Polytertiary Phosphines and Arsines. I. The Synthesis of Polytertiary Phosphines and Arsines by the Base-Catalyzed Addition of Phosphorus–Hydrogen and Arsenic–Hydrogen Bonds to Vinylphosphines[1]

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Abstract: Novel polytertiary phosphines and phosphine–arsines can be prepared by the addition of phosphorus–hydrogen and arsenic–hydrogen bonds across the carbon–carbon double bonds of vinylphosphines in the presence of a base catalyst such as phenyllithium or potassium *tert*-butoxide. Thus the reaction between diphenylphosphine and diphenylvinylphosphine gives $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. The tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ can be prepared either by the reaction between phenylphosphine and diphenylvinylphosphine or by the reaction between diphenylphosphine and phenyldivinylphosphine. The tripod tetratertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_3P$ can be prepared either by the reaction between phosphine and diphenylvinylphosphine or the reaction between diphenylphosphine and trivinylphosphine. The linear tetratertiary phosphine $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ can be prepared by the reaction between 1,2-bis(phenylphosphino)ethane and diphenylvinylphosphine. The hexatertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ can be prepared by the reaction between $H_2PCH_2CH_2PH_2$ and diphenylvinylphosphine. The phosphine–arsine $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ can be prepared by the reaction between diphenylarsine and diphenylvinylphosphine. The phosphine–diarsine $C_6H_5P[CH_2CH_2As(C_6H_5)_2]_2$ can be prepared by the reaction between diphenylarsine and phenyldivinylphosphine. Similar addition of phosphorus–hydrogen bonds across the carbon–carbon triple bond of ethynylphosphines gives olefinic ditertiary phosphines with the phosphorus atoms in trans positions, as exemplified by the reaction between diphenylphosphine and diphenylethynylphosphine to give the known *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$. The reaction between diphenylarsine and diphenylethynylphosphine gives the olefinic phosphine–arsine *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$. The infrared, proton, and ^{31}P nmr spectra and the mass spectra of the new polytertiary phosphines and phosphine–arsines are discussed.

During the past few years we have been interested in the chemistry of cyclopentadienylmetal derivatives containing tertiary phosphine ligands. For this reason we have investigated reactions of cyclopentadienylmetal–carbonyl derivatives with ditertiary phosphines such as $R_2PCH_2CH_2PR_2$ ($R = CH_3$ and C_6H_5), *cis*- and *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$, and the tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$.[3–5] Other workers have also studied extensively tertiary phosphine complexes of metal halides, carbonyls, and cyclopentadienyls.[6,7]

One of the limiting factors in the development of the chemistry of tertiary phosphine complexes of transition metals has been the availability of appropriate tertiary phosphine ligands, especially the polytertiary phosphines. Most polytertiary phosphines are prepared by reactions of organic polyhalides with alkali metal dialkylphosphides. Thus the frequently studied 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, is readily prepared by the reaction of 1,2-dichloroethane with lithium diphenylphosphide in tetrahydrofuran solution.[8] Similarly, the unsaturated ditertiary phosphines *cis*- and *trans*-1,2-bis(diphenylphosphino)ethylene can be prepared by stereospecific reactions of *cis*- and *trans*-1,2-dichloroethylene, respectively, with lithium diphenylphosphide.[9] The tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ can be prepared by reaction of the trichloride $CH_3C(CH_2Cl)_3$ with sodium diphenylphosphide in liquid ammonia and tetrahydrofuran.[8] However, attempts to extend this synthetic technique to more complex polytertiary phosphines, except for the one tetratertiary phosphine $C[CH_2P(C_6H_5)_2]_4$,[10] have been unpromising owing either to the unavailability of an appropriate polyhalide or to difficulties in obtaining complete reaction of such a polyhalide with an alkali metal dialkylphosphide. Even the preparation of the tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ from $CH_3C(CH_2Cl)_3$ and sodium diphenylphosphide[8] has presented some difficulties of this type, since the reaction of $CH_3C(CH_2Cl)_3$ with an insufficient quanitity of sodium diphenylphosphide leads to the formation of the phosphetanium salt I rather than the desired tritertiary phosphine.[11] The one known potentially tetradentate tetratertiary phosphine, tris(*o*-diphenylphosphinophenyl)phosphine (II), was prepared by treatment of phosphorus trichloride with the lithium derivative from *n*-butyllithium and *o*-bromophenyldiphenylphosphine.[12]

These considerations indicate the need for a new method for the preparation of polytertiary phosphines to supplement the reactions of alkali metal dialkylphosphides with organic polyhalides. Our interest in

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[1] For a preliminary communication of this work, see R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, **91**, 5191 (1969).

[2] Postdoctoral research associate, 1968–1969.

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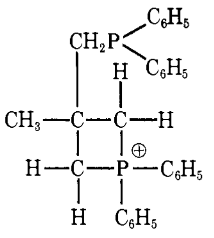
coordination chemistry led us to study the synthesis of polytertiary phosphines with the phosphorus atoms in relative positions to bond to a single metal atom, *i.e.*, to act as multidentate chelating agent. Polytertiary phosphines which act as multidentate chelating agents are of the greatest potential interest to coordination chemists because of new possibilities for the stabilization of unusual coordination numbers, oxidation states, and spin states. Furthermore, such polytertiary phosphine multidentate chelating agents might form transition metal complexes with novel catalytic properties.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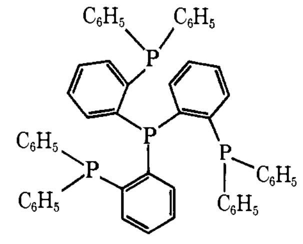
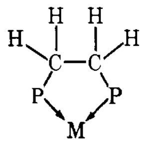
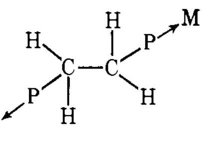

II

A useful building block for the construction of potentially multidentate chelating polytertiary phosphines is the ethane bridge between two phosphorus atoms in units of the type PCH_2CH_2P. Such PCH_2CH_2P units are useful for building polytertiary phosphines with varied coordinating properties since the two phosphorus atoms in a PCH_2CH_2P unit can either bond both to a single metal atom (IIIa) or to two different metal atoms (IIIb), as demonstrated by various studies on reactions between cyclopentadienylmetal-carbonyl derivatives and the ditertiary phosphines $R_2PCH_2CH_2PR_2$.[4,5] Furthermore, the PCH_2CH_2P building block can be generated by the addition of a phosphorus-hydrogen bond across the carbon-carbon double bond of vinylphosphines according to the following general scheme.


IIIa


IIIb

$$P{-}H + PCH{=}CH_2 \longrightarrow PCH_2CH_2P$$

The vinylphosphorus derivatives required for syntheses of this type are potentially readily obtainable by reaction of the corresponding phosphorus halide with vinylmagnesium bromide.[13] Phosphorus-hydrogen bonds are known to undergo facile base-catalyzed addition to the carbon-carbon double bonds of activated olefins such as acrylonitrile;[14] it appeared reasonable that the neighboring phosphorus atom might activate the carbon-carbon double bond in vinylphosphines similar to the neighboring sulfur atom in vinylsulfonium salts.[15] During the initial stages of our studies phenyllithium was used as the basic catalyst because of its demonstrated value for catalysis of the addition of phenylphosphine to 1,3-diynes.[16] However, in a later stage of this work potassium *tert*-butoxide was found to be a better catalyst in certain cases.

