

## Methyl(cyanomethyl)phosphines. Synthesis and Nucleophilic Reactivity

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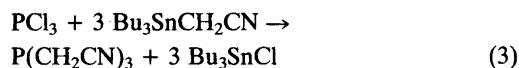
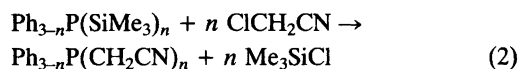
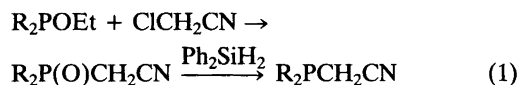
The preparation of  $\text{Me}_2\text{PCH}_2\text{CN}$ ,  $\text{MeP}(\text{CH}_2\text{CN})_2$  and  $\text{P}(\text{CH}_2\text{CN})_3$  is described, and phosphorus lone-pair ionization potentials and second order rate constants for their reactions with benzyl bromide in acetonitrile at 35 °C are determined. The rate constant for  $\text{Me}_2\text{PCH}_2\text{CN}$  is approximately the same as that for  $\text{Ph}_3\text{P}$ , whereas that for  $\text{P}(\text{CH}_2\text{CN})_3$  is  $2 \times 10^4$  times smaller. This low nucleophilic reactivity of cyanomethylphosphines is ascribed to polar effects from the cyano group(s) which contracts the phosphorus lone-pair.

(Cyanomethyl)phosphines,  $\text{R}_{3-n}\text{P}(\text{CH}_2\text{CN})_n$ , are examples of C-functionalized tertiary phosphines which have recently attracted considerable interest, mainly because of their potential as chelating ligands.<sup>1-3</sup> Introduction of functional groups close to the phosphorus atom, however, changes the donor property of phosphorus for both steric and electronic reasons, and accordingly changes the coordinating ability (towards metal centers) and nucleophilicity (towards carbon centers). Obviously it would be valuable to have quantitative information on how different functional groups change the donor property in order to help designing new phosphines with specific properties. Functionalization at the  $\alpha$ -carbon should give maximum effects, and many such substituted phosphines are now known, e.g. the trisubstituted phosphines  $\text{P}(\text{CH}_2\text{OH})_3$ ,<sup>4</sup>  $\text{P}(\text{CH}_2\text{NR}_2)_3$ ,<sup>5</sup>  $\text{P}(\text{CH}_2\text{PMe}_2)_3$ ,<sup>6</sup>  $\text{P}(\text{CH}_2\text{COOEt})_3$ ,<sup>7</sup>  $\text{P}(\text{CH}_2\text{COOH})_3$ <sup>8</sup> and  $\text{P}(\text{CH}_2\text{CN})_3$ .<sup>9</sup> However, we are aware of only one quantitative study of the nucleophilic reactivity of  $\alpha$ -substituted phosphines. The quaternization of some diphenyl-

phosphinoacetic acid derivatives with ethyl iodide has been correlated with Taft  $\sigma^*$  values and phosphorus lone-pair ionization potentials.<sup>10</sup>

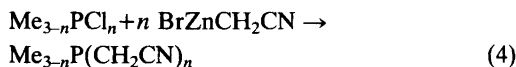
The present paper describes the preparation of two new  $\alpha$ -substituted phosphines,  $\text{Me}_2\text{PCH}_2\text{CN}$  and  $\text{MeP}(\text{CH}_2\text{CN})_2$ , a new route (eqn. (4)) to the known  $\text{P}(\text{CH}_2\text{CN})_3$ , and quantitative results on their very different nucleophilic reactivities.

