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Preliminary communication

Synthesis, characterisation, and crystal structure of a tetra(phosphino)ethene $[\mathrm{Ph\overline{PCH_2CH_2P(Ph)C}{=}}]_2$

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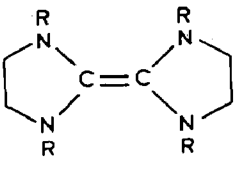
Abstract

The dilithio-1,2-bis(phenylphosphino)ethane reagent $[(\mathrm{PhPCH_2CH_2PPh})\{\mathrm{Li(THF)_2}\}_2]_2$ (THF = tetrahydrofuran) reacts with C_2Cl_4 in THF at −50 °C to give $[\mathrm{Ph\overline{PCH_2CH_2P(Ph)C}{=}}]_2$ (I), a novel alkene with a $P_2C{=}CP_2$ framework, whereas $\mathrm{Li(PPh_2)}$ and C_2Cl_4 under ambient conditions give the alkyne $\mathrm{Ph_2PC{\equiv}CPPh_2}$ (IIa), but at −78 °C give the tetra(phosphino)ethene $\mathrm{(Ph_2P)_2C{=}C(PPh_2)_2}$ (IIIa). The X-ray structure of I shows that the phosphorus atoms are in a pyramidal environment, with $\langle \mathrm{P{-}C_{sp^2}} \rangle$ 1.84(1) and C=C 1.352(15) Å.

Electron-rich alkenes such as A (abbreviated as L_2^R, R = a primary alkyl group) are strongly nucleophilic and highly reactive; they are effective precursors in the synthesis of many carbene-transition metal complexes [1a]. *N*-Aryl-substituted analogues L_2^{Ar} exhibit reduced activity for such reactions [1b]. The positive π-electron charge on the N atoms is significantly greater in L_2^{Ph} than in **A**, an effect attributed to the presence of the aromatic groups rather than the observed non-planar distortion in the crystal and molecular structure [2]. We now report the tetraphosphorus analogue of the enetetramine L_2^{Ph} (**A**, R = Ph) and the characterisation of the isolated stereoisomer I by a single crystal X-ray structural determination and by various spectroscopic methods.



(**A**)

The reaction between dilithio-1,2-bis(phenylphosphino)ethane [3] and tetrachloroethene according to eq. 1 afforded a yellow oil, which after crystallisation from

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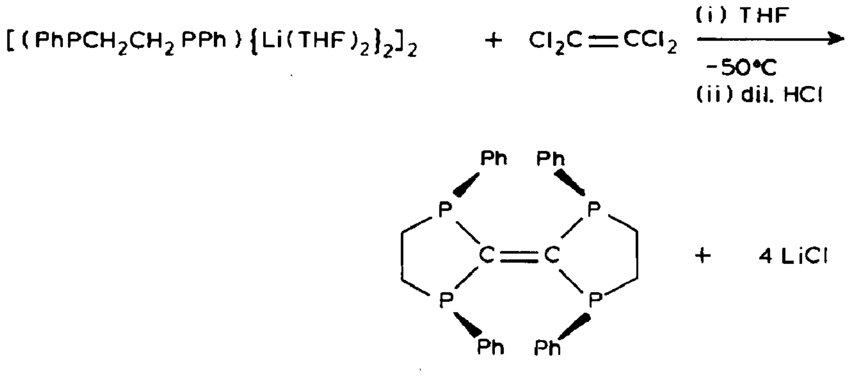

(1)

(I)

absolute ethanol gave a moderate yield of bright yellow needles of compound I *. The He(I) photoelectron spectrum of compound I showed its first ionisation potential to be 7.4 eV, which may be compared with 5.95 eV for (A, R = Et), 10.5 eV for C_2H_4, or ca. 9 eV for a simple tertiary phosphine [1b].

The X-ray diffraction study ** of the tetra(phosphino)ethene I (Fig. 1) showed that (i) there is no significant departure from the sp^2 hybridisation of the alkene carbon atoms (cf., L_2^{Ph}, which exhibits a very slight tetrahedral distortion), and (ii) the phosphorus atoms are in an unexceptional pyramidal environment (sp^3 hybridisation). There is, however, a small (7°) rotation about the C=C [C(1)C(1′)] bond of the P(1)C(1)P(2) plane relative to the plane defined by P(1)′C(1)′P(2)′. The

