Synthesis of cyclopentenones and butenolides by reaction of the lithium salt of *P,P*-diphenyl-*P*-(alkyl)(*N*-phenyl)phosphazenes with electrophilic double and triple bonds

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Lithium *P,P*-diphenyl-*P*-(alkyl)(*N*-phenyl)phosphazenes act as bidentate reagents towards electrophilic olefins and acetylenes. The reactions with dimethyl acetylenedicarboxylate (DMAD) and dimethyl maleate afford cyclopentenones, while with methyl benzoylpropiolate the products obtained are butenolides with a quaternary carbon atom in position 5 of the heterocycle. The use of less activated substrates (methyl phenylpropiolate, methyl cinnamate, and dimethyl oxalate) allowed the isolation of *C*-acylated aminoylide or phosphazene derivatives. A reaction mechanism is proposed based on a *tandem* process involving the regioselective *C*-acylation of the carbon α to the phosphorus, followed by a cyclisation process promoted by the intramolecular Michael addition of the nitrogen of the PN linkage to an electrophilic double or triple carbon–carbon bond.

Introduction

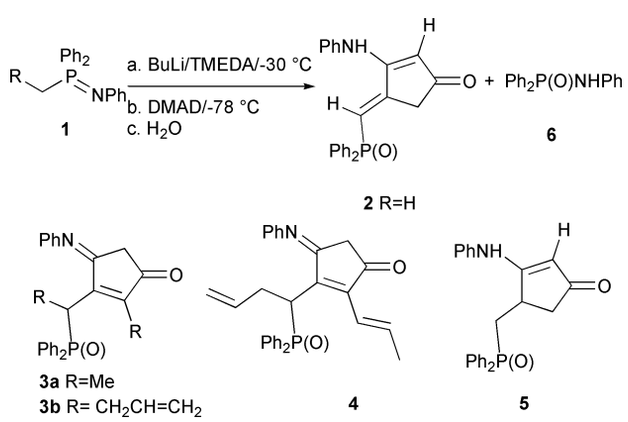
Phosphorus-stabilised carbanions are very important reactive intermediates in carbon–carbon bond formation reactions.[1] The excellent regio- and stereoselectivity achieved in the addition of electrophiles to, for example, metalated phosphine calchogenides,[2] phosphonates[3] and phosphoramides[4] has led to a large variety of synthetic applications. Lithium phosphazenes are isosteric to the corresponding phosphine oxides. However, their use in organic synthesis has been much less exploited.[5] The delocalisation of the negative charge of the CLi bond through the PN linkage suggests the possibility of acting as bidentate nucleophiles. This chemical behaviour can be correlated with the ability of phosphazenes to participate in silylotropic[6] and prototropic[7] rearrangements. These last processes are phosphazene–aminoylide tautomer equilibria, which can be influenced by the substituents on the α-carbon and on the nitrogen of the P=N group. Thus, in the case of diisopropoxyphosphazenes (Scheme 1),[8] the aminoylide

Scheme 1

tautomer is the unique species detected when X = Y = CO_2Me and R = Ph. Changing one CO_2Me for a phenyl group displaces the equilibrium to the phosphazene tautomer.

In the last few years crystal structures of α-lithium phosphazenes have been reported showing in all cases a common structural characteristic: the formation of a four-membered ring by coordination of the lithium cation to the carbon and nitrogen atoms of the phosphazene moiety.[9] Even though, all the known reactions of lithium phosphazenes with electrophiles afford exclusively the products arising from the *C*-regioselective attack of the anion.[10]

In an attempt to explore the bidentate behaviour of metalated phosphazenes we described in a previous paper,[11] the formation of cyclopentenones by reaction of the salt of lithium *P,P*-diphenyl-*P*-(alkyl)(*N*-phenyl)phosphazenes with DMAD or dimethyl maleate (Scheme 2). The mechanism we proposed



Scheme 2

was based on a *tandem* reaction with the key steps being the addition of the metalated carbon α to the PN to one carbonyl group of the DMAD and an intramolecular Michael-type addition through the nitrogen of the P=N group (see below).

This was the first example of a lithiated phosphazene acting as a bidentate nucleophile. The reaction mechanism proposed involved the formation of several intermediate compounds and an olefination reaction that represented the participation

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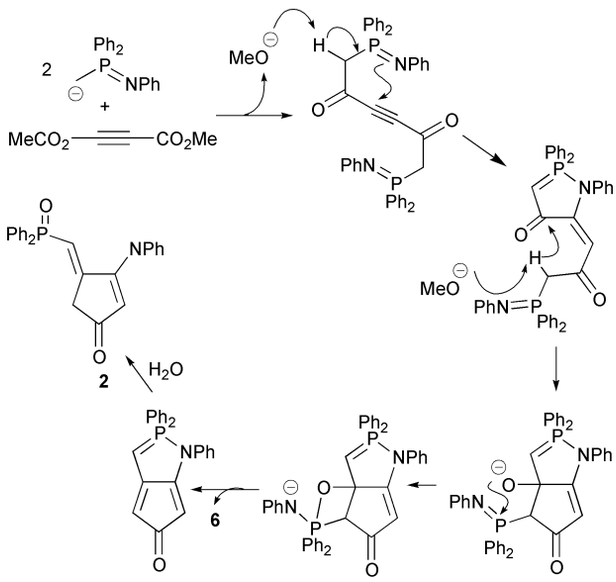
for the first time of a phosphazene in a process similar to the Wittig and Horner carbon–carbon double bond synthesis. Here we give full details of the reaction of lithium *P*,*P*-diphenyl-*P*-(alkyl)(*N*-phenyl)phosphazenes with DMAD. In order to obtain some insights to support the reaction mechanism previously proposed and to extend the scope of the reaction we will include the results obtained with other activated double and triple bonds related to DMAD. The electrophiles selected for the mechanistic studies were methyl phenylpropiolate, methyl cinnamate and dimethyl oxalate, affording in all cases the corresponding *C*-addition products. On the other hand, the use of methyl benzoylpropiolate as electrophile yielded unusual β-aminobutenolides with a quaternary γ-carbon atom in reasonable yields and high stereoselectivity. The formation of these new compounds is explained again in terms of the bidentate behaviour of metalated phosphazenes.