This paper describes the details of the study on our previously communicated[1] synthesis of polytertiary phosphines by the base-catalyzed addition of phosphorus-hydrogen bonds across the carbon-carbon double bonds of vinylphosphines. These reactions provide facile high-yield syntheses of ditertiary, tritertiary, two tetratertiary, and even one hexatertiary phosphine built from PCH_2CH_2P units. Lack of availability of appropriate starting materials presently prevents similar reactions from being used for the preparation of other types of polytertiary phosphine structures such as pentatertiary phosphines or hexatertiary phosphines other than the one prepared. In this work positions on the trivalent phosphorus atoms not occupied by the CH_2CH_2 bridges were filled with phenyl groups since the phenylphosphines $C_6H_5PH_2$ and $(C_6H_5)_2PH$ and the phenylvinylphosphines $(C_6H_5)_2PCH{=}CH_2$ and $C_6H_5P(CH{=}CH_2)_2$ are the most readily available compounds of these types. Moreover, the phenylated polytertiary phosphines were all air-stable white crystalline solids. These advantages of the phenylated polytertiary phosphines allowed us to explore the application of this new synthetic technique to a wide variety of systems, although the presence of phenyl rather than methyl groups on the phosphorus atoms is somewhat disadvantageous in coordination chemistry owing to relatively low solubility of many metal complexes. This paper also describes the synthesis of mixed phosphine-arsines such as $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ by similar base-catalyzed additions of diphenylarsine to carbon-carbon double bonds of various vinylphosphines. The phosphorus-hydrogen bond in diphenylphosphine was also found to add to the carbon-carbon triple bond in diphenylphosphinoacetylene, $(C_6H_5)_2PC{\equiv}CH$, but the $(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ produced in this reaction was the trans isomer rather than the cis isomer; the trans isomer is less useful to coordination chemists than the cis isomer since the trans isomer cannot act as a bidentate chelating agent where both phosphorus atoms bond to a single metal atom. For this reason we did not investigate additions of phosphorus-hydrogen bonds across the carbon-carbon triple bonds in ethynylphosphines in as much detail as the additions of phosphorus-hydrogen bonds across the carbon-carbon double bonds in vinylphosphines.

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., on a vapor pressure osmometer using benzene solutions. Infrared spectra (4000-600 cm^{-1}) were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer. Proton nmr spectra (Table I) were taken in chloroform-*d* solutions and were recorded at 100 MHz on a Varian HA-100 spectrometer. Phosphorus-31 nmr spectra (Table II) were taken in concentrated dichloromethane solutions and recorded at 40.5 MHz on a Varian HA-100 spectrometer. Mass spectra were taken at 70 eV on a Hitachi Perkin-Elmer RMU-6 mass spectrometer with a chamber temperature of 200 ± 20°. Relative

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Table I. Proton Nmr Spectra of Some Polytertiary Phosphines and Arsines[a]

	Chemical shifts, τ[b]	
Compound[b]	C_6H_5[c]	$=CHPR_2$ or CH_2
$Ph_2PCH_2CH_2PPh_2$	2.78	7.92 (t, 4)
$Ph_2PCH_2CH_2AsPh_2$	2.79	7.89 (s)
		7.93 (d, 4)
cis-$Ph_2PCH{=}CHPPh_2$	2.73	2.75 (t, 14.5)
trans-$Ph_2PCH{=}CHPPh_2$	2.71	3.26 (t, 14.5)
trans-$Ph_2PCH{=}CHAsPh_2$	2.68, 2.72, 2.76	3.07 (d, 14.5)[d]
		3.10 (d, 16)[d]
$PhP(H)CH_2CH_2P(H)Ph$	2.60, 2.71	8.19 (tt, 5,2)
	[τ(PH) 5.88	
	(dt, 211, 2)]	
$(Ph_2PCH_2CH_2)_2PPh$	2.71, 2.75	~8.0–8.4 (br, m)
$(Ph_2AsCH_2CH_2)_2PPh$	2.76	8.0–8.2 (m)
$(Ph_2PCH_2CH_2)_3P$	2.65	8.0–8.2 (br)
		8.4–8.6 (br)
$Ph_2PCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$	2.77	8.0–8.4 (br)
$(Ph_2PCH_2CH_2)_2PCH_2CH_2P(CH_2CH_2PPh_2)_2$	2.76	8.0–8.2 (br)
		8.5–8.6 (br)

[a] All of these spectra were taken in $CDCl_3$ solution. [b] The following abbreviations are used: Ph = phenyl, s = singlet, d = doublet, t = triplet, br = broad, m = multiplet, tt = triplet of triplets, dt = doublet of triplets. The separation (cps) is given in parentheses. [c] The phenyl resonance was complex and asymmetrical. Only the positions of peaks are given. [d] There are three possible ways of assigning the chemical shifts and coupling constants for the four nmr peaks in the olefinic proton region of *trans*-$Ph_2PCH{=}CHAsPh_2$. The assignment given in this table was selected so that the coupling constants in *trans*-$Ph_2PCH{=}CHAsPh_2$ were as close as possible to the coupling constants in the closely related *trans*-$Ph_2PCH{=}CHPPh_2$.

Table II. ^{31}P Nmr Spectra of Polytertiary Phosphines and Arsine–Phosphines[a]

	Chemical shifts[a]		
Compound[b]	$(C_6H_5)_2P$	C_6H_5P	P
$Ph_2PCH_2CH_2PPh_2$	12.9		
$Ph_2PCH_2CH_2AsPh_2$	13.0		
$PhP(CH_2CH_2PPh_2)_2$	13.5	16.6	
$PhP(CH_2CH_2AsPh_2)_2$		16.6	
$P(CH_2CH_2PPh_2)_3$	13.5		17.8
$Ph_2PCH_2CH_2PPhCH_2CH_2PPh-CH_2CH_2PPh_2$	13.1	16.6	
$(Ph_2PCH_2CH_2)_2PCH_2CH_2P-(CH_2CH_2PPh_2)_2$	13.2		17.4
trans-$Ph_2PCH{=}CHPPh_2$	7.9		
trans-$Ph_2PCH{=}CHAsPh_2$	8.0		

[a] These spectra were taken in dichloromethane solution at 40.5 MHz on a Varian HA-100 nmr spectrometer. Chemical shifts are given in parts per million upfield from external 85% phosphoric acid. [b] Ph = phenyl.

intensities are indicated in parentheses after the ion formula. Melting points were taken in capillaries and are uncorrected. A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling air-sensitive organophosphorus compounds and the phenyllithium catalyst, and (c) admitting to evacuated vessels containing potentially air-sensitive materials.

Many of these preparations were extremely malodorous. It was imperative not only to carry out all reactions involving volatile and air-sensitive organophosphorus compounds in a good hood but also to pass the effluent vapors from the more obnoxious reactions through oxidizing traps before venting them into the hood. Saturated aqueous potassium permanganate, bromine water, and a 1:1 mixture of nitric and sulfuric acids were the three most effective reagents for such traps. In some cases all three different types of traps were used in series. In one organophosphorus experiment closely related to those described in this paper where the trapping of noxious vapors was insufficient, the odors emanating from the hood exhausts were so strong that they invalidated experiments on the olfactory sense of snakes in a neighboring building. Phenylphosphine was the worst offender followed by phenyldivinylphosphine and 1,2-diphosphinoethane.

Starting Materials. Phenyllithium was purchased from Alfa Inorganics, Beverly, Mass., as a 2 *M* solution in 70:30 benzene–ether. Potassium *tert*-butoxide was used as purchased from M. S. A. Research Corporation, Pittsburgh, Pa. Tetrahydrofuran was purified by redistillation over lithium aluminum hydride. Benzene was purified by distillation over sodium spheres.

The vinyl bromide marketed 10–15 years ago when the original work on vinylmetallic compounds was carried out contained appreciable quantities of ethyl bromide and hence was unsuitable for preparation of vinylmagnesium bromide without further rather laborious purification before use.[17] However, the vinyl bromide currently marketed by Matheson Inc., East Rutherford, N. J., is manufactured by the dehydrobromination of 1,2-dibromoethane and hence does not contain the ethyl bromide impurity.[18] We therefore employed commercial vinyl bromide for this work without further purification.

The procedures used for the preparation in quantity of many of the known organophosphorus compounds required for this work are summarized below.

