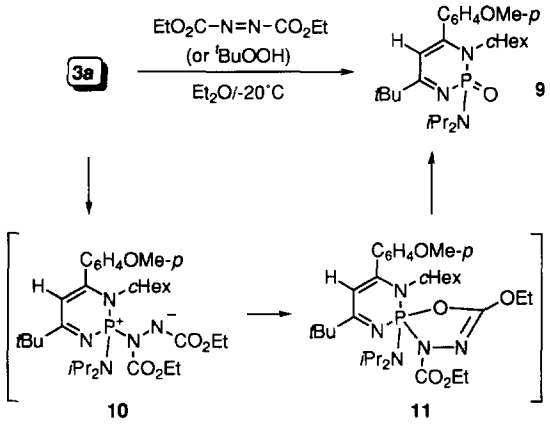
group is shortened, reflecting a mesomeric stabilization of the ylidic charge. This mesomeric form is also indicated by a slight lengthening of the corresponding carbon–oxygen bonds (C=O 1.216(3) Å; C–O 1.360(3) Å), as can be seen in comparison with the carbonyl group attached to C_6 (C–C 1.504(3) Å; C=O 1.197(3) Å; C–O 1.341(2) Å). This stabilization seems to be the driving force for the structural rearrangement from **5** to **7**.

With a sum of the bond angles of 359.6(6)°, N_9 has a planar configuration within standard deviations, probably due to a (p–σ*) interaction of nitrogen and phosphorus. This interaction is also indicated by the very short phosphorus–nitrogen interatomic distance of 1.613(2) Å, corresponding to a high phosphorus–nitrogen double bond character. The largest phosphorus–nitrogen interatomic distance (1.684(2) Å) is found for the P–N_2 bond in spite of the sp^2-character of the bonding nitrogen orbital, indicating that the sp^2-character of the orbital accommodating the lone pair prevents such a type of interaction.

The C_3–C_4–C_5 angle of 104.9(2)° derives only slightly from sp^3-geometry, leading to a non-bonding distance between C_3 and C_5 of 2.430(3) Å as was to be expected for the unperturbed case. The remaining bond lengths and angles are also in the range of expectation.

2.2. Reaction of 1,3,2-diazaphosphinines (3) with activated azo derivatives

Next, diethyl azodicarboxylate (DEAD) was chosen as another reactive substrate. When compound **3a** was reacted with DEAD in diethyl ether at −20 °C, a clean oxygen transfer reaction from the azo derivative to the starting λ^3-diazaphosphinine occurred, resulting only in the formation of the diazaphosphinine *P*-oxide **9** (80% yield; ^{31}P NMR: 4.0 ppm) (Scheme 4). On the basis of the Mitsunobi reaction [14], compounds **10** and **11** can be postulated as the reactive intermediates of the reaction. (Unsuccessful efforts were made to trap the 1,3-di-



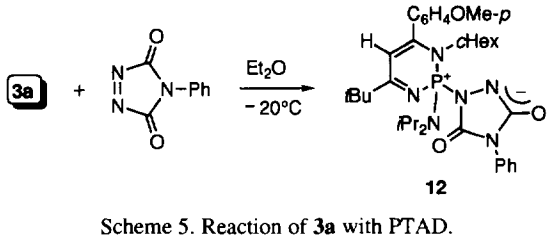
Scheme 4. Reaction of **3a** with DEAD.

pole resulting from the cycloreversion of **11** by conducting the reaction in the presence of dipolarophiles (dimethyl acetylenedicarboxylate, diethyl fumarate and *N*-phenyl maleimide.) The structure of **9** was confirmed by comparison with the product obtained by oxidation of **3a** with *tert*-butyl hydroperoxide.

To prevent the formation of intermediates of type **11** and, therefore, the occurrence of the undesirable oxidation process, we used a cyclic azo derivative, namely phenyltriazolinedione (PTAD). When the reaction of **3a** with PTAD was carried out in diethyl ether at −20 °C, a new compound **12** was formed (^{31}P NMR: 21.9 ppm) and isolated in 90% yield after purification by flash chromatography (Scheme 5). A single crystal of this adduct was grown from THF/hexane and X-ray diffraction analysis performed, showing that **12** was not the expected cycloaddition product but did have a zwitterionic structure (Fig. 2).

Crystal data of **12**: $C_{34}H_{47}N_6O_3P_1$, $M_r = 618.75$, orthorhombic, space group $P2_12_12_1$, $a = 9.433(1)$ Å, $b = 9.561(2)$ Å, $c = 38.142(9)$ Å, $V = 3440(1)$ Å^3, $Z = 4$, $D_x = 1.195$ Mg m^{-3}, Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å), $\mu = 0.122$ mm^{-1}, $F(000) = 1328$, $T = 293(2)$ K. Final conventional $R = 0.059$ and $wR_2 = 0.136$ for 2499 'observed' reflections and 396 variables.

Compound **12** crystallizes in the chiral space group $P2_12_12_1$, indicating one of the relatively rare cases of spontaneous separation of enantiomers by crystallization. The diffraction analysis reveals that the six-membered ring of **12** has almost an envelope configuration with N_1, C_1, C_2, C_3 and N_2 being nearly coplanar (maximum deviation C_3 0.108(7) Å) and the phosphorus lying 0.650(2) Å outside the plane. The shortest phosphorus–nitrogen bond (1.611(6) Å) can be found, as in the case of **7**, between the phosphorus and the nitrogen of the diisopropylamino group, the longest one being that between the phosphorus and the nitrogen of the triazoline fragment. All nitrogens are planar, as shown by the sum of the corresponding angles [358.0(16)° (N_1), 359.7(17)° (N_3) and 359.5(16)° (N_6)]. Bond lengths in the plane correspond to an extended π-system with lengthened double and shortened single bonds. The five-membered ring and the carbonyl oxygen atoms are planar (maximum deviation O_2 0.012(6) Å), with an angle of 33.8° between this plane and that of the attached phenyl group. The N_4–C_4 bond



12

Scheme 5. Reaction of **3a** with PTAD.

