Some Recent Studies on Poly(tertiary phosphines) and Their Metal Complexes

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During the past 15 years tertiary phosphines have become important ligands in coordination chemistry.[1] Certain metal complexes of tertiary phosphines have been shown to have unusual chemical properties of importance in such diverse areas as homogenous hydrogenation,[2] oxygen transfer,[3] and nitrogen fixation.[4] Such interesting applications have provided impetus to the further development of this relatively young field.

The chemical properties of metal complexes of tertiary phosphines vary with the electronic and steric properties of the ligands. For this reason further development of the coordination chemistry of tertiary phosphines is highly dependent upon the concurrent development of synthetic organophosphorus chemistry.

These considerations prompted efforts to develop new methods for the syntheses of tertiary phosphines which would possess novel coordination chemistry. One of the early objectives was synthesis of a hexa(tertiary phosphine) with the six donor phosphorus atoms situated so as to bond to a single metal atom much as do the six donor nitrogen and oxygen atoms in ethylenediaminetetraacetic acid (EDTA). The strong affinity of EDTA for a great variety of metal atoms, that in the early 1950's provided the basis for the development of complexometric analytical techniques,[5] suggested that such a chelating hexa(tertiary phosphine) might form unusual transition metal complexes with useful properties.

This research program in synthetic organophosphorus chemistry was started in late 1968 in collaboration with Dr. Pramesh Kapoor, who had had considerable prior experience in synthesizing and handling the often air-sensitive, malodorous, and toxic organophosphorus compounds. At that time the only generally useful method for the preparation of poly(tertiary phosphines) employed reactions of alkali metal dialkylphosphides and diarylphosphides with organic polyhalides. Alkali metal diphenylphosphides, $MP(C_6H_5)_2$,[6] were convenient reagents for this type of synthesis since they are readily obtained by reactions of the alkali metal with the readily available triphenylphosphine in an appropriate coordinating solvent such as tetrahydrofuran (THF) (M = Li), liquid ammonia (M = Na or Li), or dioxane (M = K). This synthetic method is exemplified by the preparation of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (I) from the reaction of lithium diphenylphosphide with 1,2-dichloroethane according to[6]

$$2LiP(C_6H_5)_2 + ClCH_2CH_2Cl \xrightarrow{THF} 2LiCl +$$
$$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$$
$$I$$
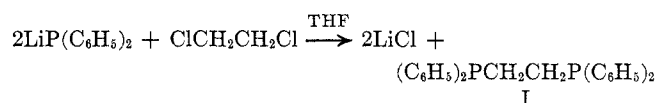
Compound I is frequently known by the trivial name "diphos," but this term is becoming confusing, since other di(tertiary phosphines) are beginning to receive considerable attention from coordination chemists. The analogous reactions between lithium diphenylphosphide and the cis and trans isomers of 1,2-dichloroethylene give stereospecifically the cis and trans isomers of the olefinic di(tertiary phosphine) $(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ according to[7]
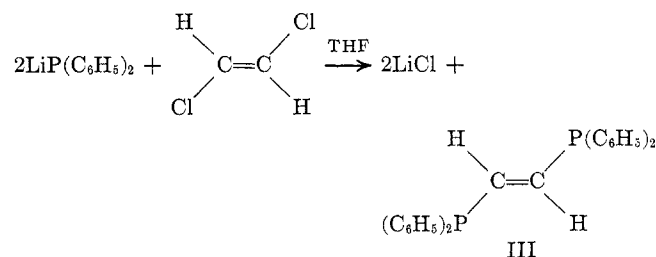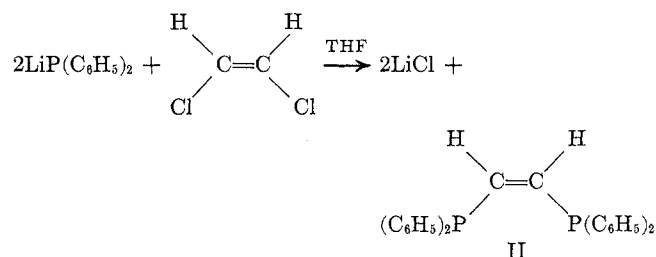
In a few cases analogous reactions of alkali metal diphenylphosphides with organic polyhalides have been

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(3) L. Vaska, *Science*, **140**, 809 (1963); *Accounts Chem. Res.*, **1**, 335 (1968).
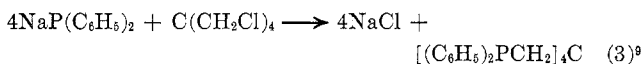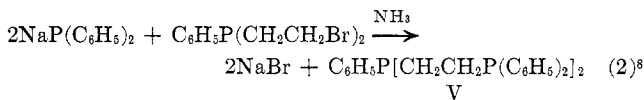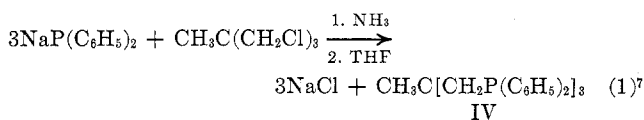
(4) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Comm.*, 79 (1967).

(5) F. J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid," Van Nostrand, Princeton, N. J., 1958.
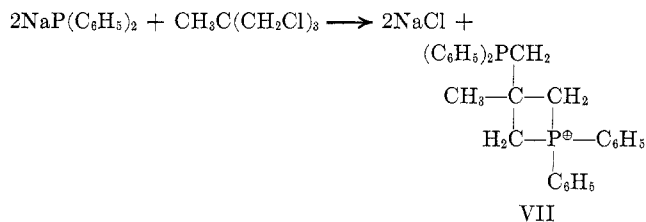
(6) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(7) A. M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, **86**, 2299 (1964).

