Structure and reactivity of tautomeric forms of zwitterionic species from the reaction of phosphorus(III) compounds with electron deficient alkenes and alkynes†

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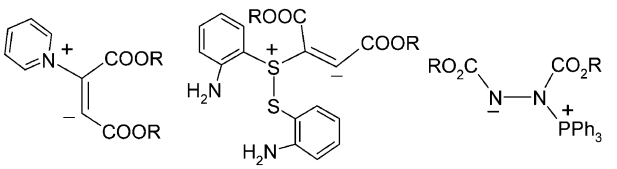
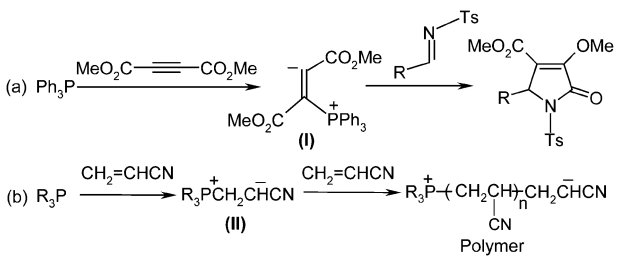
Synthesis and reactivity of tautomeric forms of the zwitterions proposed in the phosphine catalysed transformations of electron-deficient alkenes/alkynes using the heterocycles [(*t*-BuNH)PN-*t*-Bu]$_2$ (**1**) and Ph$_2$P(NH-*t*-Bu) (**2**) are discussed. Thus, compounds (*t*-BuNH)P(N-*t*-Bu)$_2$P(=N-*t*-Bu)CH=CH(CO$_2$Me) (**3**), (*t*-BuNH)P(N-*t*-Bu)$_2$P(=N-*t*-Bu)CH$_2$CH$_2$(CN) (**4**) and Ph$_2$P(N-*t*-Bu){C(Ph)=CH(CO$_2$Et)} (**5**) are isolated. A novel heterocycle [(*t*-BuNH)P(N-*t*-Bu)$_2$P[=C(CO$_2$Me)–CH(OMe)–C(O)–N(*t*-Bu)–] (**6**) obtained by utilizing **1** and MeO$_2$CC≡CCO$_2$Me is described. The structural proof for the second stage intermediate after the addition of phenols/carboxylic acids to the zwitterions formed in the reaction of electron deficient alkenes with P^{III} compounds [*e.g.* {(*t*-BuNH)P(N-*t*-Bu)$_2$P(NH-*t*-Bu)CH$_2$CH$_2$(CN)}$^+${X}$^-$ where X = PhO$^-$ + PhOH (**7** · Ph–O–H···OPh), 4-NO$_2$–C$_6$H$_4$–CO$_2^-$ + H$_2$O (**8** · H$_2$O)] is also provided for the first time. X-Ray structural characterisation of **3–8** has also been accomplished.

Introduction

A significant number of useful applications for a variety of organic transformations utilizing triphenylphosphine–dimethyl acetylenedicarboxylate (Ph$_3$P-DMAD) or a combination of a P(III) compound and an electron deficient alkene/alkyne has emerged in recent years.[1,2] The key intermediate in the reaction utilizing the Ph$_3$P-DMAD combination is assumed to be Ph$_3$P$^+$C(CO$_2$Me)=C$^-$(CO$_2$Me) (**I**) and the reaction products seem to justify this (*cf.* Scheme 1); similar intermediates are proposed utilizing other activated alkynes/alkenes. However, as shown by several workers, this combination does lead to many other products,[3] and to our knowledge, no conclusive proof for **I** is available. It is also known that phosphines initiate the polymerization of acrylonitrile and the zwitterion R$_3$P$^+$CH$_2$CH$^-$CN (**II**) has been proposed as the initiator.[4] In the first step of the phosphine catalysed Baylis–Hillman reaction also, species of type **II** may be involved.[5] By contrast, the reaction of Ph$_3$P with tetracyanoethylene (NC)$_2$C=C(CN)$_2$ leads to Ph$_3$P=N{C=C(CN)–C(CN)$_2$–C(CN)$_2$–C(CN)$_2$–}.[6] It is also important to note that in heterocyclic syntheses utilizing pyridine-DMAD or disulfide-DMAD, involvement of similar zwitterions **III–IV** are proposed, but detailed characterisation of such species is still to be undertaken.[7] The Morrison–Brunn–Huisgen intermediate (**V**) proposed in the well-known Mitsunobu reaction also has a similar betaine structure, but this intermediate has a well-defined ^{31}P NMR chemical shift of δ 44.8.[8]



In the above context, we were interested in identifying intermediates of type **I–II** in a more definitive way. Our previous success with the traditional 'inorganic heterocycle', the cyclodiphosphazane [(*t*-BuNH)PN-*t*-Bu]$_2$ (**1**) in the isolation of the tautomeric forms of Morrison–Brunn–Huisgen type intermediates[8d,e] prompted us to utilize the same precursor for the reaction with electron-deficient alkynes/ alkenes. Prior to our studies, use of the related cyclodiphosphazanes was largely on developing macrocycles and coordination complexes.[9] It is important to note that as a P^{III} substrate, compound **1** has three bulky N-*t*-Bu groups around phosphorus that could facilitate the isolation of the intermediates proposed in phospine-related organic reactions. To show that the results obtained here are common to other P(III) derivatives also, we have utilized the precursor Ph$_2$P(NH-*t*-Bu) (**2**).



