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Tetrahedron Letters
Tetrahedron Letters 48 (2007) 6987–6991

# Regio- and stereoselective nucleophilic additions of amines, thiols and aminophosphanes to the C≡C bond of *P*,*P*-diphenyl-*P*-(2-phenylethynyl)-$\lambda^5$-phosphazenes

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Received 28 June 2007; revised 17 July 2007; accepted 24 July 2007
Available online 27 July 2007

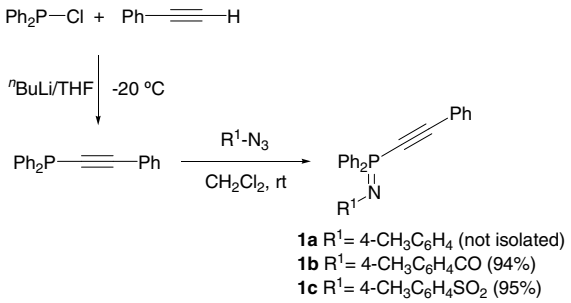
**Abstract**—Nitrogen and sulfur nucleophiles, such as amines, thiophenols, and aminophosphanes, add to the triple bond of *P*-ethynyl-$\lambda^5$-phosphazenes to give regio and diastereoselectively *P*-ethenyl-$\lambda^5$-phosphazenes. An equally selective substitution reaction, occurring by an addition–elimination pathway, on bis(iminophosphoranyl)ethenes has been also achieved.


A few examples of nucleophilic addition to the C≡C bond of some classes of *P*-alkynyl derivatives, such as phosphane oxides and sulfides, phosphonates and thiophosphonates, have been described.[1] The results of these reactions are in agreement with theoretical calculations showing that these P(V) functionalities are electron withdrawing and, consequently, play the role of activating groups in such processes.[2] We have previously disclosed that an iminophosphoranyl function successfully activate a *P*-linked C=C bond for Michael-type addition of a variety of nucleophiles.[3] In contrast, there is no precedents of similar reactivity over *P*-alkynyl-$\lambda^5$-phosphazenes. Moreover, the members of this class of compounds reported up to now are scarce.[4] To our knowledge only their hydrolysis[5] and a [3+2] cycloaddition with diazo compounds[6] have been occasionally disclosed.

Herein, we describe the synthesis of three new *P*-ethynyl-$\lambda^5$-phosphazenes and the results of the addition reaction of nucleophiles, such as amines, thiophenols, and aminophosphanes, to their C≡C bond.

The *P*-alkynyl-$\lambda^5$-phosphazenes **1a–c** are readily prepared by the stoichiometric reaction of azides and *P*,*P*-diphenyl-*P*-phenylethynylphosphane[7] under the standard conditions of the Staudinger imination reaction[8] (Scheme 1). *N*-(4-Tolyl) derivative **1a** was quite unstable to be isolated in totally pure form due to the hydrolytic sensitivity of its P=N bond, but could be used successfully in crude form in the following reactions. In contrast, the *N*-acyl and *N*-sulfonyl derivatives **1b** and **1c** were isolated in pure state as oils after a simple work-up and showed to be stable for weeks as far as they are kept under a nitrogen atmosphere.

The characterization of compounds **1** was straightforward following their spectral data. Their $^{31}P\{^1H\}$ NMR spectra show a singlet appearing between −16.9 and −0.5 ppm, remarkably deshielded in relation to the analogous *P*-alkenyl-$\lambda^5$-phosphazenes ($\Delta\delta = 16.7$–18.6 ppm). In their $^{13}C$ NMR spectra the signals attributed to the acetylenic carbons appear as doublets, in the interval 105.6–109.6 ppm for the β-carbon, and in the




**Scheme 1.** Preparation of *P*-alkynyl-$\lambda^5$-phosphazenes **1a–c**.

*Keywords*: Addition reactions; *P*-Alkynyl-$\lambda^5$-phosphazenes; Bis(iminophosphoranyl)ethenes.
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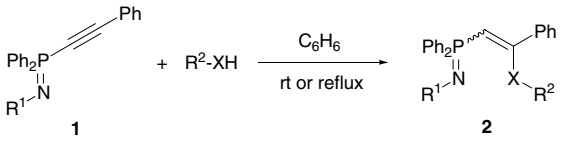
doi:10.1016/j.tetlet.2007.07.148