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* *Selected data* [NMR spectra measured in CD_2Cl_2 at ambient temperature, coupling constants in Hz, chemical shifts to high frequency of (i) 85% aq. H_3PO_4 (external) for $^{31}P\{^1H\}$ or (ii) $Si(CH_3)_4$ (external) for $^{13}C\{^1H\}$ and ^1H NMR]. Compound I, bright yellow microcrystals, m.p. 148–150 °C (Found: C, 69.4; H, 5.62. $C_{30}H_{28}P_4$ calc.: C, 70.3; H, 5.51%), M^+, 512; NMR: ^1H: δ 7.28 (8H, m, *ortho H*-Ar), 6.84 (12H, m, *meta*- and *para-H*-Ar), 1.66 ppm (8H, m, -H_2C-), $^{13}C\{^1H\}$ (in $C_6D_5CD_3$): δ 170.28 (m, *C=C*), 138.68 (m, *ipso*-Ar*C*), 132.68 (m, *ortho*-Ar*C*), 31.13 ppm (m, -H_2*C*-), $^{31}P\{^1H\}$: δ 5.5 ppm. Compound IIa, off-white microcrystals, m.p. 79–80 °C (lit. [6] 86 °C) (Found: C, 79.2; H, 5.10. $C_{26}H_{20}P_2$ calc.: C, 79.2; H, 5.12%); M^+, 394; NMR (lit. [4] values in parentheses): $^{13}C\{^1H\}$: δ 106.6 (107.7) ppm (P-*C*≡*C*-P), $^{31}P\{^1H\}$: δ −31.4 (−32.3) ppm. Compound IIb, pale yellow crystals, m.p. 201–202 °C dec., MS (FAB): $[M+1]^+$, 535; NMR: $^{31}P\{^1H\}$: δ 7.2 (lit. [4] 7.5) ppm [^1J(PSe), 784 (lit. [4] 775) Hz]. Compound IIIa, colourless microcrystals, m.p. 114–117 °C. Found: C, 73.3; H, 5.68. $C_{50}H_{40}P$ calc.: C, 77.3; H. 6.23%. Trihydrate calc.: C, 73.4; H, 5.6%; NMR: $^{13}C\{^1H\}$: δ 136.01 (m, *ipso*-Ar*C*), 134.47 (m, *ortho*-Ar*C*), 128.37 (m, *meta*-Ar*C*), 128.89 (s, *para*-Ar*C*), 95.64 ppm (m, *C=C*), $^{31}P\{^1H\}$: δ −14.7 ppm. Compounds IIIb and IIIc were identified by MS, $[M+1]^+$, and $^{31}P\{^1H\}$ NMR.

** *Crystal data for I*: $C_{30}H_{28}P_4$, $M = 512.5$, a 17.777(8), b 8.085(3), c 18.664(9) Å, β 104.96(4)°, U 2591.7 Å^3, monoclinic, space group $C2/c$, $Z = 4$. 1892 Total reflections were measured on a CAD4 diffractometer for $2 < \theta < 22°$, and 602 unique reflections with $|F^2| > \sigma(F^2)$ were used in the refinement; P and C were set anisotropic and H atoms fixed at calculated positions. A weighting scheme of $w = 1/\sigma^2(F)$ was applied for the full matrix least squares analysis. Final residuals were $R = 0.078$, $R' = 0.071$. The molecule has a two-fold crystallographic rotation axis perpendicular to the plane of the alkene through the mid-point of the C=C bond. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

