Phosphoranes

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Formation of a Dicyanotriorganophosphorane from the Reaction of Triphenylphosphane with Phenylselenocyanate**

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Whilst numerous organophosphorus(III) cyanide compounds, such as $R_2PCN/RP(CN)_2$, are known,[1,2] reports of their phosphorus(V) analogues are considerably rarer. The ionic compounds $[R_3PCN]X$ ($X = Br$, I) are readily formed from

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stoichiometric amounts of R_3P and XCN[3,4] and exist in the solid state with either covalent ($[R_3PCN]X$) or ionic ($[R_3PX]CN$) cyanide although the former predominates in solution.[4] Recent work by Verkade and co-workers has shown that Me_3SiCN converts $[(Me_2N)_3PBr]Br$ into $[(Me_2N)_3PCN]Br$, whilst the same reaction with similar azaphosphatrane systems results in the isolation of both cyano (P−CN) and isocyano (P−NC) compounds.[5] In contrast, covalent dicyanotriorganophosphoranes ($R_3P(CN)_2$) are much more elusive with only three examples known ($R_3 = Ph_2Me$, $PhMe_2$, and $(Et_2N)_3$), each obtained from the reaction of $[R_3PCN]I$ with a second equivalent of ICN, although the products were not extensively characterized.[3] Herein, we report the remarkably facile formation of the dicyanotriorganophosphorane $Ph_3P(CN)_2$ by the reaction of triphenylphosphane with phenylselenocyanate.

PhSeCN and Ph_3P were reacted in a 2:1 ratio in dry diethyl ether for 24 h; subsequent solvent reduction and the addition of hexane resulted in the precipitation of a cream solid **1**. The $^{31}P\{^1H\}$ NMR spectrum of **1** ($CDCl_3$) exhibited a resonance at $\delta = -107.3$ ppm, the extremely low frequency of which is consistent with five-coordinate phosphorus, although the signal is considerably shifted from those reported for the trigonal-bipyramidal Ph_3PF_2 ($\delta_P = -58.1$)[6] and Ph_3PCl_2 ($\delta_P = -47.0$).[7] A significantly low-frequency shift in the $^{31}P\{^1H\}$ NMR spectra of P−CN compounds relative to P−Cl analogues is consistent with similar observations for organophosphorus(III) cyanides, for example, Ph_2PCN $\delta_P = -35.7$[2] (relative to Ph_2PCl $\delta_P = 81.9$).[8] The IR spectrum of **1** (nujol) exhibits an absorption at 2150 cm^{-1} (A_2' asymmetric CN mode), whilst the Raman spectrum displays a peak at 2158 cm^{-1} (A_1'' symmetric CN mode). These observations are consistent with group-theory predictions for a $R_3P(CN)_2$ molecule of D_{3h} symmetry. The absence of a band at 2080 cm^{-1} (typical of ionic cyanide)[9] suggests **1** is covalent in the solid state. On the basis of the spectroscopic data, we assigned **1** as the dicyanophosphorane $Ph_3P(CN)_2$. A crop of suitable crystals of **1** were obtained from a solution of diethyl ether, and X-ray crystallographic analysis confirmed the formation of $Ph_3P(CN)_2$ (Figure 1).[10]

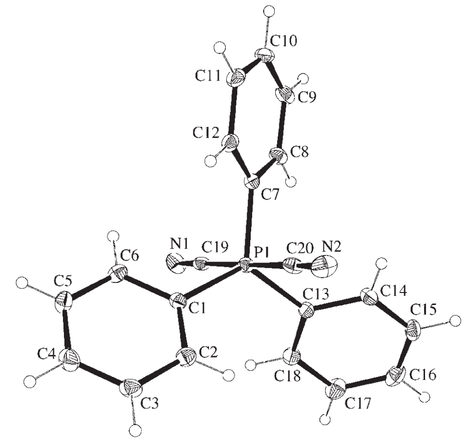

Figure 1. The molecular structure of $Ph_3P(CN)_2$ **1**. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths [Å] and angles [°]: P1-C1 1.801(3), P1-C7 1.776(4), P1-C13 1.801(3), P1-C19 1.941(3), P1-C20 1.929(3), N1-C19 1.148(5), N2-C20 1.147(5); N1-C19-P1 178.7(3), N2-C20-P1 179.0(3), C19-P1-C20 178.85(16), C1-P1-C19 89.90(15), C1-P1-C7 119.16(16).

