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Regio- and stereospecific addition of phosphines to cyanoacetylenes

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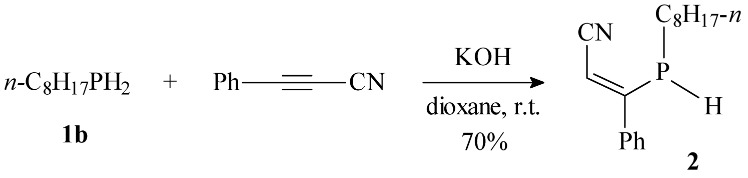
Abstract—Primary and secondary phosphines add regio- and stereospecifically to phenylcyanoacetylene and 4-hydroxy-4-methylpent-2-ynenitrile under mild conditions to form corresponding functionalized secondary and tertiary phosphines of *Z*-configuration in 70–91% yield. According to ESR and UV data, the addition of primary phosphines to phenylcyanoacetylene involves a single electron transfer process. © 2003 Elsevier Science Ltd. All rights reserved.

Addition of phosphines to acetylene and its derivatives is a convenient and atom-economic method of the C–P bond formation and the simplest route to unsaturated phosphines, prospective building blocks for chiral phosphine ligands.[1,2] Meanwhile, this reaction still remains poorly understood. It is known that vinylphosphine gives with acetylene under pressure and UV irradiation in the gas phase divinylphosphine in a very small yield (3%).[3] 2-Cyanoethylphosphine adds to heptyne-1 (AIBN, 80–85°C, 2 h) to form bis(1-heptenyl)-2-cyanoethylphosphine in 26% yield.[4] Addition of 2,6-bis(trifluoromethyl)phenylphosphine to phenylacetylene (100–110°C, 40 h) results in a mixture of corresponding *E*- and *Z*-isomers (59% total yield).[5] In the KOH–DMSO suspension, primary phosphines with phenylacetylene (60°C, 1–4 h) give predominantly or exclusively *Z*,*Z*-isomers of bis(2-phenylethenyl)organylphosphines in good yield (41–81%).[6]

In this work, to gain a better insight into peculiarities of phosphorylation of acetylenes with phosphines and to synthesize novel functionalized unsaturated secondary and tertiary phosphines, we have studied the reaction of phenylcyanoacetylene and 4-hydroxy-4-methylpent-2-ynenitrile with alkylphosphines and aryl(or hetaryl)ethylphosphines now readily available from red phosphorus and alkyl halides[7] or aryl(or hetaryl)ethenes.[8,9]

In the KOH–dioxane suspension, alkylphosphines **1a**,**b** react with phenylcyanoacetylene regio- and stereospecifically at room temperature to afford, depending on the reactant ratio, either secondary or tertiary phosphines of *Z*-configuration. Thus, *n*-octyl(*Z*-1-phenyl-2-cyanoethenyl)phosphine **2** is formed in 70% yield when equimolar amounts of the starting materials are used. Besides, a slow dropwise addition of phenylcyanoacetylene into the alkylphosphine–KOH–dioxane suspension is important in this case (Scheme 1).

In the reaction of alkylphosphines **1a**,**b** with a two-fold molar excess of phenylcyanoacetylene, *n*-alkylbis(*Z*-1-phenyl-2-cyanoethenyl)phosphines **3a**,**b** are produced in 85–91% yield (Scheme 2).



Scheme 1.

Keywords: cyanoacetylenes; primary phosphines; secondary phosphines; nucleophilic addition; single electron transfer.

