

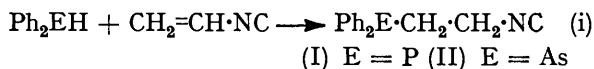
Addition of Phosphorus-Hydrogen and Arsenic-Hydrogen Bonds to Vinyl Isocyanide¹

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Addition of diphenylphosphine or diphenylarsine to vinyl isocyanide catalysed by potassium t-butoxide gives the liquid 2-diphenylphosphinoethyl (I) or diphenylarsinoethyl isocyanide (II). However, a similar addition of phenylphosphine to vinyl isocyanide in tetrahydrofuran solution gives 4,5-dihydro-3-phenyl-1,3-azaphosphole rather than phenylphosphinediylbis(ethyl isocyanide). Reactions of compounds (I) and (II) with tetracarbonylnorbornadienechromium at room temperature give the yellow polymetal derivatives $[\text{Ph}_2\text{E}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NC}]_4\text{Cr}_3(\text{CO})_{12}$ (E = P or As) rather than the simple monometal derivatives $[\text{Ph}_2\text{E}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NC}]\text{Cr}(\text{CO})_4$, in accord with the relative orientations of the two lone pairs in the ligand (I) or (II).

RECENT publications from this laboratory have described the preparation of compounds containing $\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{P}$ units by the base-catalysed addition of phosphorus-hydrogen bonds to vinylphosphines² and vinylphosphonates.³ Similar base-catalysed additions of phosphorus-hydrogen bonds across the carbon-carbon double bond of vinyl isocyanide⁴ have now been investigated in attempts to prepare compounds containing both isocyanide and tertiary phosphine functions.

The reaction between diphenylphosphine and vinyl isocyanide proceeded normally according to equation (i) (E = P). The product (I) was a pale yellow vacuum-



distillable liquid, ν_{max} 2154s cm^{-1} [$\nu(\text{CN})$], τ 6.72 and 7.66 (nonequivalent CH_2) and 2.74 (aromatic). The mass spectrum did not exhibit a molecular ion; that of highest m/e value was $\text{Ph}_2\text{PC}_2\text{H}_3^+$ ($M - \text{HCN}$). Further fragmentation processes are as expected for compounds containing Ph_2P units.^{5,6}

¹ Preliminary communication, R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, 1971, **93**, 564.

² R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, 1971, **93**, 4158.

³ R. B. King, J. C. Cloyd, jun., and P. N. Kapoor, *J.C.S. Perkin I*, 1973, 2226.

The reaction between diphenylarsine and vinyl isocyanide in the presence of potassium t-butoxide also proceeded normally [equation (i), E = As]. The product (II) exhibited the characteristic $\nu(\text{CN})$ band at 2155 cm^{-1} and the ^1H n.m.r. spectrum was essentially identical with that of the phosphorus analogue, although triplet rather than quartet multiplicity was observed for the resonance around τ 6.9 arising from the inability of the arsenic atom (spin 3/2) to couple with these protons, in contrast with the phosphorus atom (spin 1/2). A very weak molecular ion was observed in the mass spectrum under carefully controlled conditions but rapid decomposition in the mass spectrometer prevented a reliable mass spectrum from being obtained.

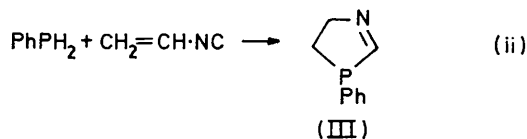
The reaction between phenylphosphine and vinyl isocyanide was investigated in an attempt to prepare phenylphosphinediylbis(ethyl isocyanide). However, this reaction proceeded according to equation (ii) to give the 1,3-azaphosphole (III), lacking isocyanide i.r. absorption in the range 2100–2200 cm^{-1} . A medium intensity broad band at ca. 1560 cm^{-1} can be assigned to $\nu(\text{C}=\text{N})$.

⁴ D. S. Matteson and R. A. Bailey, *J. Amer. Chem. Soc.*, 1968, **90**, 3761.

⁵ D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1968, **90**, 966.

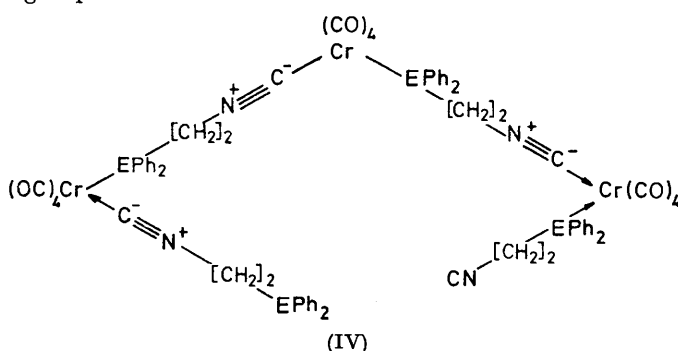
⁶ R. Colton and Q. N. Porter, *Austral. J. Chem.*, 1968, **21**, 2215.