*Synthesis.* (Cyanomethyl)phosphines have hitherto been prepared by three methods [eqn. (1)–(3)]. The first method [eqn. (1)]<sup>11</sup>



allows only one cyanomethyl group to be introduced but is otherwise fairly general. This method was chosen to prepare  $\text{Me}_2\text{PCH}_2\text{CN}$ . The second route [eqn. (2)]<sup>12</sup> involves the preparation of silylphosphines which are very reactive and sometimes difficult to obtain, and the yield is low for  $n=3$ . The third method [eqn. (3)]<sup>9</sup> seems fairly general ( $\text{Cl}_2\text{PCH}_2\text{CN}$ <sup>13</sup> and  $\text{MeP}(\text{CH}_2\text{CN})_2$ <sup>14</sup> have been similarly obtained) but its drawback is the low yield synthesis of  $\text{Bu}_3\text{SnCH}_2\text{CN}$ . To obtain  $\text{MeP}(\text{CH}_2\text{CN})_2$  and  $\text{P}(\text{CH}_2\text{CN})_3$  we therefore attempted a synthesis *via* the known<sup>15</sup> Reformatsky reagent  $\text{BrZnCH}_2\text{CN}$  [eqn. (4)], in analogy with Podla-

hová's successful syntheses of  $\text{Ph}_{3-n}\text{P}(\text{CH}_2\text{COOEt})_n$ .<sup>7</sup> The reactions when run at low temperatures ( $-78^\circ\text{C}$ ) gave  $\text{MeP}(\text{CH}_2\text{CN})_2$  and  $\text{P}(\text{CH}_2\text{CN})_3$  in fair yields. As it is a one pot synthesis from readily obtainable starting materials, this route is considered the most attractive one to prepare (cyanomethyl)phosphines with two or three cyanomethyl groups.



**Nucleophilic reactivity.**  $\text{P}(\text{CH}_2\text{CN})_3$  reacts very slowly with alkyl halides. Several days, in refluxing acetonitrile with excess benzyl bromide, were necessary to prepare  $\text{PhCH}_2\text{P}^+(\text{CH}_2\text{CN})_3\text{Br}^-$ , and refluxing with excess ethyl iodide in acetone did not give appreciable amounts of a phosphonium salt after 2 days. The above benzylophosphonium salt hydrolyzes easily at room temperature to give  $\text{PhCH}_2\text{P}(\text{O})(\text{CH}_2\text{CN})_2$ . This reflects the good leaving group ability of the cyanomethyl group which, more surprisingly, also manifests itself in the properties of  $\text{P}(\text{CH}_2\text{CN})_3$ . Although fairly stable to water and dilute HCl,  $\text{P}(\text{CH}_2\text{CN})_3$  is rapidly hydrolyzed to  $\text{HPO}_3^{2-}$  and  $\text{CH}_3\text{CN}$  by aqueous NaOH at room temperature.<sup>14</sup>  $\text{MeP}(\text{CH}_2\text{CN})_2$  and  $\text{Me}_2\text{PCH}_2\text{CN}$  react more smoothly with alkyl halides, and only  $\text{PhCH}_2(\text{Me})\text{P}^+(\text{CH}_2\text{CN})_2\text{Br}^-$  is somewhat prone to hydrolysis.

Quantitative results on the nucleophilic reactivity of  $\text{Me}_2\text{PCH}_2\text{CN}$ ,  $\text{MeP}(\text{CH}_2\text{CN})_2$  and  $\text{P}(\text{CH}_2\text{CN})_3$  were obtained from following, by conductivity measurements, their reactions with benzyl bromide in acetonitrile at  $35^\circ\text{C}$ . The

Table 1. Rate constants for quaternization, Taft  $\sigma^*$  values and phosphorus lone-pair ionization potentials of  $\text{Me}_{3-n}\text{P}(\text{CH}_2\text{CN})_n$  and  $\text{Ph}_3\text{P}$ .

	$k_2^a$ ( $\text{l mol}^{-1}\text{s}^{-1}$ )	$\Sigma\sigma^*^b$	IP <sup>c</sup> (eV)
$\text{P}(\text{CH}_2\text{CN})_3$	$1.3 \times 10^{-7}$	5.13	10.59
$\text{MeP}(\text{CH}_2\text{CN})_2$	$3.0 \times 10^{-5}$	3.42	9.83
$\text{Me}_2\text{PCH}_2\text{CN}$	$3.9 \times 10^{-3}$	1.71	9.22
$\text{Ph}_3\text{P}$	$3.0 \times 10^{-3}$	1.80	7.88

<sup>a</sup> Second order rate constant for quaternization with benzyl bromide in acetonitrile at  $35^\circ\text{C}$ . <sup>b</sup>  $\sigma^* = 0.00$  for Me, 0.60 for Ph and 1.71 for  $\text{CH}_2\text{CN}$ .<sup>10</sup> <sup>c</sup> Vertical ionization potentials.