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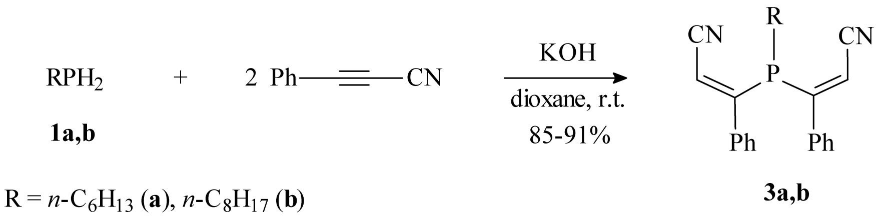
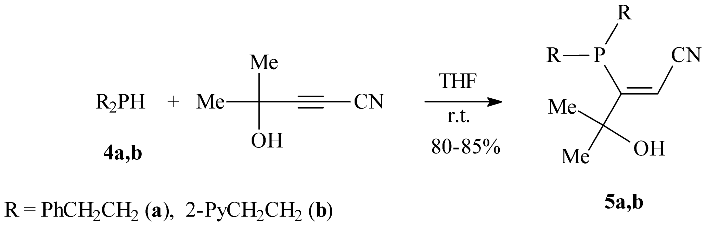


Scheme 2.



Scheme 3.

In contrast to secondary phosphines, which easily add to phenylcyanoacetylene[10] under non-catalytic conditions, the above reactions fail in the absence of KOH.

An easy stereocontrolled access to functionalized tertiary phosphines of the type **5** proves to be the addition of bis(2-phenylethyl)- and bis[2-(2-pyridyl)ethyl]phosphines **4a**,**b** to 4-hydroxy-4-methylpent-2-ynenitrile (Scheme 3).

The reaction proceeds smoothly without catalyst (THF, room temperature, 3 h). The yield of *Z*-3-[bis(2-phenylethyl)phosphino]- and *Z*-3-{bis[2-(2-pyridyl)ethyl]phosphino}-4-hydroxy-4-methylpent-2-enenitriles **5a**,**b** is 80–85%.

Configuration of phosphines **3a**,**b** follows from ^{1}H NMR spectra where the coupling $^3J_{PH}$ of 16.2 Hz corresponds to the *trans* disposition of the phosphorus and hydrogen atoms relative to the double bond.[11–13]

In contrast, from the known data,[10,11,13,14] one may suggest that the doublet of the ethenyl proton at 5.73 ppm with $^3J_{PH}$=5.6 Hz observed in the ^{1}H NMR spectrum of phosphine **2** could assign *cis* disposition of the hydrogen and phosphorus atoms. But the cross-peaks of the ethenyl and *ortho*-phenyl protons in the ^{1}H–^{1}H NOESY spectrum of phosphine **2** are only possible in their *cis*-disposition relative to the double bond, thus reliably supporting *Z*-configuration of the phosphine. The similar fact is observed for phosphines **5a**,**b** whose ^{1}H NMR spectra contain doublets of the ethenyl protons with $^3J_{PH}$=5.4, 6.6 Hz, respectively. *Z*-Configurations of the phosphines are confirmed by the cross-peaks of the ethenyl and methyl protons in the ^{1}H–^{1}H NOESY spectra, indicating their *cis*-disposition relative to the double bond.

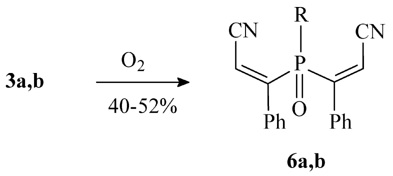
Therefore, the reactions obey the *trans*-addition rule of nucleophiles (including P-nucleophiles[11,15]) to activated acetylenes.[16]

Secondary ethenylphosphines RPHCH═CHR′ are known to transform upon heating[5,17] or in the presence of bases,[18] to highly reactive species RP═CHCH$_2$R′ with two-coordinate phosphorus. We have undertaken an attempt to effect the analogous isomerization of phosphine **2**. However, in the 1,4-diazabicyclo[2.2.2]octane–CDCl$_3$ system (a spectrometer tube, 60°C, 40 min) or in DMSO-d$_6$ (100°C, 30 min) it does not give the expected 3-(*n*-octylphosphinidene)-3-phenylpropanenitrile (^{31}P NMR). In the latter case (in the ^{31}P NMR spectrum), the peak of phosphine **2** disappears and two new peaks of approximately equal intensity arise at 33.4 ppm (J_{PH}=462 Hz) and 38.4 ppm (J_{PH}=466 Hz), which presumably correspond to *Z*- and *E*-isomers of *n*-octyl(1-phenyl-2-cyanoethenyl)phosphine oxide. Their formation can be accounted for by the oxidation of the starting phosphine **2** with dimethyl sulfoxide to the corresponding *Z*-isomer of phosphine oxide followed by isomerization of the latter to the *E*-isomer.