useful for the synthesis of certain tri- and tetra(tertiary phosphines), e.g., eq 1–3. These syntheses of tri- and

$$3NaP(C_6H_5)_2 + CH_3C(CH_2Cl)_3 \xrightarrow[\text{2. THF}]{\text{1. NH}_3}$$
$$3NaCl + CH_3C[CH_2P(C_6H_5)_2]_3 \quad (1)^7$$
$$IV$$

$$2NaP(C_6H_5)_2 + C_6H_5P(CH_2CH_2Br)_2 \xrightarrow{NH_3}$$
$$2NaBr + C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2 \quad (2)^8$$
$$V$$

$$4NaP(C_6H_5)_2 + C(CH_2Cl)_4 \longrightarrow 4NaCl +$$
$$[(C_6H_5)_2PCH_2]_4C \quad (3)^9$$

tetra(tertiary phosphines), however, have various disadvantages. In the synthesis of the tri(tertiary phosphine) IV, the mole ratio of sodium diphenylphosphide to the halide $CH_3C(CH_2Cl)_3$ is critical. If a deficiency of sodium diphenylphosphide is used, the reaction proceeds differently to form the phosphetanium salt VII.[10]

$$2NaP(C_6H_5)_2 + CH_3C(CH_2Cl)_3 \longrightarrow 2NaCl +$$

$$(C_6H_5)_2PCH_2$$
$$|$$
$$CH_3-C-CH_2$$
$$|\quad\quad\ |$$
$$H_2C-P^{\oplus}-C_6H_5$$
$$|$$
$$C_6H_5$$
$$VII$$

The synthesis of the tri(tertiary phosphine) V is reported[8] to give only a 16% yield and uses the rather unstable and difficulty accessible halide $C_6H_5P(CH_2-CH_2Br)_2$[11] as a starting material. Steric considerations prevent the tetra(tertiary phosphine) VI from acting as a tetradentate chelating agent. Only three phosphorus atoms in VI at most can bond to a single metal atom. An analogous synthetic method is not applicable for the syntheses of other tetra(tertiary phosphines) which might act as tetradentate ligands by having all four phosphorus atoms bond to a single metal atom.

These and other limitations in the reactions of alkali metal dialkylphosphides with organic polyhalides as methods for the preparations of poly(tertiary phosphines) indicate the need for a new general method for poly(tertiary phosphine) synthesis. We were particularly interested in the synthesis of poly(tertiary phosphines) with multidentate chelating properties. Compounds containing the PCH_2CH_2P and cis-$PCH=CHP$ units were, therefore, selected as synthetic objectives since both of these types of units should be bidentate. The unit PCH_2CH_2P can act either as a bidentate chelating unit as in VIIIa or as a bridging unit as in VIIIb because of free rotation around the carbon–carbon single bond.
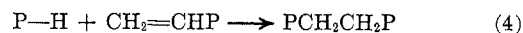
Synthesis of Poly(tertiary phosphines)

One possible method for constructing a PCH_2CH_2P

VIIIa   VIIIb   IX
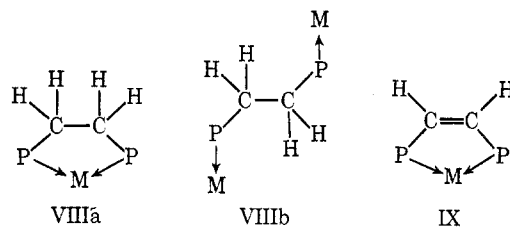
unit in a poly(tertiary phosphine) appeared to be the addition of a phosphorus–hydrogen bond across the vinyl double bond of a vinylphosphine as shown in eq 4.

$$P-H + CH_2=CHP \longrightarrow PCH_2CH_2P \quad (4)$$

Previous work on the addition of phosphorus–hydrogen bonds to other unsaturated compounds such as acrylonitrile[12] or 2,4-hexadiyne[13] suggested that a basic catalyst such as phenyllithium or potassium hydroxide might be required. The necessary vinylphosphines were generally prepared by reactions of vinylmagnesium bromide in tetrahydrofuran with the corresponding halophosphines[14,15] or alkoxyphosphines.[16]

In order to evaluate this proposed new method, the reaction between diphenylphosphine and diphenylvinylphosphine in the presence of a phenyllithium catalyst was investigated. An ~80% yield of the desired phosphine $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (I) was obtained according to eq 5.[17,18] The ditertiary phosphine was

$$(C_6H_5)_2PH + (C_6H_5)_2PCH=CH_2 \longrightarrow I \quad (5)$$
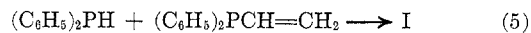
identified by comparison of its physical and spectroscopic properties with those of authentic material prepared from lithium diphenylphosphide and 1,2-dichloroethane as described above. The synthesis of I from diphenylphosphine and diphenylvinylphosphine does not offer any advantages in terms of efficiency and convenience over the previously discussed synthesis of I from lithium diphenylphosphide and 1,2-dichloroethane[6] when allowance is made for the lesser availability of both diphenylphosphine and diphenylvinylphosphine relative to triphenylphosphine, which is easily converted to lithium diphenylphosphide. However, the synthesis of I from diphenylphosphine and diphenylvinylphosphine provided the first unequivocal demonstration that the PCH_2CH_2P unit could be synthesized efficiently by the base-catalyzed addition of a phosphorus–hydrogen bond across the vinyl double bond of a vinylphosphine.

We next investigated the applicability of this new synthetic technique for the syntheses of more complex poly(tertiary phosphines) containing PCH_2CH_2P units. The tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$,

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(9) J. Ellmann and K. Dorn, Ber., 99, 653 (1966).
(10) D. L. Berglund and D. W. Meek, J. Amer. Chem. Soc., 90, 518 (1968); Inorg. Chem., 8, 2602 (1969).
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(14) L. Maier, D. Seyferth, F. G. A. Stone, and E. G. Rochow, J. Amer. Chem. Soc., 79, 5884 (1957).
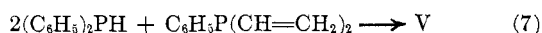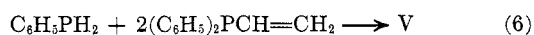(15) K. D. Berlin and G. B. Butler, J. Org. Chem., 26, 2537 (1961); R. Rabinowitz and J. Pellon, ibid., 26, 4623 (1961).
(16) M. I. Kabachnik, C. Y. Chang, and E. N. Tsvetkov, Dokl. Akad. Nauk SSSR, 135, 603 (1960); Chem. Abstr., 55, 12272 (1961).
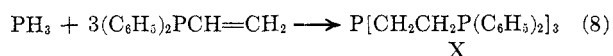(17) R. B. King and P. N. Kapoor, J. Amer. Chem. Soc., 91, 5191 (1969).
(18) R. B. King and P. N. Kapoor, ibid., 93, 4158 (1971).

