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PAPER

Facile synthesis of luminescent benzo-1,2-dihydrophosphinines from a phosphaalkene†

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The addition of 4-trifluoromethyl-1-ethynylbenzene, phenylacetylene, or 4-ethynylanisole to *P*-mesityldiphenylmethylenephosphine, **1**, produced photoluminescent 1,2-dihydrophosphinines **4a–c**, respectively, in quantitative yield *via* a [4 + 2] cycloaddition. Limited reactivity was observed between **1** and non-aromatic alkynes. *P*-[Bis(trimethylsilyl)amino][(trimethylsilyl)methylene]phosphine, **2**, and *P*-mesityl[(*t*-butyl)(trimethylsiloxy)methylene]phosphine, **3**, showed extremely limited reactivity with all alkynes examined. The reactivity of phosphaalkenes toward terminal alkynes is compared to that of alkenes as well as silenes and germenes.

Introduction

On the basis of the iconic Periodic Table, it is natural to compare the reactivity of multiply bonded compounds containing elements with the same valency, for example silenes ($R_2Si{=}CR_2$) and alkenes or phosphaalkenes ($RP{=}CR_2$) and imines. However, after three decades of research, it is now apparent that the properties and reactivity of phosphaalkenes are more similar to those of their carbon analogues, the alkenes, rather than to those of imines.[1] This so called "phosphorus–carbon analogy" has been attributed to the diagonal relationship between P and C, which focuses on the similar electronegativities of carbon (χ = 2.5) and phosphorus (χ = 2.1) rather than the number of valence electrons.[1a,b]

Like alkenes, phosphaalkene chemistry plays a significant role in synthesis and materials chemistry.[1,2,3] Cycloaddition reactions of phosphaalkenes are of particular interest since they hold much potential for the synthesis of a wide variety of phosphorus heterocycles. Several cycloadditions of phosphaalkenes have been investigated; however, the majority of work focuses on 6π electron cycloadditions and 1,3-dipolar additions.[1,3] In contrast, formal [2 + 2] cycloaddition reactions of phosphaalkenes have not been well-studied. Although these types of reactions are thermally forbidden in alkene chemistry, there have been some reports of phosphaalkenes undergoing [2 + 2] cycloadditions, presumably *via* a stepwise mechanism. A common example is the dimerization of simple phosphaalkenes, which highlights the increased reactivity of the P=C bond over the C=C bond.

Our group has been interested in the cycloaddition reactions of alkynes with silenes[4] and germenes[5] and how the reactivity of these heavy Group 14 analogues compares to that of alkenes. Unlike alkenes, silenes and germenes react readily with terminal alkynes at room temperature. Brook silenes, $((Me_3Si)_2Si{=}C(OSiMe_3)R)$, undergo a facile, regioselective cycloaddition reaction to give silacyclobutenes in high yield (Scheme 1).[6] We have found that the addition proceeds by way of a biradical intermediate.[4a,b] In contrast, naturally polarized silenes prefer to add across the CH bond of terminal alkynes.[4c] Less is known about the addition of alkynes to germenes.[7] Recently, we reported that the addition of terminal alkynes to naturally polarized germenes gives three types of products: [2 + 2] cycloadducts, σ-adducts from the insertion of the terminal alkynyl CH bond across the Ge=C bond, and ene-adducts.[5] Given the stark differences in the reactivity of silenes and germenes compared to alkenes towards alkynes, and the phosphorus–carbon analogy, we were keen to explore the reactivity of alkynes with phosphaalkenes.

The reaction between phosphaalkenes and alkynes has not been well studied: most examples reported in the literature concern the reactivity of specialized phosphaalkenes and electron rich alkynes, for example the addition of electron rich alkynes to metallophosphaalkenes,[8] phosphoranes,[9] metal-coordinated phosphaalkenes,[10] 1,2-thiaphospholes,[11] or fluorinated phosphaalkenes (Scheme 2)[12] has been examined. We were interested in studying the reactivity of a prototypical organo-substituted phosphaalkene with a range of terminal alkynes.

In this study, the reactivity of *P*-mesityldiphenylmethylenephosphine, **1**,[13] (selected as the prototypical organo-substituted

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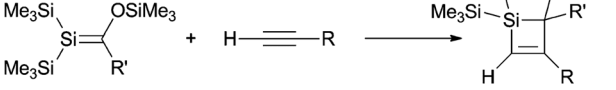
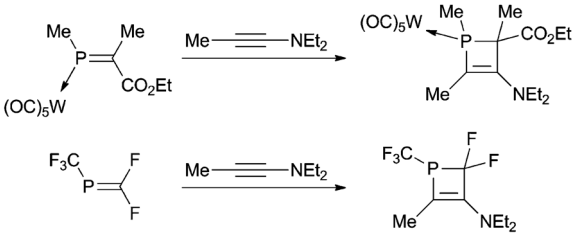
†Electronic supplementary information (ESI) available: ^{1}H NMR spectra for compounds **4a–c**, X-ray experimental and crystallography data for compounds **6a–c**, UV-VIS and fluorescence spectra for **4a–c**. CCDC reference numbers 842629–842631. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt11690a



Scheme 1 Cycloaddition of Brook silenes with alkynes.



Scheme 2 Selected examples of alkyne addition to phosphaalkenes.

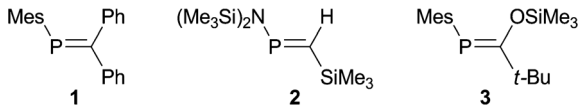


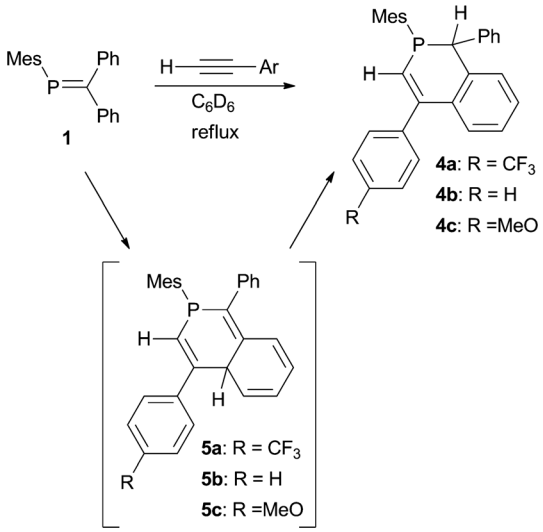
Fig. 1 Phosphaalkenes **1**, **2**, **3**.