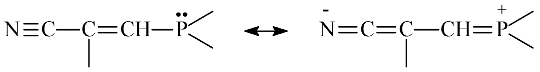
Tertiary phosphines **3a**,**b** slowly oxidize in air (2 months) to corresponding phosphine oxides **6a**,**b** (Scheme 4) of the *Z*,*Z*-configuration (their ^{1}H NMR spectra have only a doublet for the ethenyl proton, $^3J_{PH}$ of 31.9 Hz, characteristic of *Z*-configuration[13,14]).

Phosphine oxides **6a**,**b** were isolated in 40–52% yield. Under the above conditions, phosphorus-containing polymers are also formed as side products.

Unlike most tertiary phosphines which easily form phosphonium salts with alkyl halides,[19] phosphines **3a**,**b** do not react with methyl iodide (room temperature, diethyl ether, 10 h). Presumably, this is associated with a decrease of electron density at the phosphorus atom due to the through



Scheme 4.



Scheme 5.

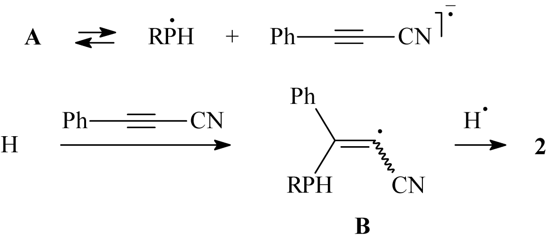
conjugation of its lone electron pair with the double bond and further with the nitrile group (Scheme 5).

Reaction of secondary phosphines with phenylcyanoacetylene was reported to proceed via a single electron transfer.[10]

We found that a dark red–brown mixture of phenylcyanoacetylene, KOH and dioxane is paramagnetic. Its ESR spectrum is an unresolved single absorption line with ΔH=0.45 mT and g-factor of 2.0028, which, seemingly, corresponds to the radical anion of phenylcyanoacetylene.[20]

In the UV spectrum of phenylcyanoacetylene in dioxane, an absorption with a well expressed vibrational structure ($\Delta\nu$ 1920 cm^{-1}) having maxima at 249, 262 and 276 nm is observed. Small amounts of KOH turn the solution dark red. Along with the above absorption, in the UV spectrum of the mixture there is a band at 379 nm, which likely belongs to the radical anion of phenylcyanoacetylene. Primary phosphines in the KOH–dioxane system remain colourless for 24 h, do not absorb in the UV region, and have no signals in the ESR spectrum.

Equimolar mixture of *n*-octylphosphine and phenylcyanoacetylene in the KOH–dioxane system gives an intense doublet (a=1.733 mT, g=2.0027) in the ESR spectrum. Upon time, the signal intensity decreases and two other signals appear: a doublet (a=2.100 mT, g=2.0034) and a singlet between the doublet lines (ΔH=0.45 mT, g=2.0028) attributable to the radical anion of phenylcyanoacetylene. The ESR-monitoring of the reaction (Fig. 1) indicates a radical giving rise to the doublet with the constant of 1.733 mT to be precursor of the radical responsible for the doublet with the constant of 2.100 mT. Under conditions of high resolution, the first doublet reveals an extra hyperfine structure (HS) composed of at least 18 lines spaced at approximately 0.05 mT. Computer simulation shows the best correlation with the experimental spectrum for the following HS constant set (mT): P(1) 1.733; N(1) 0.132; H(1) 0.120; H(5) 0.088; H(4) 0.044. According to the ^{31}P NMR, the reaction in an ESR ampoule affords not only the major product **2**, but also diadduct **3b** in the 9:1 molar ratio.



Scheme 7.