A. **Diphenylvinylphosphine.**[19] Reaction of 190 g (0.86 mol) of diphenylchlorophosphine (Eastern Chemical Co., Pequannock, N. J.) with 1.05 mol of vinylmagnesium bromide in 700 ml of tetrahydrofuran by the usual procedure[13] gave 155 g (85% yield) of diphenylvinylphosphine, bp 121° (0.4 mm).

B. **Phenyldivinylphosphine.**[13] Reaction of phenyldichlorophosphine with vinylmagnesium bromide gave only a 10% yield of phenyldivinylphosphine. However, the yield was raised to 46% by substituting the commercially available phenyldi-*n*-butoxyphosphine (Arapahoe Chemical Co., Boulder, Colo.) for phenyldichlorophosphine in this preparation.[20]

C. **Trivinylphosphine.**[13,21] Our attempts to prepare useful quantities of trivinylphosphine from vinylmagnesium bromide and either phosphorus trichloride or triphenyl phosphite were unsuccessful. We therefore prepared trivinylphosphine from vinyllithium[22] and phosphorus trichloride.

A solution of phenyllithium in diethyl ether (*without* any benzene as found in the commercial product) was prepared by the reaction of 140 g (0.89 mol) of bromobenzene with a suspension of 15 g (2.14 g-atoms) of finely cut Li metal in 200 ml of diethyl ether. The filtered brown phenyllithium solution was treated dropwise with a solution of 45 g (0.20 mol) of commercial tetravinyltin (M and T Chemical Co., Rahway, N. J.) in 200 ml of diethyl ether. The expected white precipitate of tetraphenyltin slowly separated. The resulting vinyllithium solution was treated with 27 g (0.20 mol) of phosphorus trichloride. An exothermic reaction occurred.

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After boiling under reflux for 2 hr, the reaction mixture was hydrolyzed with a saturated aqueous solution of ammonium chloride. The ether layer was dried over anhydrous sodium sulfate and then distilled under nitrogen at atmospheric pressure. First the diethyl ether was removed. Later a fraction boiling at 102–116° was collected which was sufficiently pure trivinylphosphine for the reactions described in this paper [lit.[21] bp 116.6° (760 mm)]. The yield of trivinylphosphine was 13 g (59%).

D. Phenylphosphine.[23] The phenylphosphine used in this work was prepared by the lithium aluminum hydride reduction of phenyldichlorophosphine. Highest yields were obtained when the reaction flask was cooled in a −78° bath during the initial stages of this reaction.[24] We are also indebted to Professor R. C. Taylor of this department for a gift of some of the phenylphosphine used in this work.

E. Diphenylphosphine.[25] This was prepared in 60–70% yield by reaction of triphenylphosphine with sodium in liquid ammonia followed by hydrolysis with water.

F. Diphenylarsine.[26] This was prepared in 70–95% yield by reaction of triphenylarsine with sodium in liquid ammonia followed by hydrolysis with water.

G. Diphenylethynylphosphine.[27] This was prepared by reaction of diphenylchlorophosphine with ethynylmagnesium bromide in tetrahydrofuran solution.

H. 1,2-Bis(phenylphosphino)ethane.[28] This compound was prepared either by the lithium aluminum hydride reduction of $(C_6H_5)(i\text{-}C_3H_7O)P(O)CH_2CH_2P(O)(O\text{-}i\text{-}C_3H_7)(C_6H_5)$[28] or by the cleavage of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ with sodium in liquid ammonia.[29] In our hands the latter method gave a 24% yield of diphenylphosphine and a 21% yield of 1,2-bis(phenylphosphino)ethane.

Reaction of Diphenylvinylphosphine with Diphenylphosphine. A mixture of 5.0 g (23.6 mmol) of diphenylvinylphosphine, 4.3 g (23.2 mmol) of diphenylphosphine, 4 ml of a 2 *M* benzene–ether solution of phenyllithium, and 100 ml of redistilled benzene was boiled under reflux for 20 hr. Solvent was removed from the yellow reaction mixture at ~25° (40 mm) to give a yellow solid residue which, after washing thoroughly with methanol and drying, gave 7.5 g (80% yield) of 1,2-bis(diphenylphosphino)ethane, mp 139–140° (lit.[8] mp 143–144°). The infrared spectrum of this product was identical with that of 1,2-bis(diphenylphosphino)ethane prepared from 1,2-dichloroethane and lithium diphenylphosphide.[8]

Preparation of Bis(2-diphenylphosphinoethyl)phenylphosphine. A. From Phenyldivinylphosphine and Diphenylphosphine. A mixture of 3 ml (3.0 g, 18.6 mmol) of phenyldivinylphosphine, 7 ml (6.9 g, 37.2 mmol) of diphenylphosphine, 7 ml of a 2 *M* benzene–ether solution of phenyllithium, and 50 ml of redistilled benzene was boiled under reflux for 24 hr. Solvent was then removed at ~25° (40 mm) to give a yellow paste which, after washing thoroughly with methanol and drying, gave 5.0 g (50% yield) of white crystalline $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$: mp 125–126° (lit.[30] mp 129–130°); infrared spectrum ν(CH) frequencies at 3066 (w), 3047 (vw), 3022 (vvw), 3014 (vvw), 2999 (vvw), 2924 (w), 2909 (vvw, sh), 2895 (vw), 2880 (vvw, sh), and 2865 (vvw, sh) cm^{-1}, other bands at 1580 (vw), 1479 (m), 1433 (s), 1423 (m), 1406 (vw, sh), 1384 (vw, sh), 1326 (vw,) 1317 (vw), 1304 (w), 1264 (vw, br), 1181 (vw), 1163 (w), 1155 (w), 1088 (m), 1064 (m), 1023 (m), 1010 (vvw), 995 (m), 984 (vvw), 745 (s), 727 (s), 715 (s), 698 (s), 674 (m), and 665 (m) cm^{-1}; mass spectrum (sample temperature 250°) $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5^+$ (13), $(C_6H_5)_2PCH_2CH_2P(C_2H_3)(C_6H_5)_2^+$ (4), $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2^+$ (100), $(C_6H_5)_2PCH_2CH_2PC_6H_5^+$ (39), $(C_6H_5)_3P_2H^+$ (16), $(C_6H_5)_3P_2^+$ (10), $(C_6H_5)_3PC_2H_3^+$ (14), $(C_6H_5)_3P^+$ (42), $C_{12}H_9P_2$? (11), $(C_6H_5)_2PCH_2CH_2^+$ (8), $(C_6H_5)_2PC_2H_3^+$ (6), $(C_6H_5)_2P^+$ (40), $C_{12}H_8P^+$ (85), $C_{12}H_8^+$ (13), $C_6H_5P_2^+$ (10), $C_8H_8P^+$ (7), $C_8H_7P^+$ (8), $C_8H_6P^+$ (13), $C_7H_6P^+$ (7), $C_6H_6P^+$ (13), $C_6H_5P^+$ (51), $C_6H_4P^+$ (26), $C_8H_9^+$ (5), $C_8H_8^+$ (4), $C_7H_7^+$ (11), $C_6H_6^+$ (9), and $C_6H_5^+$ (11).

Anal. Calcd for $C_{34}H_{33}P_3$: C, 76.5; H, 6.2; P, 17.3; mol wt, 534. Found: C, 76.2; H, 6.2; P, 17.2; mol wt, 527 (osmometric in benzene).

B. From Diphenylvinylphosphine and Phenylphosphine. A mixture of 10 g (47.2 mmol) of diphenylvinylphosphine, 2.6 g (23.6 mmol) of phenylphosphine, 0.5 g (4.5 mmol) of potassium *tert*-butoxide, and 100 ml of redistilled benzene was boiled under reflux for 24 hr. Solvent was removed at ~25° (40 mm) and the residue was washed with methanol and dried. Recrystallization from a mixture of benzene and methanol gave 11 g (87% yield) of white cystalline $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, mp 127°. The infrared spectrum of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ prepared by this method from diphenylvinylphosphine and phenylphosphine was identical with that of a sample prepared from phenyldivinylphosphine and diphenylphosphine as described above.