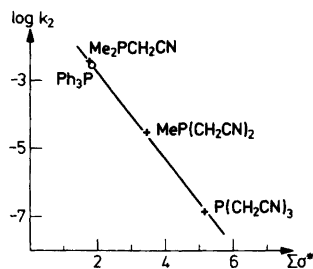


Fig. 1. Plot of rate constant versus Taft  $\sigma^*$  values for the reaction  $\text{R}_3\text{P} + \text{PhCH}_2\text{Br} \rightarrow \text{R}_3\text{PhCH}_2\text{P}^+\text{Br}^-$  in acetonitrile at  $35^\circ\text{C}$ .

second order rate constants for quaternization, including that of  $\text{Ph}_3\text{P}$  for comparison, are given in Table 1, together with the Taft  $\sigma^*$  values and the phosphorus lone-pair ionization potentials (IP). The rate data show that the cyanomethyl group decreases the nucleophilic reactivity of phosphorus very strongly.  $\text{Me}_2\text{PCH}_2\text{CN}$  reacts nearly as slowly as  $\text{Ph}_3\text{P}$ , and  $\text{P}(\text{CH}_2\text{CN})_3$  is approximately 20 000 times less reactive. The effects of multiple cyanomethyl substitution are additive as shown by a linear dependence of  $\log k_2$  with the Taft  $\sigma^*$  values (Fig. 1). The rate constants also correlate with the IP's (Fig. 2), although  $\text{Ph}_3\text{P}$  is anomalous. A correlation between gas phase (IP) and solution ( $\log k_2$ ) properties may fail for several reasons,<sup>10</sup> but the main cause of the deviation for  $\text{Ph}_3\text{P}$  is probably the different C–P–C bond angle ( $103^\circ$  for  $\text{Ph}_3\text{P}$ ,<sup>16</sup> about  $98^\circ$  for  $\text{P}(\text{CH}_2\text{CN})_3$ <sup>9</sup> and  $\text{Me}_3\text{P}$ <sup>17</sup>). A larger C–P–C angle corresponds to a more extended lone-pair (one with more *p* character) with a lower IP, as observed. The correlation of

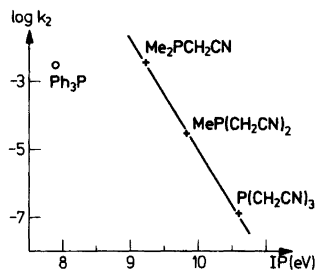


Fig. 2. Plot of rate constant versus phosphorus lone-pair ionization potential for the reaction  $\text{R}_3\text{P} + \text{PhCH}_2\text{Br} \rightarrow \text{R}_3\text{PhCH}_2\text{P}^+\text{Br}^-$  in acetonitrile at  $35^\circ\text{C}$ .

$\log k_2$  with IP for  $\text{Me}_2\text{PCH}_2\text{CN}$ ,  $\text{MeP}(\text{CH}_2\text{CN})_2$  and  $\text{P}(\text{CH}_2\text{CN})_3$  indicates that the cyano groups exert a field (or inductive) effect on the lone-pair which results in a contraction of it and thereby makes it less available for reactions.

This conclusion is corroborated by CNDO/2 calculations,<sup>18</sup> which show that the electron density in the lone pair region of  $\text{P}(\text{CH}_2\text{CN})_3$  is reduced relative to that of  $\text{Me}_3\text{P}$ . *Ab initio* calculations on  $\text{Me}_2\text{PCH}_2\text{CN}$  and low temperature X-ray diffraction studies on  $\text{P}(\text{CH}_2\text{CN})_3$  are in progress<sup>19</sup> with the aim to give more evidence on the electron distribution in these cyanomethylphosphines.