range 77.4–81.0 ppm for the α-carbon. In this context, it is well known that the polarity of a carbon–carbon triple bond is associated to the difference of the $^{13}C$ NMR chemical shifts ($\Delta\delta$) between the signals of their carbon atoms.[2] By comparing these values (for **1a**: $\Delta\delta =$ 24.66 ppm, **1b**: $\Delta\delta = 28.14$ ppm and **1c**: $\Delta\delta =$ 32.16 ppm) with that of *P*,*P*-diphenyl-*P*-phenylethynylphosphane ($\Delta\delta = 21.88$ ppm)[7b] and its oxide ($\Delta\delta =$ 22.59 ppm)[7b] it seems clear that the triple bonds of *P*-alkynyl-$\lambda^5$-phosphazenes **1a–c** are more polar than those of the precursor *P*-alkynyl phosphane and its oxide.

The reaction of *P*-alkynyl-$\lambda^5$-phosphazenes **1** with a couple of alkylamines at reflux temperature, and with 4-methoxythiophenol at room temperature, gave rise to the respective 2-substituted *P*-alkenyl-$\lambda^5$-phosphazenes **2** (Scheme 2, Table 1).

As it has been found in nucleophilic additions to the C≡C bond of other electron-deficient alkynes,[9] these reactions resulted to be totally regioselective, the nucleophilic part of the reagents adding to the β-carbon. The products were isolated as mixtures of *Z* and *E* isomers, except for the case of **2a** where the *Z* isomer is exclusively formed (Table 1). In most cases these two stereoisomers could be separated by chromatographic purification on silica gel deactivated with triethylamine (5%). The assignment of the double bond geometries was made on the basis of the coupling constants trans $^3J_{CP}$ (*Z* isomers) and cis $^3J_{CP}$ (*E* isomers) between the phosphorus atom and the *ipso* carbon of the 2-phenyl group in their $^{13}C$ NMR spectra (Fig. 1). These data show a clear and simple pattern in which trans $^3J_{CP} >$ cis $^3J_{CP}$. Furthermore, the ranges are such (trans $^3J_{CP}$ 14.1–15.3 Hz and cis $^3J_{CP}$ 4.7–8.2 Hz) that it is possible to assign the stereochemistry confidently when only a single isomer is obtained. These *J* values are in agreement with other previous reports showing that in *P*-alkenyl P(V) compounds the value of both $^3J_{CP}$ coupling constants are in the ranges: trans $^3J_{CP}$ 16.4–23.7 Hz and cis $^3J_{CP}$ 4.0–7.5 Hz.[10]




**Scheme 2.** Nucleophilic addition to *P*-alkynyl-$\lambda^5$-phosphazenes **1**.

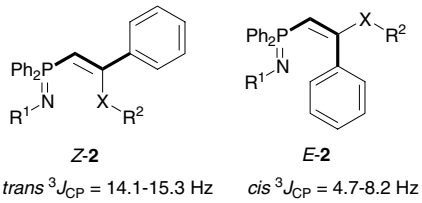


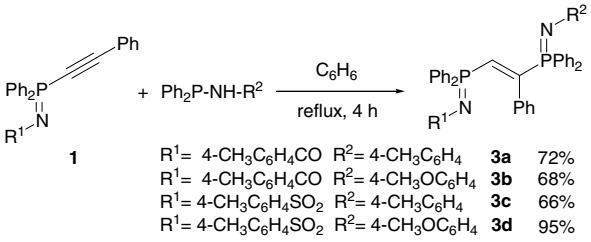

**Figure 1.** Coupling constants $^3J_{CP}$ for *Z*-**2** and *E*-**2** isomers.

It is noticeable that for the cases *Z*-**2a** and *Z*-**2b**, where *X* is an NH group, the enamino tautomer, which may form an intramolecular hydrogen bond with the phosphazene N atom, was the only one observed, whereas in similar compounds where $R^1$ and $R^2$ in structure **2** are 2,6-diisopropylphenyl groups an imino-enamino equilibrium is clearly established.[11]

On the other hand, we have reported that aminophosphanes ($R^1_2P$–NH–$R^2$)[12] are excellent nucleophilic species in reactions with activated alkyl halides[13] and carbon–carbon double bonds.[3] In such reactions, the aminophosphanes experience regioselective *P*-alkylations and consequently they behave as synthetic equivalents of iminophosphide anions $[R^1_2P{=}NR^2]^-$. For this reason they can be considered as iminophosphoranyl synthons.