The following similarly performed reactions also gave the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$. (a) Diphenylvinylphosphine (100 g, 472 mmol), phenylphosphine (25 g, 227 mmol), and 5 g (44.6 mmol) of potassium *tert*-butoxide in 400 ml of redistilled tetrahydrofuran gave 90–100 g (74–83% yield) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$. (b) Diphenylvinylphosphine (20 g, 94.5 mmol), phenylphosphine (5.2 g, 47.3 mmol), and 9 ml of a 1 *M* ether–benzene solution of phenyllithium in 150 ml of redistilled benzene gave 14 g (55% yield) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, mp 128–129°. (c) Diphenylvinylphosphine (6.0 g, 28.3 mmol), phenylphosphine (3.1 g, 28.2 mmol), and 0.5 g (4.5 mmol) of potassium *tert*-butoxide in 150 ml of benzene gave 4.0 g (53% yield based on diphenylvinylphosphine) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$.

Preparation of the Tetratertiary Phosphine Tris(2-diphenylphosphinoethyl)phosphine. A. From Trivinylphosphine and Diphenylphosphine. A mixture of 2.0 g (17.8 mmol) of trivinylphosphine, 10.0 g (53.8 mmol) of diphenylphosphine, 10 ml of a 2 *M* benzene–ether solution of phenyllithium, and 100 ml of redistilled benzene was boiled under reflux for 20 hr. Removal of solvent at 25° (40 mm) gave a yellow oil which, upon washing with methanol, solidified giving, after drying, 7.0 g (59% yield) of white crystalline $[(C_6H_5)_2PCH_2CH_2]_3P$: mp 131°; infrared spectrum ν(CH) frequencies at 3055 (vvw, sh), 3039 (vw), 3103 (vvw, br, sh), 2992 (vvw, sh), 2917 (vw), and 2881 (vw) cm^{-1}, other bands at 1479 (m), 1460 (vw, sh), 1430 (m), 1411 (m), 1386 (w, sh), 1322 (vw), 1300 (w), 1257 (vw), 1178 (vvw), 1171 (vw), 1153 (w), 1087 (m), 1062 (m), 1021 (m), 993 (w), 891 (w), 836 (vvw), 784 (vvw), 758 (vvw), 741 (s), 730 (s), 716 (s), 686 (s, br), 669 (s, sh), and 662 (s, sh) cm^{-1}.

Anal. Calcd for $C_{42}H_{42}P_4$: C, 75.3; H, 6.3; P, 18.4; mol wt, 671. Found: C, 75.1; H, 6.5; P, 17.9; mol wt, 667 (osmometric in benzene).

B. From Phosphine and Diphenylvinylphosphine in a Closed System. A mixture of 30 g (141.8 mmol) of diphenylvinylphosphine, 10 ml of a 2 *M* benzene–ether solution of phenyllithium, and 100 ml of redistilled benzene was placed in a 300-ml stainless-steel cylinder. The cylinder was closed and then charged with about 2 g (58.9 mmol) of commercial phosphine. The reaction vessel was closed and heated in an oven at 100° for 36 hr. The stainless-steel cylinder was then cooled and opened, and benzene was removed from the resulting solution at ~25° (40 mm). By vacuum distillation of the remaining brown liquid, 20 g (66.7% recovery) of diphenylvinylphosphine, bp ~121° (0.4 mm), was recovered. The residue from the vacuum distillation was crystallized from a mixture of benzene and ethanol to give 2.6 g (24% yield, 8% conversion) of $[(C_6H_5)_2PCH_2CH_2]_3P$, identified by comparison of its infrared spectrum with that of material prepared from trivinylphosphine and diphenylphosphine as described above.

Preparation of the Tetratertiary Phosphine 1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane. A mixture of 4.0 g (16.3 mmol) of 1,2-bis(phenylphosphino)ethane, $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$, 7.0 g (33.0 mmol) of diphenylvinylphosphine, 0.6 g (5.4 mmol) of potassium *tert*-butoxide, and 100 ml of redistilled benzene was boiled under reflux for 24 hr. Solvent was then removed at ~25° (40 mm). The residue was washed several times with methanol and then recrystallized from a mixture of benzene and ethanol at the boiling point to give 5.6 g (51% yield) of white crystalline $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$: mp 155–158°; infrared spectrum ν(CH) frequencies at 3071 (w), 3049 (vw, sh), 3028 (vw, sh), 3014 (vvw, sh), 3003 (vvw, sh), 2927 (vw), and 2897 (vw) cm^{-1}, other bands at 1581 (vw), 1520 (vvw), 1479 (m), 1456 (vw, sh), 1430 (s), 1420 (w, sh), 1326 (vw), 1302 (vw), 1269 (vw), 1260 (vw, sh), 1184 (w, sh), 1168 (w), 1149 (w), 1094 (m), 1065 (m), 1021 (m), 996 (w), 747 (s), 727 (s), 717 (s), 692 (vs), and 674 (m, sh) cm^{-1}.

Anal. Calcd for $C_{42}H_{42}P_4$: C, 75.3; H, 6.3; P, 18.4; mol wt, 671. Found: C, 74.3; H, 6.1; P, 17.0; mol wt, 671 (osmometric in benzene).

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Preparation of the Hexatertiary Phosphine 1,1,4,4-Tetrakis-(2-diphenylphosphinoethyl)-1,4-diphosphabutane. A mixture of 22 g (104 mmol) of diphenylvinylphosphine, 15 ml of a 1 *M* benzene–ether solution of phenyllithium, and 150 ml of redistilled benzene was treated with 2.5 g (25.6 mmol) of 1,2-diphosphinoethane[31] (from Professor R. C. Taylor of this department) in a nitrogen-filled glove bag. An exothermic reaction occurred immediately with separation of a pale yellow solid. The reaction mixture was boiled under reflux for 24 hr. Solvent was then removed at ~25° (40 mm). By vacuum distillation of the remaining pale yellow liquid, 16 g (73% recovery) of diphenylvinylphosphine, bp 121° (0.5 mm), was obtained. The residue from the distillation was recrystallized twice from mixtures of benzene and ethanol to give 1.2 g (5% conversion, 18% yield based on unrecovered diphenylvinylphosphine) of white crystalline $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$: mp 138–140°; infrared spectrum ν(CH) frequencies at 3069 (vw), 3050 (vw), 3021 (vw), 3000 (vvw), 2930 (vw), 2900 (vw), and 2890 (vw, sh) cm^{-1}, other bands at 1480 (w), 1432 (m), 1418 (w), 1326 (vvw), 1303 (vw), 1272 (vvw), 1261 (w), 1158 (vw), 1097 (vw), 1086 (vw), 1069 (vw), 1026 (vw), 1011 (vvw), 1000 (vw), 990 (vw), 749 (m), 740 (m), 726 (m), 693 (s), and 680 (w) cm^{-1}.

Anal. Calcd for $C_{58}H_{60}P_6$: C, 73.9; H, 6.4; P, 19.7; mol wt, 943. Found: C, 73.0; H, 6.4; P, 19.4; mol wt, 950 (osmometric in benzene).

Reaction of Diphenylethynylphosphine with Diphenylphosphine. A mixture of 3.0 g (14.3 mmol) of diphenylethynylphosphine, 2.6 g (14.0 mmol) of diphenylphosphine, 2.0 ml of a 2 *M* benzene–ether solution of phenyllithium, and 100 ml of redistilled benzene was boiled under reflux for 14 hr. Solvent was removed from the reaction mixture at ~25° (40 mm). The brown solid residue was washed several times with methanol and then crystallized from a mixture of benzene and methanol to give 4.0 g (72% yield) of white crystalline *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$. After another recrystallization from a mixture of benzene and methanol the product melted at 123–124° (lit.[9] mp 124–126°). The infrared spectrum of this product (KBr pellet) was identical both with the spectrum reported for the trans isomer[9] and with the spectrum of *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ prepared in our laboratory from *trans*-1,2-dichloroethylene and lithium diphenylphosphide in tetrahydrofuran. The proton nmr spectrum of the product obtained from this reaction was also identical with that reported for *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ rather than with the distinctly different spectrum (in the olefinic proton region) reported for the corresponding cis isomer.[9] Finally, reaction of 0.5 g (1.26 mmol) of this product with 0.3 g (1.16 mmol) of $CH_3Mo(CO)_3C_5H_5$ in 100 ml of acetonitrile for 24 hr gave 0.5 g (~100% yield) of yellow crystalline *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2[Mo(CO)_2(COCH_3)(C_5H_5)]_2$, mp 220° dec (lit.[4] mp 222° dec), identified further by the positions of the ν(CO) frequencies in its infrared spectrum.