Results and discussion

The lithium salts of *P*,*P*-diphenyl-*P*-(alkyl)(*N*-phenyl)phosphazenes used in this study were synthesised through the Staudinger reaction,[12] by addition of phenyl azide to the corresponding phosphine. As we have described before,[11] the metalation of *P*,*P*-diphenyl-*P*-(alkyl)(*N*-phenyl)phosphazenes (3 mmol) was carried out with *n*-BuLi and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (3 mmol) in THF at −30 °C for 30 min. Then the electrophile DMAD or dimethyl maleate (1.5 mmol) was added at −78 °C and the reaction mixture was allowed to reach room temperature. Aqueous work-up led to a mixture of two major phosphorus compounds in a relative ratio 1:1. Purification by column chromatography affords the cyclopentenones **2**–**5**, as well as the by-product *P*,*P*-diphenyl-(*N*-phenyl)phosphonamide **6** (Scheme 2). Compound **4** is isolated as a mixture 1.5:1 together with the isomer **3b** and could not be separated by recrystallisation. The structure identification of all cyclopentenones was based on the analysis of the ^{1}H, ^{13}C, DEPT, HMQC and HMBC spectra. The configuration of the exocyclic double bond in **2** was deduced from NOE observed between the *ortho* protons of the phenyl rings bonded to the phosphorus and the methylene protons of the cyclopentenone. The assignment of the structure of each component of the mixture **3b**–**4** was more challenging due to the complex multiplicity pattern and partial overlap of some signals. These difficulties could be tackled by acquiring the COSY-45 and TOCSY spectra. Fortunately, the ^{13}C NMR spectrum showed well resolved signals for both isomers, except in the aromatic region, and the differences in intensity between the signals of each compound also facilitated their assignment (see Experimental section).

The reaction was very sensitive to the substituent R of the phosphazene. No cyclopentenone could be obtained for R = Pr, ^{i}Bu, Ph, CH=CH$_2$. The failure of the reaction for R = Pr, *i*-Bu may be attributed to steric hindrance of the phosphazene anion to the electrophile, while the lack of reactivity of the phosphazenes with a phenyl or vinyl substituent can be explained by the delocalization of the negative charge through the π-system. The cyclopentenones obtained are of synthetic interest. The cyclopentenone skeleton occurs in a variety of natural products,[13] some of them with antibiotic activity.[14]

The mechanism proposed is illustrated in Scheme 3 for the synthesis of **2**. The mechanism involves the addition of two molecules of lithiated phosphazene to each of the two carbonyl groups of the DMAD. The lithium methoxide generated in this process affords a new lithium phosphazene which reacts as its aminoylide tautomer by Michael addition of the nitrogen to the activated triple bond leading to a dihydro-1,2-azaphosphol-4-one with a *P*,*P*-diphenyl-*P*-(alkyl)(*N*-phenyl)phosphazenyl substituent at position 5. This new phosphazene intermediate can be deprotonated by a second MeOLi molecule and the resulting nucleophile undergoes an intramolecular olefination

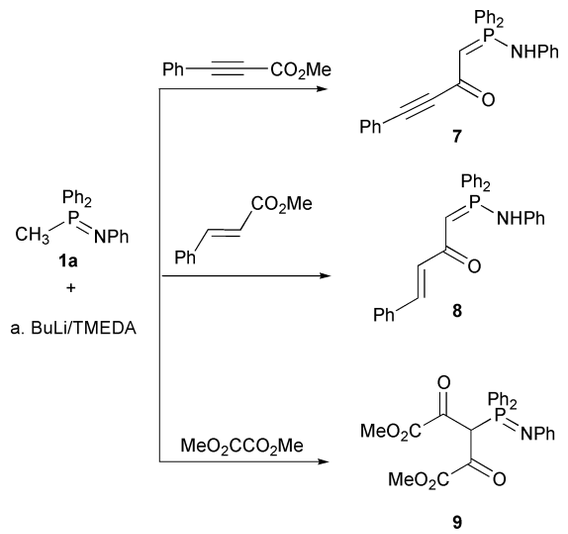


Scheme 3

reaction with the carbonyl group of the azaphosphole ring yielding a bicyclic azaphosphole and diphenyl(*N*-phenyl)phosphonamide **6**. In the aqueous work up, the P=N is hydrolysed affording the final cyclopentenone **2** after a 1,3-proton shift.

In an attempt to elucidate the reaction mechanism, we tried to follow the reaction with NMR using a sample prepared under the same reaction conditions mentioned for the Schlenk scale. Unfortunately, the ^{1}H, ^{13}C and ^{31}P NMR spectra measured at low temperature (−80 to −30 °C) showed only very broad signals, which prevented the identification of any intermediate compound.

Our next approach to the study of the reaction mechanism consisted of the use of less reactive electrophiles structurally related to DMAD and dimethyl maleate. Two obvious candidates are methyl phenylpropiolate and methyl cinnamate. The reaction with the lithium salt of *P*,*P*-diphenyl-*P*-(methyl)(*N*-phenyl)phosphazene and *n*-BuLi–TMEDA in THF at −30 °C followed by addition of the corresponding electrophile at −78 °C afforded exclusively the products **7** and **8** of regioselective *C*-acylation in the carbon next to the phosphorus (Scheme 4). Interestingly, both compounds are stabilised as



Scheme 4

aminoylides. This structural characteristic is easily deduced from their ^{1}H and ^{13}C NMR spectra. In both cases the methine proton is a doublet with a large $^{2}J_{PH}$ coupling (**7**, δ 4.22,

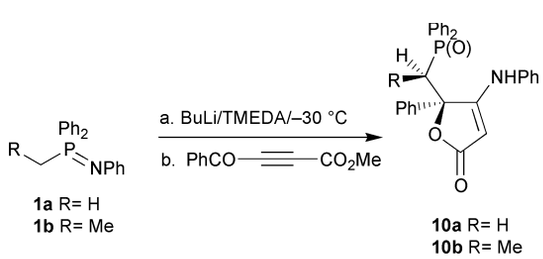
$^2J_{PH}$ 27.6 Hz; **8**, δ 3.91, $^2J_{PH}$ 34.5 Hz) as expected for a sp^2 hybridised carbon atom bonded to the phosphorus. Only the NH proton of **7** could be identified as a broad singlet at 10.02 ppm. The ylide carbon of **7** and **8** is identified as a CH through DEPT-135 and the ylidic nature is supported by the high field position of the signals as well as the large $^1J_{PC}$ observed (**7**, δ 63.36, $^1J_{PC}$ 117.0; **8**, δ 61.13, $^1J_{PC}$ 119.3 Hz).[15] Both experimental observations, the *C*-acylation and the stabilisation of the acylated product as aminoylides, support the first step of the proposed mechanism and the ability of phosphazenes to act as bidentate nucleophiles. However, the lithium derivatives of **7** and **8** are stable under the reaction conditions assayed and the possible products derived from the intramolecular Michael addition of the nitrogen to the respective carbon–carbon triple or double bond of **7** and **8** could not be detected.