Scheme 1

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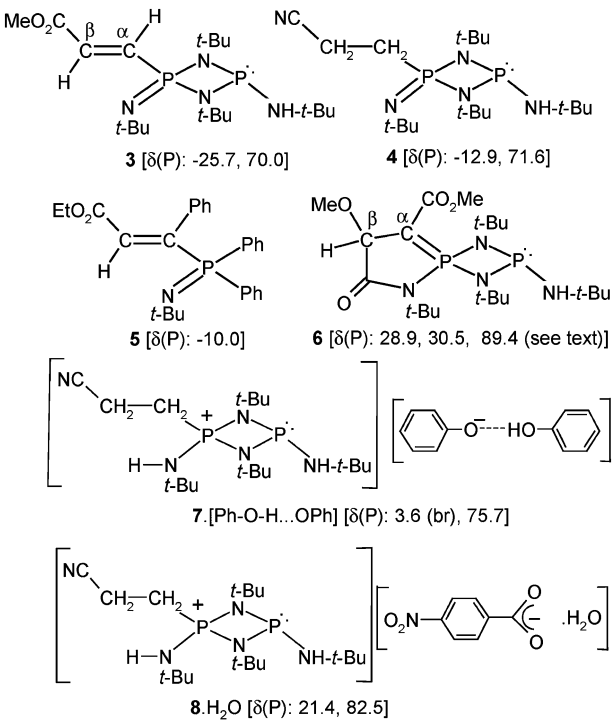
In this paper, the isolation and characterisation (X-ray structures) of the following new derivatives are reported.

(i) Tautomeric forms **3** and **4** of the expected zwitterionic compounds from the reaction of **1** with methyl propiolate [HC≡C(CO_2Me)] and acrylonitrile (H_2C=CHCN) and the compound **5** from the reaction of **2** with PhC≡CCO_2Et.

(ii) A novel heterocycle **6** in the reaction with DMAD.

(iii) The phenol/ acid addition products **7**·[Ph–O–H···OPh] and **8**·H_2O, obtained by treating **4** with phenol or 4-nitrobenzoic acid.

The stability of **3** *vis a vis* the *Z* isomer, the zwitterionic forms and the species resulting from the attack of phosphorus at the *C*(CO_2Me) centre are assessed by theoretical calculations at the B3LYP/6-31G** level. Compound **6** features a new type of ylidic phosphorus heterocycle. Isolation of **7**·Ph–O–H···OPh is also significant since similar species are invoked in the phosphine-catalysed reactions involving alcohols/ phenols.[1b,2f,q]



3 [δ(P): -25.7, 70.0] **4** [δ(P): -12.9, 71.6]

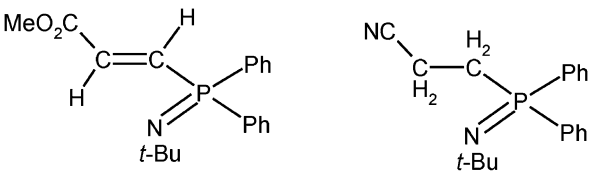
5 [δ(P): -10.0] **6** [δ(P): 28.9, 30.5, 89.4 (see text)]

7.[Ph-O-H...OPh] [δ(P): 3.6 (br), 75.7]

8.H_2O [δ(P): 21.4, 82.5]

Results and discussion

Compound **3** (Fig. 1) is formed by the direct addition of methyl propiolate to **1** in toluene. It is the tautomeric form of the zwitterion [(*t*-BuNH)P(N-*t*-Bu)$_2$P$^+$(NH-*t*-Bu)CH=C$^-$(CO_2Me); the second phosphorus remains essentially as a spectator. It is also clear from the X-ray structure that the *C*H carbon gets attached to phosphorus. In a similar fashion, the reaction of acrylonitrile with **1** leads to **4** (Fig. 2) with the *C*H_2 end attached to phosphorus. Encouraged by these results, we treated the acyclic aminophosphine Ph_2P(NH-*t*-Bu) [**2**, δ(P) 22.7] with methyl propiolate and acrylonitrile; although we are yet to isolate a pure compound, in each case a clear peak (>80%) at δ(P) −14.5 or −9.1 consistent with Ph_2P(=N-*t*-Bu)(CH=CHCO_2Me) (**VI**) and Ph_2P(=N-*t*-Bu)(CH_2CH_2CN) (**VII**), respectively, is observed. Fortunately, from the reaction of **2** with ethylphenyl propiolate [EtO_2CC≡CPh] we have been succesful in isolating the iminophosphonate Ph_2P(N-*t*-Bu){C(Ph)=CH(CO_2Et)} (**5**) (Fig. 3) in good yields. This observation clearly shows that the use of a P-NH-*t*-Bu group facilitates the isolation of P–C bonded compounds, but with the tautomeric imino structure.