phosphaalkene) with a number of different alkynes has been investigated. Both electron rich and electron deficient, aromatic and non-aromatic, alkynes were included in the study. Phosphaalkene **1** contains only carbon substituents, and thus, the P═C bond is naturally polarized, with a slight partial negative charge on carbon. The absence of any strongly electron withdrawing substituents leaves the P═C bond of **1** relatively electron rich. The reactivity of **1** was compared to the reactivity of two other representative phosphaalkenes, bis(trimethylsilyl)amino(trimethylsilyl)methylenephosphine, **2**,[14] and *P*-mesityl [(*t*-butyl)(trimethylsiloxy)]methylenephosphine, **3** (Fig. 1).[15] Both phosphaalkene **2** and **3** have substituents that greatly influence the electronic nature of the P═C bond. Both the *P*-amino group and the *C*-silyl group on **2** enhance the natural polarity of the P═C bond by increasing the electron density at carbon. The *C*-siloxy group on **3** diminishes the polarity of the P═C bond through π-donation of electron density from oxygen to phosphorus. The reactivity of phosphaalkenes towards alkynes will be compared to that of alkenes as well as silenes/germenes.

Results

A solution of *P*-mesityldiphenylmethylenephosphine, **1**, and excess aromatic alkyne (ArC≡CH; Ar = *p*-$CF_3C_6H_4$, Ph, *p*-$MeOC_6H_4$) in C_6D_6 was heated to reflux. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. In each case, a 1,2-dihydrophosphinine, **4a–c**, was obtained quantitatively (Scheme 3). A difference was noted, however, in the reaction times. The addition of *p*-$CF_3C_6H_4C$≡CH to **1** was complete after 16 h, whereas the addition of PhC≡CH and *p*-$MeOC_6H_4$-C≡CH required 4 and 6 days, respectively, to go to completion. Although in each reaction the 1,2-dihydrophosphinine, **4a–c**, was formed as the sole addition product, purification by chromatography was required to remove residual alkyne. It was difficult to obtain samples of high purity (>95%) due to the tendency of **4a–c** to oxidize in air or on silica.

The structures of 1,2-dihydrophosphinines **4a–c** were determined using ^{1}H, ^{13}C, ^{31}P, gCOSY, ^{1}H–^{13}C gHSQC and gHMBC NMR spectroscopy, and mass spectrometry. A molecular ion consistent with a 1 : 1 (**1** to alkyne) adduct was observed in the mass spectra for all addition products.



Scheme 3 Addition of aromatic alkynes to **1**.

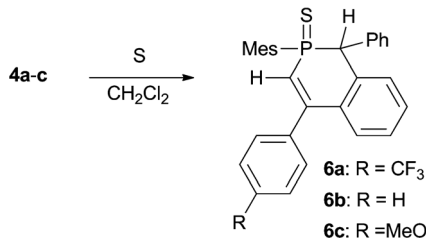
The ^{31}P signals of **4a–c** (−27 to −26 ppm) were significantly shifted upfield in comparison to the ^{31}P signal of phosphaalkene **1** (234 ppm), which is consistent with a change from two-coordinate phosphorus(III) to three-coordinate phosphorus(III).[16] The ^{1}H NMR spectra of **4a–c** all showed a doublet in the vinylic region (~6.5 ppm) with a coupling constant that ranged from 17–19 Hz, consistent with a geminal coupling between a vinylic ^{1}H and a ^{31}P(III) centre.[16] The presence of a vinylic ^{1}H geminal to the P(III) centre suggested that the terminal end of the alkyne added to the phosphorus centre of the phosphaalkene.

The ^{13}C NMR spectra of **4a–c** showed the presence of a saturated carbon adjacent to the P(III) centre; a doublet at ~46 ppm with a coupling constant of 11–13 Hz was observed in all cases.[16] This carbon signal showed a correlation in the ^{1}H–^{13}C gHSQC spectra of **4a–c** to a signal at ~5.5 ppm in the ^{1}H dimension, which integrated for one ^{1}H. Thus, this ^{1}H was situated two bonds from the ^{31}P(III) centre; however, there was no visible splitting of the ^{1}H signal due to the proximal ^{31}P(III). In addition to the saturated CH, the phosphorus was substituted with an unsaturated CH and a mesityl group to give a MesP(CH═CR_2)(CHR_2) moiety.

Upon close examination of the ^{1}H NMR spectra of **4a–c**, the integration value of the signals in the aromatic region did not correspond to the number of aromatic hydrogens present in the starting materials; there was one less hydrogen than expected. To account for the low integration value in the aromatic region, along with the presence of a ^{1}H signal on a saturated carbon next to the ^{31}P(III) centre, regioselective cycloaddition between phosphaalkene **1** and the alkyne to initially give 1,4-dihydrophosphinine **5a–c**, followed by a rapid isomerization *via* a H-transfer to re-aromatize the fused ring was proposed (Scheme 3).

Several attempts were made to crystallize 1,2-dihydrophosphinines **4a–c**, but suitable crystals for X-ray analysis were not obtained. Thus, compounds **4a–c** were oxidized with elemental sulfur to give the phosphorus(V) analogues, **6a–c** (Scheme 4).

Oxidized products **6a–c** were identified by IR, ^{1}H, ^{13}C, ^{31}P, gCOSY, ^{1}H–^{13}C gHSQC and gHMBC NMR spectroscopy, mass spectrometry, and X-ray crystallography. As expected, the ^{1}H



Scheme 4 Oxidation of **4a–c** with sulfur.