which was previously[8] obtained in only 16% yield by the reaction of sodium diphenylphosphide with the halide $C_6H_5P(CH_2CH_2Br)_2$, could now be obtained in much better yield (50–90%) and much more conveniently by the method of either eq 6 or eq 7.[17,18] Suitable basic catalysts for these reactions are phenyllithium and potassium *tert*-butoxide. Suitable solvents for these reactions are benzene and tetrahydrofuran.

$$C_6H_5PH_2 + 2(C_6H_5)_2PCH=CH_2 \longrightarrow V \qquad (6)$$

$$2(C_6H_5)_2PH + C_6H_5P(CH=CH_2)_2 \longrightarrow V \qquad (7)$$

This new synthetic approach could be used to prepare two isomeric tetra(tertiary phosphines) of the empirical composition $C_{42}H_{42}P_4$ and containing PCH_2-CH_2P structural units. The tripod tetra(tertiary phosphine) $P[CH_2CH_2P(C_6H_5)_2]_3$ (X) could be prepared in good yield by the methods of either eq 8 or eq 9.[17,18]

$$PH_3 + 3(C_6H_5)_2PCH=CH_2 \longrightarrow \underset{X}{P[CH_2CH_2P(C_6H_5)_2]_3} \quad (8)$$

$$3(C_6H_5)_2PH + P(CH=CH_2)_3 \longrightarrow X \qquad (9)$$

The reaction between PH_3 and $(C_6H_5)_2PCH=CH_2$ is especially convenient for the preparation of the tripod tetra(tertiary phosphine) X since this reaction proceeds in nearly quantitative yield in a few hours' time simply by bubbling the PH_3 generated by hydrolysis of commercial aluminum phosphide into a boiling tetrahydrofuran solution of diphenylvinylphosphine containing some potassium *tert*-butoxide catalyst.[19] The linear tetra(tertiary phosphine) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)$-$CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (XI) can be prepared by eq 10.[17,18] The preparation of the required

$$\underset{XI}{(C_6H_5)_2PCH_2CH_2\overset{|}{\underset{C_6H_5}{P}}CH_2CH_2\overset{|}{\underset{C_6H_5}{P}}CH_2CH_2P(C_6H_5)_2} \quad (10)$$
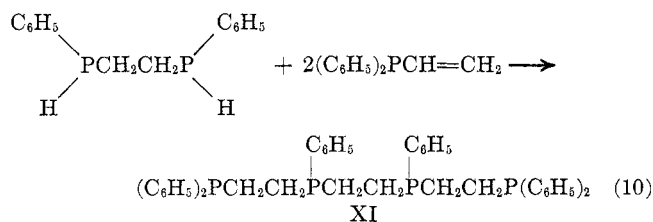
$C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ starting material for the synthesis of the linear tetra(tertiary phosphine) XI is somewhat troublesome, but can be accomplished either by reaction of $C_6H_5P(OR)_2$ (R = isopropyl, etc.) with 1,2-dibromoethane followed by lithium aluminum hydride reduction of the intermediate $C_6H_5P(O)(OR)CH_2$-$CH_2P(O)(OR)C_6H_5$[20] or by cleavage of $(C_6H_5)_2PCH_2$-$CH_2P(C_6H_5)_2$ (I) with sodium in liquid ammonia followed by protonation with ammonium chloride;[21] the latter method is less preferable because of the concurrent formation of $(C_6H_5)_2PH$ which must be removed by a careful fractional vacuum distillation.

The successful preparation of the tri(tertiary phosphine) V and the tetra(tertiary phosphines) X and XI containing PCH_2CH_2P structural units encouraged us to investigate the similar preparation of a hexa(tertiary phosphine) with PCH_2CH_2P structural units.

We found that base-catalyzed addition of the four phosphorus–hydrogen bonds in $H_2PCH_2CH_2PH_2$[22] to 4 equiv of diphenylvinylphosphine gave the hexa(tertiary phosphine) $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P-(C_6H_5)_2]_2$ (XII) according to eq 11.[17,18] This approach

$$H_2PCH_2CH_2PH_2 + 4(C_6H_5)_2PCH=CH_2 \longrightarrow$$
$$\underset{XII}{[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2} \quad (11)$$
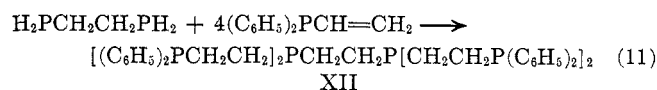
provided the first synthetic route to a hexa(tertiary phosphine) but had the disadvantage of requiring the use of the malodorous and pyrophoric $H_2PCH_2CH_2PH_2$. This disadvantage could be partially alleviated by generating the $H_2PCH_2CH_2PH_2$ by reduction of $(C_2H_5O)_2$-$P(O)CH_2CH_2P(O)(OC_2H_5)_2$ with lithium aluminum hydride in diethyl ether followed by dilute aqueous acid treatment to remove the lithium and aluminum salts. The resulting diethyl ether solution of $H_2PCH_2CH_2PH_2$ could be used directly for the preparation of the hexa-(tertiary phosphine) XII without isolation of pure $H_2PCH_2CH_2PH_2$.[23] By means of this technique, 50-g quantities of the hexa(tertiary phosphine) XII were easily obtained in a single preparation, thereby making this compound available for use as a ligand in transition metal chemistry.