Preparation of 1-Diphenylphosphino-2-diphenylarsinoethane. A mixture of 5.0 g (23.6 mmol) of diphenylvinylphosphine, 5.4 g (23.5 mmol) of diphenylarsine, 0.5 g (4.5 mmol) of potassium *tert*-butoxide, and 100 ml of redistilled benzene was boiled under reflux for 24 hr. Solvent was then removed at ~25° (40 mm) to give an orange solid residue which was washed several times with methanol to give a white solid. Recrystallization of this solid from a mixture of benzene and methanol gave 8.0 g (77% yield) of white crystalline $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$: mp 116–118°; infrared spectrum ν(CH) frequencies at 3065–2995 (w, br, unresolved), 2943 (vvw), 2912 (vvw), and 2895 (vvw, sh), cm^{-1}, other bands at 1570 (w), 1474 (w), 1458 (w, sh), 1421 (m), 1387 (w, sh), 1319 (w, sh), 1299 (w), 1261 (vw), 1193 (vw, sh), 1181 (w), 1142 (w), 1091 (vw), 1070 (w, sh), 1060 (m), 1022 (w), 995 (w), 962 (vw, sh), 934 (vvw, sh), 903 (w), 847 (w), 733 (s), 711 (s), 681 (s), 668 (s, sh), and 612 (m) cm^{-1}; mass spectrum (sample temperature 130°) $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2^+$ (60), $(C_6H_5)_2PAs(C_6H_5)_2^+$ (13), $(C_6H_5)_2PCH_2CH_2AsC_6H_5^+$ (4), $(C_6H_5)_2PAsC_6H_5^+$ (6), $(C_6H_5)_3PC_2H_3^+$ (80), $(C_6H_5)_2PC_7H_6^+$ (8), $(C_6H_5)_3P^+$ (95), $(C_6H_5)_2As^+$ (13), $C_{12}H_8As^+$ (35), $(C_6H_5)_2P^+$ (50), $C_{12}H_8P^+$ (100), $C_{12}H_{10}^+$ (17), $C_{12}H_9^+$ (11), $C_{12}H_8^+$ and/or $C_6H_5As^+$ (30), $C_8H_6P^+$ (6), $C_6H_6P^+$ (5), $C_6H_5P^+$ (26), $C_6H_4P^+$ (10), $C_7H_7^+$ (8), $C_6H_6^+$ (29), and $C_6H_5^+$ (17).

Anal. Calcd for $C_{26}H_{24}AsP$: C, 70.6; H, 5.5; As, 16.9; P, 7.0; mol wt, 442. Found: C, 69.8; H, 5.5; As, 17.5; P, 7.2; mol wt, 441 (osmometric in benzene).

If phenyllithium was substituted for the potassium *tert*-butoxide in this reaction, no $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ was obtained. Instead a 15% yield of white crystalline $(C_6H_5)_2As(O)OH$, mp 158–161° dec (lit.[32] mp 174°), was obtained.

Anal. Calcd for $C_{12}H_{11}AsO_2$: C, 55.0; H, 4.2; As, 28.6. Found: C, 54.9; H, 4.2; As, 29.6.

Preparation of *trans*-1-Diphenylphosphino-2-diphenylarsinoethylene. A mixture of 2.0 g (9.54 mmol) of diphenylethynylphosphine, 2.2 g (9.56 mmol) of diphenylarsine, 0.3 g (2.7 mmol) of potassium *tert*-butoxide, and 100 ml of redistilled benzene was boiled under reflux for 24 hr. Solvent was then removed at ~25° (40 mm) to give an orange solid. This solid was washed with several portions of methanol and then recrystallized from a mixture of benzene and methanol to give 3.5 g (83% yield) of white crystalline *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$: mp 95–96°; infrared spectrum ν(CH) frequencies at 3071 (w), 3050 (vw), 3022 (vvw), and 3001 (vvw) cm^{-1}, other bands at 1578 (vw), 1480 (m), 1432 (w), 1382 (vw, sh), 1324 (vw), 1301 (w), 1281 (w), 1263 (vvw, sh), 1195 (vvw), 1182 (vvw), 1150 (vw), 1090 (vw), 1062 (w), 1021 (m), 998 (m), 984 (w), 903 (vw), 782 (vw), 734 (s), 713 (m), 690 (s), and 654 (m) cm^{-1}; mass spectrum (sample temperature 110°) $(C_6H_5)_2PC_2H_2As(C_6H_5)_2^+$ (100), $(C_6H_5)_2PAs(C_6H_5)_2^+$ (4), $(C_6H_5)_2PC_2H_2AsC_6H_5^+$ (22), $(C_6H_5)_2PAsC_6H_5^+$ (2), $(C_6H_5)_3PC_2H^+$ (33), $(C_6H_5)_3P^+$ (78), $(C_6H_5)_2As^+$ (11), $C_{12}H_8As^+$ (22), $(C_5H_4)_2PC_3H_2^+$? (7), $(C_6H_5)_2PC_2H_2^+$ (10), $(C_6H_5)_2PC_2H^+$ (6), *m/e* 205 (8), $(C_6H_5)_2P^+$ (28), $C_{12}H_8P^+$ (60), $C_6H_5AsC_2H_2^+$ (10), $C_6H_5AsC_2H^+$ (26), $C_{12}H_{10}^+$ (10), $C_{12}H_9^+$ (8), $C_{12}H_8^+$ and/or $C_6H_5As^+$ (22), $C_6H_5PC_2H^+$ (19), $C_6H_5P^+$ (15), $C_6H_4P^+$ (10), $C_8H_9^+$ (10), $C_8H_8^+$ (8), $C_7H_7^+$ (10), $C_6H_6^+$ (22), $C_6H_5^+$ (19), and $C_6H_4^+$ (12).

Anal. Calcd for $C_{26}H_{22}AsP$: C, 70.9; H, 5.0; As, 17.1; P, 7.0; mol wt, 440. Found: C, 70.9; H, 4.9; As, 16.9; P, 7.1; mol wt, 441 (osmometric in benzene).

Preparation of Bis(2-diphenylarsinoethyl)phenylphosphine. A mixture of 2.0 g (12.4 mmol) of phenyldivinylphosphine, 5.8 g (25.2 mmol) of diphenylarsine, 0.5 g (4.5 mmol) of potassium *tert*-butoxide, and 100 ml of redistilled benzene was boiled under reflux for 20 hr. Solvent was removed from the reaction mixture at ~25° (40 mm). The brown solid residue was washed with methanol and then recrystallized from a mixture of benzene and methanol to give 3.6 g (47% yield) of white crystalline $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$: mp 160–162°; infrared spectrum ν(CH) frequencies at 3068 (w), 3048 (w), 3027 (vvw), 3018 (vvw), 2997 (vvw), 2947 (vw), and 2914 (vw) cm^{-1}, other bands at 1576 (w), 1478 (m), 1464 (vw), 1456 (vw), 1434 (s), 1421 (m), 1416 (m), 1397 (w), 1384 (vw), 1330 (vw), 1310 (vw, sh), 1303 (w), 1270 (vw, sh), 1258 (w), 1237 (vvw, sh), 1184 (m), 1177 (s), 1164 (w), 1156 (w), 1146 (w), 1109 (w), 1097 (vw), 1077 (w), 1074 (m), 1062 (w), 1023 (m), 1016 (vvw, sh), 996 (m), 986 (vvw), 907 (vw), 867 (w), 844 (vvw), 836 (vvw), 797 (vw), 781 (m), 746 (m, sh), 739 (vs), 716 (m), 698 (s, sh), 692 (s), 667 (vvw, sh), and 637 (m) cm^{-1}.