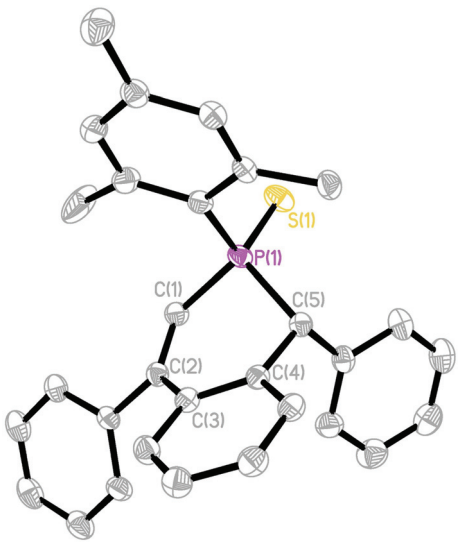


Fig. 2 Thermal ellipsoid plot (50% probability surface) of **6b**. Two molecules of **6b** were present in the asymmetric unit; the structure and parameters are given for one of the two molecules. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–C(1) = 1.7937(18), P(1)–C(5) = 1.8526(19), C(1)–C(2) = 1.343(3), C(2)–C(3) = 1.484(2), C(3)–C(4) = 1.411(2), C(4)–C(5) = 1.518(2), C(5)–P(1)–C(1) = 97.63(8), C(4)–C(5)–P(1) = 108.77(11).

and ^{13}C NMR data of **6a–c** were very similar to those of **4a–c**. Noticeably, the chemical shift of the ^{31}P signal of the oxidized structures was shifted downfield to ~30 ppm (from −26 ppm). Both the IR and mass spectra were consistent with the incorporation of sulfur into the structure. Crystals of **6a–c** were grown by slow diffusion of hexanes into a concentrated benzene–Et_2O solution. The molecular structures of **6a–c** were determined by X-ray crystallography; a thermal ellipsoid plot of **6b** is shown in Fig. 2. The phosphorus atom lies out of the plane made by the remaining carbon atoms of the six-membered ring, which gives the ring a puckered conformation. The intracyclic bond angles at phosphorus are close to 98° and the intracyclic P–C bond lengths are between 1.79–1.86 Å. The metrics of **6a–c** are comparable to those of other crystallographically characterized 1,2-dihydrophosphinines.[17] The stereochemistry of **6a–c** was determined from the molecular structures; the *P*-mesityl and the *C*-phenyl substituents were *trans* to each other in each case.

Adducts **4a–c** are bright green solids whereas the oxidized phosphorus(V) analogues, **6a–c**, are colourless. 1,2-Dihydrophosphinines **4a–c** were analyzed by UV-VIS and fluorescence spectroscopy. In addition to the absorption attributed to the aromatic substituents at ~250 nm in the UV-VIS spectra of **4a–c** (Fig. S4†), a second, lower energy absorption was observed at ~345 nm, which was assigned to the n to π* transition. There were no absorption bands present in the visible range, which was puzzling given the green colour. However, excitation at the low energy absorption (~340 nm) gave rise to a broad emission band for each compound between 450 and 500 nm (Fig. S5†), which is consistent with the observed colour of the dihydrophosphinines.

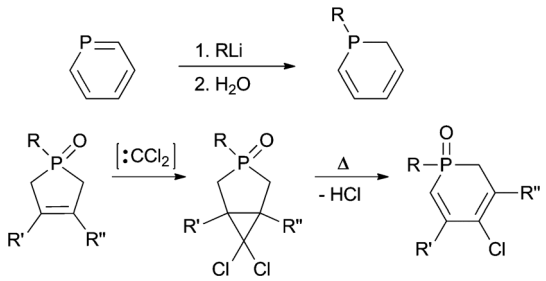
The reaction of phosphaalkene **1** with non-aromatic alkynes (RC≡CH; R = $(CH_2)_3CH_3$, *t*-Bu, $SiMe_3$, C(O)OMe) was also examined. The alkyne was present in excess; solutions (C_6D_6) were heated for at least 20 h, and in some cases, up to 6 days. The reactions were monitored by ^1H and ^{31}P NMR spectroscopy. No reaction was observed with the alkyl- and silyl-substituted alkynes (R = $(CH_2)_3CH_3$, *t*-Bu, $SiMe_3$). Upon addition of methyl propiolate (HC≡CC(O)OMe), phosphaalkene **1** was entirely consumed; however, a complex mixture of products was formed, from which no single addition product could be separated.

The reactivity of phosphaalkenes **2** and **3** with terminal alkynes was also studied. Unlike phosphaalkene **1**, neither **2** nor **3** have aromatic substituents on carbon, and thus, the [4 + 2] cycloaddition pathway is not possible. Phosphaalkenes **2** and **3** were each treated with phenylacetylene, hexyne, and methyl propiolate. No reactions were observed with phenylacetylene or hexyne, even after the reaction mixtures were refluxed in C_6D_6. These results are consistent with a previous report on the reactivity of **2** towards phenylacetylene.[18] Methyl propiolate reacted with **2** at room temperature; the phosphaalkene was entirely consumed after 2 days. Unfortunately, like the reaction of methyl propiolate with **1**, an intractable mixture was obtained and no single product could be isolated. Phosphaalkene **3** did not react with methyl propiolate at room temperature; however, a complex mixture was obtained after 5 days in refluxing C_6D_6.

Since phosphaalkenes **1**, **2**, and **3** did not appear to react with several alkynes under thermal conditions, photochemical conditions were explored. Hexane solutions of phosphaalkenes **1**, **2**, or **3** were irradiated in the cold (−70 °C) at 254 nm in the presence of either phenylacetylene or hexyne. The reactions were monitored by ^{31}P NMR spectroscopy. After 20 h of irradiation, no ^{31}P-containing products were observed in any of the reactions. In the case of phosphaalkene **3**, a small amount of isomerization from the *E*-phosphaalkene to the *Z*-isomer was observed.

Discussion

1,2-Dihydrophosphinines, such as **4a–c**, in general, are well-known phosphorus heterocycles;[19] however, the synthesis of 1,2-dihydrophosphinines *via* cycloaddition between a phosphaalkene and an alkyne has not previously been reported. Typically, 1,2-dihydrophosphinines are synthesized from either the addition of an organometallic reagent to the parent phosphinine or the ring-expansion of a dihydrophosphole (Scheme 5).[19,20,21] The syntheses of the required phosphinines and dihydrophospholes can be challenging and/or require harsh conditions, and thus, the cycloaddition of an aromatic alkyne to a *C*-aryl substituted phosphaalkene represents a facile, mild route to benzo-fused 1,2-dihydrophosphinines.



Scheme 5 Typical routes to 1,2-dihydrophosphinines.

Reactivity of phosphaalkenes with alkynes

1,2-Dihydrophosphinines **4a–c** are likely derived from a formal [4 + 2] cycloaddition followed by a H-transfer; the *C*-phenyl substituted phosphaalkene acts as the 4π component and the alkyne as the 2π component in the cycloaddition. However, the possibility of ring expansion from an intermediate 1,2-dihydrophosphete (or phosphacyclobutene), as was reported in the addition of benzophenone to a *C*-mesityl substituted Brook silene,[22] cannot be ruled out.