We also investigated the possibility of preparing mixed arsine–phosphines by the base-catalyzed addition of arsenic–hydrogen bonds across the vinyl double bonds of vinylphosphines. The base-catalyzed addition of the arsenic–hydrogen bond in diphenylarsine, $(C_6H_5)_2AsH$, across the vinyl double bond in diphenylvinylphosphine gave the mixed arsine–phosphine $(C_6H_5)_2AsCH_2CH_2P(C_6H_5)_2$ (XIII).[17,18] Similarly, the

$$(C_6H_5)_2AsH + (C_6H_5)_2PCH=CH_2 \longrightarrow$$
$$\underset{XIII}{(C_6H_5)_2AsCH_2CH_2P(C_6H_5)_2}$$
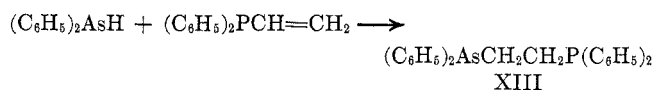
base-catalyzed addition of the arsenic–hydrogen bonds in 2 equiv of $(C_6H_5)_2AsH$ across the vinyl double bonds in $C_6H_5P(CH=CH_2)_2$ gave the mixed diarsine–phosphine $C_6H_5P[CH_2CH_2As(C_6H_5)_2]_2$ (XIV).[17,18] Potas-

$$2(C_6H_5)_2AsH + C_6H_5P(CH=CH_2)_2 \longrightarrow$$
$$\underset{XIV}{C_6H_5P[CH_2CH_2As(C_6H_5)_2]_2}$$
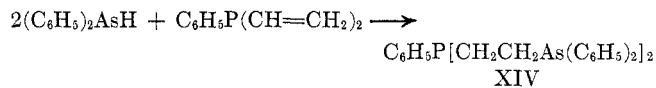
sium *tert*-butoxide was used as a catalyst for these reactions; phenyllithium appeared to be unsuitable.

The successful synthesis of poly(tertiary phosphines) with PCH_2CH_2P structural units by base-catalyzed addition of phosphorus–hydrogen bonds across the vinyl double bonds of vinylphosphines suggested that olefinic poly(tertiary phosphines) with $PCH=CHP$ structural units might be analogously prepared by base-catalyzed addition of phosphorus–hydrogen bonds across the carbon–carbon triple bonds of ethynylphosphines according to eq 12. In this reaction there is an ambiguity as to whether the two phosphorus atoms in the adduct will be in cis positions (XVc) or in trans positions (XVt). In order to elucidate the stereochem-
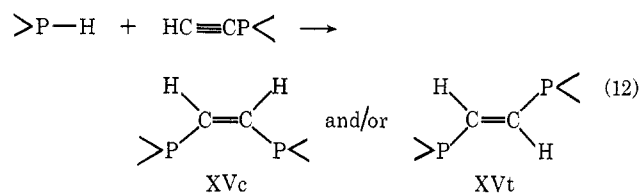
(19) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).

(20) K. Issleib and H. Weichmann, *Ber.*, **101**, 2197 (1968).

(21) K. Sommer, *Z. Anorg. Allgem. Chem.*, **376**, 37 (1970).

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(23) R. B. King and M. S. Saran, *Inorg. Chem.*, **10**, 1861 (1971).

$$>P-H \ + \ HC\equiv CP< \ \longrightarrow$$

$$\text{(12)}$$

XVc   and/or   XVt

istry, the reaction between diphenylphosphine and diphenylethynylphosphine was investigated because both the cis (II) and the trans (III) isomers of the olefinic di(tertiary phosphine) $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ are well-characterized compounds.[7] The reaction between diphenylphosphine and diphenylethynylphosphine afforded a product, $(C_6H_5)_2PCH=CHP(C_6H_5)_2$, which was shown to be the pure trans isomer III on the basis of infrared and proton nmr spectra as well as its reaction with $CH_3Mo(CO)_3C_5H_5$ in acetonitrile solution to give a bridged product $(C_6H_5)_2PCH=CHP(C_6H_5)_2$-$[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ rather than a chelate $[(C_6H_5)_2PCH=CHP(C_6H_5)_2]_2Mo(CO)_2$.[24] Thus the reaction between diphenylphosphine and diphenylethynylphosphine occurs in a syn fashion to give a trans product.

Poly(tertiary phosphines) with trans-PCH=CHP bridges are of less value to coordination chemists because both phosphorus atoms of the trans-PCH=CHP moiety cannot bond to the same metal atom (i.e., to form chelates). This reaction was therefore not extended to other examples. However, an olefinic mixed phosphine-arsine, trans-$(C_6H_5)_2PCH=CHAs(C_6H_5)_2$ (XVI), was prepared[17,18]

$$(C_6H_5)_2AsH \ + \ (C_6H_5)_2PC\equiv CH \ \longrightarrow$$


XVI
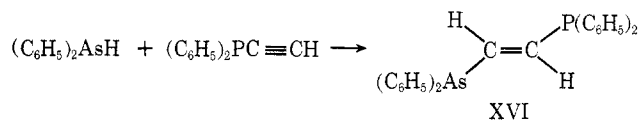
This reaction demonstrates that arsenic–hydrogen bonds can add to the carbon–carbon triple bonds of ethynylphosphines just as they can add to the vinyl carbon–carbon double bonds of vinylphosphines as discussed above.

Synthesis of Other Trivalent Phosphorus and Arsenic Derivatives

The successful base-catalyzed addition of phosphorus–hydrogen and arsenic–hydrogen bonds across the vinyl bonds of vinylphosphines suggested investigation of base-catalyzed additions of phosphorus–hydrogen and arsenic–hydrogen bonds across multiple bonds in other types of compounds in order to synthesize other organophosphorus and organoarsenic compounds of potential value as ligands. Vinyl isocyanide, CH_2=CHNC,[25] was first investigated because of the usefulness of isocyanides as ligands in coordination chemistry.