The proton n.m.r. spectrum exhibited resonances at τ 1.73, 2.78, 5.8, 8.05, and 8.16 arising from the single olefinic proton, the five phenyl protons, the $\text{CH}_2\cdot\text{N}$



system, and the two non-equivalent $\text{P}\cdot\text{CH}_2$ protons, respectively. The splitting patterns were complex, but a large $\text{P},\text{H}-2$ coupling (56 Hz) was clearly observed. The mass spectrum exhibited the molecular ion as well as the ion $\text{PhP}\cdot\text{CH}_2\cdot\text{CH}_2^+$ ($M - \text{HCN}$; supported by observation of the expected metastable ion).

Compounds (I) and (II) are of potential interest as ligands in co-ordination chemistry; tertiary phosphines⁷ and isocyanides⁸ both form extensive series of metal complexes. However, the linear sp hybridization of both the carbon and the nitrogen atom of the isocyanide group directs the lone pair on the isocyanide carbon atom so that it cannot co-ordinate with the same metal atom as the lone pair on the phosphorus or arsenic atom. This effect should prevent the compounds from acting as simple bidentate ligands on a single metal atom.⁹ In accord with this view, the reactions of (I) and (II) with tetracarbonylnorbornadienechromium did not give the simple monometal complex $[\text{Ph}_2\text{E}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NC}]\text{Cr}(\text{CO})_4$; instead yellow crystalline polymetal products, $[\text{Ph}_2\text{E}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NC}]_4\text{Cr}_3(\text{CO})_{12}$, were obtained. The i.r. spectra of these products exhibited the $\nu(\text{CO})$ bands expected for a *cis*- $\text{L}_2\text{Cr}(\text{CO})_4$ derivative,¹⁰ indicating that the stereochemistry of the norbornadiene complex had been retained. The compounds can be formulated as (IV) ($\text{E} = \text{P}$ or As), in which three *cis*- $\text{Cr}(\text{CO})_4$ units are bridged by two $\text{Ph}_2\text{E}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NC}$ ligands, with two additional monodentate $\text{Ph}_2\text{E}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NC}$ ligands as end groups.



EXPERIMENTAL

Microanalyses and molecular weight determinations were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and by Schwarzkopf Microanalytical Laboratory, Woodside, New York. I.r. spectra were taken

⁷ G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 1.

⁸ (a) L. Malatesta, *Progr. Inorg. Chem.*, 1959, **1**, 283; (b) L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley, London, 1969.

⁹ R. B. King, *J. Coord. Chem.*, 1971, **1**, 67.

for liquid films (Perkin-Elmer 621 spectrometer with grating optics) and ^1H n.m.r. spectra for solutions in CDCl_3 [Varian HA-100 (100 MHz) or Hitachi-Perkin-Elmer R-20 (60 MHz) spectrometer]. Mass spectra were taken at 70 eV and 210° chamber temperature with either the University of Georgia Hitachi-Perkin-Elmer RMU-6 spectrometer or the Rutgers University RMU-7 instrument; only the most abundant ions are listed. A nitrogen atmosphere was generally used for carrying out reactions and for handling organo-phosphorus and organoarsenic compounds.

Diphenylphosphine,¹¹ diphenylarsine,¹² phenylphosphine,¹³ and vinyl isocyanide⁴ were prepared by published procedures. Potassium t-butoxide was used as received from MSA Research Corp., Pittsburgh, Pennsylvania. Benzene and tetrahydrofuran were purified before use by distillation under nitrogen over sodium benzophenone ketyl.