For a phosphaalkene to behave as the 4π component, there must be some delocalization between the P═C bond and at least one of the aromatic rings on carbon. Detailed studies of the structure of **1** have lead to the conclusion that conjugation between the P═C bond and *C*-aryl substituents is present, but of minor importance to the stability of this phosphaalkene.[23] The conclusion has been extended to other *C*-aryl substituted phosphaalkenes.[24]

Analogous [4 + 2] chemistry has been reported for related heavier main group systems: the addition of an aldehyde to a *C*-aryl substituted germene, dimesitylfluorenylidenegermane, gave a 1,2-oxagermin.[25] Interestingly, the fluorenylidene substituent ensures the C-substituted aromatic ring is held coplanar to the Ge═C bond. There are no reported examples involving an alkyne.

Simple, non-aromatic 1-phosphabutadienes also undergo [4 + 2] cycloaddition reactions upon treatment with dienophiles.[26] Examples of cycloadditions between 1-phosphabutadienes and alkynes have been reported; however, the addition products are generally 1,4-dihydrophosphinines, rather than 1,2-dihydrophosphinines.[26,27] Re-aromatization of the fused ring system likely promotes the isomerization of 1,4-dihydrophosphinines **5a–c** to 1,2-dihydrophosphinines **4a–c** (Scheme 3) in the reactions between phosphaalkene **1** and the aromatic alkynes.

Cycloadducts **4a–c** are formed regio- and stereospecifically; only a single diastereomer was obtained for each compound. Although the exact factors governing the regiochemistry of alkyne addition to phosphaalkene **1** are unclear, we note that the dipoles of the phosphaalkene and the alkyne are aligned when the terminal alkynyl carbon approaches the phosphorus centre.[28] Most likely, steric interactions also play a role in governing the regiochemistry of the reaction. The stereoselectivity of the reaction is consistent with a concerted [4 + 2] cycloaddition followed by a suprafacial H-transfer. Since stepwise cycloaddition mechanism would potentially lead to a mixture of diastereomers, the formation of one diastereomer was taken as evidence for a concerted cycloaddition reaction pathway.

In carbon chemistry, a concerted [4 + 2] cycloaddition is typically favoured when an electron rich diene interacts with an electron deficient dienophile. Interestingly, the reaction between phosphaalkene **1** and 4-trifluoromethyl-1-ethynylbenzene, the aromatic alkyne with the strongest electron withdrawing group, took the least amount of time (16 h), compared to the time required to react with phenylacetylene (4 days) or with the (relatively) electron rich 4-ethynylanisole (6 days). Thus, phosphaalkene **1**, when acting as a diene, appears to follow similar reactivity trends as carbon-based dienes. The enhanced reactivity with electron deficient alkynes also provides evidence that phosphaalkene **1** is electron rich and that conjugation between the P═C bond and at least one C–Ph substituent is present.[23] With this analysis, it is not surprising then that there was no reaction observed with the aliphatic alkynes since alkyl groups are known to be electron donating.

Methyl propiolate, an electron deficient alkyne, reacted with phosphaalkene **1**; however, the reaction was not clean. The presence of the ester functionality in methyl propiolate, in addition to the C≡C triple bond, likely leads to side reactions between the phosphaalkene and the carbonyl group.

Phosphaalkenes **2** and **3** showed limited reactivity towards alkynes. Neither phosphaalkene reacted with phenylacetylene or hexyne and only complex product mixtures were formed upon treatment with methyl propiolate. In the absence of an *C*-aryl substituent, the [4 + 2] cycloaddition pathway is unavailable and, without this reaction pathway, it appears that phosphaalkenes do not readily react with alkynes, which is consistent with a thermally forbidden [2 + 2] cycloaddition. The electronic nature of the substituents on the phosphaalkene did not have any significant influence on the reactivity of these phosphaalkenes.

Once again, phosphaalkenes mimic the chemistry of alkenes more so than silenes in terms of their reactivity towards alkynes. In alkene chemistry, [2πs + 2πs] cycloaddition reactions are thermally forbidden;[29] the same reaction appears to be thermally forbidden in phosphaalkene chemistry as evidenced by the lack of [2 + 2] cycloaddition between phosphaalkenes **1–3** and the terminal alkynes. The previously reported examples of formal [2 + 2] cycloadditions between phosphaalkenes and alkynes all involved electron rich–electron poor combinations of reagents,[8,10] which likely promoted stepwise addition mechanisms. In contrast, the [2 + 2] cycloaddition of alkynes to the relatively non-polar Brook silenes occurs readily to give a silacyclobutene[4a,b,6] and naturally polarized silenes add readily across the CH bond of terminal alkynes.[4c] In general, silenes appear to be more reactive than phosphaalkenes.[3,6,30] On the other hand, [4πs + 2πs] cycloaddition reactions are thermally allowed in carbon chemistry. The preference for phosphaalkenes to undergo [4 + 2] rather than [2 + 2] cycloaddition reactions suggests that the [4 + 2] pathway is lower in energy than a stepwise [2 + 2] pathway. The observed reactivity of phosphaalkenes **1–3** with alkynes provides further support for the diagonal relationship between the chemistry of low valent phosphorus and carbon compounds.[1]

Under photochemical conditions, a [2πs + 2πs] cycloaddition of alkenes is symmetry allowed. Since phosphaalkenes **1–3** appear to behave in a similar manner to alkenes, alkyne cycloaddition may be achieved through excitation of the P═C bond. Unfortunately, this was not observed. *E*/*Z* isomerization of the P═C bond in phosphaalkene **3** was observed providing evidence

that the P=C bond was indeed being excited; however, the excited state may have an extremely short lifetime making reaction with the alkyne unlikely. Under the conditions examined, an excited state may not have been achieved with phosphaalkenes **1** and **2**.

Properties of 1,2-dihydrophosphinines 4a–c

Based on the UV-VIS spectral data, the central six-membered ring and the fused aromatic ring of 1,2-dihydrophosphinines **4a–c** are conjugated. π-Conjugated organophosphorus derivatives are of current interest due to their interesting optical and electronic properties.[31] Phospholes, in particular, have been investigated extensively in the development of new materials for solar cells and organic light emitting diodes.[32] In contrast to pyrroles, phospholes do not exhibit a high degree of aromaticity. The lone pair does not interact with the π-system very efficiently since phosphorus has a much higher barrier for planarization than nitrogen. The small amount of aromatic character that is present in phospholes arises from hyperconjugation between the exocyclic P–R σ-bond and the π-system. Phospholes also have a high electron affinity, similar to that of siloles. The combination of low aromaticity, σ–π hyperconjugation, and high electron affinity separates phospholes from both pyrroles and thiophenes in terms of optical and electronic properties, which makes them desirable as materials in various photonic applications.