To the best of our knowledge, $Ph_3P(CN)_2$ is the first crystallographically characterized dicyanotriorganophosphorane and exhibits trigonal-bipyramidal geometry at the phosphorus center, with axial cyanide groups and equatorial phenyl groups, as predicted by valence-shell electron-pair repulsion (VSEPR) theory. The structure of **1** may be compared with analogous Ph_3PX_2 systems, the solid-state structures of which vary considerably depending upon the nature of X; four-coordinate Ph_3P-X-X "spoke" structures are observed for X = Br or I,[11,12] whereas trigonal-bipyramidal compounds are formed for X = Cl or F,[7,13–14] although the chloride system also yields a dinuclear ionic species in dichloromethane.[15] The trigonal-bipyramidal structure exhibited by **1** is consistent with the high electronegativity of the CN^- ion (3.84 on the Pauling scale),[16] which lies between that of chlorine (3.16) and fluorine (3.98).[17] In $Ph_3P(CN)_2$, the NC-P-CN bond angle is essentially linear (C19-P1-C20: 178.85(16)°) and displays none of the distortions from regular trigonal-bipyramidal geometry observed for Ph_3PCl_2.[7] The P−C bonds to the cyano groups (P1-C19: 1.941(3), P1-C20: 1.929(3) Å) are substantially longer than those to the phenyl rings (P1-C1: 1.801(3), P1-C7: 1.776(4), P1-C13: 1.801(3) Å) and are considerably longer than in ionic $[\{2,4,6\text{-}(MeO)_3C_6H_2\}_3PCN]I$ (P-CN: 1.78(2) Å)[4] and the cyano phosphatrane $[N(CH_2CH_2N\mathit{i}Bu)_3PCN]Br$ (P-CN: 1.854(2) Å);[5] however, these P−CN bonds are closer to the axial P−CN bond length of 1.915(5) Å in the $[P(CN)_3Cl]^-$ ion.[18] The C≡N bond lengths (C19-N1: 1.148(5), C20-N2: 1.147(5) Å) are, however, very similar to the C≡N bond length of 1.148(3) Å in $[N(CH_2CH_2N\mathit{i}Bu)_3PCN]Br$,[5] but rather shorter than that of 1.19(5) Å observed for $[\{2,4,6\text{-}(MeO)_3C_6H_2\}_3PCN]I$.[4]

The formation of $Ph_3P(CN)_2$ in this reaction was unanticipated and is in contrast to the analogous reactions of "PhSeI" (a centrosymmetric dimer $(Ph_2Se_2I_2)_2$ in the solid state)[19] with tertiary phosphanes, which result in cleavage of the weak Se−Se bond and formation of either charge-transfer $R_3PSe(Ph)I$ compounds[20] or ionic $[R_3PSePh]I$ salts,[21] depending on the basicity of the phosphane. Given the significantly different reactivity of PhSeCN and $(Ph_2Se_2I_2)_2$ towards Ph_3P and the intriguing loss of selenium from the former, we sought to further explore the processes involved in the formation of **1** by performing the reaction on an NMR-tube scale with a number of different solvents ($[D_{10}]$diethyl ether, $[D_8]$toluene, and $[D_6]$acetone), thus monitoring the reaction in situ by $^{77}Se\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. In all solvents, the only peaks observed in the $^{77}Se\{^1H\}$ NMR spectra were PhSeCN ($\delta_{Se} = 319.2$), Ph_2Se_2 ($\delta_{Se} = 461.9$), and small amounts of Ph_3PSe ($\delta_{Se} = -269.2$). The formation of Ph_2Se_2 may imply the operation of a radical process, which involves homolytic cleavage of the Se−CN bond with subsequent recombination of $PhSe^{\bullet}$ and $CN^{\bullet}$ radicals to afford Ph_2Se_2 and $(CN)_2$; the latter species reacting with Ph_3P to produce **1**. However, we have not further explored this supposition.