In the UV spectrum of the above reaction mixture, at the starting moment there are absorption bands of phenylcyanoacetylene in the 225–300 nm region and an absorption band at 369 nm, presumably resulting from the phenylcyanoacetylene radical anion. Shortly thereafter, another absorption band (454 nm) appears. Upon time, the intensities of the bands at 369 and 454 nm decrease, vibrational structure of the absorption at 225–300 nm flattens, and in the spectrum of the final product a broad band of phosphine **2** at 276 nm remains (it is supported by ^{31}P NMR).

The data imply that phosphide-anion reacts with phenylcyanoacetylene to give radical ion pair **A**, which further undergoes protonation subsequent to coupling to form secondary phosphine **2** (Scheme 6).

Spontaneous exit of phosphinyl radical from the radical ion pair and its addition to phenylcyanoacetylene results in the

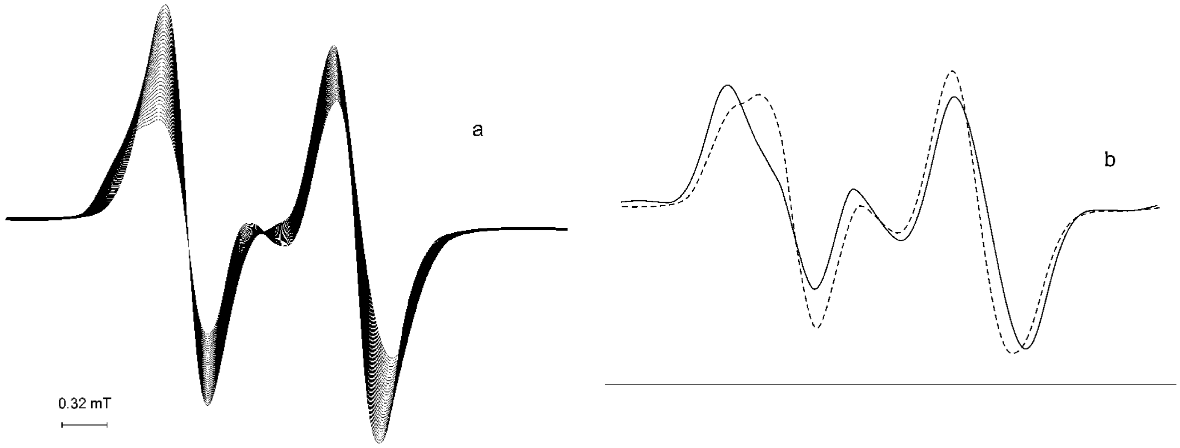
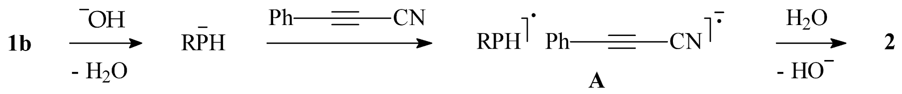
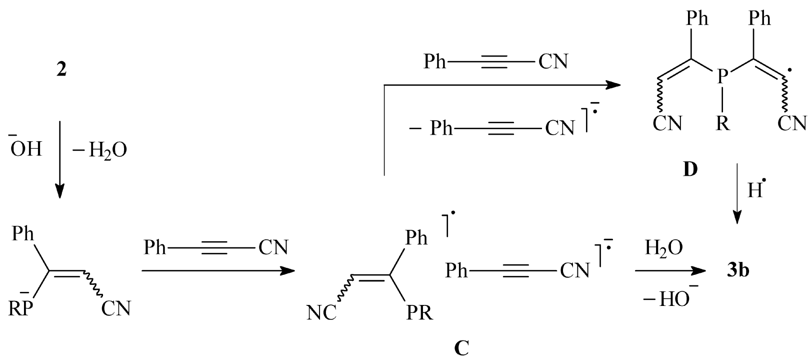


Figure 1. ESR-monitoring of the reaction of *n*-octylphosphine with phenylcyanoacetylene (1:1) in the KOH–dioxane system: (a) for 78 min; (b) dashed line: 1.5 h after the reaction start; solid line: 2.5 h after the reaction start.



Scheme 6.



Scheme 8.