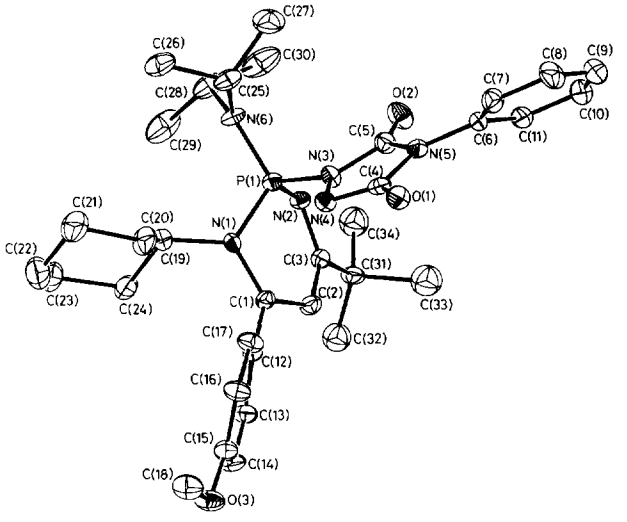


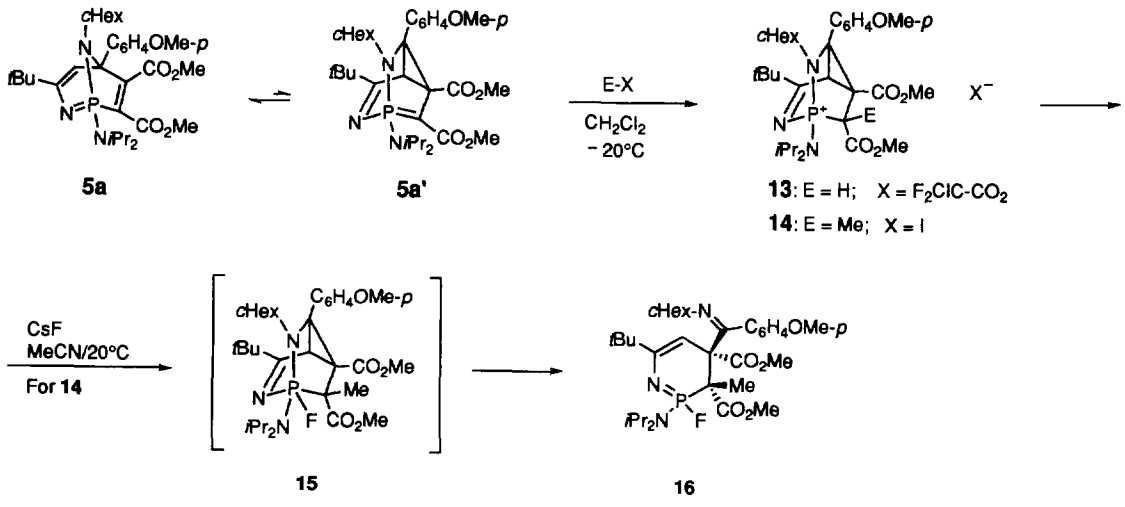
Fig. 2. Crystal structure of **12**. Selected bond lengths (pm) and bond angles (°): P1–N1 164.4(5), P1–N2 162.5(5), N1–C1 141.3(9), C1–C2 135.2(10), C2–C3 144.0(9), N2–C3 132.4(8), P1–N6 161.1(6), P1–N3 165.6(6), N4–C4 132.3(9), N3–C5 136.8(9), C4–O1 124.4(9), C5–O2 122.0(9), N5–C4 145.1(9), N5–C5 137.7(9), N3–N4 145.1(8); N6–P1–N2 110.8(3), N6–P1–N1 114.8(3), N2–P1–N1 107.2(3), N6–P1–N3 109.9(3), N2–P1–N3 110.6(3), N1–P1–N3 103.3(3), C1–N1–P1 112.8(5), C1–N1–C19 122.8(6), C19–N1–P1 122.4(5), C25–N6–C28 116.5(6), C25–N6–P1 117.6(5), C28–N6–P1 125.4(5), N4–C4–N5 110.4(7), N3–C5–N5 104.1(7).

length of 1.323(9) Å corresponds to a strong carbon–nitrogen double bond character, while the carbon–oxygen double bond is lengthened (1.244(9) Å), indicating that the negative charge is accommodated in the nitrogen and oxygen centers. All other bond parameters are in the range of expectation.

2.3. Reaction of 1-phospha-2,8-diaza-bicyclo[3,2,1]-octa-1,3,6-triene (5a) with electrophiles

The reactivity of the new imine phosphorane **5a** towards electrophiles was tested further (Scheme 6). We found that the reaction of **5a** with difluorochloroacetic acid and methyl iodide furnished phosphonium salts **13** (^{31}P NMR: 46.4 ppm) and **14** (^{31}P NMR: 48.5 ppm) respectively in 66–73% yield after crystallization. This means that the homoconjugated C-7 atom of structure **5a** is the exclusive reactive ylidic center of the molecule rather than the expected N_2 or C_4 atoms. This finding is in agreement with the participation of the valence isomer **5a'**. Moreover, both the protonation and the methylation processes take place stereoselectively through the *exo* face of **5a**, which can easily be explained by the steric hindrance of one of the sides of the molecule by ester and *tert*-butyl groups. An X-ray analysis of **13** allowed us to establish the structure of adducts **13** and **14** [11].

