Reaction of the Phospha-alkyne ArC≡P (Ar = 2,4,6-$Bu^t_3C_6H_2$) with Nucleophiles: A New Approach to 1,3-Diphosphabutadiene Synthesis

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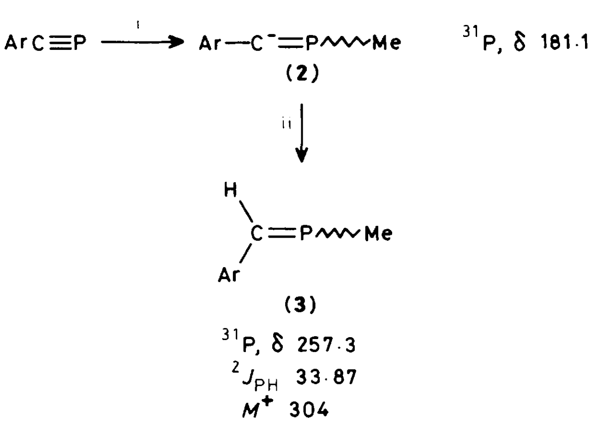
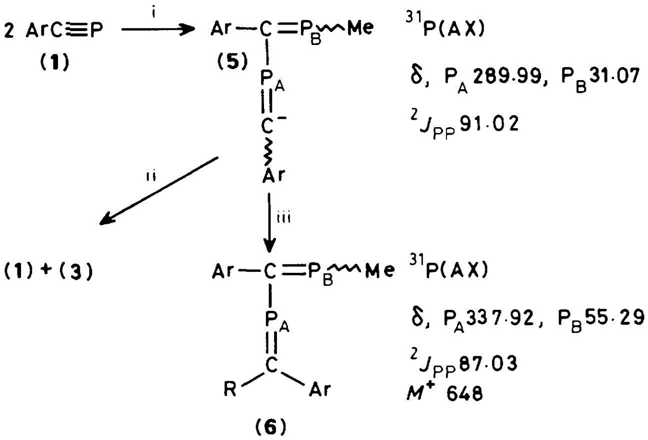
The reactions of ArC≡P (Ar = 2,4,6-$Bu^t_3C_6H_2$) with the nucleophiles MeLi and Li[$BHEt_3$] are described; the *X*-ray crystal structure of ArC≡P is also reported.

Nitriles have proved to be extremely useful synthons for organic synthesis.[1] It is only more recently, however, that the synthetic potential of the corresponding phospha-alkynes, RC≡P, has begun to be appreciated. To date, the principal use of phospha-alkynes has been the synthesis of heterocyclic compounds by means of cycloaddition reactions.[2] We report (i) the first examples of the reaction of a phospha-alkyne with nucleophiles, (ii) the conversion of a phospha-alkyne to a phospha-alkene, (iii) a new approach to the synthesis of 1,3-diphosphabutadienes, and (iv) the first *X*-ray crystallographic determination of the phosphorus–carbon triple bond length for an unco-ordinated phospha-alkyne.

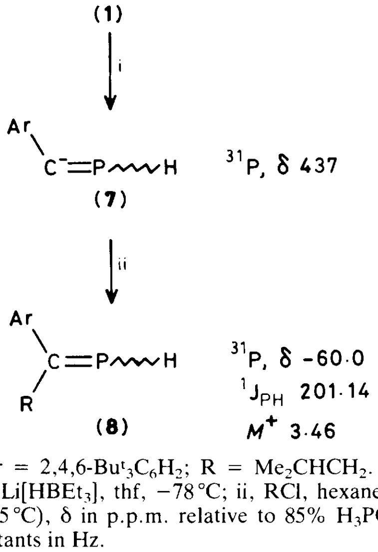
The phospha-alkyne ArC≡P (**1**) (Ar = 2,4,6-$Bu^t_3C_6H_2$) was prepared *via* the reaction of ArC(O)Cl with Li[(P($SiMe_3$)$_2$] in



Scheme 1. Ar = 2,4,6-$Bu^t_3C_6H_2$. *Reagents and conditions.* i, MeLi, tetrahydrofuran (thf), −78 °C; ii, H_2O, hexane, −78 °C, ^{31}P n.m.r. (thf, 25 °C), δ in p.p.m. relative to 85% H_3PO_4 (external), coupling constants in Hz.



Scheme 2. Ar = 2,4,6-$Bu^t_3C_6H_2$, R = Pr^i. *Reagents and conditions*, i, MeLi, thf, −78 °C; ii, H_2O, hexane, −78 °C; iii, RCl, hexane, −78 °C. ^{31}P n.m.r. (thf, 25 °C), δ in p.p.m. relative to 85% H_3PO_4 (external), coupling constants in Hz.



Scheme 3. Ar = $2,4,6\text{-}Bu^t_3C_6H_2$; R = Me_2CHCH_2. *Reagents and conditions.* i, $Li[HBEt_3]$, thf, −78 °C; ii, RCl, hexane, −78 °C. ^{31}P n.m.r. (thf, 25 °C), δ in p.p.m. relative to 85% H_3PO_4 (external), coupling constants in Hz.

1,2-dimethoxyethane solution.† Compound (**1**) was characterised by *X*-ray crystallography (Figure 1).‡ The P≡C bond length of 1.516(13) Å in (**1**) compares favourably with the distances of 1.5421(5) and 1.544(4) Å found by microwave spectroscopy for HC≡P[3] and MeC≡P,[4] respectively.