The base-catalyzed additions of $(C_6H_5)_2EH$ (E = P or As) to vinyl isocyanide gave the expected addition

products $(C_6H_5)_2ECH_2CH_2NC$ (XVII, E = P or As) according to eq 13.[26] The presence of an isocyanide
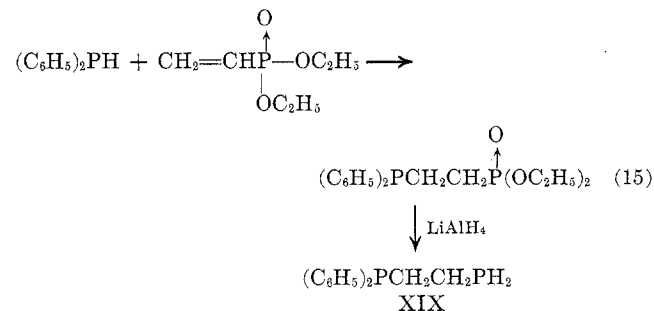
$$(C_6H_5)_2EH \ + \ CH_2=CHNC \ \longrightarrow \ (C_6H_5)_2ECH_2CH_2NC \quad (13)$$
$$E = P \text{ or As} \qquad\qquad XVII, E = P \text{ or As}$$
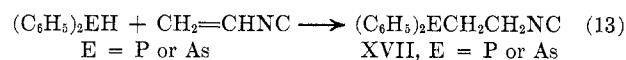
group in the products was demonstrated by a strong infrared absorption frequency around 2150 cm^{-1}. The reactions of $(C_6H_5)_2EH$ (E = P or As) with vinyl isocyanide thus proceed by 1,2 addition of the phosphorus–hydrogen or arsenic–hydrogen bond across the vinyl double bond of the vinyl isocyanide.

In an attempt to prepare the phosphine diisocyanide $C_6H_5P(CH_2CH_2NC)_2$, the base-catalyzed reaction of phenylphosphine with vinyl isocyanide was investigated. This reaction instead gave the 3-azaphosphole derivative XVIII[26] (eq 14). The absence of an isocy-

$$C_6H_5PH_2 \ + \ CH_2=CHNC \ \longrightarrow$$

$$\text{(14)}$$
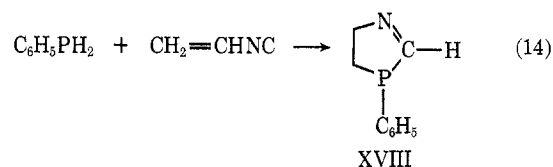
XVIII

anide group in the 3-azaphosphole product XVIII is demonstrated by the absence of an isocyanide infrared frequency around 2150 cm^{-1}. The reaction of phenylphosphine with vinyl isocyanide thus proceeds by 1,4 addition of the phosphorus–hydrogen bonds across the multiple bonds of the conjugated vinyl and isocyanide groups. Compound XVIII is of interest as the first simple derivative of the 3-azaphosphole system to be prepared. It is potentially a very reactive molecule because of the presence of both a trivalent phosphorus atom and a carbon–nitrogen multiple bond; however, its chemistry has not yet been investigated.

We also investigated the base-catalyzed addition of diphenylphosphine to the carbon–carbon double bond of diethyl vinylphosphonate, $CH_2=CHP(O)(OC_2H_5)_2$. This reaction gave a viscous pasty residue which was not characterized but which instead was reduced with lithium aluminum hydride to give the colorless, malodorous, air-sensitive compound $(C_6H_5)_2PCH_2CH_2PH_2$ (XIX), apparently according to reaction sequence 15.[27]

$$(C_6H_5)_2PH \ + \ CH_2=CHP(O)-OC_2H_5 \ \longrightarrow$$
$$\qquad\qquad\qquad\qquad\qquad\quad OC_2H_5$$

$$(C_6H_5)_2PCH_2CH_2P(O)(OC_2H_5)_2 \quad (15)$$

$$\downarrow \text{LiAlH}_4$$

$$(C_6H_5)_2PCH_2CH_2PH_2$$
XIX

$(C_6H_5)_2PCH_2CH_2PH_2$ is the first known compound incorporating both the primary phosphine and the tertiary phosphine functional groups. Its ^{31}P nmr spectrum exhibits a singlet and a triplet of approximately equal intensities. The triplet arises from the phos-

(24) R. B. King, L. W. Houk, and P. N. Kapoor, Inorg. Chem., 8, 1792 (1969).
(25) D. S. Matteson and R. A. Bailey, J. Amer. Chem. Soc., 90, 3761 (1968).

(26) R. B. King and A. Efraty, ibid., 93, 564 (1971).
(27) R. B. King and P. N. Kapoor, Angew. Chem., Int. Ed. Engl., 10, 734 (1971).

phorus of the PH_2 group, split by the two hydrogen atoms directly bonded to it. The singlet arises from the tertiary phosphorus atom.

The conversion of $(C_6H_5)_2PH$ to $(C_6H_5)_2PCH_2CH_2$-PH_2 as discussed above is the first useful method for converting a P–H bond to a $PCH_2CH_2PH_2$ unit. Further applications of this synthetic technique for the preparation of compounds containing $PCH_2CH_2PH_2$ units have been hampered by the disagreeable, pervasive, and persistent odors of most primary phosphines, including compounds of this type. The value of compounds containing the $PCH_2CH_2PH_2$ unit as building blocks for the syntheses of poly(tertiary phosphines) is demonstrated by the base-catalyzed addition of the two phosphorus–hydrogen bonds in $(C_6H_5)_2$-$PCH_2CH_2PH_2$ to the vinylic moieties in 2 equiv of diphenylvinylphosphine to give the tripod tetra(tertiary phosphine) $P[CH_2CH_2P(C_6H_5)_2]_3$ (X) (eq 16).[27] X

$$(C_6H_5)_2PCH_2CH_2PH_2 + 2(C_6H_5)_2PCH=CH_2 \longrightarrow$$
$$P[CH_2CH_2P(C_6H_5)_2]_3 \quad (16)$$
$$X$$
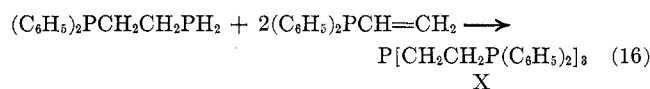
prepared by this method was shown by its infrared spectrum, melting point, and complexing properties with nickel chloride to be identical with authentic tetra(tertiary phosphine) X prepared by the base-catalyzed reaction of phosphine with 3 equiv of diphenylvinylphosphine as described above.