Other types of phosphorus-containing ring systems, such as phosphinines and 1,2-dihydrophosphinines, have not been studied to the same extent as phospholes with respect to their potential for use in π-conjugated materials. Like phospholes, 1,2-dihydrophosphinines **4a–c** are photoluminescent; absorption of light in the UV range gives rise to emission in the visible range at ~450 nm. In general, 1,2-dihydrophosphinines are not photoluminescent;[19] however, the additional π-conjugation from the fused aromatic ring appears to significantly influence the photoluminescent properties in **4a–c**. The phosphorus(III) centre, in addition to the extended conjugated π-system, apparently plays an important role in the photoluminescence of **4a–c** since the corresponding phosphine sulfides **6a–c** are colourless. Although it has not been determined whether there is any σ–π hyperconjugation between the exocyclic P–Mes bond and the cyclic diene moiety, it seems likely that σ–π hyperconjugation is present in **4a–c** since modification of the geometry at P, through oxidation, affects the emission. A crystal structure of the P(III) derivative is needed to give insight into the geometry at phosphorus in **4a–c**. The emissive behaviour of these systems is interesting. The preparation of **4a–c** is simple and could easily be performed on a large scale, which may promote future interest in these systems; however, a larger substituent on phosphorus will be required to prevent oxidation under ambient conditions.

Conclusions

We have examined the addition of simple alkynes to three different phosphaalkenes (**1**, **2**, **3**) under thermal and photochemical conditions. Luminescent 1,2-dihydrophosphinines **4a–c** were formed quantitatively when 4-trifluoromethyl-1-ethynylbenzene, phenylacetylene, or 4-ethynylanisole was added to $MesP{=}CPh_2$ (**1**) although isolated yields are only moderate due to oxidation at the P(III) centre upon chromatography. Phosphaalkene **1** can be produced readily in large quantities, is easy to handle, and is stable under an inert atmosphere for extended periods of time. Furthermore, several phenyl-substituted derivatives of **1** can be synthesized in good yield,[13b] and thus, the addition of alkynes to phosphaalkenes may offer a simple, direct route to a variety 1,2-dihydrophosphinines from readily available starting materials.

Phosphaalkene **1** acts as the 4π component in the cycloaddition reactions with aromatic terminal alkynes, through the use of the *C*-phenyl substituent, to yield bicyclic phosphorus heterocycles. The addition of a number of aliphatic alkynes to **1** was also attempted; however, no products were observed or isolated. Phosphaalkenes **2** and **3** showed very little reactivity towards terminal alkynes and no reaction was observed upon irradiation of any of the phosphaalkenes (**1**, **2**, or **3**) with phenylacetylene or hexyne.

The general lack of reactivity with terminal alkynes emphasizes that phosphaalkenes do indeed mimic alkenes in terms of their cycloaddition chemistry. Regardless of the polarity of the phosphaalkene examined, [2 + 2] cycloaddition with aromatic/aliphatic terminal alkynes does not appear to be a favoured reaction.

Experimental

General experimental details

All reactions were carried out under an inert atmosphere (argon) in flame-dried NMR tubes. The C_6D_6 was distilled from $LiAlH_4$, degassed prior to use, and then stored over 4 Å molecular sieves. Hexanes and dichloromethane were dried using a solvent purification system (Innovative Technologies Inc., Newburyport, Massachusetts) in which the solvent was passed through an alumina-packed column. Phenylacetylene, 4-trifluoromethyl-1-ethynylbenzene, 4-ethynylanisole, hexyne, *t*-butylacetylene, trimethylsilylacetylene, and methyl propiolate were purchased from the Aldrich Chemical Co. and stored over 4 Å molecular sieves. *P*-Mesityldiphenylmethylenephosphine, **1**,[13b] *P*-[bis(trimethylsilyl)amino][(trimethylsilyl)methylene]phosphine, **2**,[14] and *P*-mesityl [(*t*-butyl)(trimethylsiloxy)methylene]phosphine, **3**,[15] were prepared according to reported procedures.

The NMR spectra were recorded on a Varian Mercury 400, Inova 400 or Inova 600 spectrometer. The internal NMR standards used were residual C_6D_5H (7.15 ppm) for ^1H NMR spectra and the central signal of C_6D_6 (128.00 ppm) for ^{13}C NMR spectra. An external standard of 85% H_3PO_4 (0 ppm) was used for the ^{31}P NMR spectra and C_6F_6 (−164.9 ppm) was used for the ^{19}F NMR spectra. Electron impact mass spectra were obtained using a MAT model 8400 mass spectrometer using an ionizing voltage of 70 eV. Mass spectral data are reported in mass-to-charge units, *m*/*z*. IR spectra were recorded (cm^{-1}) from thin films on a Bruker Tensor 27 FT-IR spectrometer.

General procedure for the addition of aromatic alkynes to phosphaalkene 1

A solution of phosphaalkene (100 mg, 0.3 mmol) and excess alkyne in C_6D_6 (1.5 mL) was heated to reflux. The reaction was

monitored by ^{1}H and ^{31}P NMR spectroscopy. Phosphaalkene **1** was completely consumed after 20 h, 4 days, or 6 days of heating with 4-trifluoromethyl-1-ethynylbenzene, phenylacetylene, or 4-ethynylanisole, respectively. Upon completion of the reaction, the solvent and excess alkyne were removed under vacuum. The crude products were sticky yellow solids. Preparative thin-layer chromatography was performed to purify the crude products (silica gel, 1 : 1 CH_2Cl_2–hexanes) yielding 1,2-dihydrophosphinine **4a–c** (23–33% isolated yields) as bright green waxy solids. Compounds **4a–c** oxidized slowly in air and upon adsorption to silica, and thus, it was difficult to obtain samples of high purity (>95%). The products were stored under nitrogen to prevent further oxidation.