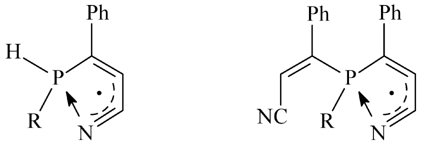
intermediate radical **B** (Scheme 7), which seems to be the one detected in the spectra (the major doublet with a=1.733 mT and g=2.0027 in the ESR and the absorption band at 454 nm in the UV).

It is unlikely that we detect phosphorus-centred radicals since radicals AlkP˙H are unstable and thus invisible in the ESR spectra under ordinary conditions, whereas the hyperfine coupling constants at the phosphorus atom for the known PhP˙H radicals are an order higher.[21]

The paramagnetic particles are registered also for the nucleophilic addition of n-octylphosphine to two-fold molar excess of phenylcyanoacetylene. In this case, two signals are instantly observed in the ESR spectrum: a doublet (a=1.733 mT, g=2.0027) and a singlet (ΔH=0.45 mT, g=2.0028), although the intensity of the central singlet increases much faster than in the case of equimolar ratio of the reactants. These data give even a stronger support for the conclusion that the singlet in the ESR spectrum corresponds to the radical anion of phenylcyanoacetylene. After 2.5 h, the doublet constant in the ESR spectrum becomes equal to 2.100 mT (g=2.0034).

This may be described by involving the radical ion pair **C** and the paramagnetic particle **D** (a=2.100 mT, g=2.0034). The latter signal is also detected in the ESR spectrum of the equimolar mixture of monoadduct **2** and phenylcyanoacetylene in the KOH–dioxane system (Scheme 8).

When the reaction (Scheme 1) is carried out in the presence of a radical process inhibitor (hydroquinone, 3 wt% of the reactants' weight), predominant formation of diadduct **3b** occurs (^{31}P NMR). The ESR spectrum shows the doublets of radicals **B** and **D** and no signal of phenylcyanoacetylene radical anion. This suggests that being inactive towards the comparatively stable radicals **B** and **D**, hydroquinone quenches phenylcyanoacetylene radical anion. In this case, polymeric products are formed in a lower amount compared to the experiments without hydroquinone, i.e. the latter inhibits polymerization of the starting phenylcyanoacetylene and resultant functional unsaturated phosphines.



B **D**

Scheme 9.

The observed stereospecificity uncommon for free radical processes may be rationalized as resulted from a through space stabilization of the intermediate radicals **B** and **D** in Z-configurations (Scheme 9).

No paramagnetic particles are registered for the nucleophilic addition of bis(2-phenylethyl)phosphine to 4-hydroxy-4-methylpent-2-ynenitrile. It is not improbable that radicals, similar to the described above, do form in the process but they are less stable and too reactive to be registered by ESR.

In conclusion, primary and secondary phosphines add to cyanoacetylenes regio- and stereospecifically under mild conditions to afford corresponding functionalized secondary and tertiary phosphines in good to high yields. These reactions represent a new general atom-economic approach to the synthesis of versatile reactive building blocks for organic synthesis and prospective polydentate and amphiphilic ligands for design of metal complex catalysts.[22,23]

1. Experimental

1.1. General

^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX 400 and Jeol FX-90Q (CDCl$_3$) spectrometers, respectively. IR spectra were run on a Bruker IFS 25 instrument. UV spectra were measured using a Specord UV–Vis instrument. ESR spectra were taken on a SE/X-2547 spectrometer (Radiopan, Poland), equipped with a magnetometer and a high frequency meter. WINEPR SimFonia ver. 1.25 software (Bruker, Inc. 1996) was used for computer simulation of the ESR spectra.