The reaction of equimolar quantities of (**1**) and MeLi (Scheme 1) results in the formation of the deep purple carbanion, (**2**). The electron-impact mass spectrum (e.i.m.s.) of (**2**) exhibited a peak at *m/z* 304 which was presumably due to hydrolysis of (**2**) to phospha-alkene (**3**) during sample preparation. This hypothesis was confirmed by addition of the stoicheiometric quantity of deoxygenated water to (**2**) (Scheme 1).

Interestingly, the reaction of (**1**) with MeLi in 2:1 stoicheiometry produced the novel 1,3-diphosphabutadienyl anion (**5**) (Scheme 2). As in the case of carbanion (**2**), the e.i.m.s. featured a peak corresponding to $M^+ + 1$. However, treatment of (**5**) with deoxygenated H_2O results in cleavage of one P–C bond and the production of equimolar quantities of (**1**) and (**3**) (Scheme 2). The identity of (**5**) was confirmed by reaction with alkyl halides; *e.g.* treatment of (**5**) with Pr^iCl afforded the 1,3-diphosphabutadiene (**6**). Note that the assignments of the ^{31}P chemical shifts of (**5**) and (**6**) are based on the generalisation that the attachment of substituents with lone pairs to the carbon atom of phospha-alkenes results in upfield ^{31}P chemical shifts.[5]

Preliminary experiments have also been conducted with other nucleophiles. For example, the reaction of (**1**) with $Li[HBEt_3]$ affords the carbanion (**7**) (Scheme 3). We were not able to detect a ^{31}P–^{1}H coupling constant for (**7**) at 25 °C owing to severe broadening of the ^{31}P n.m.r. signal. Nevertheless, the synthesis of (**7**) was clear from the fact that reaction of this carbanion with Me_2CHCH_2Cl produced the phospha-alkene (**8**).

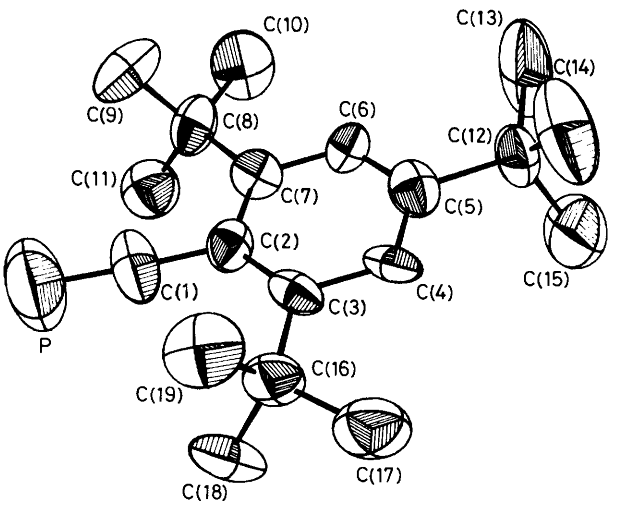


Figure 1. Molecular structure of ArC≡P (**1**) (Ar = $2,4,6\text{-}Bu^t_3C_6H_2$).

The reaction of phospha-alkynes with nucleophiles represents a new method of synthesis for phospha-alkenes and 1,3-diphosphabutadienes. The only previous examples of the latter class of compound were prepared *via* the reaction of the phosphaketene, ArP=C=O, with silyl-phosphorus reagents.[6]

The reaction of nitriles with organo-lithium reagents results in the formation of iminolithium compounds, $[R_2C{=}NLi]_x$.[7] The observation that phospha-alkynes react with nucleophiles in the opposite sense to nitriles is due to the reversal of polarity, *i.e.* $\overset{\delta-\ \delta+}{C\equiv P}$ *vs.* $\overset{\delta+\ \delta-}{C\equiv N}$. The fact that the phosphorus atom constitutes the positive end of the dipole also explains the implied reaction of (**2**) with (**1**) to form the 1,3-diphosphabutadienyl anion (**3**) (Scheme 2).§

We thank the United States Army Research Office, the National Science Foundation, and the Robert A. Welch Foundation for support.

Received, 6th July 1987; Com. 952

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† Compound (**1**) has been synthesised previously *via* the reaction of Ar(CO)Cl with $(Me_3Si)_3$, see P. G. Märkl and H. Sejpka, *Tetrahedron Lett.*, 1986, **27**, 171. For the As analogue, see G. Märkl and H. Sejpka, *Angew. Chem.*, 1986, **98**, 286.

‡ *Crystal data* for (**1**): $C_{19}H_{29}P$, monoclinic, $P2_1/n$ (No. 14), a = 9.997(4), b = 11.276(9), c = 16.599(5) Å, β = 96.13(3)°, U = 1860.4 Å^3, Z = 4, D_c = 1.030 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 1.3 cm^{-1}. A total of 1114 unique reflections was collected over the range $3.0 \leq 2\theta \leq 46.0°$ on an Enraf-Nonius CAD-4 diffractometer at 25 °C. The data were corrected for Lorentz, polarisation, decay, and absorption and the structure was solved (direct methods) and refined (difference Fourier, full-matrix, least-squares) using 962 reflections with $I > 3.0\sigma(I)$. The final residuals were R = 0.061 and R_w = 0.074. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ It is recognised that steric effects might also influence the mode of addition.