When a couple of *N*-aryl aminophosphanes were reacted with *P*-alkynyl phosphazenes **1** the presumed asymmetrically substituted bis(iminophosphoranes) **3a–d**[14] derived from 1-phenyl-1,2-bis(diphenylphosphino)ethene, were obtained in good yields (Scheme 3). These nucleophilic additions proceed with total regio- and diastereoselectivity, affording exclusively the *E*-isomers.

A careful scrutiny of the NMR data of compounds **3**, paying particular attention to the values of the $^3J_{HP}$, $^3J_{CP}$, and $^3J_{PP}$ coupling constants allowed the unambiguous assignment of their *E*-geometries (Fig. 2). For




**Scheme 3.** Synthesis of *E*-bis(iminophosphoranyl)ethenes **3** by addition of *N*-aryl aminophosphanes to *P*-alkynyl-$\lambda^5$-phosphazenes **1**.

**Table 1.**

| Compound | X | $R^1$ | $R^2$ | Ratio *Z*/*E* | *Z* (%) | *E* (%) |
|---|---|---|---|---|---|---|
| **2a** | NH | 4-$CH_3C_6H_4$ | $^i$Pr | 100/0 | 41 | — |
| **2b** | NH | 4-$CH_3C_6H_4SO_2$ | $PhCH_2$ | 63/37 | 44 | 22 |
| **2c** | S | 4-$CH_3C_6H_4$ | 4-$CH_3OC_6H_4$ | 80/20 | 49 | 12 |
| **2d** | S | 4-$CH_3C_6H_4CO$ | 4-$CH_3OC_6H_4$ | 80/20 | —[a] | —[a] |

[a] Global yield: 76%, *E* and *Z* isomers not separated.

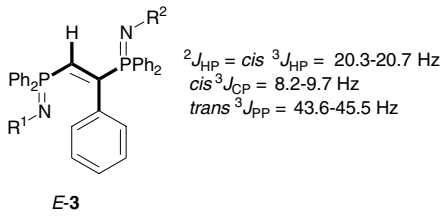
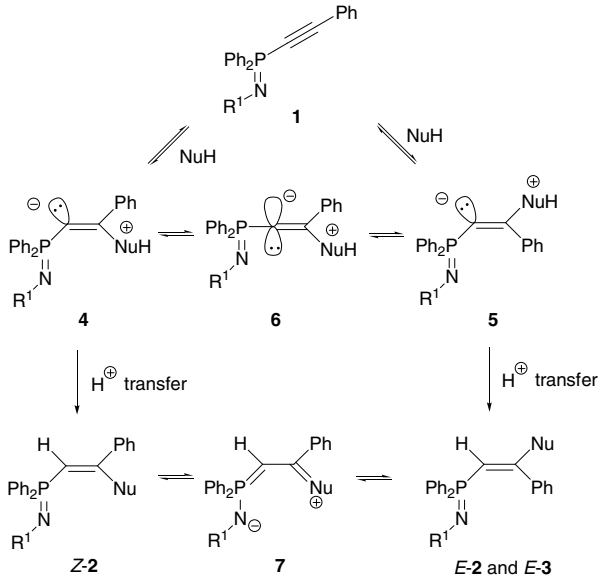



**Figure 2.** Significant coupling constant values of compounds **3**.

example, in their $^1$H NMR spectra the value of $^3J_{HP}$ is close to 21 Hz, coincident with other reports of cis $^3J_{HP}$ coupling constant in *P*-vinyl-$\lambda^5$-phosphazenes[3a] and analogous bis(sulfides) or bis(oxides).[10a,15] In addition, the quaternary *ipso* carbon of the *C*-phenyl group show a $^3J_{CP} = 8$–10 Hz, which is in the typical range of cis $^3J_{CP}$ values of comparable structures.[10a,15,16] The most significant data of their $^{31}$P NMR is the $^3J_{PP}$ value, close to 45 Hz, in agreement with typical values found for two phosphorus(V) atoms in trans-1,2-positions of a carbon–carbon double bond.[15–17]

The stereochemical course of these latter addition reactions is difficult to rationalize on the basis of the well established general mechanism of the nucleophilic additions to electron-deficient alkynes.[18] Following this general mechanism, the attack of a neutral nucleophile NuH on activated alkyne **1** should initially occur in an *anti* fashion to give *Z*-vinyl zwitterion **4** in preference to *E* isomer **5**, although both intermediates can isomerize across the linear sp-hybridized zwitterion **6** and its various resonance contributors. The formation of the final products (*Z*-**2**, of kinetic control, or *E*-**2** and *E*-**3**, of thermodynamic control) will depend on the relative rates of isomerization versus proton transfer (Scheme 4). In addition, the initially formed *Z* or *E* isomers can directly isomerize, via the intermediacy of zwitterionic form **7**, which may rotate around the central C–C single bond.