(**VI**) (**VII**)

Formation of the heterocycle **6** [Scheme 2; Fig. 4] involves a novel cyclization in which a phosphazene nitrogen attacks the carbonyl carbon of the DMAD [MeO_2CC≡CCO_2Me] residue. Although reactions involving a C=O or C=NTs group and acetylenes in the presence of PPh_3 also leads to ring formation with methoxy migration,[1b,c,10] in our case cyclization involves a nitrogen which was a part of a P(III) component and attack of nitrogen occurs at the carbomethoxy group

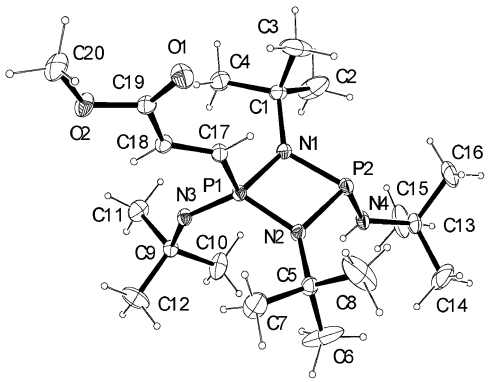


Fig. 1 Molecular structure of **3** with displacement ellipsoids at the 10% probability level.

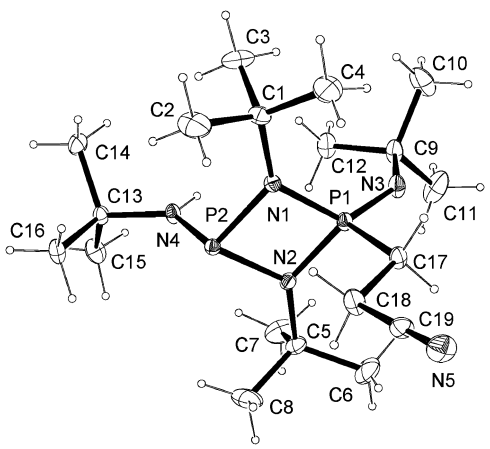


Fig. 2 Molecular structure of **4** with displacement ellipsoids at the 10% probability level.

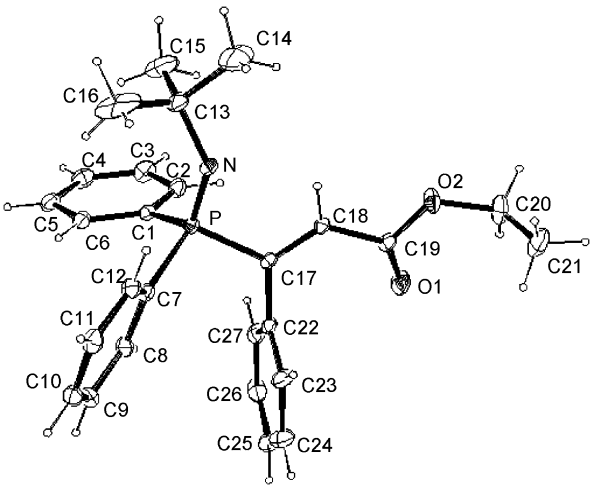
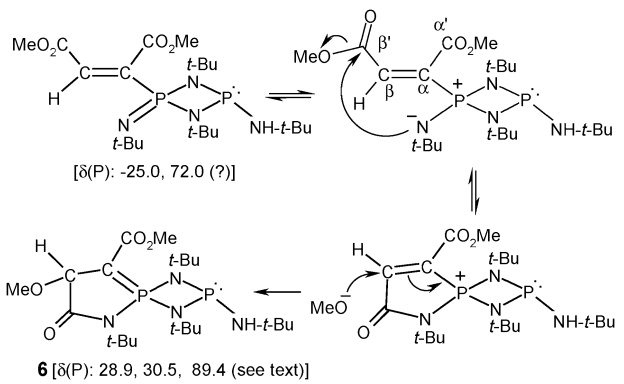


Fig. 3 Molecular structure of **5** with displacement ellipsoids at the 10% probability level. Selected bond distances (Å): P–N 1.525(4), P–C(1) 1.815(4).

connected to the carbon β to the phosphorus. This feature adds another interesting facet to the phosphine–alkyne combination. The initial reaction mixture, when **1** was treated with DMAD, showed major peaks (85%) at δ 72.2 (br), −25.0 (br), −35.3 (br), with the combined intensity of the peaks at δ −25.0 and −35.3 [P(v) region] nearly the same as the one at δ 72.2 [P(III) region]. These are clearly different from those for the final product **6**, but the peaks at δ 72.2 and −25.0 are close to that for **3** and clearly show that formation of **6** occurs *via* a species similar to **3**.