Lacking a triple bond, but still related to the DMAD is diethyl oxalate. Again the reaction with the lithium salt of *P*,*P*-diphenyl-*P*-(methyl)(*N*-phenyl)phosphazene proceeds exclusively through the carbon α to the phosphorus. In this case the *C*-diacylated derivative **9** is obtained (Scheme 4). The proton (δ 4.81) and carbon (δ 60.55) atoms of the methine group both show a large coupling to the phosphorus ($^2J_{PH}$ 27.6 Hz, $^1J_{PC}$ 117.9 Hz). The double *C*-acylation observed promotes the enhanced acidity of the methylene protons in the intermediate *C*-monoacylated phosphazene. As a consequence the unreacted lithium phosphazene will act as a base and favour the monoacylated compound. The new anion formed will add to a second molecule of dimethyl oxalate affording **9**. A similar behaviour has been previously observed when dimethyl disulfide was used as electrophile.[10b] Surprisingly, compound **9** is stabilised as the phosphazene tautomer instead of the expected aminoylide.

No evidence could be obtained for the olefination involved in the reaction mechanism proposed for the obtention of cyclopentenones **2**–**5**. When we reported the synthesis of these compounds there were no precedents of the participation of phosphazenes in carbon–carbon double bond forming reactions. In the mean time, we have demonstrated that phosphazenes do react with carbonyl compounds in the presence of *n*-BuLi yielding di-, tri- and tetrasubstituted olefins.[16]

As mentioned above, we were also interested in exploring the reactivity of lithium phosphazenes towards DMAD-like activated acetylenes with two carbonyl groups of different reactivity bonded to the triple bond. This is the case for methyl benzoylpropiolate. This reagent was prepared using the procedure already described in the literature.[17]

When the reaction between lithiated phosphazene **1a** and methyl benzoylpropiolate was performed under the same conditions used for DMAD, with a 2:1 molar ratio anion: electrophile, a 1:1 mixture of two compounds was obtained, with δ(^{31}P) 5.70 and 29.35 ppm. The high field signal corresponded to the starting phosphazene, *i.e.*, only one equivalent of the nucleophile was consumed in the reaction. The process was then repeated using equimolecular amounts of the reagents under otherwise identical reaction conditions. After aqueous work-up the ^{31}P NMR spectrum of the crude product indicated the formation of the new compound **10a** in 50% yield (Scheme 5). Column chromatography using ethyl acetate as eluent afforded pure **10a**, which was characterised on the basis of its spectroscopic data.



Scheme 5

Table 1 Crystal data and structure refinement for **10b**

Empirical formula	$C_{30}H_{26}NO_3P$
Formula weight	479.49
Temperature	293(2) K
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 11.271(11) Å
	b = 9.216(14) Å β = 92.27(6)°
	c = 24.270(13) Å
Volume	2519(5) Å^3
Z, Calculated density	4, 1.264 Mg m^{-3}
Absorption coefficient	0.141 mm^{-1}
Reflections collected/unique	5192/4931 [R(int) = 0.090]
Data/restraints/parameters	4931/0/412
Goodness-of-fit on F_2	0.896
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0492, $wR2$ = 0.0850
R indices (all data)	$R1$ = 0.3456, $wR2$ = 0.1502
Largest diff. peak and hole	0.279 and −0.436 e Å^{-3}

Thus, the mass spectrum showed the molecular ion at *m*/*z* 465, corresponding to the condensation of one molecule of phosphazene with one molecule of electrophile plus the loss of one molecule of MeOH and the addition of a molecule of water. The formal incorporation of H_2O to **10a** suggests that the starting PN linkage has been hydrolysed and, therefore, **10a** should contain one amine and one phosphine oxide structural fragment. The ^{31}P chemical shift at 29.35 ppm supports this assignment.[18] The structural identification was carried out through the combined analysis of the 2D HMQC and HMBC spectra. The butenolide structure is deduced from the correlations of the methylene and methine protons of the molecule. The diastereotopic methylene protons at 3.62 (dd, $^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 8.8 Hz) and 3.23 ppm (dd, $^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 12.5 Hz) of the CH_2 next to the phosphorus, correlate with four quaternary carbons in the HMBC spectrum at δ 85.29, 129.73 ($^1J_{PC}$ 105.3 Hz), 136.08, and 165.79 ppm. They are easily assigned based on the magnitudes of the chemical shifts and coupling constants to the phosphorus as follows: δ 85.29 the sp^3 carbon bonded to the oxygen atom, δ 129.73 the *ipso* carbon of one phenyl ring bonded to phosphorus, δ 136.08 the *ipso* carbon of the phenyl ring substituent of the quaternary carbon of the butenolide, and δ 165.79 the C-4 of the heterocyclic ring, highly deshielded because of the bonding to one heteroatom and the conjugation with the carbonyl group. The enaminic proton at 5.38 ppm appears as a singlet and correlates with two carbons already assigned (δ 85.29 and 165.79 ppm) and a third one at 172.38 ppm, corresponding to the carbonyl of the lactone moiety.