4a: green waxy solid; UV-VIS (THF): λ_{max} = 344 nm, λ_{em} = 449, 476 nm; ^{1}H NMR (C_6D_6) δ 1.93 (s, 3 H, Mes *p*-CH_3), 2.47 (s, 6 H, Mes *o*-CH_3), 5.53 (br s, 1 H, P–CHPh), 6.43 (d, J_{PC} = 17 Hz, 1 H, P–CH=CAr), 6.58 (br s, 2 H, Mes–H), 6.87–6.90 (m, 3 H, Bi–Ar 2/3/4-H), 6.95–6.97 (m, 1 H, Ph *p*-H), 7.02–7.06 (m, 3 H, Ph *m*-H/Bi–Ar 1-H), 7.11–7.12 (m, 2 H, Ar *o*-H), 7.33–7.35 (m, 4 H, Ph *o*-H/Ar *m*-H); ^{13}C NMR (C_6D_6) δ 20.85 (Mes *p*-CH_3), 24.14 (d, J_{PC} = 16 Hz, Mes *o*-CH_3), 45.90 (d, J_{PC} = 12 Hz, P–CHPh), 125.07 (q, J_{FC} = 270 Hz, CF_3), 125.61 (q, J_{FC} = 4.0 Hz, Ar *m*-C), 126.63 (d, J_{PC} = 21 Hz, Mes *i*-C), 126.91 (Bi-Ar 3-C), 126.96 (d, J_{PC} = 2.9 Hz, Ph *p*-C), 128.1[33] (Bi-Ar 4-C), 128.53 (Bi-Ar 2-C), 128.65 (d, J_{PC} = 5.7 Hz, Bi-Ar 1-C), 128.79 (Ph *m*-C), 128.89 (d, J_{PC} = 2.9 Hz, Ar *o*-C), 129.30 (q, J_{FC} = 18 Hz, Ar *p*-C), 130.21 (d, J_{PC} = 3.9 Hz, Mes *m*-C), 130.40 (d, J_{PC} = 8.6 Hz, Ph *o*-C), 132.78 (d, J_{PC} = 19 Hz, P–CH=CAr), 136.20 (d, J_{PC} = 2.9 Hz, PCH–C=CAr), 138.33 (d, J_{PC} = 13 Hz, PCHPh–C=C), 139.90 (Mes *p*-C), 140.42 (d, J_{PC} = 12 Hz, Ph *i*-C), 142.90 (d, J_{PC} = 12 Hz, P–CH=CAr), 145.66 (d, J_{PC} = 15 Hz, Mes *o*-C), 146.65 (Ar *i*-C); ^{31}P NMR (C_6D_6) δ −26.0; ^{19}F NMR (C_6D_6) δ −62.1; High-Resolution EI-MS for $C_{31}H_{26}PF_3$ *m*/*z* calcd 486.1724, found 486.1716.

4b: green waxy solid; UV-VIS (THF): λ_{max} = 336 nm, λ_{em} = 449, 478 nm; ^{1}H NMR (C_6D_6) δ 1.92 (s, 3 H, Mes *p*-CH_3), 2.48 (s, 6 H, Mes *o*-CH_3), 5.56 (br s, 1 H, P–CHPh), 6.52 (d, J_{PH} = 19 Hz, 1 H, P–CH=CAr), 6.57 (br s, 2 H, Mes–H), 6.87–6.88 (m, 2 H, Bi-Ar 2/4-H), 6.95 (t, J = 7.5 Hz, 1 H, Ph *p*-H), 7.02–7.05 (m, 3 H, Ph *m*-H/Bi–Ar 1-H), 7.10–7.13 (m, 1 H, Ar *p*-H), 7.15–7.18 (m, 3 H, Bi–Ar 3-H/Ar *m*-H), 7.32–7.34 (m, 2 H, Ar *m*-H), 7.36 (d, J = 8.4 Hz, 2 H, Ph *o*-H); ^{13}C NMR (C_6D_6) δ 20.86 (Mes *p*-CH_3), 24.16 (d, J_{PC} = 17 Hz, Mes *o*-CH_3), 45.99 (d, J_{PC} = 11 Hz, P–CHPh), 126.77 (Ph *p*-C), 126.80 (Bi–Ar 4 or 2-C), 127.18 (d, J_{PC} = 22 Hz, Mes *i*-C), 127.43 (Ar *p*-C), 128.30, 128.50, 128.53, 128.66, 128.68, 128.70 (Ph *m*-C/Bi–Ar 1 and 3-C/Bi–Ar 2 or 4-C/Ar *o*- and *m*-C), 130.13 (d, J_{PC} = 3.5 Hz, Mes *m*-C), 130.42 (d, J_{PC} = 8.0 Hz, Ph *o*-C), 130.69 (d, J_{PC} = 18 Hz, P–CH=CAr), 136.89 (d, J_{PC} = 3.5 Hz, PCHPh–C=C), 138.38 (d, J_{PC} = 13 Hz, PCHPh–C=C), 139.56 (Mes *p*-C), 140.82 (d, J_{PC} = 11 Hz, Ph *i*-C), 143.32 (d, J_{PC} = 2.3 Hz, Ar *i*-C), 144.43 (d, J_{PC} = 10 Hz, P–CH=CAr), 145.68 (d, J_{PC} = 16 Hz, Mes *o*-C); ^{31}P NMR (C_6D_6) δ −27.0; High-Resolution EI-MS for $C_{30}H_{27}P$ *m*/*z* calcd 418.1850, found 418.1844.