When we added DMAD to triphenylphosphine (1 : 1 stoichiometry) in C_6D_6 solution, we obtained a rather complicated ^{31}P NMR spectrum[11] but there was a broad peak at δ 48.3 (40–50%) close to that known for the Morrison–Brunn–Huisgen intermediate **V** [δ(P) 44.8].[8] The broadness of the peak at δ 48.3 suggests an equilibrium between **I** and other species, as suggested by earlier workers.[3a]

In the phosphine catalysed nucleophilic addition to alkynoates/alkenoates, species such as **VIII–IX** are proposed as intermediates.[2a,b,h,j,k,l,n] The first structural proof for these is provided by compounds **7**·[Ph–O–H···OPh] (Fig. 5) and **8**·H_2O (Fig. 6).[12] The ^{31}P NMR spectrum of the reaction



Scheme 2

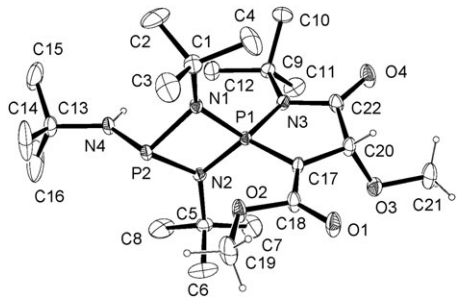


Fig. 4 Molecular structure of **6** with displacement ellipsoids at the 15% probability level (*tert*-butyl hydrogen atoms not shown).

mixture from [**3** + phenol] exhibited mainly two peaks (*ca.* 85%) at δ 71.9 and −16.4 corresponding to **7**·[Ph–O–H···OPh]; thus there is a downfield shift of ∼9 ppm for the tetracoordinate region consistent with the protonated phosphonium salt.

The hydrogen-bonded complex $Ph_3P^+CH_2CH{=}CH(Me)–O^-\cdots HOAr$ was proposed recently in the phosphine–phenol cocatalysed Morita–Baylis–Hillman (MBH) reaction using methyl vinyl ketone.[5c] Although hydrogen-bonding in **7** is different from this (note: acrylonitrile is also used in MBH reaction), it may be fruitful to study hydrogen-bonding effects in these cocatalysed reactions in greater depth.

It can be noted that at least four other isomeric forms (**3a–3d**) are feasible for **3** (Fig. 7). To check the stability of these isomers, we have performed theoretical calculations (B3LYP/6-31G**) on the observed structure **3** and the isomeric forms **3a–3d**. Destabilization (kcal mol^{-1}) with respect to the crystallographically observed form **3** is as follows: **3** (0.00) < **3a** (+7.40) < **3b** (+30.68) and **3c** (+4.94) < **3d** (+36.38). Thus the theory agrees well with the experimental results. The difference in energy between the *E* (*i.e.* **3**) and *Z* (*i.e.* **3a**) forms is not large. Hence, *E* and *Z* forms for the intermediate [(*t*-BuNH)P(N-*t*-Bu)$_2$P(=N-*t*-Bu)C(CO$_2$Me)=CH(CO$_2$Me) from the reaction of **1** with DMAD are also likely to be close in energy, facilitating the attack of

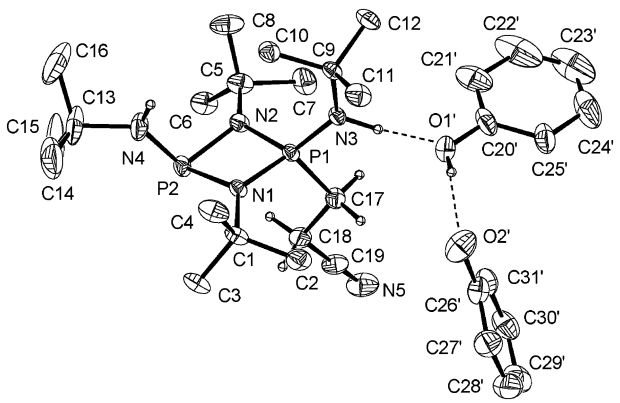


Fig. 5 An ORTEP drawing of **7**·[Ph–O–H···OPh] with displacement ellipsoids at the 15% probability level (*tert*-butyl and phenyl hydrogen atoms omitted). Hydrogen bond parameters (Å, Å, Å, °): N3–H3···O1′ 1.02(3), 1.62(4), 2.626(3), 168(3); O1′–H1′···O2′ 0.93(6), 1.77(7), 2.525(5), 137(6). [Symmetry code: (i) 1 + *x*, 1 + *y*, *z*.]

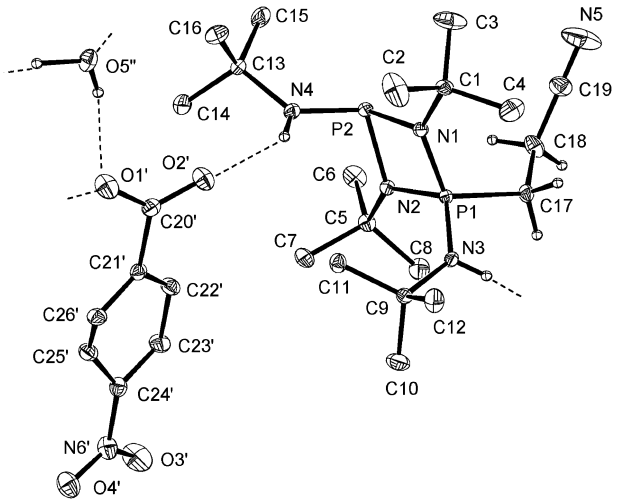


Fig. 6 Molecular structure of $\mathbf{8}\cdot H_2O$ with displacement ellipsoids at the 15% probability level. Hydrogen bond parameters (Å, Å, Å, °): N4–H4···O2′ 0.75(3), 2.54(3), 3.188(4), 147(3); O5″–H5A″···O1′ 0.78(3), 2.03(3), 2.782(3) 164(3); O5″–H5B″···O1‴ 1.12(7), 1.69(7), 2.789(3), 167(6); N3–H3···O5⁗ 0.80(3), 2.03(3), 2.824(3), 173(3). [Symmetry codes: (i) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$, (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$, (iii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$, (iv) $2-x, 1-y, 1-z$.]

nitrogen on the carbonyl group at the β-carbon in the cyclization leading to **6**.