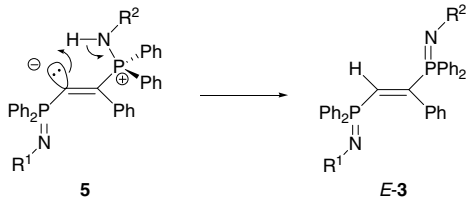



**Scheme 4.** Mechanistic proposal for the formation of compounds **2** and **3**.

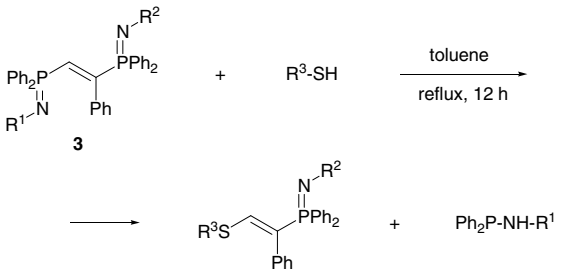
The most diastereoselective addition reactions on compounds **1** among all presented here are those leading to **3a**–**d**, which yield exclusively *E* isomers. This selectivity can be tentatively interpreted as resulting from a rapid internal proton transfer occurring at intermediate *E* zwitterions **5**. In these cases, the cis relationship between the carbanionic sp$^2$ orbital and the proton-releasing aminophosphonium unit facilitates such proton transfer, via a 5-center transition state (Scheme 5), thus making this step particularly rapid when compared with the alternative, presumably intermolecular proton transfer collapsing of **4** to *Z*-**2**.

In view of the presumed acceptor properties of the C=C bond of 1,2-bis(iminophosphoranyl)ethenes **3**, bearing one electron withdrawing group at each carbon, we decided to test their reactions with thiophenols, although keeping in mind the possibility that such reactions could not be highly regioselective (as the chemodifferentiation between the two terms of the C=C bonds seems, a priori, minimal). Rather surprisingly, the products of these reactions were not mixtures of the expected two regioisomeric addition products but instead $\lambda^5$-phosphazenes **8**[19] and the corresponding acyl or sulfonyl aminophosphane **9** were the only isolated products. Note that the reactions required slightly harsher conditions for completion than others here previously disclosed (toluene, reflux) (Scheme 6).

Thus, the R$^3$S group has replaced regio- and stereoselectively one of the two iminophosphoranyl groups at the




**Scheme 5.** Intramolecular proton transfer in intermediate **5** via a 5-center transition state.



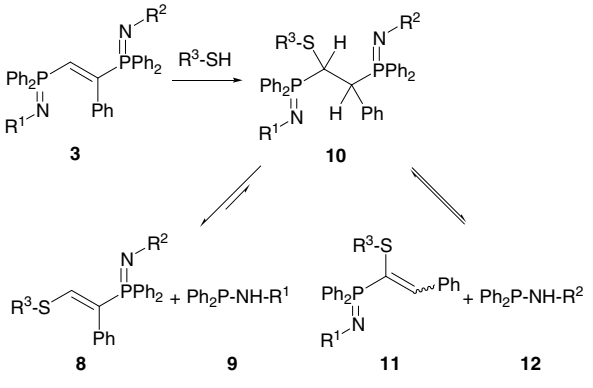

$R^2$ = 4-$CH_3C_6H_4$, $R^3$ = 4-$CH_3C_6H_4$ **8a** 75% $R^1$ = 4-$CH_3C_6H_4SO_2$ **9a** 60%
$R^2$ = 4-$CH_3OC_6H_4$, $R^3$ = 4-$CH_3OC_6H_4$ **8b** 93% $R^1$ = 4-$CH_3C_6H_4CO$ **9a** 50%
$R^2$ = 4-$CH_3C_6H_4$, $R^3$ = 4-$CH_3OC_6H_4$ **8c** 83% $R^1$ = 4-$CH_3C_6H_4SO_2$ **9b** 52%
$R^2$ = 4-$CH_3OC_6H_4$, $R^3$ = 4-$CH_3OC_6H_4$ **8b** 80% $R^1$ = 4-$CH_3C_6H_4SO_2$ **9b** 47%

**Scheme 6.** Selective substitution reaction of one iminophosphoranyl group of bis(iminophosphoranyl)ethenes **3**.

C=C double bond, more specifically that bearing $R^1$ (ArCO or $ArSO_2$), which is now found in aminophosphane **9**, whereas the second iminophosphoranyl function bearing $R^2$ (Ar) remains at its original place.