Anal. Calcd for $C_{34}H_{33}As_2P$: C, 65.6; H, 5.3; As, 24.1; P, 5.0; mol wt, 622. Found: C, 65.4; H, 5.3; As, 24.0; P, 5.1; mol wt, 623 (osmometric in benzene).

In a larger scale preparation of $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$ a mixture of 35 g (216 mmol) of phenyldivinylphosphine, 100 g (435 mmol) of diphenylarsine, 4.0 g (35.6 mmol) of potassium *tert*-butoxide, and 400 ml of redistilled tetrahydrofuran gave 120 g (89% yield) of $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$.

Discussion

The base-catalyzed addition of phosphorus–hydrogen bonds across the carbon–carbon double bonds of vinylphosphines is a special case of the Michael addition reaction.[33] The carbon–carbon double bonds of the vinylphosphorus derivative $CH_2{=}CHP(O)(OC_2H_5)_2$[34] and of dimethylvinylsulfonium salts,[15] $(CH_3)_2SCH{=}CH_2^+$, have previously been shown to undergo Michael addition reactions; vinylsulfonium salts of the type $R_2SCH{=}CH_2^+X^-$ contain a cation isoelectronic with the vinylphosphines of the type $R_2PCH{=}CH_2$ used in this study. Phosphorus–hydrogen derivatives such as $(C_6H_5)_2PH$ readily lose their

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[33] E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, **10**, 179 (1959).

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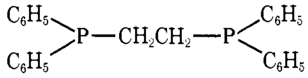
protons in the presence of strong bases to form dialkylphosphide anions $(C_6H_5)_2P^-$; they are thus similar to the acidic carbonyl compounds such as dialkyl malonates, ethyl acetoacetate, etc., which undergo Michael addition reactions.[33]

The first reaction between vinylphosphines and phosphorus–hydrogen compounds to be investigated in this work was the addition of diphenylphosphine to diphenylvinylphosphine, since it was expected to give the known 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (IV), according to the following equation.

$$(C_6H_5)_2PCH{=}CH_2 + (C_6H_5)_2PH \longrightarrow (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$$

The white crystalline product obtained from this reaction using a phenyllithium catalyst was identical in all respects (melting point and infrared and nmr spectra) with authentic 1,2-bis(diphenylphosphino)ethane prepared by the published method[8] from 1,2-dichloroethane and lithium diphenylphosphide. The 80% yield obtained in this preliminary reaction encouraged us to apply this technique to the preparation of more complex polytertiary phosphines of potential interest to coordination chemists.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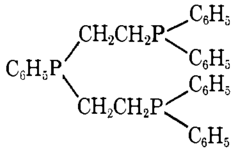
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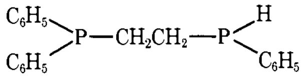

VI

The next objective in this work was the preparation of the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (V), previously obtained in only 14% yield from sodium diphenylphosphide and the relatively difficultly accessible phenylbis(2-bromoethyl)phosphine.[30] This tritertiary phosphine V could be obtained in good yield (up to ~90%) either by addition of 2 equiv of diphenylphosphine to the carbon–carbon double bonds of phenyldivinylphosphine or by addition of the phosphorus–hydrogen bonds of phenylphosphine to the carbon–carbon double bonds in 2 equiv of diphenylvinylphosphine according to the following equations.

$$C_6H_5P(CH{=}CH_2)_2 + 2(C_6H_5)_2PH \longrightarrow [(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$$

$$2(C_6H_5)_2PCH{=}CH_2 + C_6H_5PH_2 \longrightarrow [(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$$

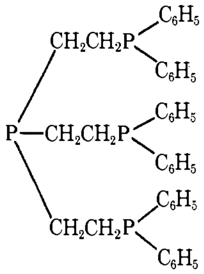
The latter method was preferred since much higher yields are obtained in the preparation of diphenylvinylphosphine from vinylmagnesium bromide and diphenylchlorophosphine than in the preparation of phenyldivinylphosphine from vinylmagnesium bromide and either phenyldichlorophosphine or phenyldi-*n*-butoxyphosphine. Either potassium *tert*-butoxide or phenyllithium could be employed as catalysts for this reaction, with potassium *tert*-butoxide giving slightly better results. The reaction between diphenylvinylphosphine and phenylphosphine in a 1:1 mole ratio gave the tritertiary phosphine V rather than the phosphorus–hydrogen compound $(C_6H_5)_2PCH_2CH_2P(H)C_6H_5$ (VI), indicating that the addition of VI to vinylphosphines is about as fast as or faster than the addition of diphenylphosphine to vinylphosphines.

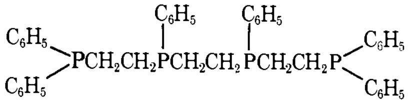
This new synthetic method was used to prepare two isomeric tetratertiary phosphines $C_{42}H_{42}P_4$. Thus the "tripod" tetratertiary phosphine tris(2-diphenylphosphinoethyl)phosphine, $[(C_6H_5)_2PCH_2CH_2]_3P$ (VII), could be prepared either by addition of the phosphorus–hydrogen bonds in phosphine to the carbon–carbon double bonds in 3 equiv of diphenylvinylphosphine or by the addition of 3 equiv of diphenylphosphine to the carbon–carbon double bonds in trivinylphosphine according to the following equations.

$$3(C_6H_5)_2PCH{=}CH_2 + PH_3 \longrightarrow [(C_6H_5)_2PCH_2CH_2]_3P$$

$$(CH_2{=}CH)_3P + 3(C_6H_5)_2PH \longrightarrow [(C_6H_5)_2PCH_2CH_2]_3P$$

The products obtained from both of these reactions were identical. Later, after the work described in this paper was completed, large quantities of the "tripod" tetratertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_3P$ were required for a study of its metal complexes. At that time a more convenient preparation[35] of $[(C_6H_5)_2PCH_2CH_2]_3P$ was developed which consisted of bubbling phosphine generated by hydrolysis of aluminum phosphide into a boiling tetrahydrofuran solution of diphenylvinylphosphine containing the potassium *tert*-butoxide catalyst. Substitution of benzene for the tetrahydrofuran solvent in this atmospheric pressure reaction between phosphine and diphenylvinylphosphine gave negative results.[35]


VII


VIII

The other tetratertiary phosphine prepared in this work was the "linear" tetratertiary phosphine 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (VIII), obtained by addition of the phosphorus–hydrogen bonds in 1,2-bis(phenylphosphino)ethane to the carbon–carbon double bonds in 2 equiv of diphenylvinylphosphine according to the following equation.

$$2(C_6H_5)_2PCH{=}CH_2 + C_6H_5P(H)CH_2CH_2P(H)C_6H_5 \longrightarrow (C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$$

The white crystalline tetratertiary phosphine VIII had distinctly different melting point and ir and nmr spectra than those of the isomeric tetratertiary phosphine VII.