Attempts to trap **5b** did not afford analogous polycyclic compounds under the same conditions, but yielded **7b** quantitatively.



Scheme 6. Formation of polycycles **13** and **14** from **5a** and electrophiles and rearrangement into azaphosphinine **16**.

To see if, in spite of the steric overcrowding, a σ^5-phosphorus compound **15** could be obtained, we tried to exchange iodide with fluoride by taking advantage of the strength of the phosphorus–fluorine bond (Scheme 6). Thus, compound **13** was allowed to react with cesium fluoride in acetonitrile at room temperature for 12 h. The spectral data of the product revealed that, in addition to the fluorine–phosphorus covalent bond formation, a new skeletal rearrangement had occurred. The reaction led to λ^5-5,6-dihydro-1,2-azaphosphinine **16** (90% yield; ^{31}P NMR: 38.0 ppm; $^1J_{P-F}$ = 1094.7 Hz) as a ca. 93:7 mixture of diastereoisomers. The formation of the phosphorus pentacoordinate species **15** followed by a [4 + 2] cycloreversion accounts well for the transformation of **13** into **16**. Note that this reaction allows the high yield synthesis of heterocycles with three chiral centers, including a phosphorus atom, with full control of the relative stereochemistry.

In summary, it is shown in this report for the first time that the 1,2-dihydro-1,3,2-diazaphosphinines **3** behave as 1,5-dipoles towards dimethyl acetylenedicarboxylate, leading to novel cyclic iminophosphoranes **5**. These cycloadducts undergo thermal 1,7-rearrangement to **7**. The valence isomer **5a'** was trapped with electrophiles, e.g. methyl iodide and difluorochloroacetic acid, to afford new complex heteropolycyclic structures **13** and **14**. In contrast, activated azo derivatives, like diethyl azodicarboxylate and *N*-phenyltriazolinedione, do not give the corresponding [5 + 2] cycloadducts, but oxidation of the starting diazaphosphinine or simple phosphorus nucleophilic addition respectively were observed.

3. Experimental details

All reactions were carried out under nitrogen. Solvents were purified by standard methods [15]. Chemicals were of reagent grade. Compounds **1** were prepared according to literature procedures [16]. Flash column chromatography was carried out on silica gel 60 (230–400 mesh). Melting points were obtained on a Büchi–Tottoli apparatus using open capillary tubes and are uncorrected. NMR spectra were run on Bruker AC200 and AC300 spectrometers. Mass spectra were determined on HP 5987A (EIMS) and Finnigan MAT 95 (HRMS) spectrometers.

3.1. Preparation of 4-tert-butyl-1-cyclohexyl-2-diisopropylamino-6-(4-methoxyphenyl)-1,2-dihydro-1,3,2-diazaphosphinine (3a)

The aminoazadiene **1a** (4.85 g, 15.4 mmol) was added slowly to a well-stirred solution of dichloro(diisopropylamino)phosphane (3.12 g, 15.4 mmol) in CH_2Cl_2/NEt_3 (20 ml/5 ml) at 0 °C. After stirring for 6 h at 20 °C the solvent was removed under reduced pressure, the residue was treated with ether and the salts were filtered off. Compound **3a** was obtained as a yellow oil after evaporation of the solvent (6.40 g, 94%) and used without further purification.

^{31}P NMR: 57.9 ppm.

^{13}C NMR: 174.6 (d, ^2J(P,C) = 12.5 Hz, C=N); 159.0 (s, CarO); 131.1 (s, C*C*ar); 127.8 (s, CHar); 112.9 (s, CH); 102.1 (d, ^3J(P,C) = 14.6 Hz, CH); 60.1 (d, ^2J(P,C) = 22.2 Hz, NCH); 45.9 (d, ^2J(P,C) = 10.4 Hz, CH); 37.9 (d, ^3J(P,C) = 11.1 Hz, $C(CH_3)_3$); 33.9 (d, ^3J(P,C) = 17.3 Hz, CH_2); 32.5 (d, ^3J(P,C) = 9.7 Hz, CH_2); 27.8 (s, CH_3); 25.6 (s, CH_2); 25.1 (s, CH_2); 24.4 (s, CH_2); 24.0 (d, ^3J(P,C) = 7.6 Hz, CH_3); 23.6 (d, ^3J(P,C) = 5.6 Hz, CH_3) ppm.

^{1}H NMR: 7.3–6.8 (m, 4H, CHar); 5.7 (s, 1H, CH); 3.8 (s, 3H, OCH_3); 3.4–3.0 (m, 3H, NCH); 2.2–0.7 (m, 31H, CH_2 + CH_3) ppm.

3.2. Preparation of 2-diisopropylamino-1,4-bis(4-methylphenyl)-6-phenyl-1,2-dihydro-1,3,2-diazaphosphinine (3b)

Dichloro(diisopropylamino)phosphane (1.33 g, 6.6 mmol) was dissolved at 0 °C in Et_2O/NEt_3 (10 ml/2 ml) and 2.2 g (6.6 mmol) of the aminoazadiene **1b** in ether (20 ml) was slowly added. The reaction was stirred overnight, the precipitated salts were filtered off and the solvent removed under reduced pressure. The product was crystallized from hexane as a yellow powder (2.7 g, 90%).