The $^{31}P\{^1H\}$ NMR spectrum of the reaction in [D$_6$]acetone recorded immediately after preparation displayed three major resonances at $\delta = -109.0$ (**1**), -4.1 (Ph_3P), and 27.5 ppm. A fourth (minor) resonance, which displayed selenium satellites, $^1J(\text{Se-P}) = 741$ Hz, was observed at $\delta = 36.5$ ppm and is assigned to Ph_3PSe by comparison with literature values ($\delta_P = 36.1$ ppm, $^1J(\text{Se-P}) = 738$ Hz).[22] The formation of Ph_3PSe suggests that PhSeCN behaves to some degree similarly to KSeCN, which is routinely used to oxidize R_3P to R_3PSe,[23] although the resonance remained a minor product when the sample was monitored over several days. The reaction was monitored over 48 h, with a number of different species being observed (Table 1). The limited stability of **1** in [D$_6$]acetone is highlighted by the rapid disappearance of the resonance at $\delta = -109.0$ ppm, concomitant with the appearance of a peak at $\delta = -25.5$ ppm, which we tentatively assign to the ionized form of **1**, [Ph_3PCN]CN, since other [R_3PCN]$^+$ ions have been observed at similar chemical shifts.[4,5] This species is only stable for a few hours in acetone, and after 48 h the only major resonance present in the $^{31}P\{^1H\}$ NMR spectrum is that observed at $\delta = 29.1$ ppm, along with a few minor species. A similar situation was observed when the reaction was followed in [D$_8$]toluene and [D$_{10}$]diethyl ether, although the reaction occurs at a slower rate, with Ph_3P persisting in the mixture over several days. Additionally, **1** is significantly more stable in these solvents, as it survives for several days in both cases. Over longer periods, the $^{31}P\{^1H\}$ NMR spectra in these solvents resemble that observed in [D$_6$]acetone, with the resonance at $\delta = 29.1$ ppm predominating after several weeks.

Whilst the isolation in bulk of the species observed at $\delta = 29.1$ ppm in the $^{31}P\{^1H\}$ NMR spectrum remains elusive, we were fortuitous in obtaining structural data because of the formation of crystals from the acetone solution upon standing for several days. The structure of the unusual bridged tetracyanodiiminophosphorane **2** was thus elucidated (Figure 2).[24]

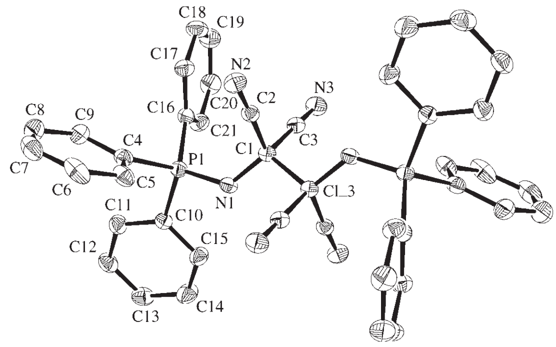

Figure 2. The molecular structure of $Ph_3PNC(CN)_2C(CN)_2NPPh_3\cdot 2\,(CH_3)_2CO$ (**2**). Thermal ellipsoids are set at the 30% probability level, and hydrogen atoms and solvent of crystallization are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-N1 1.577(3), P1-C4 1.809(3), P1-C10 1.800(3), P1-C16 1.797(3), N1-C1 1.406(4), C1-C2 1.502(4), C1-C3 1.505(4), C1-C1_3 1.592(4), C2-N2 1.138(4), C3-N3 1.137(4); C4-P1-N1 113.45(15), P1-N1-C1 128.3(2), N1-C1-C2 116.3(3), N1-C1-C3 113.9(2), N1-C1-C1_3 108.5(2), C1-C2-N2 177.5(3), C1-C3-N3 177.4(3). Symmetry operation used to generate equivalent atoms: $1-x$, $1-y$, $1-z$.