Some of the 1,2-bis(phenylphosphino)ethane required for the preparation of the linear tetratertiary phosphine VIII was prepared by the published method[28] which utilizes the lithium aluminum hydride reduction of $(C_6H_5)(i\text{-}C_3H_7O)P(O)CH_2CH_2P(O)(O\text{-}i\text{-}C_3H_7)(C_6H_5)$. The cleavage of phenyl groups from $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ with sodium in liquid ammonia[29] was explored as an alternate route to 1,2-bis(phenylphosphino)-

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[35] Results described in paper IV: R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, 10, 1851 (1971).

ethane. This reaction appeared to proceed according to the following two pathways.

$$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 + 4Na \longrightarrow C_6H_5P(Na)CH_2CH_2P(Na)C_6H_5 + 2NaC_6H_5$$

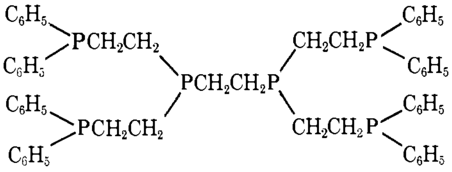
$$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 + 2Na \longrightarrow 2(C_6H_5)_2PNa + CH_2{=}CH_2$$

Protonation of the resulting reaction mixture with ammonium chloride gave about equal quantities of diphenylphosphine and 1,2-bis(phenylphosphino)ethane. Difficulties in separating these two compounds by vacuum distillation made this preparation of 1,2-bis(phenylphosphino)ethane less desirable than the previously reported preparation.[28]

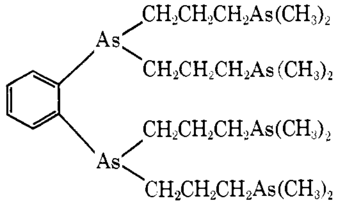
Our interest in a potentially hexadentate tertiary phosphine ligand led to the preparation of the hexatertiary phosphine 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphosphabutane, $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ (IX), by the addition of the phosphorus–hydrogen bonds in 1,2-diphosphinoethane, $H_2PCH_2CH_2PH_2$,[31] to the carbon–carbon double bonds in four equivalents of diphenylvinylphosphine according to the following equation.

$$4(C_6H_5)_2PCH{=}CH_2 + H_2PCH_2CH_2PH_2 \longrightarrow [(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$$

Scaling up this reaction to prepare sufficient quantities of the hexatertiary phosphine IX to study its coordination chemistry was hampered by difficulties in preparing and handling large quantities of the relatively volatile and pyrophoric $H_2PCH_2CH_2PH_2$. This difficulty was later[36] circumvented by generating the $H_2PCH_2CH_2PH_2$ by the lithium aluminum hydride reduction of $(C_2H_5O)_2P(O)CH_2CH_2P(O)(OC_2H_5)_2$[37] and utilizing directly the dried ether layer from this reaction for the reaction with excess diphenylvinylphosphine after removal of the lithium and aluminum salts by hydrolysis and filtration. This technique provided a relatively facile (although rather malodorous) preparation of the hexatertiary phosphine IX in ~50-g quantities.[36] Apparently the hexatertiary phosphine IX is the first hexatertiary phosphine to be prepared; the hexatertiary arsine X is known.[38]



IX



X

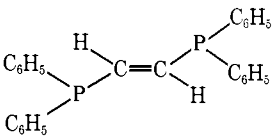
The success in the preparation of polytertiary phosphines with PCH_2CH_2P units from vinylphosphines and phosphorus–hydrogen compounds suggested the preparation of polytertiary phosphines with PCH=CHP units from ethynylphosphines and phosphorus–hydrogen compounds according to the following general scheme.

$$P{-}H + PC{\equiv}CH \longrightarrow PCH{=}CHP$$

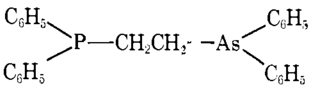
A reaction of this type could lead to either cis or trans stereochemistry around the carbon–carbon double bond of the olefinic ditertiary phosphine unit in the product. This stereochemical ambiguity was clarified by an investigation of the following reaction between diphenylethynylphosphine and diphenylphosphine.

$$(C_6H_5)_2PC{\equiv}CH + (C_6H_5)_2PH \longrightarrow (C_6H_5)_2PCH{=}CHP(C_6H_5)_2$$

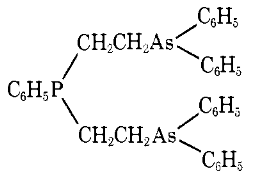
Both the cis and trans isomers of $(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ are readily available and well-characterized compounds with distinctive spectroscopic and chemical properties.[9] The product from the reaction between diphenylethynylphosphine and diphenylphosphine was identified as the trans isomer XI from both its spectroscopic properties (infrared and proton nmr) and its reaction with $CH_3Mo(CO)_3C_5H_5$ in acetonitrile to give a (diphos)$[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ derivative rather than a (diphos)$_2$Mo(CO)$_2$ derivative.[4] Formation of the trans isomer XI rather than the corresponding cis isomer from the reaction between diphenylethynylphosphine and diphenylphosphine maximizes the distance between the relatively bulky diphenylphosphino substituents on the carbon–carbon double bond.



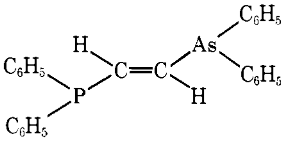
XI



XII



XIII



XIV

Some preparations of mixed tertiary phosphine–arsines by additions of the arsenic–hydrogen bond in diphenylarsine across the carbon–carbon double bonds of vinylphosphines were also investigated. The potentially bidentate ligand $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ (XII) and potentially tridentate ligand $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$ (XIII) were prepared by the following reactions.

$$(C_6H_5)_2PCH{=}CH_2 + (C_6H_5)_2AsH \longrightarrow (C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$$

$$C_6H_5P(CH{=}CH_2)_2 + 2(C_6H_5)_2AsH \longrightarrow [(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$$

In both cases potassium *tert*-butoxide was used as the catalyst. Attempts to prepare $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ from diphenylvinylphosphine and diphenylarsine using phenyllithium as a catalyst led to negative results: instead of the desired mixed phosphine–arsine the arsenic derivative $(C_6H_5)_2As(O)(OH)$ was

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[36] Results described in paper V: R. B. King and M. S. Saran, *Inorg. Chem.*, 10, 1861 (1971).

[37] A. H. Ford-Moore and J. W. Williams, *J. Chem. Soc.*, 1465 (1947).

[38] G. A. Barclay, C. M. Harris and J. V. Kingston, *Chem. Commun.*, 965 (1968).

isolated from the reaction mixture. The addition of the arsenic–hydrogen bond in diphenylarsine to the carbon–carbon triple bond in diphenylethynylphosphine gave the unsaturated phosphine–arsine *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$ (XIV) according to the following equation.

$$(C_6H_5)_2PC{\equiv}CH + (C_6H_5)_2AsH \longrightarrow \textit{trans}\text{-}(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$$

This product is formulated as the trans isomer for the following reasons: (1) analogy between this reaction and the reaction of diphenylethynylphosphine with diphenylphosphine discussed above, and (2) the nmr chemical shift of the olefinic protons in *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$ (Table I) being much closer to that of the olefinic protons in *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ than to that of the olefinic protons in the corresponding cis isomer.

The polytertiary phosphines and phosphine–arsines prepared in this work are all white air-stable crystalline solids with characteristic melting points ranging from 95–96° for *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$ (XIV) to 160–162° for $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$ (XIII). They are sparingly soluble in methanol but readily soluble in benzene and chloroform. The solubility decreases somewhat with increasing molecular weight. Mixtures of benzene and methanol are suitable for recrystallization of the polytertiary phosphines and phosphine–arsines.

The new polytertiary phosphines and phosphine–arsines were all characterized by complete elemental analyses and molecular weight determinations in benzene solution; the latter were more sensitive indicators of the nature of the products since each additional phosphorus atom made a large contribution to the molecular weight because of the accompanying one or two phenyl groups. When possible, the infrared, proton, and ^{31}P nmr, and mass spectra were determined. In all cases they support the proposed structures as discussed below.

The infrared spectra of the polytertiary phosphines and phosphine–arsines were relatively complex, exhibiting a large number of bands in the 1600–600-cm^{-1} region. The spectra in this region were useful for identifying specific polytertiary phosphines and phosphine–arsines and therefore are described in detail in the Experimental Section. Strong absorptions around 1200 cm^{-1} were absent, indicating the absence of phosphine oxide impurities.[39] As expected, the unsaturated polytertiary phosphine–arsine *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$ exhibited several relatively weak ν(CH) frequencies in the range 3000–3070 cm^{-1}, whereas the saturated polytertiary phosphines and phosphine–arsines exhibited additional weak ν(CH) frequencies in the range 2850–3000 cm^{-1}.