M.p. 146–150 °C.

IR: 3026, 2962, 2926, 2866, 1592, 1561, 1509, 1483, 1362, 1312, 1295, 1256, 1180, 1122, 1067, 1016, 692, 797, 773, 752, 700, 647, 508 cm^{-1}.

^{31}P NMR: 78.3 ppm.

^{13}C NMR: 163.2 (d, $^2J(P,C) = 8.0$ Hz, C=N); 154.8 (b, N–C); 143.2 (d, $^2J(P,C) = 13.1$ Hz, N*C*ar); 139.6 (s, C*C*ar); 139.0 (s, C*C*ar); 137.7 (d, $^3J(P,C) = 8.0$ Hz, C*C*ar); 134.1 (s, C*C*ar); 128.8 (s, CH); 128.7 (s, CH); 128.1 (s, CH); 128.0 (s, CH); 127.9 (s, CH); 127.0 (s, CH); 126.9 (s, CH); 102.2 (d, $^3J(C,P) = 7.3$ Hz, NCCH); 47.0 (d, $^2J(P,C) = 7.3$ Hz, NCH); 25.0 (d, $^3J(P,C) = 5.8$ Hz, CH_3); 24.2 (d, $^3J(P,C) = 4.4$ Hz, CH_3); 21.2 (s, CH_3); 20.6 (s, CH_3) ppm.

^1H NMR: 8.1–8.0 (m, 2H, CHar); 7.6–7.0 (m, 11H, CHar); 6.4 (s, 1H, CH); 3.6–3.5 (m, 2H, NCH); 2.6 (s, 3H, CH_3); 2.3 (s, 3H, CH_3); 1.5–1.4 (m, 12H, CH_3) ppm.

3.3. Preparation of 3-tert-butyl-8-cyclohexyl-1-diisopropylamino-5-(4-methoxyphenyl)-6,7-bis(methoxycarbonyl)-bicycle[3,2,1]-1-phospha-2,8-diaza-1,3,6-octatriene (5a)

A solution of DMAD (0.45 g, 3.2 mmol) in 5 ml of ether was added at −20 °C to a well-stirred solution of **3a** (1.41 g, 3.2 mmol) in 30 ml of ether. The mixture was kept at −20 °C overnight, the solvent evaporated at reduced pressure and the product crystallized from hexane at low temperature to afford compound **5a** as a yellow–orange solid (1.5 g, 80%).

M.p. 106–109 °C (decomp.).

MS (*m/e*): 585 (M^+); 544 ($M^+ - C_3H_6$); 502 ($M^+ - C_6H_{11}$); 419 ($M^+ - C_6H_4OCH_3 - CO_2CH_3$); 402 ($M^+ - C_6H_{11} - N(C_3H_7)_2$).

^{31}P NMR: 48.2 ppm.

^{13}C NMR: (THF-d_8, −30 °C) 167.1 (s, N–*C*=C); 166.1 (d, $^3J(P,C) = 18.0$ Hz, C=O); 165.6 (d, $^2J(P,C) = 13.0$ Hz; C=O); 161.9 (s, CarO); 137.5 (d, $^2J(P,C) = 11.3$ Hz, PC*C*); 133.9 (s, CHar), 132.6 (d, $^3J(P,C) = 9.5$ Hz, C*C*ar), 131.0 (s, CHar); 115.9 (s, CHar); 114.0 (s, CHar); 96.5 (d, $^1J(P,C) = 129.2$ Hz, PC); 84.6 (d, $^3J(P,C) = 13.2$ Hz, CH); 67.2 (d, $^2J(P,C) = 13.2$ Hz, *C*Car); 56.6 (s, OCH_3 + NCH); 53.4 (s, OCH_3); 52.8 (s, OCH_3); 48.9 (d, $^2J(P,C) = 8.6$ Hz, NCH); 48.3 (s, NCH); 40.5 (d, $^3J(P,C) = 22.3$ Hz, *C*$(CH_3)_3$); 36.6 (s, CH_2); 33.3 (s, CH_2); 30.8 (s, C(*C*$H_3)_3$); 29.3 (s, CH_2); 29.0 (s, CH_2); 27.7 (s, CH_2); 25.7 (s, CH_3); 22.6 (s, CH_3), 22.6 (s, CH_3); 22.1 (s, CH_3) ppm.

^1H NMR: 7.4–6.6 (m, 4H, CHar); 4.5 (s, 1H, CH); 4.2–4.0 (s, 1H, NCH); 3.6 (s, 3H, $ArOCH_3$); 3.7–3.4 (m, 2H, NCH); 3.4 (s, 3H, OCO_3); 3.3 (s, OCH_3); 2.7–2.6 (m, 1H); 1.9–0.7 (m, 30H, $CH_2 + CH_3$).

3.4. Reaction of diazaphosphinine (3a) with (phenylethynylmethoxymethylene)pentacarbonyl chromium: synthesis of 6

To a well-stirred solution of **3a** (0.42 g, 0.9 mmol) in CH_2Cl_2 (10 ml) were added at −80 °C 0.32 g (0.7 mmol) of chromium carbene complex in 5 ml of CH_2Cl_2. The solution was allowed to warm overnight to room temperature. After evaporation of the solvent and flash column chromatography (SiO_2/CH_2Cl_2), the product crystallized from CH_2Cl_2/ether as an orange solid (0.4 g, 73%).

M.p. 168–170 °C.

IR: 2971, 2933, 2861, 2041, 1959, 1915, 1903, 1878, 1605, 1582, 1513, 1486, 1462, 1454, 1401, 1372, 1368, 1300, 1289, 1252, 1199, 1175, 1152, 1133, 1100, 1078, 1022, 987, 967, 897, 834, 817, 765, 733, 701, 676, 661, 586, 556 cm^{-1}.