The structure of **2** consists of two {Ph_3P} units linked by a $-NC(CN)_2C(CN)_2N-$ bridge. The molecule has a centre of symmetry, with the $N-PPh_3$ units adopting an *anti* configuration along the C1−C1_3 bond. The P−N linkage in **2** (P1-N1: 1.577(3) Å) is consistent with a P=N double bond, with the P1-N1-C1 bond angle of 128.3(2)° being somewhat larger than the idealized 120° expected for an sp^2 nitrogen atom. The P=N bond is shorter than those observed for other cyano-substituted imino phosphoranes, for example, 1.615(2) Å for $Ph_3P{=}N\text{-}(\textit{cyclo}\text{-}C_5(CN)_7)$.[25] The C1−N1 linkage of 1.406(4) Å is typical for a CN single bond, while the terminal CN bond lengths are consistent with C≡N triple bonds. In the extended structure, individual molecules are linked by short intermolecular N···H contacts to phenyl protons (N2···H12: 2.48(4) Å; compared with the sum of the van der Waals radii: 2.75 Å).

The origin of **2** remains unclear and provides further evidence for the complexity of this reaction. Whilst **2** has thus far resisted more comprehensive characterization (because of contamination with Ph_2Se_2 and PhSeCN), the $^{31}P\{^1H\}$ NMR spectrum of the crystals confirms that **2** is the species observed at $\delta = 29.1$ ppm and is the most stable phosphorus-containing product obtained from the reaction, thus showing no sensitivity towards air or moisture. The mechanism for the formation of **2** is unclear, but it appears that it forms both in competition with and through the decomposition of **1**. The elimination of $(CN)_2$ from **1**, followed by attack of Ph_3P at the nitrogen atom is likely to result in the initial formation of unsaturated bridged species, such as $Ph_3P{=}N{-}C{\equiv}C{-}N{=}PPh_3$. This unit would be susceptible to successive addition of $(CN)_2$ across the unsaturated carbon–carbon bonds, thus resulting finally in **2**, the stability of which may be enhanced by the presence of cyano groups, which have previously been reported to stabilize iminophosphoranes.[25]

The reaction of PhSeCN with Ph_3P appears to offer a convenient synthetic route to dicyanotriorganophosphoranes, which are otherwise difficult to prepare and have been rarely studied, and $Ph_3P(CN)_2$, described herein, represents the first Group 15 triorganodicyanide compound to be crystallographically characterized. We are continuing to explore the bounds of this fascinating reaction with a view to preparing a range of $R_3P(CN)_2$ compounds, whose reactivity towards metal pow-

Table 1: Relative ratios over time of species present in the $^{31}P\{^1H\}$ NMR spectrum of the reaction of PhSeCN and Ph_3P (2:1) in [D$_6$]acetone.

t [h]	Chemical shift [ppm] of species present in solution							
	36.5 (Ph_3PSe)	29.1 (**2**)	27.5	22.0	15.1	−4.1 (Ph_3P)	−25.5 ((Ph_3PCN)CN)	−109.0 (**1**)
0	1	0	5	0	0	5	0	5
2.5	1	3	0	1	1	0	10	0
6	1	4	0	1	3	0	8	0
48	1	10	0	1	0	0	0	0

ders may mirror other R_3PX_2 compounds and may yield a new route to novel metal–cyanide complexes.