The proton nmr spectra (Table I) of the polytertiary phosphines and phosphine–arsines with CH_2CH_2 bridges exhibited resonances from the phenyl protons around τ 2.7 and resonances from the protons of the CH_2CH_2 bridges around τ 8. In $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ the protons of the CH_2CH_2 bridge appear as a triplet (separation 4 cps), arising from strong phosphorus–hydrogen coupling. In $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$, where one of the two phosphorus atoms is replaced by a magnetically inactive arsenic atom, the protons of the CH_2CH_2 bridge appear as a doublet (separation 4 cps) and a singlet separated by a chemical shift difference of ~0.04 ppm. This indicates the slight nonequivalence of the two methylene groups in the bridge of $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ (XII) and that only one of the methylene groups is coupled to the phosphorus atom. The chemical shift difference between the protons of the two different methylene groups in XII is apparently too small for appreciable proton–proton coupling to occur.

The methylene nmr resonances of the more complex polytertiary phosphines and phosphine–arsines appeared in the τ 8 region but either were broad and featureless or complex asymmetric multiplets which defied simple analysis. However, the resonances of methylene protons bonded to phosphorus atoms bonded only to other methylene groups occurred at appreciably higher chemical shifts than resonances of methylene protons bonded to phosphorus atoms bonded to phenyl groups. This effect was illustrated most clearly in the proton nmr spectrum of $[(C_6H_5)_2PCH_2CH_2]_3P$ (VII), where two featureless humps of equal relative intensities were observed in the τ 8 region, one covering the range τ 8.0–8.2 and the other the range τ 8.4–8.6. The structure of VII contains three methylene groups bonded to a $(C_6H_5)_2P$ phosphorus atom and three methylene groups bonded to a phosphorus atom bearing two other methylene groups. The assignment of the higher field resonance to the latter three methylene groups is indicated by the absence of a resonance in this region in the nmr spectrum of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ which contains only methylene groups bonded to $(C_6H_5)_2P$ phosphorus atoms.

A comparison of the nmr spectrum of the olefinic protons of the mixed olefinic phosphine–arsine *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$ (XIV) with that of the corresponding ditertiary phosphine is of interest. The proton nmr spectrum of the ditertiary phosphine *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ exhibits a triplet (separation 14.5 cps) centered at τ 3.26 arising from strong phosphorus–hydrogen and phosphorus–phosphorus coupling as in $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ discussed above. In the mixed phosphine–arsine *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$ (XIV) two doublets with slightly different chemical shifts are observed. This indicates the slight nonequivalence of the two protons in the bridge of XIV but that both of these protons are coupled to the single phosphorus atom, albeit by slightly different coupling constants. The coupling of the bridge protons to the single phosphorus atom in the olefinic phosphine–arsine *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$ (XIV) is thus different from that in the saturated phosphine–arsine $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ (XII), since in the olefinic derivative XIV the protons on both carbon atoms of the bridge are coupled to the phosphorus atom, whereas in the saturated derivative XII only the protons on one carbon atom of the bridge are coupled to the phosphorus. This is reasonable in view of the availability of the π electrons in the carbon–carbon double bond of the olefinic phosphine–arsine XIV for transmission of the coupling from the phosphorus atom to the proton on the more remote carbon atom.

The phosphorus-31 nmr spectra of the polytertiary phosphines and phosphine–arsines (Table II) provided

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[39] D. E. C. Corbridge, *Top. Phosphorus Chem.*, **6**, 235 (1969).

excellent confirmation of the proposed structures. Phosphorus atoms in the environments $(C_6H_5)_2PCH_2CH_2$–, $C_6H_5P(CH_2CH_2–)_2$, $P(CH_2CH_2–)_3$, and $(C_6H_5)_2PCH{=}CH$– consistently exhibited ^{31}P resonances in the distinct ranges 12.9–13.5, 16.6, 17.4–17.8, and 7.9–8.0 ppm, respectively (all upfield from external 85% H_3PO_4), thereby providing an excellent means for unequivocally elucidating the structures of relatively complex polytertiary phosphines. The trends observed upon changing aromatic groups on the phosphorus atoms to aliphatic and olefinic groups parallel closely similar trends found in the ^{31}P nmr spectra of simple tertiary phosphines with one phosphorus atom.[40] In all cases the ^{31}P nmr resonances were broad unresolved peaks.

Attempts to obtain mass spectra of the polytertiary phosphines and phosphine–arsines were limited by the low volatility of some of the more complex derivatives arising from the presence of a large number of phenyl groups. Sample temperatures of 110–150° gave enough vapor pressure to obtain satisfactory mass spectra of the compounds with four phenyl groups and two phosphorus or arsenic atoms $(C_6H_5)_2PCH_2CH_2E(C_6H_5)_2$ (E = P or As) and *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$. However, the much higher sample temperature of 250° was used to produce enough vapor pressure to obtain a satisfactory mass spectrum of the compound $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (V) with three phosphorus atoms and five phenyl groups.

The mass spectra of the polytertiary phosphines and phosphine–arsines which could be obtained exhibited general features similar to those previously[41] found in the mass spectra of ditertiary phosphines and arsines of the type $(C_6H_5)_2E(CH_2)_nE(C_6H_5)_2$ (E = P or As, n = 1 or 2). Cleavage of the carbon–phosphorus and/or carbon–arsenic bonds predominated in the early stages of the fragmentation process. Thus, in the mass spectrum of the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, the molecular ion readily lost a diphenylphosphino group to give the ion $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2^+$, the strongest ion of the mass spectrum. Further fragmentation processes in this mass spectrum involved primarily loss of either the CH_2CH_2 bridges or the phenyl groups. In some cases the neutral leaving group removed one proton from the CH_2CH_2 bridge leaving a C_2H_3 group attached to the phosphorus atom resulting in ions such as $(C_6H_5)_nPC_2H_3^+$ (n = 1, 2, and 3). Some ions with three phenyl groups attached to a single phosphorus atom were observed in the mass spectrum of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$; the presence of $(C_6H_5)_3PC_2H_3^+$ indicates that these ions arise from some type of phenyl-transfer process rather than by simple pyrolysis to triphenylphosphine at the very high inlet temperatures.

The mass spectra of the mixed phosphine–arsines $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ and *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$ exhibited ions of the types $(C_6H_5)_2E^+$, $C_{12}H_8E^+$, and $C_6H_5E^+$, containing either phosphorus or arsenic. Ions containing three phenyl groups attached to a single phosphorus atom were also observed [$(C_6H_5)_3P^+$ and $(C_6H_5)_2PC_2H_3^+$ in the mass spectrum of $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ and $(C_6H_5)_3P^+$ and $(C_6H_5)_2PC_2H^+$ in the mass spectrum of *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$]. However, none of the mass spectra of the mixed phosphine–arsines contained any ions with three phenyl groups attached to a single arsenic atom. This suggests that a phenyl group can be transferred from arsenic to phosphorus but not from phosphorus to arsenic. The mass spectra of both mixed phosphine–arsines contained the ion $(C_6H_5)_3PAs^+$ but not the ions $(C_6H_5)_3P_2^+$ or $(C_6H_5)_3P_2^+$, indicating concurrent elimination of the two-carbon bridge and formation of a phosphorus–arsenic bond. If the ion $(C_6H_5)_2PAs^+$ were produced by combination of $(C_6H_5)_nP$ and $(C_6H_5)_nAs$ units produced during pyrolysis and/or fragmentation, the ions $(C_6H_5)_3P_2^+$ and $(C_6H_5)_3As_2^+$ would also be formed in statistical quantities.

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(40) S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, 32, 781 (1967).

(41) R. Colton and Q. N. Porter, *Aust. J. Chem.*, 21, 2215 (1968).