MS (*m/e*): 779 (M^+), 741, 639 ($M^+ - 5CO$), 588 ($M^+ - Cr(CO)_5$).

^{31}P NMR: 44.8 ppm.

^{13}C NMR: 225.1 (s, CO_{trans}); 219.8 (s, CO_{cis}); 205.5 (d, $^3J(P,C) = 19.6$ Hz, C–Cr); 189.7 (d, $^2J(P,C) = 6.3$ Hz, C=N); 164.7 (d, $^2J(P,C) = 14.9$ Hz, C=*C*=C); 161.6 (s, CarO); 161.3 (b, *C*Car); 136.6 (d, $^2J(P,C) = 25.0$ Hz, C*C*ar); 132.7 (b, CHar); 130.0 (b, CHar); 129.2 (d, $^3J(P,C) = 7.1$ Hz, C*C*ar); 127.9 (s, CHar); 125.9 (s, CHar); 114.3 (b, CHar); 110.9 (d, $^3J(P,C) = 24.3$ Hz, CH); 85.2 (d, $^1J(P,C) = 156.5$ Hz, PC); 65.5 (s, OCH_3); 59.5 (s, NCH); 55.3 (s, OCH_3); 49.4 (b, NCH); 40.7 (d, $^3J(P,C) = 20.4$ Hz, *C*$(CH_3)_3$); 36.2 (s, CH_2); 32.6 (s, CH_2); 28.4 (s, C(*C*$H_3)_3$); 26.6 (s, CH_2); 26.2 (s, CH_2); 23.3 (b, CH_3); 22.0 (b, CH_3) ppm.

^1H NMR: 7.9–6.9 (m, 9H, CHar); 6.4 (s, 1H, CH); 4.2–3.5 (m, 3H, NCH); 3.9 (s, 3H, OCH_3); 3.0 (s, 3H, OCH_3); 2.5 (b, 1H, CH); 1.9–0.5 (m, 31H, $CH_2 + CH_3$) ppm.

3.5. Preparation of 6-tert-butyl-8-cyclohexyl-1-diisopropylamino-4-(4-methoxyphenyl)-2,3-bis(methoxycarbonyl)-bicycle[3,2,1]-1-phospha-7,8-diaza-1,3,6-octatriene (7a)

Compound **3a** (0.3 g, 0.5 mmol) was dissolved in 5 ml of CH_2Cl_2 and left overnight at room temperature. Then the solvent was removed under reduced pressure

and the product crystallized from ether/hexane (0.25 g, 85%).

M.p. 134–136 °C (decomp.).

IR: 1656, 1311, 1167, 1104 cm^{-1}.

MS (*m/e*): 585 (M^+); 544 ($M^+ - C_3H_6$); 502 ($M^+ - C_6H_{11}$); 402 ($M^+ - C_6H_{11} - N(C_3H_7)_2$).

M^+: 585.333175; M^+_{calc}: 585.333160.

^{31}P NMR: 56.5 ppm.

^{13}C NMR: 181.4 (d, $^2J(P,C)$ = 5.6 Hz, C=N); 169.4 (d, $^3J(P,C)$ = 19.4 Hz, C=O); 165.2 (d, $^2J(P,C)$ = 10.4 Hz, C=O); 157.3 (s, CarO); 135.1 (d, $^3J(P,C)$ = 13.2 Hz, *C*Car); 131.7 (s, C*C*ar); 130.2 (s, CHar); 112.8 (s, CHar); 104.6 (d, $^2J(P,C)$ = 2.1 Hz, PC*C*); 62.3 (d, $^2J(P,C)$ = 20.1 Hz, NCH); 54.6 (s, OCH_3); 53.4 (d, $^2J(P,C)$ < 2 Hz, CH); 52.3 (d, $^1J(P,C)$ = 148.4 Hz, PC); 51.0 (s, OCH_3); 49.8 (s, OCH_3); 47.8 (d, $^2J(P,C)$ = 5.6 Hz, N*C*H$(CH_3)_2$); 37.2 (d, $^3J(P,C)$ = 20.8 Hz, *C*$(CH_3)_3$); 32.4 (d, $^3J(P,C)$ = 6.3 Hz, CH_2); 29.5 (s, CH_2); 28.1 (s, C(*C*$H_3)_3$); 26.1 (s, CH_2); 26.0 (s, CH_2); 25.4 (s, CH_2); 22.7 (d, $^3J(P,C)$ = 2.1 Hz, CH_3); 22.6 (s, CH_3) ppm.

^1H NMR: 7.3–6.7 (m, 4H, CHar); 4.8 (d, 1H, $^3J(P,H)$ = 24.1 Hz, CH); 3.8 (m, 2H, NCH); 3.7 (s, 3H, OCH_3); 3.5 (s, 3H, OCH_3); 3.1 (m, 1H, NCH); 1.4 (d, 2H, $^4J(P,H)$ = 6.3 Hz, CH_3); 1.2 (d, $^4J(P,H)$ = 6.7 Hz, CH_3); 0.9 (s, 9H, CH_3); 2.3–0.7 (m, 10H, CH_2) ppm.