These results can be reasonably approximated by assuming an addition–elimination sequence of events. First, a regioselective addition of thiol to the C=C bond takes place,[20] incorporating the $R^3S$ fragment to the less substituted carbon of the starting alkene, to give **10** (Scheme 7). Then a β-elimination of aminophosphane $Ph_2P–NH–R^1$ should occur for leading to final products **8** and **9**. Note that the N atom of the P=N function, notably electronegative by virtue of the contribution of the ylidic $^+P–N^-$ resonance form, can reasonably act as an internal base promoting a 5-center concerted β-elimination. However, a second alternative β-elimination is also conceivable involving the other iminophosphoranyl group of **10** and leading to the functionalized alkene **11** and aminophosphane **12** $Ph_2P–NH–R^2$. Having no doubt the reaction products are exclusively **8** and **9**, we interpret the course of these processes as resulting of a thermodynamic equilibrium between the product couples **8/9** and **11/12** established across the sterically congested tetrasubstituted ethane **10** under the reaction conditions, in which the final composition of the reaction mixture (**8** + **9**) is determined by the rather irreversible transformation step **10**→**8** + **9**. The inverse reaction **8** + **9**→**10** should be quite slow due to the low nucleophilicity of *N*-acyl or sulfonyl aminophosphane **9** as a result of the delocalization of the N lone pair over the conjugated C=O or S=O bonds. On the contrary, *N*-aryl aminophosphane **12** is able of adding efficiently to **11**, thus sustaining their reversible equilibrium with **10**. In support of this last proposal, we have previously established that *N*-aryl aminophosphanes add to the C=C bond of *P*-alkenyl phosphazenes to yield 1,2-bis(iminophosphoranyl)ethanes.[3b]

In summary the present investigations have explored the addition of amines, thiols and aminophosphanes to *P*-ethynyl-*P*,*P*-diphenyl-$\lambda^5$-phosphazenes. The resulting tri-substituted alkenes have been obtained with total regioselectivity and high levels of diastereoselectivity. We have also shown that one iminophosphoranyl group of 1,2-bis(iminophosphoranyl)ethenes, differently substituted at their two N atoms, can be replaced by an ArS residue in a totally controlled way, under thermodynamic equilibrium conditions, via an addition–elimination sequence.




**Scheme 7.**

## Acknowledgments

This work was supported by the *MEC* and *FEDER* (Project CTQ2005-02323/BQU) and *Fundación Séneca-CARM* (Project 00458/PI/04). P.L.-L. also thanks *Fundación Séneca-CARM* for a fellowship.