A brief description of the X-ray structures

The P–N (imino) distances in **3–5** (Table 1 and Fig. 3) are in the range 1.523 ± 0.003 Å and are close to that found in $(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})_2P[(N\text{-}t\text{-Bu})(N\text{–}(CO_2Et)\text{–}N(H)(CO_2Et))]$ [1.533(1) Å].[8e] These are in the range expected for P=N bonds.[13] Compounds $\mathbf{7}\cdot$[Ph–O–H···OPh] and $\mathbf{8}\cdot H_2O$ are phosphonium salts with a P–N single bond as reflected by the comparatively longer bond distances [1.580(2) and 1.600(2) Å, respectively]. However, these latter distances are significantly shorter than the P–N distance in the heterocycle **6** [1.704(3)], most likely due to favourable additional π-interactions.[14] The P–C distances are also in line with the structures as written, and the one for **6** is the shortest, as expected. The structure of **6** can also be written in the phosphonium form (**6′**), but considering the short P–C distance contribution from this structure may not be very significant. No *cis–trans* isomerization of the NH-*t*-Bu substituents had taken place

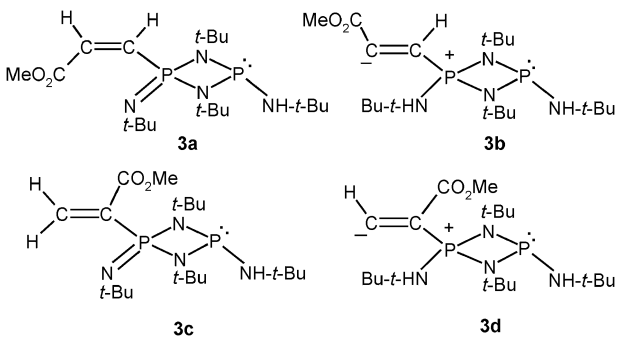
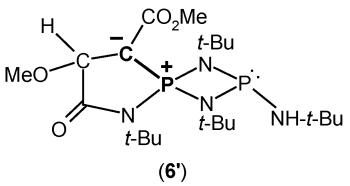


Fig. 7 Isomeric structures for **3** that were used for calculations.

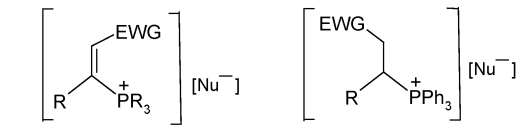
Table 1 P–N and P–C bond distances (Å) with e.s.d.s for **3**, **4**, **6**, $\mathbf{7}\cdot$[Ph–O–H···OPh] and $\mathbf{8}\cdot H_2O$

Compound	**3**	**4**	**6**	$\mathbf{7}\cdot$[Ph–O–H···OPh]	$\mathbf{8}\cdot H_2O$
P(1)–N(1)	1.680(3)	1.678(2)	1.639(3)	1.647(2)	1.641(2)
P(1)–N(2)	1.679(2)	1.681(2)	1.657(3)	1.643(2)	1.641(2)
P(1)–N(3)	1.521(2)	1.526(2)	1.704(3)	1.580(2)	1.600(2)
P(1)–C(17)	1.791(3)	1.819(2)	1.697(4)	1.805(3)	1.812(2)
P(2)–N(1)	1.744(3)	1.735(2)	1.765(3)	1.747(2)	1.764(2)
P(2)–N(2)	1.731(2)	1.734(2)	1.756(3)	1.759(2)	1.773(2)
P(2)–N(4)	1.651(3)	1.657(2)	1.626(4)	1.629(3)	1.639(2)

during these reactions.



(6′)



EWG = CO_2R, C(O)R etc
R = Alkyl, CO_2Me etc
Nu = -OAr, -OR, thiobenzamidato etc

(VIII)

EWG = CN, CO_2R, C(O)Me
Nu = oximato

(IX)

In compounds $\mathbf{7}\cdot$[Ph–O–H···OPh] and $\mathbf{8}\cdot H_2O$, there are additional hydrogen bonding interactions involving the phenolate or carboxylate oxygen atoms. Although the presence of additonal phenol in $\mathbf{7}\cdot$[Ph–O–H···OPh] looks rather awkward, analgous hydrogen bonding situations may be responsible for bringing the reactants together. As noted above, this aspect needs further study.