3.6. Preparation of 1-diisopropylamino-2,3-bis(methoxycarbonyl)-6,8-bis(4-methylphenyl)-4-phenylbicycle[3,2,1]-1-phospha-7,8-diaza-1,3,6-octatriene (7b)

Compound **3b** (0.53 g, 1.1 mmol) was dissolved in 20 ml of ether and a solution of DMAD (0.17 g, 1.1 mmol) in ether (5 ml) was added at −70 °C. The mixture was allowed to stand overnight at −20 °C, the solvent removed at low temperature under reduced pressure and the product **5b** precipitated as an orange solid with 10 ml of hexane. This compound was dissolved again in CH_2Cl_2 and left for 30 min at room temperature. After filtration through SiO_2 and evaporation of the solvent, **7b** is obtained as a yellow–orange oil (0.6 g, 85%).

^{31}P: 56.8 ppm.

^{13}C NMR: 168.9 (d, $^2J(P,C)$ = 19.6 Hz, C=N); 165.8 (d, $^3J(P,C)$ = 11.0 Hz, CO); 162.9 (s, CO); 142.6 (s, CarN); 139.2 (s, *C*arC); 137.2 (s, *C*arC); 136.8 (d, $^3J(P,C)$ = 18.3 Hz, Car*C*); 136.5 (s, Car); 129.9 (s, Car); 126.9 (s, Car); 129.5 (d, $J(P,C)$ = 24.3 Hz, C–Car); 129.0 (s, Car); 128.8 (s, Car); 128.1 (d, $^3J(C,P)$ = 3.9 Hz, Car); 127.5 (s, Car); 126.3 (s, Car); 106.8 (d, $^2J(P,C)$ = 3.9 Hz; PC*C*); 73.5 (d, $^2J(P,C)$ = 18.8 Hz, NCH); 54.5 (d, $^1J(P,C)$ = 151.8 Hz, PC); 51.2 (s, OCH_3); 50.0 (s, OCH_3); 48.2 (s, NCH); 48.1 (s, NCH); 22.8 (s, CH_3); 22.3 (d, $^3J(P,C)$ = 2.4 Hz, CH_3); 21.4 (s, CH_3); 20.9 (s, CH_3) ppm.

^1H NMR: 7.5–6.6 (m, 13H, CHar); 5.3 (d, $^3J(P,H)$ = 22.9 Hz, CH); 3.8–3.6 (m, 2H, NCH); 3.7 (s, 3H, CH_3); 2.4 (s, 3H, CH_3); 2.3 (s, 3H, CH_3); 1.5 (d, 3H, $^4J(P,H)$ = 6.4 Hz, CH_3); 0.97 (d, 3H, $^4J(P,H)$ = 6.7 Hz, CH_3) ppm.

3.7. Preparation of 4-tert-butyl-1-cyclohexyl-2-diisopropylamino-6-(4-methoxyphenyl)-1,2-dihydro-1,3,2-diazaphosphinine-P-oxide (9)

Method A. 0.3 g (2 mmol) of azodicarboxylic acid diethylester in 5 ml of CH_2Cl_2 was added dropwise at −20 °C to a well-stirred solution of 0.8 g (1.8 mmol) of **3a** in 20 ml of CH_2Cl_2. The reaction mixture was kept for a few hours at low temperature and then allowed to warm slowly to room temperature. The solvent was removed at reduced pressure and the product isolated by flash column chromatography (SiO_2/CH_2Cl_2) followed by crystallization from ether/hexane to give **9** as white crystals (0.7 g, 85%).

Method B. To a solution of 0.36 g (0.8 mmol) of **3a** in 15 ml of CH_2Cl_2 was added dropwise 0.5 ml of a 3 N solution of *tert*-butylhydroperoxide in 2,2,4-trimethylpentane. The mixture was stirred for 30 min and the solvent removed under reduced pressure to give a residue which was purified as above (0.35 g, 90%).

M.p. 142–144 °C.

IR: 1801, 1750, 1605, 1593, 1574, 1521, 1496, 1452, 1377, 1303, 1292, 1253, 1234, 1203, 1186, 1097, 1024, 993, 954, 821, 810, 698, 650 cm^{-1}.

MS (*m/e*): 459 (M^+); 416 ($M^+ - C_3H_7$); 376 ($M^+ - C_6H_{11}$); 360 ($M^+ - N^iPr_2 + H$); 334 ($M^+ - C_6H_{11} - C_3H_6$); 277 ($M^+ - N^iPr_2 - C_6H_{11}$).

^{31}P NMR: 3.9 ppm.

^{13}C NMR: 160.4 (d, $^2J(P,C)$ = 3.5 Hz, C=N); 159.8 (s, CarO); 130.1 (b, C*C*ar); 128.9 (b, CHar); 113.5 (b, CH); 100.7 (d, $^3J(P,C)$ = 21.5 Hz, CH); 61.0 (b, NCH); 55.2 (s, OCH_3); 46.2 (s, NCH); 46.1 (s, NCH); 39.0 (d, $^3J(P,C)$ = 22.3 Hz, *C*$(CH_3)_3$); 34.3 (s, CH_2); 31.2 (b, CH_2); 28.3 (s, *C*$(CH_3)_3$); 26.5 (s, CH_2); 26.3 (s, CH_2); 24.8 (s, CH_2); 23.2 (s, CH_3); 22.3 (s, CH_3) ppm.

^1H NMR: 7.3–6.8 (m, 4H, CH); 5.4 (s, 1H, CH); 3.8 (s, 3H, OCH_3); 3.2–2.8 (m, 2H, NCH); 2.1 (m, 1H, NCH); 1.7 (m, 1H, CH); 1.6–0.8 (m, 30H, $CH_3 + CH_2$) ppm.