## EXPERIMENTAL

Analyses were performed by the microanalytical department of this laboratory.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a JEOL FX 90 Q Fourier NMR spectrometer. Chemical shifts (ppm) are given relative to internal TMS for  $^1\text{H}$  spectra ( $\delta_{\text{H}}$ ) and external 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  spectra ( $\delta_{\text{P}}$ ), and are given as positive for low-field shifts. The He(I) photoelectron spectra were obtained on a Perkin-Elmer PS 18 spectrometer calibrated using the 2P<sub>3/2</sub> peaks of Ar and Xe. Ionization potentials were reproducible within  $\pm 0.03$  eV. The kinetic measurements were performed at  $35.0 \pm 0.2^\circ$  using the conductivity method of Henderson and Buckler.<sup>20</sup> A Radiometer CDM 2 Conductivity Meter and a cell with platinized platinum electrodes with a cell constant of  $0.97 \text{ cm}^{-1}$  was used. Acetonitrile (Merck "Uvasol") was purified through a column of neutral  $\text{Al}_2\text{O}_3$  (Woelm N-Super I) and deoxygenated by bubbling Ar through it for 10 min. The solvent thus purified had a conductivity of less than  $0.2 \mu\text{ohm}^{-1} \text{ cm}^{-1}$ . The solutions were prepared at  $20^\circ\text{C}$  and corrected for concentration changes upon heating to  $35^\circ\text{C}$ . The reactions were followed until a few percent of the phosphine had reacted. The rate constants were calculated from the linear approximation  $kt = x/ab$ .<sup>20</sup> Benzyl bromide and phosphine concentrations were varied to prove that the reactions were second order. Up to ten times molar excess of benzyl bromide was used for the more slowly reacting phosphines to ensure convenient rates. The calculated rate constants (Table 1) are the results of duplicate runs, which were reproducible within  $\pm 10\%$ . All manipulations with phosphines were carried out under  $\text{N}_2$  or Ar.

*P,P*-dimethylphosphinoacetonitrile ( $\text{Me}_2\text{P}(\text{O})\text{CH}_2\text{CN}$ ).  $\text{Me}_2\text{POBu}$ <sup>21</sup> (3.35 g, 25

mmol) was added in 0.5 ml portions to  $\text{ClCH}_2\text{CN}$  (3.8 g, 50 mmol) at  $75^\circ\text{C}$  with stirring. After 1 h at  $75^\circ\text{C}$  BuCl and excess  $\text{ClCH}_2\text{CN}$  were removed *in vacuo* and the residue recrystallized from ethyl acetate to give  $\text{Me}_2\text{P}(\text{O})\text{CH}_2\text{CN}$  (1.90 g, 65%), m.p.  $75\text{--}78^\circ\text{C}$  (hygroscopic). Anal.  $\text{C}_4\text{H}_8\text{NOP}$ : C, H, N. NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$  38.0;  $\delta_{\text{H}}$  1.76 ( $\text{CH}_3$ , d,  $^2J_{\text{PH}}$  13.2 Hz), 3.04 ( $\text{CH}_2$ , d,  $^2J_{\text{PH}}$  15.1 Hz).

*P,P*-dimethylphosphinoacetonitrile ( $\text{Me}_2\text{PCH}_2\text{CN}$ ). A mixture of  $\text{Me}_2\text{P}(\text{O})\text{CH}_2\text{CN}$  (1.75 g, 15 mmol) and  $\text{Ph}_2\text{SiH}_2$  (2.76 g, 15 mmol) was heated with stirring to  $175^\circ\text{C}$  for 6 h. Vacuum distillation through a small Claisen head gave  $\text{Me}_2\text{PCH}_2\text{CN}$  (1.24 g, 82%), b.p.  $58\text{--}59^\circ\text{C}/12 \text{ mmHg}$ . The purity was more than 97% according to  $^1\text{H}$  and  $^{31}\text{P}$  NMR. NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$   $-50.1$ ;  $\delta_{\text{H}}$  1.19 ( $\text{CH}_3$ , d,  $^2J_{\text{PH}}$  3.8 Hz), 2.40 ( $\text{CH}_2$ , d,  $^2J_{\text{PH}}$  5.6 Hz).