Conclusions

Herein, we have provided good structural evidence for the initial phosphorus–carbon bond formation proposed in the phosphine-catalysed reactions of activated alkynes/alkenes through the isolation of the tautomeric forms of the expected betaines. It is possible that the zwitterions can be stabilized by using groups such as $-NR_2$ that do not contain a tautomerizable proton, but we are yet to succeed in isolating them. We have characterised a novel heterocycle **6** featuring phosphorus from the reaction of a P(III) precursor with DMAD. We have also been successful in reactions with vinyl sulfones, dimethyl maleate, *etc*. and hence the reaction is quite general; utility of the compounds thus synthesized needs to be explored.[15]

Experimental

Chemicals were procured from Aldrich/ Fluka or from local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[16] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^1H, ^{13}C and $^{31}P\{H\}$ NMR spectra were recorded on a Bruker 200 MHz or 400 MHz spectrometer in $CDCl_3$ solutions (unless stated otherwise), with shifts

referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$). IR spectra were recorded on a JASCO FT/ IR-5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C or Thermo Finnigan EA1112 analyzer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected.

Precursors **1** and **2** were prepared using literature procedures.[17]

Compound 3

To a solution of **1** (0.572 g, 1.64 mmol) in toluene (10 cm^3), methyl propiolate (0.137 g, 1.64 mmol) was added *via* syringe at room temperature and mixture was stirred for 4 h; the solution was concentrated *in vacuo* (to *ca.* 1.5 cm^3) and cooled for 24 h at −4 °C to obtain crystals of **3**. Yield: 0.638 g (90%) (found: C 55.33, H 9.67, N 12.78. $C_{20}H_{42}N_4O_2P_2$ requires C 55.54, H 9.78, N 12.95%); mp 96–100 °C; ν_{max}(KBr)/cm^{-1} 3347, 2971, 1717, 1632, 1368, 1327, 1232; δ_H (400 MHz, $CDCl_3$) 1.32 and 1.38 (2 s, 36H, *t*-Bu-*H*), 2.81 (br, d, 1H, ^2J(P–H) ∼ 6.0 Hz, N*H*), 3.76 (s, 3H, CO_2CH_3), 6.59 (dd, 1H, ^3J(HH) = 8.0 Hz, ^2J(P–H) = 16.0 Hz, PC*H*), 6.79 (dd, 1H, ^3J(P–H) = 16.0 Hz, ^3J(HH) = 8.0 Hz, PCC*H*); δ_C (50 MHz, $CDCl_3$) 32.0 (t, ^3J(P–C) = 5.0 Hz, two of $C(CH_3)_3$), 33.4 (d, ^3J(P–C) = 10.0 Hz, $C(CH_3)_3$), 34.6 (d, ^3J(P–C) = 12.0 Hz, $C(CH_3)_3$), 51.4 (s, $C(CH_3)_3$), 51.7 (s, CO_2CH_3), 51.9 (d, ^2J(P–C) = 7.5 Hz, $C(CH_3)_3$), 52.5 (d, ^2J(P–C) = 10.0 Hz, $C(CH_3)_3$), 132.2 (s, *C*H (COOCH$_3$)), 147.5 (d, ^1J(P–C) = 168.9 Hz, P*C*), 166.3 (d, ^3J(P–C) = 25.0 Hz, CO_2CH_3); δ_P (160 MHz, $CDCl_3$) −25.7, 70.0.

Compound 4

The procedure was the same as that for **3** using **1** (0.571 g, 1.63 mmol) and acrylonitrile (0.086 g, 1.63 mmol) [reaction time 2 d]. Yield 0.59 g (90%) (found: C 56.63, H 10.25, N 17.19. $C_{19}H_{41}N_5P_2$ requires C 56.84, H 10.29, N 17.44%); mp 88–91 °C; ν_{max}(KBr)/cm^{-1} 3345, 2959, 2255, 2236, 1470, 1333, 1209; δ_H (400 MHz, $CDCl_3$) 1.29, 1.34, 1.41 (3 s, 36H, *t*-Bu-*H*), 2.29 (br, 4H, PCH_2CH_2), 2.96 (br, d, 1H, ^2J(P–H) = 16.0 Hz, N*H*); δ_C (50 MHz, $CDCl_3$) 12.1 (s, $PCCH_2$), 29.0 (d, ^1J(P–C) = 135.0 Hz, P*C*), 31.9 (s, NC(CH_3)$_3$), 32.8 (d, ^3J(P–C) = 10.0 Hz, (C(CH_3)$_3$), 34.2 (d, ^3J(P–C) = 12.0 Hz, NC(CH_3)$_3$), 51.9–52.4 (many lines, $C(CH_3)_3$), 119.5 (s, *C*N); δ_P (160 MHz, $CDCl_3$) −12.9, 71.6.

Compound 5

The procedure was the same as that for **3** using Ph_2P(NH-*t*-Bu) (**2**) [δ(P) 22.7 (lit.,[17] 22.5)] (0.82 g, 3.18 mmol) and ethyl phenyl propiolate (0.55 g, 3.18 mmol) [reaction time 24 h]. Yield: 1.16 g (85%) (found: C 75.42, H 6.96, N 3.17. $C_{27}H_{30}NO_7P$ requires: C 75.14, H 7.00, N 3.26%); mp 101–104 °C; ν_{max}(KBr)/cm^{-1} 3055, 2963, 1728, 1620, 1437, 1265, 1194; δ_H (400 MHz, $CDCl_3$) 1.01 (t, 3H, ^3J(H–H) = 7.0 Hz, OCH_2CH_3), 1.13 (s, 9H, *t*-Bu-*H*), 4.00 (qrt, 2H, ^3J(H–H) = 7.0 Hz, OCH_2CH_3), 6.58 (d, ^3J(P–H) ∼ 7.0 Hz 1H, PCC*H*), 7.00–7.65 (m, 15H, Ar*H*); δ_C (50 MHz, $CDCl_3$) 13.7 (s, OCH_2CH_3), 31.5 (s, C(CH_3)$_3$), 32.9 (d, ^3J(P–C) = 10.0 Hz, C(CH_3)$_3$), 34.7 (br, C(CH_3)$_3$), 52.0 (br, $C(CH_3)_3$), 60.1 (s, $CO_2CH_2CH_3$), 127.3, 128.1, 128.7, 131.2, 131.6, 131.8, 140.0, 133.6 (Ar–C + PC + PCC), 165.0 (br, *C*=O); δ_P (80 MHz, $CDCl_3$) −8.5.