Metal Complexes of Poly(tertiary phosphines)

The new synthetic techniques in organophosphorus (and organoarsenic) chemistry discussed in this Account provide a wide range of new ligands of considerable interest to coordination chemists. We have made a survey of the reactions of several of the new poly(tertiary phosphines) with transition metal halides, metal carbonyls, and cyclopentadienylmetal carbonyls. The ligands studied include the tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (V), the isomeric tetra(tertiary phosphines) $P[CH_2CH_2P(C_6H_5)_2]_3$ (X) and $(C_6$-$H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (XI), and the hexa(tertiary phosphine) $[(C_6H_5)_2$-$PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ (XII).

The Tri(tertiary phosphine) V. The tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (V: abbreviated as Pf–Pf–Pf) can bond to transition metals in the following six fundamentally different ways:[28] monoligate monometallic (XXa or XXb), biligate monometallic (XXc), triligate monometallic (XXd), biligate
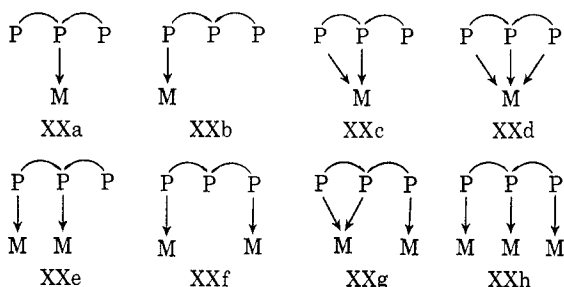
bimetallic (XXe or XXf), triligate bimetallic (XXg), and triligate trimetallic (XXh). (The phenyl rings are omitted in these and the following structures and the CH_2CH_2 bridges are represented by a simple arc.) We have been able to prepare complexes which exemplify each of these six fundamentally different types of bonding of the tri(tertiary phosphine) V to transition metals. However, currently available physical and/or chemical techniques have not yet made possible a distinction between the two different types of monoligate monometallic complexes XXa and XXb and between the two different types of biligate bimetallic complexes XXe and XXf. Factors affecting the types of complexes (XXa through XXb) formed in a reaction with a particular transition metal derivative include the ease of generating vacant coordination positions on the transition metal and the number of vacant positions so generated.

Preparation of a monoligate monometallic complex (XXa or XXb) of the tri(tertiary phosphine) Pf–Pf–Pf (V) requires a transition metal system in which exactly one vacant coordination position is readily generated and where the rate of reaction with tertiary phosphines is sufficiently sluggish that only one phosphorus atom will be complexed. These conditions seem to be satisfied by the methyliron complex $CH_3Fe(CO)_2C_5H_5$ which reacts with the tri(tertiary phosphine) Pf–Pf–Pf (V) in boiling acetonitrile to form the monoligate monometallic acetyliron derivative $CH_3COFe(CO)(Pf-Pf-Pf)$-(C_5H_5)[28] (eq 17). This reaction corresponds to the re-

$$CH_3Fe(CO)_2C_5H_5 + Pf-Pf-Pf \xrightarrow[\Delta]{CH_3CN}$$
$$CH_3COFe(CO)(Pf-Pf-Pf)(C_5H_5) \quad (17)$$

XXI
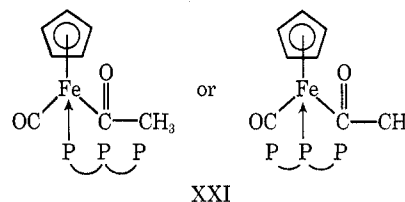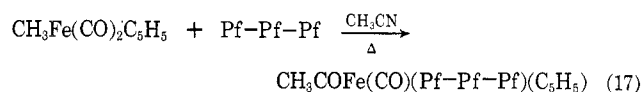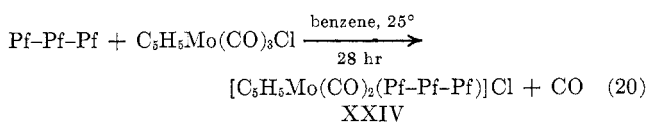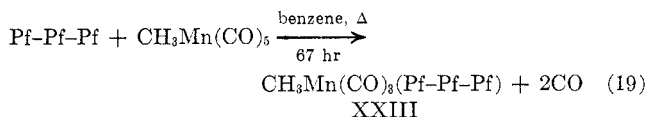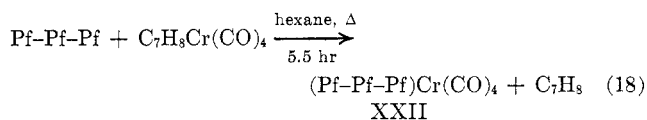
action of $CH_3Fe(CO)_2C_5H_5$ with mono(tertiary phosphines) (e.g., triphenylphosphine) to form similar acetyl derivatives of the type $CH_3COFe(CO)(PR_3)$-(C_5H_5).[29] The availability of exactly one coordination position in the methyliron derivative $CH_3Fe(CO)_2C_5H_5$ for replacement by a tertiary phosphine appears to be a consequence of the availability of exactly one methyliron bond to remove one carbonyl ligand by insertion of carbon monoxide to form an acetyl–iron bond.
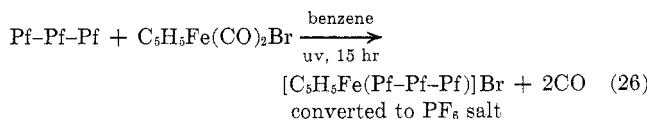
Biligate monometallic complexes (XXc) of the tri(tertiary phosphine) Pf–Pf–Pf (V) are considerably more common than monoligate monometallic complexes (XXa or XXb) because there are several types of metal carbonyl derivatives in which exactly two reactive coordination positions are readily generated by loss of carbonyl groups and/or other ligands. Specific

(28) R. B. King, P. N. Kapoor, and R. N. Kapoor, Inorg. Chem., **10**, 1841 (1971).