4c: green waxy solid; UV-VIS (THF): λ_{max} = 344 nm, λ_{em} = 467 nm; ^{1}H NMR (C_6D_6) δ 1.93 (s, 3 H, Mes *p*-CH_3), 2.52 (s, 6 H, Mes *o*-CH_3), 3.33 (s, 3 H, OCH_3), 5.58 (br s, 1 H, P–CHPh), 6.53 (d, J_{PH} = 18 Hz, 1 H, P–CH=CAr), 6.58 (br s, 2 H, Mes–H), 6.78–6.80 (m, 2 H, Ar *m*-H), 6.89–7.00 (m, 3 H, Ph *p*-H/Bi–Ar 2- and 3-H), 7.03–7.06 (m, 3 H, Ph *m*-H/Bi–Ar 1-H), 7.26–7.28 (m, 3 H, Bi–Ar 4-H/Ar *o*-H), 7.38 (d, J = 7.8 Hz, 2 H, Ph *o*-H); ^{13}C NMR (C_6D_6) δ 20.85 (Mes *p*-CH_3), 24.18 (d, J_{PC} = 17 Hz, Mes *o*-CH_3), 46.04 (d, J_{PC} = 13 Hz, P–CHPh), 54.82 (OCH_3), 114.18 (Ar *m*-C), 126.76 (Ph *p*-C), 127.38 (d, J_{PC} = 23 Hz, Mes *i*-C), 128.27–128.29 (Bi–Ar 2/3-C), 128.50–128.54 (Bi–Ar 1/4-C), 128.68 (Ph *m*-C), 129.50 (d, J_{PC} = 18 Hz, P–CH=CAr), 129.81 (d, J_{PC} = 3.5 Hz, Ar *o*-C), 130.15 (d, J_{PC} = 4.7 Hz, Mes *m*-C), 130.43 (d, J_{PC} = 9.2 Hz, Ph *o*-C), 135.64 (d, J_{PC} = 3.5 Hz, Ar *i*-C), 137.12 (d, J_{PC} = 3.5 Hz, PCHPh–C=C), 138.55 (d, J_{PC} = 12 Hz, PCHPh–C=C), 139.50 (Mes *p*-C), 140.89 (d, J_{PC} = 11 Hz, Ph *i*-C), 144.10 (d, J_{PC} = 10 Hz, P–CH=CAr), 145.69 (d, J_{PC} = 15 Hz, Mes *o*-C), 159.59 (Ar *p*-C); ^{31}P NMR (C_6D_6) δ −27.3; High-Resolution EI-MS for $C_{31}H_{29}PO$ *m*/*z* calcd 448.1956, found 448.1966.

Oxidation of 1,2-dihydrophosphinine 4a–c with sulfur

Sulfur powder (25 mg, 0.75 mmol) was added to a solution of **4a–c**[34] (0.3 mmol)[35] in dichloromethane (3 mL) at room temperature. The reaction mixture was allowed to stir overnight. The excess sulfur powder was removed by filtration and the product mixture was purified by preparative thin-layer chromatography (silica gel, 9 : 1 hexanes–acetone). 1,2-Dihydrophosphinine sulfides **6a–c** were obtained as white solids (20–23% isolated yields). Compounds **6a–c** were contaminated with a small amount of the corresponding phosphinine oxides. Colourless crystals were grown by the slow diffusion of hexanes into an ether–benzene solution of **6a–c** and the molecular structures were determined by X-ray crystallography.

6a: colourless solid; IR cm^{-1} 701 (m), 739 (s, P=S), 824 (w), 1018 (w), 1067 (m), 1128 (m), 1168 (m), 1265 (m), 1323 (s), 1407 (w), 1451 (w), 1605 (w), 2850 (w), 2919 (w), 3052 (w); ^{1}H NMR (C_6D_6) δ 1.79 (s, 3 H, Mes *p*-CH_3), 2.64 (br s, 6 H, Mes *o*-CH_3), 5.17 (d, J_{PH} = 14 Hz, 1 H, P–CHPh), 6.03 (d, J_{PH} = 15 Hz, 1 H, P–CH=CAr), 6.43 (d, J_{PH} = 3.6 Hz, 2 H, Mes–H), 6.63–6.69 (m, 3 H, Bi–Ar 2/3/4-H), 6.74–6.75 (m, 1 H, Bi–Ar 1-H), 7.07–7.10 (m, 3 H, Ar *o*-H/Ph *p*-H), 7.22 (t, J = 7.5 Hz, 2 H, Ph *m*-H), 7.29–7.31 (m, 2 H, Ar *m*-H), 7.56 (d, J = 7.8 Hz, 2 H, Ph *o*-H); ^{13}C NMR (C_6D_6) δ 20.54 (Mes *p*-CH_3), 24.73 (Mes *o*-CH_3), 50.10 (d, J_{PC} = 47 Hz, P–CHPh), 124.75 (q, J_{FC} = 270 Hz, CF_3), 125.54 (d, J_{PC} = 73 Hz, P–CH=CAr), 125.86 (q, J_{FC} = 3.5 Hz, Ar *m*-C), 127.62 (d, J_{PC} = 3.5 Hz, Ph *p*-C), 128.1[33] (Ph *m*-C), 128.2[33] (Bi–Ar 3-C), 128.52 (d, J_{PC} = 3.3 Hz, Bi–Ar 4-C), 128.6[33] (d, J_{PC} = 90 Hz,[36] Mes *i*-C), 128.84 (Ar *o*-C), 129.72 (Bi–Ar 2-C), 130.44 (d, J_{PC} = 4.7 Hz, Ph *o*-C), 130.75 (q, J_{FC} = 32 Hz, Ar *p*-C), 130.87 (d, J_{PC} = 8.1 Hz, Bi–Ar 1-C), 131.49 (d, J_{PC} = 12 Hz, Mes *m*-C), 133.97 (d, J_{PC} = 4.7 Hz, Ph *i*-C), 134.46 (d, J_{PC} = 14 Hz, PCHPh–C=C), 136.03 (d, J_{PC} = 5.7 Hz, PCHPh–C=C), 140.09 (d, J_{PC} = 2.4 Hz, Mes *p*-C), 140.63 (d, J_{PC} = 9.2 Hz, Mes *o*-C), 143.28 (d, J_{PC} = 15 Hz, Ar *i*-C), 147.04 (*P*-CH=CAr); ^{31}P NMR (C_6D_6) δ 30.0; ^{19}F NMR (C_6D_6) δ −62.4; High-Resolution EI-MS for $C_{31}H_{26}F_3PS$ *m*/*z* calcd 518.1445, found 518.1435.

6b: colourless solid; IR cm^{-1} 685 (m), 698 (s, P=S), 735 (m), 780 (m), 850 (w), 1031 (w), 1076 (w), 1266 (w), 1444 (m), 1494 (m), 1556 (w), 1603 (m), 2922 (w), 3028 (w), 3058 (w); ^{1}H NMR (C_6D_6) δ 1.78 (s, 3 H, Mes *p*-CH_3), 2.69 (br s, 6 H,