Experimental Section

All reactions were performed under an inert argon atmosphere using standard Schlenk techniques. Diethyl ether (BDH) was distilled over sodium/benzophenone ketyl and hexane (BDH) was distilled from sodium wire. Triphenylphosphane (Aldrich) and phenylselenocyanate (Acros) were used as supplied without further purification. ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained using a Bruker DPX400 machine operating at 399.9 and 100.6 MHz, respectively. ^{31}P{^{1}H} and ^{77}Se{^{1}H} NMR spectra were obtained using a Bruker DPX200 machine operating at 81.8 and 38.2 MHz, respectively. Peak positions are quoted relative to external trimethylsilane {^{1}H/^{13}C}, 85 % H_3PO_4 {^{31}P}, and Me_2Se {^{77}Se} using the high-frequency positive convention throughout. All spectra were recorded at 300 K. IR spectra were recorded on a Nicolet-Nexus combined FT-IR/FT-Raman spectrometer as nujol mulls held between KBr plates. Elemental analyses were performed by the University of Manchester, Chemistry Department, Microanalytical Service.

1: Ph_3P (0.820 g, 3.12 mmol) was dissolved in freshly distilled diethyl ether (30 mL), and PhSeCN (0.797 mL, 6.49 mmol) was added dropwise by syringe. The yellow solution was left to stir overnight, the volume was reduced to 5 mL, and freshly distilled hexane (10 mL) was added, thus resulting in precipitation of a cream solid which was isolated and dried in vacuo (yield = 0.647 g, 65.8 %). M.p. 102–104 °C; elemental analysis calcd (%) for $C_{20}H_{15}N_2P$: C 76.4, H 4.8, P 9.9; found: C 75.4, H 4.9, P 9.8; NMR ($CDCl_3$): $\delta_H = 8.12$–8.01 (m, 6H, Ar), 7.74–7.53 ppm (m, 9H, Ar); $\delta_C = 133.9$ (d, $^1J_{PC} = 76.3$ Hz, C_i), 132.3 (d, $^4J_{PC} = 12.6$ Hz, C_P), 132.2 (d, $^2J_{PC} = 18.4$ Hz, C_o), 129.9 ppm (d, $^3J_{PC} = 18.4$ Hz, C_m), (the resonance of the cyanide carbon atom was obscured by aromatic peaks); $\delta_P = -107.3$ ppm (s); IR (Nujol): $\tilde{\nu} =$ 2150 cm^{-1}, asymm. ν(CN); Raman: 2158 cm^{-1}, sym. ν(CN).

Crystallography: Diffraction data were recorded on a Nonius κ-CCD four-circle diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 150(2) K. Structural data were solved by direct methods, with full-matrix least-squares refinement on F^2 using the SHELX-97 program.[26] Absorption corrections by the multiscan method were applied with the SORTAV program. Non-hydrogen atoms were refined with anisotropic thermal parameters, all hydrogen atoms were located in the data. The figures were generated using ORTEP-3 for Windows.[27] CCDC-282250 (**1**) and -282249 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[24] Crystallographic details for **2** ($C_{48}H_{42}N_6P_2O_2$): orange prism, $0.20 \times 0.20 \times 0.20$ mm^3, monoclinic, $P2_1/n$ (no. 14), $a = 9.9274(3)$, $b = 14.9426(5)$, $c = 14.8579(5)$ Å, $\alpha = 90$, $\beta = 92.986(2)$, $\gamma = 90°$, $V = 2201.05(12)$ Å^3, $\rho_{calcd} = 1.202$ g cm^3, $\theta_{max} = 26.00°$, reflections/unique/parameters 15569/4307/325, $F(000)$ 836, $\mu = 0.144$ mm^{-1}, $T_{max} = 0.9718$, $T_{min} = 0.9718$, $R = 0.0722$, $wR2 = 0.2247$, largest diff. peak + hole 0.783, −0.377 Å^{-3}.

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