Reaction of Diphenylphosphine with Vinyl Isocyanide.—A mixture of diphenylphosphine (11.0 g, 59.3 mmol), vinyl isocyanide (4.75 g, 90 mmol), potassium t-butoxide (0.8 g, 7.1 mmol), and benzene (100 ml) was boiled under reflux for 20 h with stirring. Solvent was then removed at 50° and 40 mmHg. The residue was extracted with a mixture of dichloromethane (*ca.* 40 ml) and hexane (*ca.* 60 ml). Solvent was removed from the filtered extracts at 25° and 40 mmHg. The liquid was then vacuum distilled to give yellow viscous 2-diphenylphosphinoethyl isocyanide (I) (7.5 g, 53%), b.p. 133–144° at 0.07 mmHg. This product still contained a small amount of diphenylphosphine, as indicated by a weak $\nu(\text{PH})$ band at *ca.* 2280 cm^{-1} . A sample of b.p. 139–142° at 0.05 mmHg was obtained by a second vacuum distillation [Found: C, 75.1; 75.7; H, 6.2, 5.7; N, 5.6, 5.3; P, 13.1%; M , 238 (vapour pressure osmometer; solvent benzene). $\text{C}_{15}\text{H}_{14}\text{NP}$ requires C, 75.4; H, 5.9; N, 5.9; P, 12.9%; M , 239; $\nu(\text{CH})$ 3066m, 3052m, 3023vw,sh, 3012vw, 2999vw, 2930w,br, and 2853vw,br cm^{-1} ; $\nu(\text{CN})$ 2154s cm^{-1} ; other bands at 1660m, 1650m, 1586w, 1573vw, 1483m, 1454w, 1437s, 1350w, 1307vw, 1274vw, 1228vw, 1214vw, 1185vw, 1158vw, 1119vw, 1097m, 1071w, 1027m, 1000w, 954w, 929w, 910w, 740s, and 698s cm^{-1} ; τ 2.74 (complex m), 6.72 (apparent q, J 8 Hz), and 7.66 (t, J 8 Hz) (*ca.* 10 : 2 : 2, respectively); mass spectrum (sample temp. 50°) $\text{Ph}_2\text{PCH}_2\cdot\text{CH}_2\cdot\text{NC}^+$ (<1%), $\text{Ph}_2\text{PC}_2\text{H}_3^+$ (50), Ph_2PH^+ (25), $\text{C}_{12}\text{H}_8\text{P}^+$ (27), PhPCN^+ and/or $\text{C}_8\text{H}_7\text{P}^+$ (23), PhP^+ (100), $\text{C}_6\text{H}_4\text{P}^+$ (51), $\text{C}_6\text{H}_3\text{P}^+$ (36), $\text{C}_4\text{H}_2\text{P}^+$ (39), C_4HP^+ and/or C_6H_8^+ (56), PCN^+ and/or PC_2H_2^+ (29), and $\text{C}_2\text{H}_2\text{N}^+$ (135).

A similar reaction in boiling tetrahydrofuran rather than boiling benzene gave only a 12% yield of (I).

Reaction of Diphenylarsine with Vinyl Isocyanide.—A mixture of diphenylarsine (6.0 g, 26 mmol), vinyl isocyanide (7.0 g, 133 mmol), potassium t-butoxide (0.6 g, 5.4 mmol), and benzene (75 ml) was boiled under reflux for 24 h. Isolation of the product by a procedure similar to that for compound (I) gave pure 2-diphenylarsinoethyl isocyanide (II) (2.3 g, 31%), b.p. 153° and 2 mmHg after a single distillation [Found: C, 63.8; H, 5.1; As, 26.4; N, 5.1%; M , 284 (vapour pressure osmometer; solvent benzene). $\text{C}_{15}\text{H}_{14}\text{AsNP}$ requires C, 63.6; H, 5.0; As, 26.4; N, 4.9%; M , 283; $\nu(\text{CH})$ 3076m, 3061m, 3034vw, 3020vw, 3004vw, 2937w, and 2872vw,br cm^{-1} ; $\nu(\text{CN})$ 2155s cm^{-1} ; other bands at 1584m, 1487s, 1453m, 1439s, 1351m, 1308w,

¹⁰ F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

¹¹ W. Gee, R. A. Shaw, and B. C. Smith, *Inorg. Synth.*, 1967, **9**, 19.

¹² F. G. Mann and M. J. Pragnell, *J. Chem. Soc.*, 1965, 4120.

¹³ W. Kuchen and H. Buchwald, *Chem. Ber.*, 1958, **91**, 2296.

1287w, 1190w, 1161vw, 1085m, 1080m, 1074w, 1030m, 1003m, 924m, 895m, 853vw, 743s, and 702s cm^{-1} ; τ 2.90 (m), 6.80 (t, J 8 Hz), and 7.87 (t, J 8 Hz) (*ca.* 10 : 2 : 2, respectively). Instability of the compound in the mass spectrometer prevented a reliable mass spectrum from being obtained. A weak molecular ion peak was detected at m/e 283. Other more abundant ions were $\text{Ph}_2\text{AsC}_2\text{H}_3^+$, Ph_2AsH^+ , Ph_2As^+ , $\text{C}_{12}\text{H}_8\text{As}^+$, $\text{C}_{12}\text{H}_{10}^+$, $\text{C}_{12}\text{H}_8\text{As}^+$ and/or PhAs^+ , C_6H_6^+ , C_6H_5^+ , and $\text{C}_2\text{H}_2\text{N}^+$; the relative intensities changed continuously as the sample decomposed.