All experiments were carried out under argon atmosphere. Phenylcyanoacetylene was prepared according to the published procedure.[24] 4-Hydroxy-4-methyl-2-pentynenitrile was synthesized by the known technique.[25]

1.1.1. *n*-Octyl(Z-1-phenyl-2-cyanoethenyl)phosphine 2. To a solution of 0.25 g (1.7 mmol) of n-octylphosphine in 3 ml of absolute dioxane, 0.04 g (0.6 mmol, 35% relative to the phosphine) of powdered KOH·0.5H_2O (15% water content) was introduced. To the suspension obtained, a solution of 0.22 g (1.7 mmol) of phenylcyanoacetylene in 4 ml of dioxane was added dropwise upon stirring during 1.5 h. The reaction mixture was stirred at room temperature for 5 days (no stirring overnight). Then 0.04 g (0.7 mmol) of ammonium chloride was added, the precipitate was filtered off and dioxane was removed from the filtrate under reduced pressure to give 0.33 g (70%) of phosphine **2**, a viscous product of yellow colour [purified on silica gel (40/100), eluent: ether]. [Found: C 74.41; H 8.94; N 5.40; P 11.13. $C_{17}H_{24}NP$ requires C 74.70; H 8.85; N 5.12; P 11.33%]; ν_{max} 2211 (ν C≡N), 2273 (ν P–H) cm^{-1}; δ_H 7.45–7.35 (m, 5H, Ph), 5.73 (d, 1H, =CH, $^3J_{PH}$=5.6 Hz), 4.63 (ddd, 1H, P–H, $^1J_{PH}$=223.6 Hz, $^3J_{HH'}$=9.5 Hz, $^3J_{HH''}$=5.1 Hz), 1.68–1.14 (m, 14H, CH_2), 0.85 (t, 3H, Me, $^3J_{HH}$=6.9 Hz); δ_P −50.5.

1.2. Synthesis of phosphines 3a,b (a typical procedure)

To a solution of alkylphosphine (2.4 mmol) in 4 ml of absolute dioxane, 0.06 g (0.9 mmol, 38% relative to the phosphine) of powdered KOH·0.5H_2O (15% water content) was introduced. To the suspension obtained, a solution of 0.61 g (4.8 mmol) of phenylcyanoacetylene in 4 ml of absolute dioxane was added dropwise during 10 min. The reaction mixture was stirred at room temperature for 3 h and then quenched with 0.06 g (1.1 mmol) of ammonium chloride. The precipitate was filtered off and dioxane was removed from the filtrate under reduced pressure.

1.2.1. *n*-Hexylbis(Z-1-phenyl-2-cyanoethenyl)phosphine 3a. Yield 91%. A honey-like product of amber colour [purified on silica gel (40/100), eluent: ether]. [Found: C 77.68; H 6.95; N 7.36; P 8.05. $C_{24}H_{25}N_2P$ requires C 77.40; H 6.76; N 7.52; P 8.32%]; ν_{max} 2210 (ν C≡N) cm^{-1}; δ_H 7.38–7.22 (m, 10H, Ph), 5.84 (d, 2H, =CH, $^3J_{PH}$= 16.2 Hz), 1.65–1.22 (m, 10H, CH_2), 0.86 (t, 3H, Me, $^3J_{HH}$=6.8 Hz); δ_P −1.4.

1.2.2. *n*-Octylbis(Z-1-phenyl-2-cyanoethenyl)phosphine 3b. Yield 85%. A honey-like product of amber colour [purified on silica gel (40/100), eluent: ether]. [Found: C 77.70; H 7.45; N 7.22; P 7.45. $C_{26}H_{29}N_2P$ requires C 77.97; H 7.29; N 6.99; P 7.73%]; ν_{max} 2210 (ν C≡N) cm^{-1}; δ_H 7.44–7.32 (m, 10H, Ph), 5.92 (d, 2H, =CH, $^3J_{PH}$= 16.2 Hz), 1.51–1.15 (m, 14H, CH_2), 0.91 (t, 3H, Me, $^3J_{HH}$=6.9 Hz); δ_P −1.0.

1.3. Synthesis of phosphines 5a,b (a typical procedure)

To a solution of starting phosphine **4a**,**b** (1.5 mmol) in 3 ml of absolute THF, a solution of 0.16 g (1.5 mmol) of 4-hydroxy-4-methylpent-2-ynenitrile in 3 ml of absolute THF was added dropwise during 10 min. The mixture was stirred at room temperature for 3 h, passed through a layer of Al_2O_3 (1 cm), then THF was removed under reduced pressure.