Mes *o*-CH_3), 5.19 (d, J_{PH} = 15 Hz, 1 H, P–CHPh), 6.11 (d, J_{PH} = 17 Hz, 1 H, P–CH=CAr), 6.42 (d, J_{PH} = 3.0 Hz, 2 H, Mes–H), 6.62–6.66 (m, 2 H, Bi–Ar 2/3-H), 6.76 (d, J = 6.0 Hz, 1 H, Bi–Ar 1-H), 6.93 (d, J = 9.0 Hz, 1 H, Bi–Ar 4-H), 7.05 (t, J = 7.2 Hz, 1 H, Ph *p*-H), 7.10–7.14 (m, 3 H, Ar *m*,*p*-H), 7.19 (t, J = 7.2 Hz, 2 H, Ph *m*-H), 7.28 (d, J = 6.6 Hz, 2 H, Ar *o*-H), 7.64 (d, J = 7.2 Hz, 2 H, Ph *o*-H); ^{13}C NMR (C_6D_6) δ 20.53 (Mes *p*-CH_3), 24.68 (Mes *o*-CH_3), 50.18 (d, J_{PC} = 48 Hz, P–CHPh), 123.80 (d, J_{PC} = 75 Hz, P–CH=CAr), 127.45 (d, J_{PC} = 2.9 Hz, Ph *p*-C), 128.0[33] (Bi–Ar 3-C), 128.1[33] (Ph *m*-C), 128.64 (Ar *o*-C), 128.91 (Bi–Ar 4-C), 128.94 (Ar *m*-C), 129.01 (Ar *p*-C), 129.10 (d, J_{PC} = 81 Hz, Mes *i*-C), 129.41 (Bi–Ar 2-C), 130.51 (d, J_{PC} = 5.0 Hz, Ph *o*-C), 130.75 (d, J_{PC} = 8.7 Hz, Bi–Ar 1-C), 131.43 (d, J_{PC} = 11 Hz, Mes *m*-C), 134.25 (d, J_{PC} = 3.9 Hz, Ph *i*-C), 135.21 (d, J_{PC} = 14 Hz, PCHPh–C=C), 136.19 (d, J_{PC} = 5.7 Hz, PCHPh–C=C), 139.78 (d, J_{PC} = 3.0 Hz, Mes *p*-C), 139.96 (d, J_{PC} = 14 Hz, Ar *i*-C), 140.63 (d, J_{PC} = 9.6 Hz, Mes *o*-C), 148.78 (P–CH=CAr); ^{31}P NMR (C_6D_6) δ 30.3; High-Resolution EI-MS for $C_{30}H_{27}PS$ *m*/*z*, calcd 450.1571, found 450.1560.

6c: colourless solid; IR cm^{-1} 670 (s), 695 (s), 735 (s), 778 (m), 812 (m), 933 (w) 1031 (s), 1178 (s), 1253 (s), 1292 (m), 1331 (m), 1376 (w), 1411 (w), 1451 (m), 1510 (s), 1552 (w), 1606 (s), 2837 (w), 2929 (w), 2964 (w), 3033 (w); ^{1}H NMR (C_6D_6) δ 1.79 (s, 3 H, Mes *p*-CH_3), 2.72 (br s, 6 H, Mes *o*-CH_3), 3.32 (s, 3 H, OCH_3), 5.20 (d, J_{PH} = 14 Hz, 1 H, P–CHPh), 6.09 (dd, J_{PH} = 16 Hz, J = 1.8 Hz, 1 H, P–CH=CAr), 6.44 (d, J_{PH} = 3.6 Hz, 2 H, Mes–H), 6.65 (t, J = 7.5 Hz, 1 H, Bi–Ar 2-H), 6.70 (t, J = 7.5 Hz, 1 H, Bi–Ar 3-H), 6.72–6.75 (m, 2 H, Ar *m*-H), 6.76–6.78 (m, 1 H, Bi–Ar 1-H), 7.03–7.07 (m, 2 H, Bi–Ar 4-H/Ph *p*-H) 7.20–7.24 (m, 4 H, Ph *m*-H/Ar *o*-H), 7.66 (d, J = 7.8 Hz, 2 H, Ph *o*-H); ^{13}C NMR (C_6D_6) δ 20.54 (Mes *p*-CH_3), 24.69 (Mes *o*-CH_3), 50.19 (d, J_{PC} = 48 Hz, P–CHPh), 54.92 (OCH_3), 114.50 (Ar *m*-C), 122.09 (d, J_{PC} = 76 Hz, P–CH=CAr), 127.41 (d, J_{PC} = 3.5 Hz, Ph *p*-C), 127.92 (Bi–Ar 3-C), 128.0[33] (Ph *m*-C), 128.97 (d, J_{PC} = 2.4 Hz, Bi–Ar 4-C), 129.31 (d, J_{PC} = 79 Hz, Mes *i*-C), 129.37 (Bi–Ar 2-C), 130.01 (Ar *o*-C), 130.53 (d, J_{PC} = 4.5 Hz, Ph *o*-C), 130.77 (d, J_{PC} = 9.2 Hz, Bi–Ar 1-C), 131.43 (d, J_{PC} = 10 Hz, Mes *m*-C), 132.00 (d, J_{PC} = 15 Hz, Ar *i*-C), 134.33 (d, J_{PC} = 4.7 Hz, Ph *i*-C), 135.41 (d, J_{PC} = 14 Hz, PCHPh–C=C), 136.35, (d, J_{PC} = 5.7 Hz, PCHPh–C=C), 139.71 (d, J_{PC} = 2.3 Hz, Mes *p*-C), 140.59 (d, J_{PC} = 10 Hz, Mes *o*-C), 148.65 (P–CH=CAr), 160.87 (Ar *p*-C); ^{31}P NMR (C_6D_6) δ 30.4; High-Resolution EI-MS for $C_{31}H_{29}OPS$ *m*/*z* calcd 480.1677, found 480.1666.

General procedure for the addition of alkynes to phosphaalkenes 1, 2, and 3

A solution of phosphaalkene (0.3 mmol) and excess alkyne in C_6D_6 (1.5 mL) was heated to reflux. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. There was never any indication of reaction, except for when methyl propiolate was used. In that case, the solvent was removed by rotary evaporation yielding a yellow residue. Chromatographic separation of the crude product was attempted; however, no single compound was isolated.

General procedure for the addition of alkynes to phosphaalkenes 1, 2, and 3 under photochemical conditions

A solution of phosphaalkene (0.3 mmol) and excess alkyne in hexanes (1.5 mL) was irradiated at 254 nm in the cold (−70 °C) for 20 h using a Rayonet Photochemical Reactor. The choice of irradiation wavelength was made upon examination of the UV-VIS absorption data of the phosphaalkenes. The lowest energy absorptions were assigned to π to π* transitions: **1** 324 nm,[13b] **2** 280 nm (this work), **3** 310 nm.[37] The reaction was monitored by ^{31}P NMR spectroscopy. The ^{31}P signal for the phosphaalkene (**1–3**) was unchanged and no new signals were observed.

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