(29) J. P. Bibler and A. Wojcicki, ibid., **5**, 889 (1966); P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, ibid., **5**, 1177 (1966).

examples of biligate monometallic complexes of the tri(tertiary phosphine) Pf–Pf–Pf (V) include reactions 18–20.

$$Pf\text{–}Pf\text{–}Pf + C_7H_8Cr(CO)_4 \xrightarrow[\text{5.5 hr}]{\text{hexane, }\Delta}$$
$$(Pf\text{–}Pf\text{–}Pf)Cr(CO)_4 + C_7H_8 \quad (18)$$
$$\text{XXII}$$

$$Pf\text{–}Pf\text{–}Pf + CH_3Mn(CO)_5 \xrightarrow[\text{67 hr}]{\text{benzene, }\Delta}$$
$$CH_3Mn(CO)_3(Pf\text{–}Pf\text{–}Pf) + 2CO \quad (19)$$
$$\text{XXIII}$$

$$Pf\text{–}Pf\text{–}Pf + C_5H_5Mo(CO)_3Cl \xrightarrow[\text{28 hr}]{\text{benzene, }25°}$$
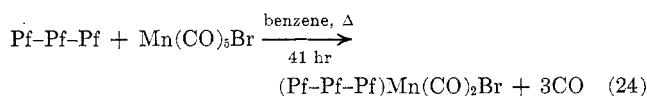$$[C_5H_5Mo(CO)_2(Pf\text{–}Pf\text{–}Pf)]Cl + CO \quad (20)$$
$$\text{XXIV}$$
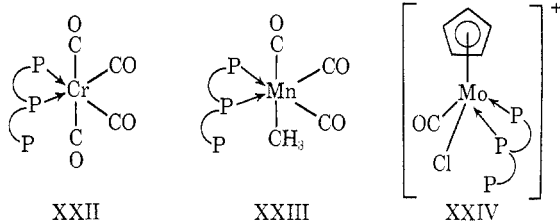
Triligate monometallic complexes (XXd) of the tri(tertiary phosphine) Pf–Pf–Pf (V) are formed if the ligand acts as a tridentate chelating agent. Examples of complexes of this type include reactions 21–26. For-

$$Pf\text{–}Pf\text{–}Pf + MCl_4^{2-} \xrightarrow{H_2O\text{–}EtOH} [(Pf\text{–}Pf\text{–}Pf)MCl]Cl + 2Cl^- \quad (21)$$
$$M = Pd \text{ or } Pt \qquad \text{converted to } PF_6^- \text{ salt}$$

$$Pf\text{–}Pf\text{–}Pf + RhCl_3 \cdot 3H_2O \xrightarrow{EtOH}$$
$$(Pf\text{–}Pf\text{–}Pf)RhCl_3 + 3H_2O \quad (22)$$

$$Pf\text{–}Pf\text{–}Pf + M(CO)_6 \xrightarrow{\text{xylene, }\Delta}$$
$$M = Cr, Mo, \text{ and } W$$
$$(Pf\text{–}Pf\text{–}Pf)M(CO)_3 + 3CO \quad (23)$$

$$Pf\text{–}Pf\text{–}Pf + Mn(CO)_5Br \xrightarrow[\text{41 hr}]{\text{benzene, }\Delta}$$
$$(Pf\text{–}Pf\text{–}Pf)Mn(CO)_2Br + 3CO \quad (24)$$

$$Pf\text{–}Pf\text{–}Pf + C_5H_5Mo(CO)_3Cl \xrightarrow[\text{uv, 41 hr}]{\text{benzene}}$$
$$C_5H_5Mo(Pf\text{–}Pf\text{–}Pf)Cl + 3CO \quad (25)$$

$$Pf\text{–}Pf\text{–}Pf + C_5H_5Fe(CO)_2Br \xrightarrow[\text{uv, 15 hr}]{\text{benzene}}$$
$$[C_5H_5Fe(Pf\text{–}Pf\text{–}Pf)]Br + 2CO \quad (26)$$
$$\text{converted to } PF_6 \text{ salt}$$
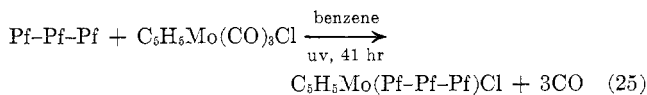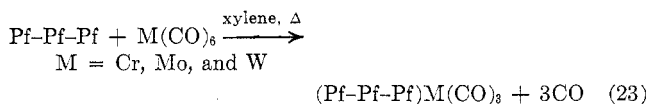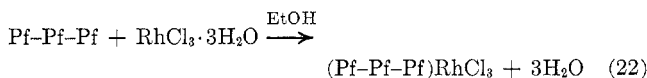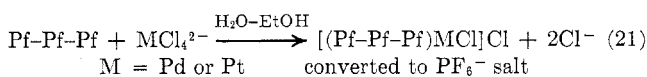
mation of a triligate monometallic complex (XXd) from the tri(tertiary phosphine) Pf–Pf–Pf (V) and a transition metal derivative only requires that three reactive coordination positions on the transition metal atom can be readily generated. This occurs in reactions of the tri(tertiary phosphine) Pf–Pf–Pf (V) with most metal halide derivatives but less frequently with metal carbonyl derivatives, since, when carbonyl groups in metal carbonyls are successively replaced with poorer π acceptors such as tertiary phosphines, the remaining carbonyl groups become more firmly bonded to the central transition metal atom because of increased back-bonding using filled metal d orbitals and antibonding carbon monoxide π* orbitals.