3.8. Reaction of diazaphosphinine (3a) with 4-phenyl-1,2,4-triazoline-3,5-dione: synthesis of 12

To a well-stirred solution of 1.12 g (2.5 mmol) of **3a** in 7 ml of CH_2Cl_2 at −30 °C was added 0.44 g (2.5 mmol) of phenyltriazolinedione in 20 ml of CH_2Cl_2. An instant color change took place. The mixture was allowed to warm slowly to room temperature and the solvent was removed at reduced pressure. The residue was purified by flash column chromatography using

$SiO_2/CH_2Cl_2/THF$ as eluent, and the product finally isolated by precipitation with ether (1.4 g, 90%).

M.p. 194–197 °C (decomp.).

MS (*m/e*): 618 (M^+); 575 ($M^+ - C_3H_7$); 519 ($M^+ + H - N(C_3H_7)_2$); 459 ($M^+ - C_8H_5N_3O$); 360 ($M^+ - N(C_3H_7)_2 - C_8H_5N_3O$).

IR: 2970, 2931, 2859, 1714, 1651, 1606, 1580, 1480, 1420, 1377, 1294, 1255, 1230, 1207, 1176, 1151, 1138, 1105, 1076, 1062, 1033, 991, 906, 893, 877, 841, 831, 800, 767, 736, 713, 688, 651, 640, 626 cm^{-1}.

^{31}P NMR: 21.9 ppm.

^{13}C NMR: 192.6 (d, $^2J(P,C) = 8.0$ Hz, C=N); 160.7 (s, CarO); 156.2 (d, $^2J(P,C) = 16.7$ Hz, C=O); 153.5 (d, $^3J(P,C) = 11.1$ Hz, C=O); 133.2 (s, Car–N); 130.9 (b, C*C*ar); 127.6 (CHar); 127.4 (CHar); 125.3 (CHar); 112.6 (CHar); 111.3 (d, $^3J(P,C) = 31.2$ Hz, C=*C*H); 60.0 (b, NCH); 54.5 (s, OCH_3); 48.3 (b, CH); 40.3 (d, $^3J(P,C) = 22.2$ Hz, *C*$(CH_3)_3$); 34.1 (b, CH_2); 32.1 (b, CH_2); 27.6 (s, C(*C*$H_3)_3$); 25.7 (b, CH_2); 24.7 (b, CH_2); 24.0 (b, CH_2); 22.5 (b, CH_3); 21.4 (b, CH_3) ppm.

^1H NMR: 7.5–6.9 (m, 9H, CHar); 6.3 (s, 1H, CH); 4.0 (m, 2H, CH); 3.8 (s, 3H, CH_3); 2.4 (m, 1H, CH); 1.6–0.8 (m, 31H, $CH_2 + CH_3$) ppm.

*3.9. Reaction of bicycle[3,2,1]-1-phospha-2,8-diaza-1,3,6-octatriene (**5a**) with difluorochloroacetic acid: synthesis of **13***

Compound **5a** (0.59 g, 1 mmol) was dissolved in 10 ml of CH_2Cl_2 at −20 °C and an excess of chlorodifluoroacetic acid (ca. 1 ml) was added. The mixture was allowed to warm to room temperature, the solvent evaporated under reduced pressure and the product crystallized from ether (0.6 g, 70%). It was obtained as an adduct with a molecule of acid according to X-ray diffraction.

M.p. 115 °C (decomp.).

IR: 3051, 3974, 2955, 2940, 2859, 1746, 1699, 1583, 1543, 1438, 1377, 1306, 1283, 1258, 1219, 1177, 1161, 1049, 1031, 997, 966, 856, 842, 779, 715 cm^{-1}.

MS (FAB): 586 $M^+ - F_2ClCCO_2$.

^{31}P NMR: 46.4 ppm.

^{13}C NMR: 206.1 (d, $^2J(P,C) = 7.8$ Hz, N=C); 164.7 (d, $^3J(P,C) = 11.7$ Hz, C=O); 163.5 (s, C=O); 161.4 (t, $^2J(F,C) = 29.7$ Hz, CO_2); 160.7 (s, OCar); 133.1 (s, CHar); 121.1 (d, $^3J(P,C) = 8.61$ Hz, C*C*ar); 119.0 (t, $^1J(F,C) = 304.4$ Hz, *C*F_2Cl); 114.9 (s, CHar); 113.5 (s, CHar); 57.8 (d, $^2J(P,C) = 9.4$ Hz, *C*Car); 56.4 (s, NCH); 55.2 (s, CH_3); 53.6 (s, CH_3); 53.1 (s, CH_3); 50.5 (b, NCH); 48.3 (b, NCH); 44.4 (d, $^3J(P,C) = 19.6$ Hz, *C*$(CH_3)_3$); 36.1 (d, $^2J(P,C) = 1.6$ Hz, PC*C*); 33.9 (d, $^3J(P,C) = 28.2$ Hz, CH); 33.0 (s, CH_2); 32.3 (d, $^1J(P,C) = 73.4$ Hz, P*C*); 31.1 (s, CH_2); 27.3 (s, C(*C*$H_3)_3$); 26.2 (s, CH_2); 25.8 (s, CH_2); 24.3 (s, CH_2); 24.0 (b, CH_3); 20.5 (b, CH_3); 20.0 (b, CH_3).

^1H NMR: 7.5–6.9 (m, 4H, CHar); 4.9 (d, $^3J(P,H) = 21.3$ Hz), 1H, CH); 4.5–3.1 (m, 13H, CH + OCH_3); 1.8–0.6 (m, 31H, $CH_2 + CH_3$).