In the case of phosphazene **1b**, the lactone **10b** has two new stereogenic centers. The ^{1}H and ^{31}P NMR spectra of the crude product showed signals for only one diastereoisomer, indicating that the reaction is highly stereoselective. The assignment of the relative stereochemistry of the two stereocentres based on NMR data ($^3J_{PC}$ values and proton NOE enhancements) was uncertain. Fortunately, crystals suitable for X-ray diffraction could be grown from hexane–dichloromethane. The crystal structure of **10b** and the numbering scheme used is shown in Fig. 1. Crystal data are given in Table 1 and some selected geometrical parameters are summarised in Fig. 1. The arrangement of the two stereocentres corresponds to a (*R**,*R**) configuration. They adopt a distorted alternated conformation where the phosphorus lies almost antiperiplanar to the oxygen atom of the heterocycle (torsion angle P–C6–C5–O1 163.4(3)°). This distortion may be derived from the hydrogen bond formed between the PO group and the NH of the aniline substituent of the butenolide (bond distance O3–H1 = 1.69(7) Å). This hydrogen bond fixes the position of the diphenylphosphinoyl moiety and explains the stereoselective formation of **10b** in terms of favourable steric interactions of the methyl group

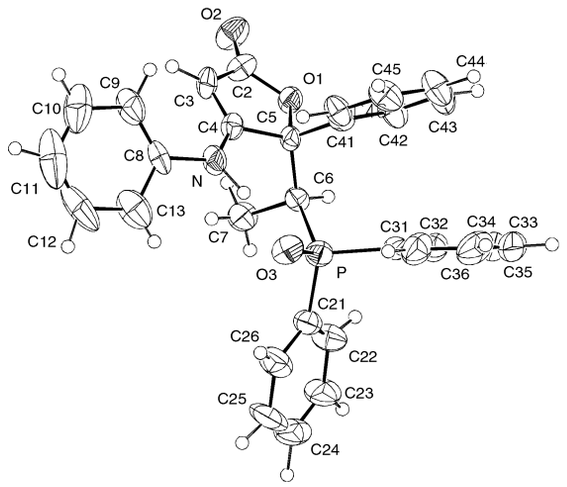
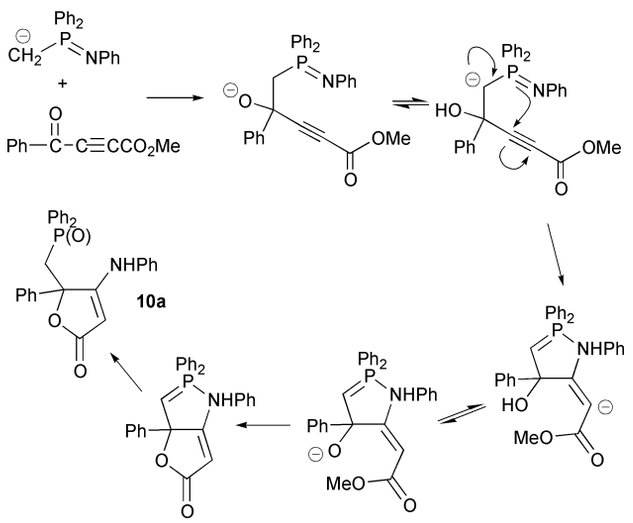


Fig. 1 Euclid plot, showing 50% probability displacement ellipsoids and the relevant atomic numbering scheme. Selected structural data, bond distances (Å) P–O(3) 1.504(4), P–C(21) 1.806(6), P–C(31) 1.815(6), P–C(6), 1.831(5), C(5)–C(6) 1.553(7), C(4)–C(5) 1.524(7), C(3)–C(4) 1.350(8), C(2)–C(3) 1.428(8), C(2)–O(1) 1.366(6), C(2)–O(2) 1.366(6), C(4)–N 1.356(7), C(3)–H(3) 0.92(4), C(5)–C(41) 1.529(7). Bond angles(°): C(6)–P–C(21) 111.2(3), C(6)–P–C(31) 111.0(3), C(6)–P–O(3) 113.5(2), C(3)–C(4)–N 132.3(6), C(3)–C(2)–O(1) 109.7(6), C(4)–C(5)–O(1) 102.5(4), C(5)–C(5)–C(41) 113.6(5). Torsion angles(°): C(7)–C(6)–P–C(31) −80.3(5), C(5)–C(6)–P–C(21) 166.5(4), N–C(4)–C(5)–C(41) −74.5(7), C(7)–C(6)–C(5)–C(41) 176.3(5), C(9)–C(8)–N–C(4) −40.0(9), C(3)–C(4)–C(5)–O(1) −5.6(6), O(1)–C(2)–C(3)–C(4) −3.1(7), C(4)–C(5)–C(41)–C(42) −159.5(5).

compared to the (*R**,*S**) diastereoisomer. The butenolide ring is practically planar (torsion angle C2–C3–C4–C5 5.4(7)°), as well as the nitrogen atom of the aniline substituent (bond angle C4–NC8 124.5(5)°), while the phenyl ring bonded to the nitrogen is rotated 138.7(2)° clockwise relative to the plane of the heterocycle.

The formation of compounds **10** can be explained through a mechanism similar to the one proposed for the reaction with DMAD (Scheme 6). The most reactive carbonyl group is the



Scheme 6

ketone. Consequently, the first step of the reaction would be the addition of the lithiated phosphazene to this carbonyl group. The resulting alcoholate will regenerate an anion α to the PN through an acid–base equilibrium, which will undergo a Michael addition to the triple bond as its aminoylide tautomer leading to a 1,2-azaphosphole ring. A new acid–base equilibrium affords an alcoholate anion that by intramolecular attack on the carbonyl ester in the 1,5 position produces a bicyclic intermediate, which is finally hydrolysed to yield the lactone **10**. Aminobutenolides have been previously obtained by reaction of amines and ammonia with methyl esters of acetylenic hydroxy acids.[19] Functionalised butenolides are very important compounds because the dihydrofuranone structural fragment is contained in a variety of biologically active compounds.[20] To the best of our knowledge, this is the first time that butenolides have been obtained by reaction of lithium phosphazenes with acetylenic esters.

Conclusions

The reaction of *P*,*P*-diphenyl-*P*-(alkyl)(*N*-phenyl)phosphazenes under basic conditions with highly activated double and triple carbon–carbon bonds reflects their bidentate character. Depending on the electrophile used, interesting cyclopentenones (electrophile: DMAD and dimethyl maleate) and lactones (electrophile: methyl benzoylpropiolate) are obtained. Insight into the reaction mechanism is provided by the isolation of *C*-acylated aminoylides in the reaction of lithium phosphazenes with monoester acetylenic and olefinic reagents, methyl phenylpropiolate and methyl cinnamate, respectively. The reaction with dimethyl oxalate proceeds in a similar way, although in this case the final products are *C*-diacylated phosphazenes due to the high acidity of the CH α to the phosphorus in the monoacylated intermediate compound. The extension of the reactivity shown here to other electrophilic unsaturated systems and functionalised phosphazenes is currently under study.