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14. Bis(iminophosphoranyl)ethene **3a**: Yield: 72%; mp 76–78 °C (yellow prisms from dichloromethane/diethyl ether); $^{1}$H NMR (200 MHz, $CDCl_3$): $\delta$ 2.29 (s, 3H, $CH_3$), 2.43 (s, 3H, $CH_3$), 6.49 (d, 2H, $^{3}J_{HH} = 8.0$ Hz, $H_{arom}$), 6.64 (t, 2H, $^{3}J_{HH} = 7.6$ Hz, $H_{arom}$), 6.84 (d, 2H, $^{3}J_{HH} = 8.0$ Hz, $H_{arom}$), 6.85–6.89 (m, 1H, $H_{arom}$), 6.98 (d, 2H, $^{3}J_{HH} = 8.0$ Hz, $H_{arom}$), 7.14–7.52 (m, 18H, $2H_{arom} + Ph_2$), 7.69–7.79 (m, 4H, $Ph_2$), 8.06 (t, 1H, $^{2}J_{HP} = {}^{3}J_{HP} = 20.4$ Hz, C*H*=C), 8.20 (d, 2H, $^{3}J_{HH} = 8.0$ Hz, $HH_{arom}$); $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ 20.76 ($CH_3$), 21.63 ($CH_3$), 124.21 (d, $^{3}J_{CP} = 16.1$ Hz), 126.95, 127.24 (*q*), 127.39 ($d_{right}$, $C_i$), 127.59, 128.44 (d, $^{3}J_{CP} = 11.2$ Hz, 2 $C_m$), 128.56, 129.35–129.47 (aromatics), 129.67 (d, $J_{CP} = 1.7$ Hz), 131.70–131.88 ($C_o + 2C_p$), 133.13 (d, $^{2}J_{CP} = 9.0$ Hz, $C_o$), 133.47 (d, $^{2}J_{CP} = {}^{3}J_{CP} = 8.4$ Hz, *q*), 135.83 (d, $^{3}J_{CP} = 18.7$ Hz, *q*), 136.33 (dd, $^{1}J_{CP} = 66.9$ Hz, $^{2}J_{CP} = 12.2$ Hz, P*C*H=CP), 140.95 (*q*), 148.18 (d, $^{2}J_{CP} = 2.0$ Hz, *q*), 150.38 (d, $^{1}J_{CP} = 61.8$ Hz, PCH=*C*P), 176.82 (d, $^{2}J_{CP} = 17.7$ Hz, CO); $^{31}P\{^{1}H\}$ NMR (81 MHz, $CDCl_3$): $\delta$ 6.77 (d, $^{3}J_{PP} = 44.1$ Hz), 7.98 (d, $^{3}J_{PP} = 44.1$ Hz); IR (Nujol): $\nu = 1540$, 1505, 1439, 1337, 1176, 1114 $cm^{-1}$; MS (FAB+): *m*/*z* (%) = 712 (45) [$M^+$+2], 711 (95) [$M^+$+1], 710 (48)[$M^+$], 303 (100); Anal. Calcd for $C_{47}H_{40}N_2OP_2$ (710.78): C, 79.42; H, 5.67; N, 3.94. Found: C, 79.59; H, 5.76; N, 3.82.
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19. Iminophosphorane **8c**: Yield: 87%; mp 124–126 °C (yellow prisms from chloroform/pentane); $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.22 (s, 3H, $CH_3$), 3.77 (s, 3H, $OCH_3$), 6.74 (d, 2H, $^{3}J_{HH} = 8.0$ Hz, $H_{arom}$), 6.79 (d, 2H, $^{3}J_{HH} = 8.8$ Hz, $H_{arom}$), 6.87 (d, 2H, $^{3}J_{HH} = 8.0$ Hz, $H_{arom}$), 7.01 (m, 2H, $H_{arom}$), 7.19 (d, 2H, $^{3}J_{HH} = 8.8$ Hz, $H_{arom}$), 7.20–7.25 (m, 3H, $H_{arom}$), 7.31–7.36 (m, 4H, $Ph_2$), 7.41–7.45 (m, 2H, $Ph_2$), 7.59–7.64 (m, 4H, $Ph_2$), 7.79 (d, 1H, $^{3}J_{HP} = 16.5$ Hz, CHS) $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 20.64 ($CH_3$), 55.42 ($OCH_3$), 114.90, 123.44 (d, $^{3}J_{CP} = 17.7$ Hz), 124.93 (*q*), 126.35 (*q*), 126.69 (d, $^{1}J_{CP} = 89.7$ Hz, CH=*C*P), 128.02 (d, $^{5}J_{CP} = 1.5$ Hz), 128.34 (d, $^{3}J_{CP} = 11.9$ Hz, $C_m$), 128.60, 129.33, 129.76 (d, $^{3}J_{CP} = 4.0$ Hz), 130.00 (d, $^{1}J_{CP} = 100.3$ Hz, $C_i$), 131.58 (d, $^{4}J_{CP} = 2.6$ Hz, $C_p$), 132.62, 132.88 (d, $^{2}J_{CP} = 9.3$ Hz, $C_o$), 135.56 (d, $^{2}J_{CP} = 8.8$ Hz, *q*), 148.40 (*q*), 148.58 (d, $^{2}J_{CP} = 12.6$ Hz, CHS), 159.67 (*q*); $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$): $\delta$ 2.43; IR (Nujol): $\nu = 1505$, 1439, 1335, 1172, 1110 $cm^{-1}$; MS (EI): *m*/*z* (%) = 532 (22) [$M^+$+1], 531 (54) [$M^+$], 291 (100); Anal. Calcd for $C_{34}H_{30}NOPS$ (531.65): C, 76.81, H, 5.69, N, 2.63. Found: C, 76.75, H, 5.77, N, 2.71.
20. The basicity of the phosphazene functions may contribute to promote the addition of relatively acidic neutral nucleophiles such as thiols.