*3.10. Reaction of bicycle[3,2,1]-1-phospha-2,8-diaza-1,3,6-octatriene (**5a**) with methyl iodide: synthesis of **14***

Compound **5a** (0.59 g, 1 mmol) was dissolved in 10 ml of CH_2Cl_2 at −20 °C and an excess of methyl iodide (ca. 2 ml) was added. The mixture was allowed to warm to room temperature, the solvent evaporated under reduced pressure and the product crystallized from 5 ml ether (0.7 g, 95%).

M.p. 165–170 °C (decomp.).

IR: 2956, 2935, 2855, 1735, 1610, 1552, 1517, 1465, 1454, 1438, 1412, 1374, 1285, 1255, 1207, 1175, 1118, 1086, 1048, 1025, 843 cm^{-1}.

^{31}P NMR: 48.5 ppm.

^{13}C NMR: 205.3 (d, $^2J(P,C) = 8.6$ Hz, C=N); 165.8 (s, CO); 164.2 (d, $^3J(P,C) = 13.3$ Hz, CO); 160.1 (s, CarO); 132.4 (s, CHar); 130.2 (s, CHar); 120.4 (d, $^3J(P,C) = 8.6$ Hz, C*C*ar); 114.5 (s, CHar); 113.1 (s, CHar); 57.8 (d, $^2J(P,C) = 10.2$ Hz; *C*Car); 56.1 (s, NCH); 55.0 (s, OCH_3); 53.2 (s, OCH_3); 53.0 (s, OCH_3); 49.7 (b, NCH); 43.9 (d, $^3J(P,C) = 19.6$ Hz, *C*$(CH_3)_3$); 40.2 (d, $^1J(P,C) = 73$ Hz, PC); 38.9 (s, PC*C*); 34.9 (d, $^3J(P,C) = 28.2$ Hz, CH), 32.6 (b, CH_2); 30.4 (b, CH_2); 26.9 (s, C(*C*$H_3)_3$); 25.8 (s, CH_2); 25.4 (s, CH_2); 23.8 (s, CH_2); 20–22 (b, CH_3); 15.5 (d, $^2J(P,C) = 7.0$ Hz, PC*C*H_3) ppm.

^1H NMR: 7.3–6.8 (m, 4H, CHar); 4.1 (s, 1H, CH); 4.1–3.8 (m, 1H, NCH); 3.7 (s, 3H, OCH_3), 3.6 (s, 3H, OCH_3); 3.3 (s, 3H, OCH_3); 3.4–2.9 (m, 2H, NCH); 2.1 (d, 3H, $^3J(P,H) = 15.9$ Hz, PCCH_3); 1.6–0.4 (m, 31H, $CH_2 + CH_3$) ppm.

*3.11. Rearrangement of **14** with cesium fluoride: synthesis of **16***

0.4 g (0.9 mmol) of **14** was dissolved in 5 ml of acetonitrile and 1 g of CsF was added. The mixture was stirred for 12 h at room temperature and the solvent removed under reduced pressure. The residue was dissolved in CH_2Cl_2, purified by flash column chromatography (SiO_2/CH_2Cl_2) and finally crystallized from CH_2Cl_2/hexane (0.3 g, 90%).

M.p. 124–126 °C.

IR: 2977, 2947, 2932, 2855, 1725, 1652, 1608, 1509, 1451, 1370, 1345, 1235, 1181, 1139, 1124, 1001, 870, 835, 816, 768, 673, 629 cm^{-1}.

MS (*m/e*): 619 (M^+); 562 ($M^+ - C_4H_9$); 403 ($M^+ - C_6H_{11}NCC_6H_4OCH_3$); 216 ($C_6H_{11}NCC_6H_4OCH_3$).

M^+: 619.353221; M^+_{calc}: 619.355038.

^{31}P NMR: 38.0 (d, $^1J(P,F) = 1094.7$ Hz) ppm.

^{13}C NMR: 173.4 (s, C=N); 171.5 (dd, $^2J(P,C) = 7.1$ Hz, $^3J(F,C) = 3.1$ Hz, C–N); 165.9 (d, $^3J(P,C) =$

10.2 Hz, CO); 158.9 (d, ^{2}J(P,C) = 7.0 Hz, CO); 158.5 (s, CarO); 128.7 (s, C*C*ar); 128.0 (s, CHar); 112.8 (s, CHar); 92.6 (dd, ^{3}J(P,C) = 19.6 Hz, ^{4}J(F,C) = 4.7 Hz, CH); 65.1 (d, ^{2}J(P,C) = 3.1 Hz, PC*C*); 60.4 (s, NCH); 54.8 (s, OCH_3); 51.6 (s, OCH_3); 51.2 (s, OCH_3); 48.0 (dd, ^{1}J(P,C) = 76.7 Hz), ^{2}J(F,C) = 18.0 Hz), PC); 47.9 (b, NCH); 37.4 (d, ^{3}J(P,C) = 22.7 Hz, *C*$(CH_3)_3$); 32.9 (s, CH_2); 28.4 (s, C(*C*$H_3)_3$); 25.4 (s, CH_2); 23.8 (s, CH_2); 22.9 (s, CH_3); 22.1 (s, CH_3); 16.9 (s, PC*C*H_3) ppm.

^{1}H NMR: 7.3–6.8 (m, 4H, CHar); 4.1 (m, 1H); 3.8 (s, 3H, CH_3); 3.7 (s, 3H, CH_3); 3.7 (s, 3H, CH_3); 3.4 (m, 2H, NCH); 3.0 (m, NCH); 1.7–0.9 (m, 25H); 0.9 (s, 9H, C$(CH_3)_3$) ppm.

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