Experimental

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were distilled before use. THF and TMEDA were dried with sodium and potassium respectively, using benzophenone as indicator, and distilled under nitrogen. Phosphazenes[12] and methyl benzoylpropiolate[17] were synthesized as previously described in the literature. All other reagents were commercially available through Sigma-Aldrich Química S.A., except *n*-BuLi, and were distilled prior to their use. TLC was performed on Merck plates with aluminium backing and silica gel 60 F_{254}. For column chromatography silica gel 60 (40–63 μm) from Scharlau was used.

Melting points were recorded on a Büchi-Tottoli apparatus and are uncorrected. Infrared spectra were obtained in KBr pellets using a UNICAM Mattson 3020 FT spectrometer. Mass spectra were determined by electron impact on a Hewlett-Packard 5987A or 1100. NMR spectra were recorded on a Bruker AC300 or AMX 400. Chemical shifts are referenced to internal tetramethylsilane for ^{1}H and ^{13}C, and to external 85% H_3PO_4 for ^{31}P. 2D NMR correlation spectra (COSY, TOCSY, NOESY, HMQC and HMBC) were acquired on a AMX400 spectrometer using standard Bruker software and processing routines. In the assignment of the ^{1}H and ^{13}C NMR spectra the following notation has been used: phenyl rings bonded to carbon, nitrogen and phosphorus are labeled as Ph, NPh and PPh, respectively. The superscripts *o*, *m*, and *p*, are the identifiers of atoms in position *ortho*, *meta* and *para*, respectively, of a phenyl ring. The superscripts *c*, *t* are used to label protons in a *cis* or *trans* arrangement, respectively.

X-Ray †

Most relevant crystal and refinement parameters are collected in Table 1. Data were recorded on a Nonius CAD4 single-crystal diffractometer. On all reflections, profile analysis were

† CCDC reference number 207/491. See http://www.rsc.org/suppdata/p1/b0/b005131o/ for crystallographic files in .cif format.

performed.[21] The structure was solved by direct methods using SHELXS-97,[22] and isotropic least-squares refinement on F^2 using SHELXL-97.[23] An empirical absorption correction was applied at this stage, using XABS2.[24] During the final stages of the refinements, all positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H-atoms were isotropically refined. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[25] Plots were made with the EUCLID package.[26] Geometrical calculations were made with PARST.[27] All calculations were made at the Scientific Computer Centre of the University of Oviedo.

General procedure for the synthesis of 7–10

To a solution of 3.1 mmol of *n*-BuLi in 10 ml of dry THF at −30 °C was added dropwise a solution of 3 mmol of the corresponding phosphazene in 20 ml of THF. Once the addition was completed, a solution of 3 mmol of TMEDA in 10 ml of THF was added. The mixture was stirred during 30 minutes and then was cooled to −78 °C. Then 1.5 mmol of DMAD dissolved in 20 ml of THF was added. The solution was allowed to reach room temperature overnight, quenched with water and extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried with $MgSO_4$ and solvents were evaporated under reduced pressure. Purification is specified in each case (see below). For compounds **7**, **8**, **9** and **10** the stoichiometry used was phosphazene : *n*-BuLi : electrophile 1 : 1.1 : 1. The electrophiles were respectively diethyl cinnamate, ethyl propiolate, dimethyl oxalate and methyl benzoylpropiolate.

3-Phenylamino-4-[2-(diphenylphosphoryl)ethenyl]cyclopent-2-en-1-one 2. Purification by column chromatography using ethyl acetate as eluent followed by recrystallisation in hexane–dichloromethane. Yellow solid ($C_{24}H_{20}NO_2P$, found: C, 74.71; H, 5.32; N, 3.57%, requires C, 74.80; H, 5.23; N, 3.63%); yield 85%; mp 207–208 °C; ν_{max}/cm^{-1} 3434 (NH), 1710 (C=O); δ_H (300.13 MHz, $CDCl_3$) 2.68 (2H, t, $^4J_{HH} = {}^4J_{PH}$ 1.6, CH_2), 5.68 (1H, d, $^5J_{PH}$ 2.8, =C*H*), 7.0–7.9 (16H, m, 15H^{ar} + =C*H*), 9.11 (1H, s, NH); δ_C (75.5 MHz, $CDCl_3$) 38.42 (d, $^3J_{PC}$ 5.4, CH_2), 107.14 (=CH), 114.17 (d, $^1J_{PC}$ 101.1, =CH), 122.17 (*C*^{o}-NPh), 124.99 (*C*^{p}-NPh), 128.7 (d, $^3J_{PC}$ 12.2, *C*^{m}-PPh), 129.16 (*C*^{m}-NPh), 130.89 (d, $^2J_{PC}$ 10.0, *C*^{o}-PPh), 132.50 (d, $^1J_{PC}$ 106.1, *C*^{ipso}-PPh), 132.07 (*C*^{p}-PPh), 139.42 (*C*^{ipso}-NPh), 151.25 (d, $^2J_{PC}$ 3.0, =C), 164.15 (d, $^3J_{PC}$ 16.6, =CN), 199.98 (CO); δ_P (121.4, $CDCl_3$) 23.92; *m*/*z* (EI) 385 (M^+, 8%), 261 (20), 201 (100).