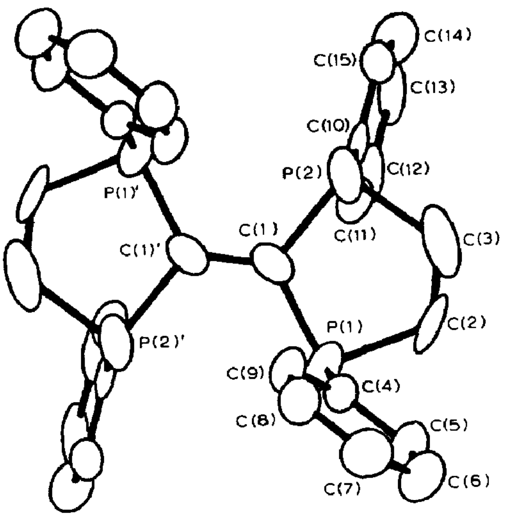
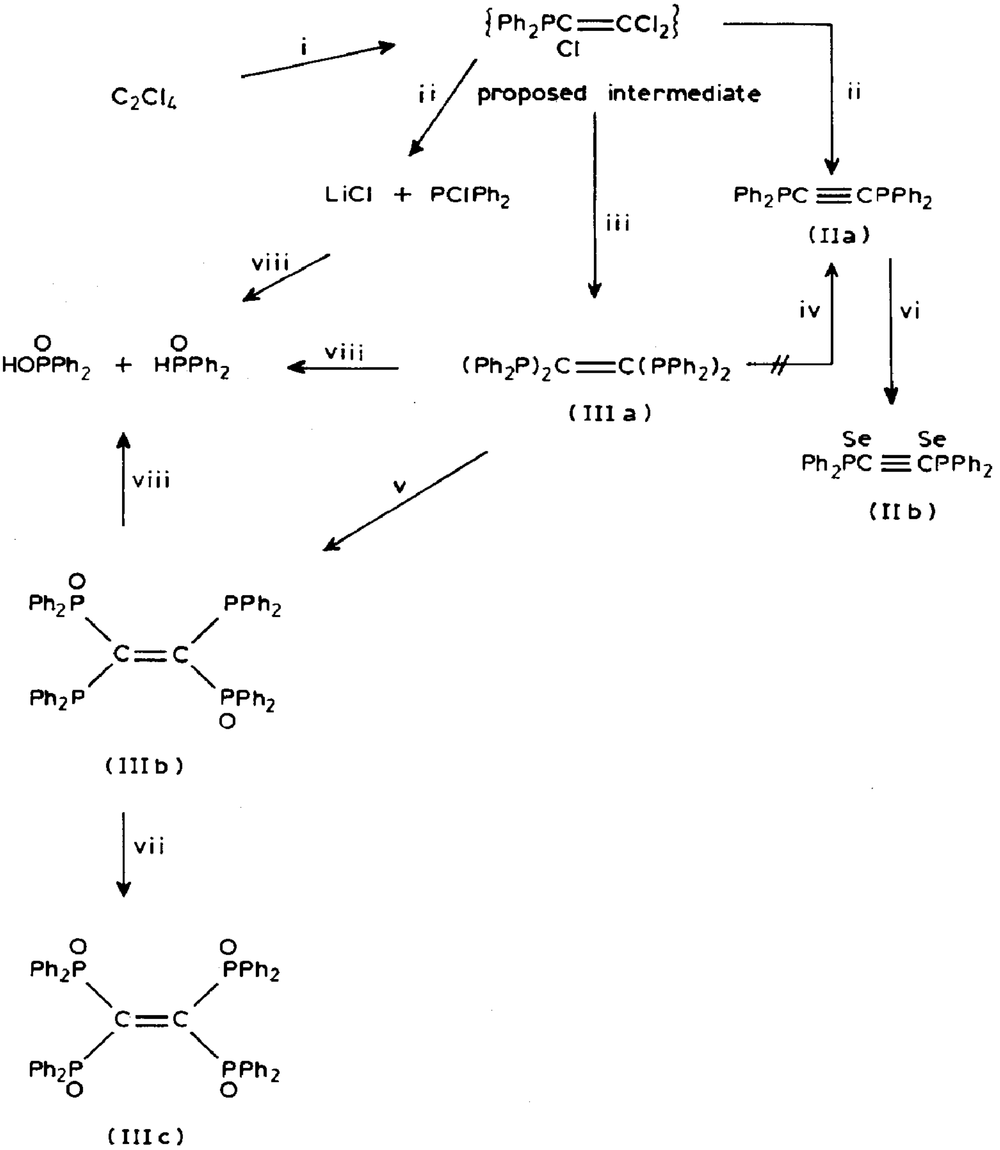


Fig. 1. The molecular structure of $[\{\overline{\mathrm{PhPCH_2CH_2P(Ph)C}}{=}\}_2]$ (I). Selected bond lengths: C(1)–C(1)′, 1.352(15); P(1)–C(1), 1.846(10); P(1)–C(2), 1.844(14); P(1)–C(4), 1.806(13); P(2)–C(1), 1.834(13); P(2)–C(3), 1.848(12); P(2)–C(10), 1.854(14) Å. Selected bond angles: C(1)–P(1)–C(2), 94.7(6); C(1)–P(1)–C(4), 103.8(5); C(2)–P(1)–C(4), 99.3(6); C(1)–P(2)–C(3), 93.3(6); C(1)–P(2)–C(10), 105.1(6); C(3)–P(2)–C(10), 99.6(6); P(1)–C(1)–P(2), 114.8(6); P(1)–C(1)–C(1)′, 122.4(9); P(2)–C(1)–C(1)′, 122.8(8)°.

C(1)–C(1)′ bond length is 1.352(15) Å [cf., 1.372(6) in L_2^{Ph} [2]], and is thus comparable to that in an unfunctionalised alkene, 1.34 Å. The P–C(1) bond length, 1.846(10) Å, is normal for a P–C single bond. We conclude that there is a strictly localised electronic environment in the $P_2C_2P_2$ moiety, with no interaction between the four P lone-pair and the alkene π-orbitals. The estimated directions of the phosphorus lone pairs are such that each makes an angle of ca. 33° with the nodal plane of the C=C bond, implying minimal interaction between the lone pairs and the double bond.