Reaction of Phenylphosphine with Vinyl Isocyanide.—A mixture of phenylphosphine (4.3 g, 39 mmol), potassium *t*-butoxide (0.75 g, 6.7 mmol), and tetrahydrofuran (100 ml) was treated gradually with vinyl isocyanide (8.0 g, 150 mmol). After the initial exothermic reaction had subsided, the mixture was boiled under reflux for 12 h. Tetrahydrofuran and the excess of vinyl isocyanide were then removed at 25° and 0.3 mmHg. Distillation of the residue gave a pale yellow air-sensitive liquid (6.0 g, 95%), b.p. 64° at 0.07 mmHg, shown to be 4,5-dihydro-3-phenyl-1,3-azaphosphole (III) [Found: C, 66.3; H, 6.0; N, 8.5; P, 19.0%; M , 186 (vapour pressure osmometer; solvent benzene). $\text{C}_6\text{H}_{10}\text{NP}$ requires C, 66.4; H, 6.1; N, 8.6; P, 19.0%; M , 163]; $\nu(\text{CH})$ 3055w, 2980w, 2932m, and 2856w cm^{-1} ; no $\nu(\text{CN})$; other bands at 1594sh, 1583sh, 1566m, 1482w, 1431m, 1304w, 1264m, 1168w, 1132vw, 1092m, 1065w, 1020w, 993w, 955s, 900w, 852w, 781w, 733s, and 684s cm^{-1} ; τ (*neat liquid*) 1.73 (dt, J 56 and 2 Hz), 2.78 (complex m), 5.80 (complex m), 8.05 (m), and 8.16 (m) (*ca.* 1 : 5 : 2 : 1 : 1, respectively); mass spectrum (sample temp. 100°) $\text{PhPC}_3\text{-H}_5\text{N}^+$ (32%), $\text{PhPC}_2\text{H}_4^+$ (35), PhP^+ (100), $\text{C}_6\text{H}_4\text{P}^+$ (36), and $\text{C}_2\text{H}_2\text{N}^+$ (89).

When benzene rather than tetrahydrofuran was used as a solvent, no identifiable organophosphorus compounds were obtained.

Attempted Reactions of Phosphine with Vinyl Isocyanide.—

Phosphine generated from aluminium phosphide (20 g, 345 mmol) and an excess of water was passed during 4 h into a mixture of vinyl isocyanide (10 g, 189 mmol), potassium *t*-butoxide (1.0 g, 8.9 mmol), and tetrahydrofuran (100 ml) at the b.p. under reflux. Attempts to isolate a product from this mixture or from a mixture obtained after a similar reaction in boiling benzene rather than boiling tetrahydrofuran failed.

Reaction of Compounds (I) and (II) with Tetracarbonylnorbornadienechromium.—A mixture of compound (I) or (II) (3 mmol), the norbornadiene complex (0.69 g, 3.2 mmol), and benzene (40 ml) was stirred for 18 h at room temperature. Solvent was then removed at 40° and 35 mmHg. Unchanged norbornadiene complex was removed by washing with boiling cyclohexane (500 ml) in several portions. The residue was dissolved in diethyl ether. Solvent was removed from the filtered solution at *ca.* 25° and 40 mmHg to give yellow solids of the approximate stoichiometries $[\text{Ph}_2\text{E}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NC}]_4\text{Cr}_3(\text{CO})_{12}$ (E = P or As) in the indicated yields. The phosphine complex (1.1 g, 100%) had m.p. 125—127° (decomp.) [Found: C, 59.6; 59.4; H, 4.5; 4.4; N, 3.3; O, 14.2. 13.9; P, 7.8%; M , 1040 (vapour pressure osmometer; solvent benzene). $\text{C}_{72}\text{H}_{56}\text{Cr}_3\text{N}_4\text{O}_{12}\text{P}_4$ requires C, 59.7; H, 3.9; N, 3.9; O, 13.3; P, 8.6%; M , 1448]; $\nu(\text{CN})$ 2144m,br cm^{-1} (KBr); $\nu(\text{CO})$ 2010s, 1920vs, 1905vs, and 1883vs cm^{-1} (CS_2 solution). The arsine complex (0.65 g, 49%) had m.p. 157—160° (decomp.) [Found: C, 53.2; H, 3.7; As, 16.8; Cr, 11.2; N, 3.1; O, 12.2; M , 1776 (vapour pressure osmometer; solvent benzene). $\text{C}_{72}\text{H}_{56}\text{-As}_4\text{Cr}_3\text{N}_4\text{O}_{12}$ requires C, 53.2; H, 3.4; As, 18.5; Cr, 9.6; N, 3.4; O, 11.8%; M , 1624]; $\nu(\text{CN})$ 2143m,br cm^{-1} (KBr); $\nu(\text{CO})$ at 2011s, 1940vs, and 1905vs cm^{-1} (CS_2 solution).

We thank the Air Force Office of Scientific Research for partial support of this work.

[3/2556 Received, 17th December, 1973]