1.3.1. *Z*-3-[Bis(2-phenylethyl)phosphino]-4-hydroxy-4-methylpent-2-enenitrile 5a. The resultant product was dissolved in diethyl ether, insoluble part filtered off, and the ether was removed under reduced pressure to give 0.42 g (80%) of phosphine **4a**. Yellow oil. [Found: C 74.98; H 7.55; N 3.76; P 9.05. $C_{22}H_{26}NOP$ requires C 75.19; H 7.46; N 3.99; P 8.81%]; ν_{max} 2210 (ν C≡N), 3300 (ν OH) cm^{-1}; δ_H 7.27–7.15 (m, 10H, Ph), 6.45 (d, 1H, =CH, $^3J_{HP}$= 5.4 Hz), 2.75–2.60 (m, 4H, CH_2Ph), 1.95–1.81 (m, 4H, CH_2P), 1.41 (s, 6H, Me); δ_P −28.9.

1.3.2. *Z*-3-{Bis[2-(2-pyridyl)ethyl]phosphino}-4-hydroxy-4-methylpent-2-enenitrile 5b. Yield 85%. Yellow oil. [Found: C 67.68; H 7.02; N 11.60; P 8.97. $C_{20}H_{24}N_3OP$ requires C 67.97; H 6.85; N 11.89; P 8.76%]; ν_{max} 2215 (ν C≡N), 3276 (ν OH) cm^{-1}; δ_H 8.50 (d, 2H, CH=N, pyridine ring protons, $^3J_{HH}$=12.5 Hz), 7.64 (dd, 2H, pyridine ring protons, $^3J_{HH}$=7.8, 7.8 Hz), 7.24 (d, 2H, pyridine ring protons, $^3J_{HH}$=7.8 Hz), 7.18 (dd, 2H, pyridine ring protons, $^3J_{HH}$=7.8, 12.5 Hz), 6.25 (d, 1H, =CH, $^3J_{HP}$=6.6 Hz), 3.01–2.91 (m, 4H, CH_2), 2.69–2.58 m and 2.41–2.30 m (4H, CH_2P), 1.43 (s, 6H, Me); δ_P −25.1.

1.4. Synthesis of phosphine oxides 6a,b (a typical procedure)

Phosphines **3a**,**b** were kept in air for 2 months. The resultant viscous products of a dark colour were washed with diethyl ether (3×4 ml), the ether extracts were combined, passed through a layer of Al_2O_3 (1 cm), the ether was removed under reduced pressure.

1.4.1. *n*-Hexylbis(Z-1-phenyl-2-cyanoethenyl)phosphine oxide 6a. Yield 40%. A honey-like reddish product. [Found: C 73.93; H 6.69; N 6.96; P 7.69. $C_{24}H_{25}N_2OP$ requires C 74.21; H 6.49; N 7.21; P 7.97%]; ν_{max} 2210 (ν C≡N), 1180 (ν P=O) cm^{-1}; δ_H 7.55–7.26 (m, 10H, Ph), 6.07 (d, 2H, =CH, $^3J_{PH}$=31.9 Hz), 1.68–1.15 (m, 10H, CH_2), 0.83 (t, 3H, Me, $^3J_{HH}$=6.8 Hz); δ_P 31.1.

1.4.2. *n*-Octylbis(Z-1-phenyl-2-cyanoethenyl)phosphine oxide 6b. Yield 52%. A honey-like reddish product. [Found: C 74.70; H 7.19; N 6.45; P 7.71. $C_{26}H_{29}N_2OP$ requires C 74.98; H 7.02; N 6.73; P 7.44%]; ν_{max} 2210 (ν C≡N), 1180 (ν P=O) cm^{-1}; δ_H 7.44–7.34 (m, 10H, Ph), 6.08 (d, 2H, =CH, $^3J_{PH}$=31.9 Hz), 1.52–1.01 (m, 14H, CH_2), 0.86 (t, 3H, Me, $^3J_{HH}$=6.8 Hz); δ_P 31.5.

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