2-Methyl-3-[1-(diphenylphosphoryl)ethyl]-4-(phenylimino)-cyclopent-2-en-1-one 3a. Purification by column chromatography using ether as eluent followed by recrystallisation in ether–dichloromethane. Light orange solid ($C_{26}H_{24}NO_2P$, found: C, 75.62; H, 5.89; N, 3.24%, requires C, 75.53; H, 5.85; N, 3.39%); yield 28%; mp 213–214 °C; ν_{max}/cm^{-1} 1714 (C=O); δ_H (400.13 MHz, $CDCl_3$) 1.55 (3H, dd, $^3J_{HH}$ 7.4, $^3J_{PH}$ 15.5, CHCH_3), 2.3 (3H, s, CH_3), 2.33 (1H, dd, $^2J_{HH}$ 21.0, $^5J_{PH}$ 2.6, CH_2), 2.49 (1H, d, $^2J_{HH}$ 21.0, CH_2), 4.66 (1H, dq, $^3J_{HH}$ 7.1, $^2J_{PH}$ 8.2, CH), 6.65–8.05 (18H, m, H^{ar}); δ_C (100.62 MHz, $CDCl_3$) 10.46 (=C*C*H$_3$), 11.35 (d, $^2J_{PC}$ 4.2, CH_3), 30.75 (d, $^1J_{PC}$ 65.9, CH), 35.07 (CH_2), 119.08 (*C*^{o}-NPh), 124.41 (*C*^{p}-NPh), 128.62–132.14 (14C^{ar}), 150.83 (*C*^{ipso}-NPh), 151.41 (d, $^3J_{PC}$ 5.9, =*C*Me), 159.04 (d, $^2J_{PC}$ 5.6, =C), 166.89 (d, $^3J_{PC}$ 4.4, C=N), 201.59 (d, $^4J_{PC}$ 2.4, CO); δ_P (121.4 MHz, $CDCl_3$) 33.01; *m*/*z* (EI) 413 (M^+, 12%), 212 (100), 194 (40).

3-[1-(Diphenylphosphoryl)but-3-enyl]-4-(phenylimino)-2-(prop-2-en-1-yl)cyclopent-2-en-1-one 3b. Purification by column chromatography using ethyl acetate as eluent. Isolated together with **4**. Oil ($C_{30}H_{28}NO_2P$, found: C, 77.48; H, 55.97; N, 3.56%, requires C, 77.40; H, 56.06; N, 3.01%); yield 20%; ν_{max}/cm^{-1} 1720 (C=O); δ_H (400.13 MHz, $CDCl_3$) 2.33 (1H, dd, $^2J_{HH}$ 21.0, $^5J_{PH}$ 2.5, COCH_2), 2.52 (1H, d, $^2J_{HH}$ 21.0, COCH_2), 2.6 (1H, m, CHCH_2), 2.9 (1H, m, CHCH_2), 3.41 (1H, m, =CCH_2), 3.97 (1H, dd, $^3J_{HH}$ 6.8, $^2J_{HH}$ 14.6, =CCH_2), 4.81 (1H, m, PC*H*), 4.98 (1H, app dq, $^2J_{HH} = {}^4J_{HH}$ 1.6, $^3J_{HH}$ 17.2, CHCH$_2$CH=C*H*′$_2$), 5.0 (1H, app dq, $^2J_{HH} = {}^4J_{HH}$ 1.6, $^3J_{HH}$ 10.3, CHCH$_2$CH=C*H*$^c_2$), 5.02 (1H, app dq, $^2J_{HH} = {}^4J_{HH}$ 1.6, $^3J_{HH}$ 10.2, =CCH$_2$CH=C*H*$^c_2$), 5.11 (1H, app dq, $^2J_{HH} = {}^4J_{HH}$ 1.6, $^3J_{HH}$ 17.2, =CCH$_2$CH=C*H*′$_2$), 5.57 (1H, m, CH$_2$=C*H*CH$_2$C=), 5.83 (1H, m, CH$_2$=C*H*CH$_2$CH), 7.04–7.95 (15H, m, H^{ar}); δ_C (100.62 MHz, $CDCl_3$) 29.40 (=C*C*H$_2$), 31.10 (CH*C*H$_2$), 35.26 (*C*H$_2$CO), 36.02 (d, $^1J_{PC}$ 64.6, PCH), 116.86 (*C*H$_2$=CHCH$_2$C=), 117.16 (*C*H$_2$=CHCH$_2$CH), 119.04 (*C*^{o}NPh), 124.36–132.43 (15C^{ar}), 132.96 (CH$_2$=*C*H-CH$_2$C=), 134.68 (d, $^3J_{PC}$ 14.0, CH$_2$=*C*HCH$_2$CH), 150.73 (*C*^{ipso}NPh), 152.13 (d, $^3J_{PC}$ 5.9, C=*C*CH$_2$), 157.79 (d, $^2J_{PC}$ 5.8, *C*=CCH$_2$), 167.37 (d, $^3J_{PC}$ 4.7, C=N), 201.12 (C-1); δ_P (161.92 MHz, $CDCl_3$) 31.55.

3-[1-(Diphenylphosphoryl)but-3-enyl]-4-(phenylimino)-2-(prop-1-en-1-yl)cyclopent-2-en-1-one 4. Purification by column chromatography using ethyl acetate as eluent. Isolated together with **2c**. Oil, ($C_{30}H_{28}NO_2P$, found: C, 77.48; H, 55.97; N, 3.56%, requires C, 77.40; H, 56.06; N, 3.01%); yield 30%; ν_{max}/cm^{-1} 1720 (C=O); δ_H (400.13 MHz, $CDCl_3$) 1.95 (3H, dd, $^3J_{HH}$ 6.8, $^4J_{HH}$ 1.6, CH_3), 2.37 (1H, dd, $^2J_{HH}$ 21.0, $^5J_{PH}$ 2.9, COCH_2), 2.55 (1H, dd, $^2J_{HH}$ 21.0, $^5J_{PH}$ 0.9, COCH_2), 2.6 (1H, m, CHCH_2), 2.9 (1H, m, CHCH_2), 4.81 (1H, m, PCH), 4.85 (1H, app dq, $^2J_{HH} = {}^4J_{HH}$ 1.6, $^3J_{HH}$ 10.3, CH=C*H*$^c_2$), 4.95 (1H, dq, $^2J_{HH} = {}^4J_{HH}$ 1.6, $^3J_{HH}$ 17.2, CH=C*H*′$_2$), 5.57 (1H, m, C*H*=CH$_2$), 7.05 (1H, m, C*H*=CHCH$_3$), 7.27 (1H, m, CH=C*H*CH$_3$), 7.04–7.95 (15H, m, H^{ar}); δ_C (100.62 MHz, $CDCl_3$) 20.29 (CH_3), 30.92 (*C*H$_2$CH), 36.32 (d, $^1J_{PC}$ 65.8, PCH), 36.60 (*C*H$_2$CO), 116.92 (*C*H$_2$=CH), 119.17 (*C*^{o}NPh), 122.11 (d, $^4J_{PC}$ 2.6, *C*H=CHCH$_3$), 124.36–132.43 (15C^{ar}), 134.49 (d, $^3J_{PC}$ 13.6, CH$_2$=*C*H), 140.29 (d, $^5J_{PC}$ 1.9, CH=*C*HCH$_3$), 145.66 (d, $^3J_{PC}$ 5.6, =CH*C*=C), 151.06 (*C*^{ipso}NPh), 153.79 (d, $^2J_{PC}$ 5.8, =CHC=*C*), 167.0 (d, $^3J_{PC}$ 5.0, C=N), 200.85 (CO); δ_P (161.92 MHz, $CDCl_3$), 31.58.