Compound 6

To a solution of **1** (0.554 g, 1.58 mmol) in toluene (15 cm^3), DMAD (0.225 g, 1.58 mmol) was added *via* syringe at 0 °C and the mixture was stirred for 20 min, the solution was stirred further at room temperature for 20 min. The reaction mixture at this stage showed the following major peaks in the ^{31}P NMR: δ 90.2, 72.2 (br), 31.8, 30.1, −25.0 (br), −35.3 (br). The intensity of the broad peaks corresponded to *ca.* 85%. The solution was concentrated *in vacuo* (to *ca.* 1 cm^3) and cooled at −4 °C for 48 h to obtain crystals of **6**. Yield: 0.697 g (90%) (found: C 53.86, H 9.06, N 11.67. $C_{22}H_{44}N_4O_4P_2$ requires C 53.86, H 9.04, N 11.42%); mp 174–178 °C; ν_{max}(KBr)/cm^{-1} 3337, 2971, 1713, 1655, 1223, 1061; δ_H (400 MHz, $CDCl_3$) 1.34, 1.36, 1.40, 1.44, 1.46, 1.75 (many lines, together 36H, *t*-Bu-*H*), 3.30 (br, 1H, NH), 3.56 (minor) and 3.61 (major) [2 s, 6H, OCH_3 + CO_2CH_3], 4.42 and 4.55 (2 d, the one at 4.55 is minor, ^3J(PH) = 18.8 and 18.8 Hz, respectively, 1H, C*H*(OCH_3); δ_C (50 MHz, $CDCl_3$): 28.5 (s, NC(CH_3)$_3$), 32.0 (d, ^3J(P–C) = 5.0 Hz, NC(CH_3)$_3$), 32.5 (d, ^3J(P–C) = 10 Hz, NC(CH_3)$_3$), 44.1, 44.3, 47.3, 48.8, 49.7, 52.1, 52.4, 54.5, 55.5, 54.8, 55.0, 57.2, 57.9 and 59.0 (many signals, $C(CH_3)_3$, OCH_3), 78.9, 79.2, 164.2, 174.8, 175.5 (as mentioned elsewhere,[3] the ^{13}C NMR spectrum was not very clear-cut in the assignment of signals); δ_P (160 MHz, $CDCl_3$) 28.9, 30.5, 89.4. The combined intensity of the tetracoordinate region (δ 28.9, 30.5) was nearly equal to the intensity of the signal at δ 89.4. This together with the ^{1}H NMR data suggests equilibrium in solution with an isomeric form for which the P(III) region is the same but the tetracoordinate phosphorus chemical shift is different.

Compound 7 · [Ph–O–H···OPh]

To a solution of **4** (0.599 g, 1.49 mmol) in toluene (10 cm^3), phenol (0.20 g, 2.13 mmol) was added all at once at room temperature and the mixture was stirred for 6 h, later the solution was concentrated *in vacuo* (to *ca.* 1.5 cm^3) and cooled to −4 °C for 24 h to obtain crystals of **7** · [Ph–O–H···OPh]. Yield: 0.58 g (65%) (found: C 63.24, H 9.02, N 11.82. $C_{31}H_{53}N_5O_2P_2$ requires C 63.13, H 9.06, N 11.86%); mp 92–95 °C; ν_{max}(CH_2Cl_2)/cm^{-1} 3380, 3100, 2971, 2180, 1589, 1472, 1370, 1071; δ_H (400 MHz, $CDCl_3$) 1.31, 1.45, 1.46 (3 s, 36H, *t*-Bu-*H*), 2.15 (br, 2H, $PCCH_2$), 2.48 (br, 3H, PCH_2 + N*H*), 3.40 (br, 1H, N*H*), 6.62–7.26 (m, 11H, Ar*H* + O*H*); δ_C (50 MHz, $CDCl_3$) 10.9 (s, $PCCH_2$), 26.6 (d, ^1J(P–C) = 121.3 Hz, P*C*), 31.8 (s, C(CH_3)$_3$), 32.3 (d, ^3J(P–C) = 9.0 Hz, C(CH_3)$_3$), 33.3 (d, ^3J(P–C) = 9.7 Hz, C(CH_3)$_3$), 52.0 (d, ^2J(P–C) = 14.5 Hz, $C(CH_3)_3$), 53.2 (s, N$C(CH_3)_3$), 53.5 (d, ^2J(P–C) = 10.0 Hz, $C(CH_3)_3$), 116.3, 118.8, 119.0,129.1 and 129.5 (*C*N and Ar*C*), 158.2 (s, Ar*C*O); δ_P (80 MHz, $CDCl_3$) 75.9 and 75.6 (probably a doublet, J ∼ 24.0 Hz), 3.6 (br).