*Benzyl(cyanomethyl)dimethylphosphonium bromide* ( $\text{PhCH}_2\text{Me}_2\text{P}^+\text{CH}_2\text{CN Br}^-$ ). A mixture of  $\text{Me}_2\text{PCH}_2\text{CN}$  (0.20 g, 2 mmol) and  $\text{PhCH}_2\text{Br}$  (0.68 g, 4 mmol) in dry ether (10 ml) was kept at  $20^\circ\text{C}$  for 6 days. The precipitate was washed with ether, dried and recrystallized from 2-propanol to give the product (0.33 g, 60%), m.p.  $120\text{--}121.5^\circ\text{C}$ . Anal.  $\text{C}_{11}\text{H}_{15}\text{BrNP}$ : C, H, N, Br. NMR ( $\text{CD}_3\text{CN}$ ):  $\delta_{\text{P}}$  31.7.

*P*-methylphosphinediylacetonitrile ( $\text{MeP}(\text{CH}_2\text{CN})_2$ ). A solution of  $\text{BrCH}_2\text{CN}$  (7.20 g, 60 mmol) in dry THF (30 ml) was added during 20 min to a stirred suspension of Zn (Riedel-de Haën "chem. rein. geraspelt", freshly etched with 0.2 M HCl followed by washing with water, acetone, ether and drying; 3.92 g, 60 mmol) in dry THF (10 ml). The temperature was kept at *ca.*  $20^\circ\text{C}$  by occasional immersion in an ice-bath. The resulting green to brown solution was cooled to  $-78^\circ\text{C}$  and  $\text{MePCl}_2$  (3.51 g, 30 mmol) in dry THF (10 ml) added with stirring during 20 min. The reaction mixture was allowed to reach room temperature slowly (over *ca.* 6 h), filtered through a glasswool plug and the precipitate washed with THF ( $2 \times 10 \text{ ml}$ ). The solvent was removed at 10 mmHg and the residue dissolved in deoxygenated water (20 ml). The product was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 20 \text{ ml}$ ) and the  $\text{CH}_2\text{Cl}_2$  solution washed with water (20 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvent and distillation *in vacuo* through a small Claisen head gave  $\text{MeP}(\text{CH}_2\text{CN})_2$  (1.13 g, 30%), b.p.  $99\text{--}102^\circ\text{C}/0.20 \text{ mmHg}$ . The purity was higher than 97% according to  $^1\text{H}$  and  $^{31}\text{P}$  NMR. NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$   $-38.2$ ;  $\delta_{\text{H}}$  1.37 ( $\text{CH}_3$ , d,  $^2J_{\text{PH}}$  5.5 Hz), 2.63 ( $\text{CH}_2$ , AB part of ABX spectrum,  $\Delta_{\text{AB}}$  0.04 ppm,  $^2J_{\text{AB}}$  17.2,  $^2J_{\text{PH}}$  5.4 and 6.0 Hz).

*P*-methylphosphonoacetonitrile ( $\text{MeP}(\text{O})(\text{CH}_2\text{CN})_2$ ).  $\text{MeP}(\text{CH}_2\text{CN})_2$  (0.13 g, 1

mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) was oxidized by bubbling  $\text{NO}_2$  through the solution until a green colour remained. Evaporation of the solvent and recrystallization of the residue from abs. ethanol gave the product (0.09 g, 60%), m.p. 93–94 °C. Anal.  $\text{C}_5\text{H}_7\text{N}_2\text{OP}$ : C, H, N. NMR ( $(\text{CD}_3)_2\text{CO}$ ):  $\delta_{\text{p}}$  31.1;  $\delta_{\text{H}}$  1.90 ( $\text{CH}_3$ , d,  $^2J_{\text{PH}}$  13.8 Hz), 3.49 ( $\text{CH}_2$ , d,  $^2J_{\text{PH}}$  14.5 Hz).