4-[(Diphenylphosphoryl)methyl]-3-(phenylamino)cyclopent-2-en-1-one 5. Purification by column chromatography using ethyl acetate as eluent followed by recrystallisation in hexane–dichloromethane. Light yellow solid ($C_{24}H_{22}NO_2P$, found: C, 74.49; H, 5.78; N, 3.52%, requires C, 74.41; H, 5.72; N, 3.62%); yield 20%; 197–198 °C; ν_{max}/cm^{-1} 3416 (NH), 1601 (C=O); δ_H (300.13 MHz, $CDCl_3$) 2.32 (1H, ddd, $^2J_{HH}$ 18.5, $^3J_{HH}$ 2.5, $^4J_{PH}$ 1.1, CH_2CO), 2.90 (1H, dd, $^2J_{HH}$ 18.5, $^3J_{HH}$ 6.2, CH_2CO), 3.58 (1H, app t, $^2J_{HH} = {}^2J_{PH}$ 13.8, PCH_2), 3.73 (1H, t, $^2J_{HH} = {}^2J_{PH}$ 13.8, PCH_2), 4.64 (1H, m, CH), 5.71 (1H, dd, $^4J_{HH}$ 1.8, $^5J_{PH}$ 3.6, =CH), 6.68–7.85 (16H, m, 15H^{ar} + NH); δ_C (75.5 MHz, $CDCl_3$) 33.09 (d, $^1J_{PC}$ 61.0, PCH$_2$), 43.78 (*C*H$_2$CO), 56.63 (d, $^2J_{PC}$ 2.0, CH), 112.94 (*C*^{o}NPh), 117.66 (*C*^{p}NPh), 128.65–132.60 (15C^{ar}), 134.05 (d, $^4J_{PC}$ 7.1, =CH), 168.34 (d, $^3J_{PC}$ 9.2, =CN), 205.36 (CO); δ_P (121.4 MHz, $CDCl_3$) 31.16; *m*/*z* (EI): 387 (M^+, 8%), 201 (19), 186 (100).

1-[Diphenyl(*N*-phenylamino)phosphoranylidene]-4-phenylbut-3-yn-2-one 7

Purification by recrystallisation in hexane–dichloromethane. Orange solid ($C_{28}H_{22}NOP$, found: C, 80.27; H, 5.32; N, 3.2%, requires C, 80.18; H, 5.29; N, 3.34%); yield 71%; mp 170–171 °C; ν_{max}/cm^{-1} 1492 (C=O); δ_H (300.13 MHz, $CDCl_3$) 4.22 (1H, d, $^2J_{PH}$ = 27.6, H-1), 6.92 (2H, d, $^3J_{HH}$ = 7.1, *H*^{o}NPh), 6.99 (1H, t, *H*^{p}NPh), 7.21 (2H, t, *H*^{m}NPh), 7.4 (5H, m, Ph), 7.5–7.7 (6H, m, *H*^{m},*H*^{p}PPh), 7.92 (4H, m, *H*^{o}PPh), 10.02 (1H, s, NH); δ_C (75.5 MHz, $CDCl_3$) 63.36 (d, $^1J_{PC}$ 117.0, =CH), 82.65 (Ph*C*≡), 90.86 (d, $^3J_{PC}$ 25.4, ≡*C*CO), 119.64 (d, $^3J_{PC}$ 7.0, *C*^{o}NPh), 122.10 (*C*^{p}NPh), 122.31 (*C*^{ipso}Ph), 126.23 (d, $^1J_{PC}$ 102.7, *C*^{ipso}PPh), 128.15, 128.61, 129.07, 129.08 (d, $^3J_{PC}$ 13.0,

C^{m}PPh), 132.16, 132.29 (d, $^{2}J_{PC}$ 11.2, C^{o}PPh), 132.95 (d, $^{4}J_{PC}$ 2.5, C^{p}PPh), 139.91 (C^{ipso}NPh), 169.29 (CO); δ_P (121.4 MHz, $CDCl_3$) 32.29; *m*/*z* (EI) 419 (M^+, 4%), 418 (8), 292 (100), 215 (25), 201 (89).

1-[Diphenyl(*N*-phenylamino)phosphoranylidene]-4-phenylbut-3-en-2-one 8. Purification by recrystallisation in ether. Yellow solid ($C_{28}H_{24}NOP$, found: C, 79.87; H, 5.68; N, 3.40%, requires C, 79.79; H, 5.74; N, 3.32%); yield 90%; mp 140–141 °C; ν_{max}/cm^{-1} 1602 (C=O); δ_H (300.13 MHz, $CDCl_3$) 3.91 (1H, d, $^{2}J_{PH}$ 34.5, P=CH), 6.73 (1H, d, $^{3}J_{HH}$ 15.7, COCH=), 6.7–8.0 (21H, m, 20H^{ar} + =C*H*Ph); δ_C (75.5 MHz, $CDCl_3$) 61.13 (d, $^{1}J_{PC}$ 119.3, P=CH), 119.31 (d, $^{3}J_{PC}$ 7.4, C^{o}NPh), 121.41 (C^{p}NPh), 126.60 (CO*C*H=), 127.27 (d, $^{1}J_{PC}$ 100.6, C^{ipso}PPh), 127.94–132.57 (17C^{ar}), 133.53 (=*C*HPh), 136.31 (C^{ipso}Ph), 140.55 (C^{ipso}NPh), 181.53 (CO); δ_P (121.4 MHz, $CDCl_3$) 32.13; *m*/*z* (EI) 421 (M^+, 27%), 329 (41), 291 (49), 201 (100).