Compound 8 · H_2O

To a solution of **4** (0.378 g, 0.94 mmol) in toluene (10 cm^3) 4-NO_2-benzoic acid (0.158 g, 0.94 mmol) was added all at once, the mixture was stirred for 6 h, concentrated *in vacuo*

Table 2 Crystal data for compounds **3**–**6**, **7**·[PhOH···OPh] and **8**·H_2O[a]

Compound	**3**	**4**	**5**[b]	**6**[c]	**7**·[Ph–O–H···OPh]	**8**·H_2O
Empirical formula	$C_{20}H_{42}N_4O_2P_2$	$C_{19}H_{41}N_5P_2$	$C_{27}H_{30}NO_7P$	$C_{22}H_{44}N_4O_4P_2$	$C_{31}H_{53}N_5O_2P_2$	$C_{26}H_{48}N_6O_5P_2$
M	432.52	401.51	431.49	490.55	589.72	586.64
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$Iba2$	Cc	$P\bar{1}$	$P2_1/c$
a/Å	18.0981(11)	9.5160(6)	19.157(4)	17.7038(18)	9.7355(6)	9.5994(4)
b/Å	9.9666(6)	16.5945(11)	25.897(6)	9.5956(10)	11.2481(6)	15.8414(7)
c/Å	16.1701(9)	15.9106(10)	9.9046(15)	17.7697(18)	17.0595(1)	21.0477(9)
α/°	90	90	90	90	92.455(1)	90
β/°	112.870(1)	91.692(1)	90	106.530(2)	105.381(1)	91.500(1)
γ/°	90	90	90	90	93.314(1)	90
V/Å^3	2687.4(3)	2511.4(3)	4913.7(16)	2893.9(5)	1794.9(2)	3199.6(2)
Z	4	4	8	4	2	4
D_{calc}/g cm^{-3}	1.069	1.062	1.167	1.126	1.091	1.218
μ/mm^{-1}	0.182	0.185	0.134	0.181	0.153	0.179
$F(000)$	944	880	1840	1064	640	1264
Data/ restraints/ parameters	4730/0/ 270	4417/0/251	3486/1/ 284	5050/2/ 300	6317/ 10/ 415	5637/ 0/ 380
S	1.064	1.038	0.926	1.053	1.069	1.090
$R1$ [$I > 2\sigma(I)$]	0.0629	0.0536	0.0498	0.0647	0.0602	0.0585
$wR2$ [all data]	0.2011	0.1647	0.1325	0.1880	0.1905	0.1458
Max., min. residual electron density/e Å^{-3}	0.427, −0.254	0.453, −0.316	0.321, −0.171	0.616, −0.268	0.375, −0.257	0.477, −0.233

[a] $R1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$. [b] Flack parameter 0.02(16). [c] Flack parameter 0.03(13).

(*ca.* 2 cm^3) and cooled at −4 °C for 24 h to obtain crystals of **8**·H_2O. Yield: 0.48 g (90%) (found: C 53.32, H 8.28, N 14.32. $C_{26}H_{48}N_6O_5P_2$ requires C 53.23, H 8.24, N 14.32%); mp 120–122 °C; ν_{max}(KBr)/cm^{-1} 3368 (w), 3281, 2969, 2254, 1618, 1519, 1523, 1458, 1368, 1198; δ_H (400 MHz, $CDCl_3$) 1.34, 1.53, 1.56 (3 s, br, 36H, *t*-Bu-*H*), 2.34–2.44 (br, 4H, PCH_2 + PCCH_2), 3.22–3.42 (br, 4H, 2N*H* + H_2O), 8.17 (s, 4H, Ar*H*); δ_C (50 MHz, $CDCl_3$) 10.0 (s, PC*C*H$_2$), 23.3 (d, ^1J(P–C) = 101.0 Hz, P*C*), 31.1 and 31.7 (2 s, C(*C*H$_3$)$_3$), 32.5 (d, ^3J(P–C) = 9.0 Hz, NC(*C*H$_3$)$_3$), 52.8, 54.6, 55.3 (3 s, *C*(CH$_3$)$_3$), 117.6 (d, ^3J(P–C) = 20.0 Hz, *C*N), 122.8, 130.2, 145.5, 148.5 (Ar*C*), 178.8 (s, *C*O$_2^-$); δ_P (160 MHz, $CDCl_3$) 21.4, 82.5.

X-Ray structural analysis

X-Ray crystallography. Single crystal X-ray data were collected on an Enraf-Nonius MACH$_3$ or on a Bruker AXS-SMART diffractometer, using Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by full-matrix least squares methods using standard procedures.[18] Absorption corrections were done using the SADABS program, where applicable. In some cases, the terminal carbon atoms of the *tert*-butyl groups (especially **5**) showed high thermals and hence were refined using a suitable disorder model. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a difference Fourier and refined isotropically. The crystal data are provided in Table 2.

CCDC reference numbers 285610–285614 and 604148. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605430g

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