**Benzylidicyanomethylmethylphosphonium bromide** ( $\text{PhCH}_2\text{MeP}^+(\text{CH}_2\text{CN})_2 \text{Br}^-$ ). A mixture of  $\text{MeP}(\text{CH}_2\text{CN})_2$  (0.50 g, 4 mmol) and  $\text{PhCH}_2\text{Br}$  (1.37 g, 8 mmol) in  $\text{CH}_3\text{CN}$  (5 ml) was refluxed for 20 h. The solvent was removed *in vacuo* and the residue washed with hexane to remove excess  $\text{PhCH}_2\text{Br}$ . Recrystallization from a small amount of  $\text{CH}_3\text{CN}$  gave the product (0.47 g, 40%), m.p. 121.5–122.5 °C. Anal.  $\text{C}_{12}\text{H}_{14}\text{BrN}_2\text{P}$ : C, H, N, Br. NMR ( $\text{CD}_3\text{CN}$ ):  $\delta_{\text{p}}$  33.2.

**Phosphinetriyltriacetonitrile** ( $\text{P}(\text{CH}_2\text{CN})_3$ ). This phosphine was prepared in the same way as  $\text{MeP}(\text{CH}_2\text{CN})_2$ , from  $\text{BrCH}_2\text{CN}$  (7.20 g, 60 mmol), Zn (3.92 g, 60 mmol) and  $\text{PCl}_3$  (2.20 g, 16 mmol) in THF (50 ml). The reaction mixture, after reaching room temperature, was heated to reflux with active carbon and then filtered through a glasswool plug. The solvent was removed *in vacuo* and the brown residue was dissolved in hot, deoxygenated water (5 ml). Cooling to 0 °C gave a crystalline product which was recrystallized once from water, with addition of active carbon, to give  $\text{P}(\text{CH}_2\text{CN})_3$  (1.07 g, 45%), m.p. 110–111.5 °C (lit.<sup>9</sup> 110.5–112.5 °C).

**Benzyltris(cyanomethyl)phosphonium bromide** ( $\text{PhCH}_2\text{P}^+(\text{CH}_2\text{CN})_3 \text{Br}^-$ ). A mixture of  $\text{P}(\text{CH}_2\text{CN})_3$  (0.76 g, 5 mmol) and  $\text{PhCH}_2\text{Br}$  (3.4 g, 20 mmol) in  $\text{CH}_3\text{CN}$  (7 ml) was heated to reflux for 4 days. The precipitate, after cooling, was filtered off and recrystallized from  $\text{CH}_3\text{CN}$  to give the product (1.02 g, 64%), m.p. 199–201 °C. Anal.  $\text{C}_{13}\text{H}_{13}\text{BrN}_3\text{P}$ : C, H, N, Br. NMR ( $\text{CD}_3\text{CN}$ ):  $\delta_{\text{p}}$  31.6;  $\delta_{\text{H}}$  4.69 ( $\text{CH}_2\text{CN}$ , d,  $^2J_{\text{PH}}$  15.5 Hz), 4.74 ( $\text{CH}_2\text{Ph}$ , d,  $^2J_{\text{PH}}$  14.9 Hz), 7.54 (Ph).

**P-benzylphosphonyldiacetonitrile** ( $\text{PhCH}_2\text{P}(\text{O})(\text{CH}_2\text{CN})_2$ ).  $\text{PhCH}_2\text{P}^+(\text{CH}_2\text{CN})_3 \text{Br}^-$  (0.32 g, 1 mmol) and water (3 ml) were heated to give a clear solution. The product crystallized on cooling (0.19 g, 87%), m.p. 163.5–165 °C. Anal.  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{OP}$ : C, H, N. NMR ( $\text{CD}_3\text{CN}$ ):  $\delta_{\text{p}}$  32.0;  $\delta_{\text{H}}$  3.18 ( $\text{CH}_2\text{CN}$ , d,  $^2J_{\text{PH}}$  13.4 Hz), 3.52 ( $\text{CH}_2\text{Ph}$ , d,  $^2J_{\text{PH}}$  14.8 Hz), 7.36 (Ph).

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