Dimethyl 3-[triphenylphosphorimidoyl]-2,4-dioxopentane-1,5-dioate 9. Purification by column chromatography using ethyl acetate as eluent followed by recrystallisation in hexane–dichloromethane. White solid (Found: C, 64.87; H, 4.65; N, 3.13%. $C_{25}H_{22}NO_6P$ requires C, 64.79; H, 4.78; N, 3.02%); yield 51%; mp 165–166 °C; ν_{max}/cm^{-1} 1724, 1695, 1690 (C=O), 1230 (P=N); δ_H (300.13 MHz, $CDCl_3$) 3.95 (6H, s, 2 × CH_3), 4.81 (1H, d, $^{2}J_{PH}$ 27.6, CH), 6.89–7.15 (5H, m, NPh), 7.45–7.87 (10H, m, PPh); δ_C (75.5 MHz, $CDCl_3$) 52.29 (2 × CH_3), 60.55 (d, $^{1}J_{PC}$ 117.9, CH), 119.25 (d, $^{3}J_{PC}$ 7.2, C^{o}NPh), 122.04 (C^{p}NPh), 125.97 (d, $^{1}J_{PC}$ 102.2, C^{ipso}PPh), 129.03 (d, $^{2}J_{PC}$ 12.9, C^{m}PPh), 129.05 (C^{m}NPh), 132.28 (d, $^{2}J_{PC}$ 11.0, C^{o}PPh), 133.12 (d, $^{4}J_{PC}$ 2.3, C^{p}PPh), 139.57 (d, $^{2}J_{PC}$ 2.2, C^{ipso}NPh), 165.87 (d, $^{3}J_{PC}$ 23.4, 2 × CO), 172.58 (d, $^{2}J_{PC}$ 3.4, 2 × CO); δ_P (121.4 MHz, $CDCl_3$) 30.29; *m*/*z* (EI) 463 (M^+, 0.5%), 462 (1.5), 418 (5), 292 (23), 215 (56), 201 (100).

2-[(Diphenylphosphoryl)methyl]-2-phenyl-3-(*N*-phenylamino)-5-oxo-2,5-dihydrofuran 10a. Purification by column chromatography using ethyl acetate as eluent, then recrystallisation in hexane–dichloromethane. Light yellow solid ($C_{29}H_{24}NO_3P$, found: C, 74.90; H, 5.27; N, 3.1%, requires C, 74.83; H, 5.20; N, 3.01%); yield 50%; mp 255–256 °C; ν_{max}/cm^{-1} 3325 (NH), 1672 (C=O); δ_H (400.13 MHz, $CDCl_3$) 3.23 (1H, dd, $^{2}J_{HH}$ 15.2, $^{2}J_{PH}$ 12.5, CH_2), 3.62 (1H, dd, $^{2}J_{HH}$ 15.2, $^{2}J_{PH}$ 8.8, CH_2), 5.38 (1H, s, =CH), 6.87 (2H, m, H^{o}NPh), 6.96 (1H, m, H^{p}NPh), 7.08–7.80 (21H, m, H^{ar}), 11.56 (1H, s, NH); δ_C (100.62 MHz, $CDCl_3$) 40.77 (d, $^{1}J_{PC}$ 67.6, CH_2), 85.19 (d, $^{4}J_{PC}$ 3.6, =CH), 85.29 (*C*Ph), 119.89 (C^{o}NPh), 124.14 (C^{p}NPh), 126.51 (C^{m}Ph), 126.68 (C^{p}Ph), 127.86 (C^{m}NPh), 128.42 (d, $^{3}J_{PC}$ 13.0, C^{m}PPh), 129.46 (C^{o}Ph), 129.73 (d, $^{1}J_{PC}$ 105.3, C^{ipso}PPh), 129.11 (d, $^{3}J_{PC}$ 11.7, C^{m}PPh), 130.15 (d, $^{2}J_{PC}$ 9.5, C^{o}PPh), 130.58 (d, $^{2}J_{PC}$ 9.5, C^{o}PPh), 131.53 (d, $^{4}J_{PC}$ 2.9, C^{p}PPh), 132.43 (d, $^{4}J_{PC}$ 2.1, C^{p}PPh), 132.83 (d, $^{1}J_{PC}$ 103.9, C^{ipso}PPh), 136.08 (C^{ipso}Ph), 140.08 (C^{ipso}NPh), 165.79 (=CN), 172.38 (CO); δ_P (121.4 MHz, $CDCl_3$) 29.35; *m*/*z* (EI) 465 (M^+, 100%), 421 (40), 321 (70), 201 (50).

(*RS*,*RS*)-2-[1-(Diphenylphosphoryl)ethyl]-2-phenyl-3-(*N*-phenylamino)-5-oxo-2,5-dihydrofuran 10b. Purification by column chromatography using ethyl acetate as eluent, then recrystallisation in hexane–dichloromethane. Light yellow solid (Found: C, 75.19; H, 5.38; N, 3.02%. $C_{30}H_{26}NO_3P$ requires C, 75.14; H, 5.46; N, 2.92; O, 10.01; P, 6.46%); yield 45%; mp 277–278 °C; ν_{max}/cm^{-1} 3320 (NH), 1673 (C=O); δ_H (300.13 MHz, $CDCl_3$) 1.2 (3H, dd, $^{3}J_{HH}$ 7.3, $^{2}J_{PH}$ 16.7, CH_3), 3.62 (1H, dq, $^{3}J_{HH}$ 7.3, $^{3}J_{PH}$ 6.8, CH), 5.48 (1H, s, =CH), 6.85–7.80 (20 H, m, H^{ar}), 11.56 (1H, s, NH); δ_C (75.5 MHz, $CDCl_3$) 10.98 (CH_3), 42.30 (d, $^{1}J_{PC}$ 71.4, CH), 87.06 (*C*Ph), 88.90 (d, $^{4}J_{PC}$ 6.2, =CH), 120.00–140.03 (19C^{ar}), 136.28 (C^{ipso}Ph), 140.03 (C^{ipso}NPh), 163.60 (=CN), 173.06 (CO); δ_P (121.4 MHz, $CDCl_3$) 35.69; *m*/*z* (EI) 479 (M^+, 100%), 201 (40), 144 (50).

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