Compound I is air- and moisture-stable for appreciable periods. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet ($\delta + 5.5$ ppm.) and the $^{13}C\{^1H\}$ NMR spectrum the expected [4] signals assigned to C_{sp^2} and CH_2 second order at δ 170.3 and 31.1 ppm, respectively; cf., for (i) L_2^{Me}, $^{13}C\{^1H\}$: δ 129.6 (C-"alkene") and 52.7 (NCH_2CH_2N) ppm [5]; and (ii) 1,1-(diphenylphosphino)ethene, $^{31}P\{^1H\}$: -3.9 ppm and $^{13}C\{^1H\}$: 148.4 ppm [$(Ph_2P)_2C{=}CH_2$] [4].

In a similar reaction to that of eq. 1, $4/n(LiPPh_2)_n$ and C_2Cl_4 at ambient temperature afforded the unexpected elimination product, the alkyne $Ph_2PC{\equiv}CPPh_2$ IIa. The target alkene, $(Ph_2P)_2C{=}C(PPh_2)_2$ (IIIa), was isolated from the low temperature reaction in THF solution (Scheme 1). We suggest that initial substitution leads to an intermediate $Cl_2C{=}C(Cl)(PPh_2)$, which upon warming in the presence of excess $LiPPh_2$ (a very strong nucleophile) affords compound IIa, LiCl, and Ph_2PCl. [Evidence for the formation of the chlorodiphenylphosphine rests on the aerobic work-up, which leads to, inter alia, $HP(O)Ph_2$ and $HOP(O)Ph_2$]. Compounds IIa and IIIa were formed in good yield (> 75% after recrystallisation). Pyrolysis (> 200 °C) or photolysis of compound IIIa did not yield the alkyne IIa; the latter was characterised by comparison with published data [4,6] and by its



Scheme 1. Synthesis and some reactions of the phospha-alkyne IIa and phospha-alkene IIIa. Conditions and reagents: i followed by ii, THF, ca. 20 °C, $4LiPPh_2$, and subsequent hydrolysis, Et_2O extraction, and crystallisation (EtOH); i followed by iii, THF −78 °C, $4LiPPh_2$, and subsequently as above; iv, 200 °C in vacuo or photolysis in THF; v followed by vii, THF, O_2, and subsequent fractional crystallisation (Et_2O–EtOH); vi, C_6H_6, Se, ca. 20 °C, 12 h, and subsequent crystallisation (EtOH); viii, aerobic hydrolysis.

derivatisation, e.g., with selenium to yield $Ph_2(Se)PC\equiv CP(Se)Ph_2$ (IIb) [4] (Scheme 1).

The tetra(phosphino)alkene IIIa was obtained as white, air- and moisture-sensitive crystals. Controlled hydrolysis (at ca. 25 °C during 48 h) of IIIa afforded $P(O)HPh_2$. Oxidation of IIIa yielded two more novel compounds: a dioxide IIIb and the tetroxide IIIc. Compound IIIb was isolated by fractional crystallisation and was NMR-characterised. $^{31}P\{^1H\}$ δ 33.4 and 23.9 ppm $J(PP')$ 217.3 Hz {cf.,

$Ph_2P[Ph_2P(E)]CH_2$; E = O [7], S, or Se (J = 91.9 Hz) [4]}. The oxidative behaviour is characteristic of phospha-alkenes [7], and contrasts with the chemiluminescent formation of the *N,N′*-dialkyl (or diaryl)imidazolidinone (L^R=O) from L^R_2 upon exposure to the atmosphere [8].

In conclusion, although the tetraphosphaethenes have a forerunner, MePP(Me)P(Me)C=CP(Me)P(Me)PMe [9], compound I is the first example of a structurally characterised *P,P′,P″,P‴-exo*(bicyclo)alkene {the unsaturated analogue, PhPCHCHP(Ph)C=CP(Ph)CH=CHPPh, has recently been reported [10]}. The formation of the ethyne IIa is rationalised by an extension of the known elimination-substitution reactions of halogeno-alkenes mediated by a strong base [11]. Finally, the novel phosphorus compounds here described are expected to have an interesting coordination chemistry, and will provide a notable extension to the variety of multidentate phosphorus-containing ligands currently in use. For example, we have observed the compound $[\{Rh(acac)\}_2(I)]$ in which each of the four phosphorus atoms of I is bonded to rhodium, the $^{31}P\{^1H\}$ NMR spectrum being of $X_2A_2B_2$ type.

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