The formation of transition metal complexes of the tri(tertiary phosphine) Pf–Pf–Pf (V) with two or more transition metals attached to a single Pf–Pf–Pf (V) ligand requires more unusual transition metal systems since the following conditions must be satisfied. (1) The number of vacant coordination positions generated on the transition metal must be limited. Otherwise the tritertiary phosphine Pf–Pf–Pf (V) will form a triligate monometallic complex (XXd). (2) The reactivity of the transition metal system must be sufficiently high that it reacts rapidly with trivalent phosphorus ligands. Otherwise only one transition metal will be attached to the Pf–Pf–Pf (V) ligand.
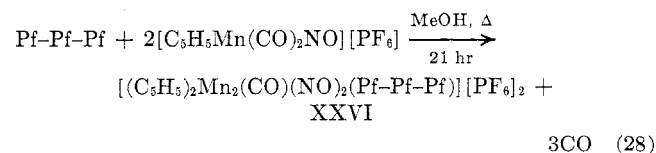
The one suitable reaction for preparing a biligate bimetallic complex of the tri(tertiary phosphine) Pf–Pf–Pf (V) uses the bimetallic cyclopentadienyliron carbonyl $[C_5H_5Fe(CO)_2]_2$ according to eq 27. (Pf–Pf–Pf)-

$$Pf\text{–}Pf\text{–}Pf + [C_5H_5Fe(CO)_2]_2 \longrightarrow$$
$$(Pf\text{–}Pf\text{–}Pf)Fe_2(CO)_2(C_5H_5)_2 + 2CO \quad (27)$$

$Fe_2(CO)_2(C_5H_5)_2$ probably has structure XXV because of the potential stability of the unusual six-membered chelate ring containing two iron atoms, two phosphorus atoms, and two carbon atoms. The infrared spectrum of this complex exhibits only a single bridging ν(CO) frequency at 1672 cm^{-1}; no terminal ν(CO) frequencies were observed. The green color and other spectroscopic properties of (Pf–Pf–Pf)Fe$_2$(CO)$_2$(C$_5$H$_5$)$_2$ resemble those of recently reported[30] (diphos)Fe$_2$(CO)$_2$-(C$_5$H$_5$)$_2$ complexes in accord with the proposed bonding of only two of the three phosphorus atoms of the tri(tertiary phosphine) Pf–Pf–Pf (V) in XXV.
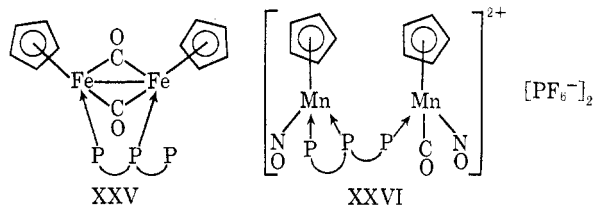
The one suitable reaction for preparing a triligate bimetallic complex of the tri(tertiary phosphine) Pf–Pf–Pf (V) uses the cation $[C_5H_5Mn(CO)_2NO]^+$ according to eq 28. The two carbonyl groups in the

$$Pf\text{–}Pf\text{–}Pf + 2[C_5H_5Mn(CO)_2NO][PF_6] \xrightarrow[\text{21 hr}]{\text{MeOH, }\Delta}$$
$$[(C_5H_5)_2Mn_2(CO)(NO)_2(Pf\text{–}Pf\text{–}Pf)][PF_6]_2 +$$
$$\text{XXVI}$$
$$3CO \quad (28)$$

cation $[C_5H_5Mn(CO)_2NO]^+$ are known[31] to be easily displaced by tertiary phosphines and other related ligands by mild heating; however, both the nitrosyl and cyclopentadienyl groups in this cation are resistant to substitution with tertiary phosphines. The reactivity of the cation $[C_5H_5Mn(CO)_2NO]^+$ in boiling methanol or acetone is so high that it reacts with all available trivalent phosphorus atoms in the system. The availability of two reactive coordination positions in [C$_5$H$_5$-

(30) R. J. Haines and A. L. Du Preez, J. Organometal. Chem., 21, 181 (1970).
(31) R. B. King and A. Efraty, Inorg. Chem., 8, 2374 (1969).

$Mn(CO)_2NO]^+$ causes $[C_5H_5Mn(CO)_2NO]^+$ to form the triligate bimetallic (XXg) complex $[(C_5H_5)_2Mn_2(CO)(NO)_2(Pf-Pf-Pf)][PF_6]_2$ (XXVI) upon reaction with the tritertiary phosphine Pf-Pf-Pf (V).

A suitable reaction for preparing a triligate trimetallic complex of the tri(tertiary phosphine) Pf-Pf-Pf (V) uses the methylmolybdenum derivative $CH_3Mo(CO)_3$-C_5H_5 in acetonitrile solution according to eq 29. The

$$Pf-Pf-Pf + 3CH_3Mo(CO)_3C_5H_5 \xrightarrow{\text{CH}_3\text{CN, 25}^\circ}$$
$$(Pf-Pf-Pf)[Mo(CO)_2(COCH_3)(C_5H_5)]_3 \quad (29)$$
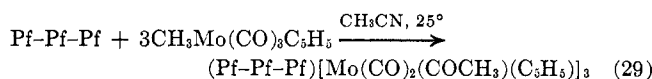
methylmolybdenum derivative $CH_3Mo(CO)_3C_5H_5$ in acetonitrile solution easily provides one coordination position (possibly through an acyl intermediate of the type $CH_3COMo(CO)_2(NCCH_3)(C_5H_5)$) and thus reacts very readily with any and all available trivalent phosphorus atoms. However, only one coordination position is easily generated, and therefore each CH_3Mo-$(CO)_3C_5H_5$ unit can only complex with a single trivalent phosphorus atom. This means that $CH_3Mo(CO)_3$-C_5H_5 in acetonitrile solution has the unusual ability of complexing individually with all available trivalent phosphorus atoms to produce a complex containing one metal atom for each trivalent phosphorus atom.

The Two Tetra(tertiary phosphines) X and XI. The observed coordination chemistry of the tri(tertiary phosphine) Pf-Pf-Pf (V) demonstrates that complexes with any of the six fundamentally different modes of bonding XXa through XXh of the ligand to metal atoms can be obtained if appropriately selected transition metal systems are used. The primary factors affecting the type of complex formed are the ease of providing reactive coordination positions and the number of such positions that can be readily generated on each metal atom. The tetra(tertiary phosphines) X (abbreviated as $P(-Pf)_3$) and XI (abbreviated as Pf-Pf-Pf-Pf) can bond to one or more transition metal atoms in the following ten fundamentally different ways: (a) monoligate monometallic; (b) biligate monometallic; (c) triligate monometallic; (d) tetraligate monometallic; (e) biligate bimetallic; (f) triligate bimetallic; (g) tetraligate bimetallic; (h) triligate trimetallic; (i) tetraligate trimetallic; (j) tetraligate tetrametallic. Because of the complexity of the systems, complexes with not all of the ten possible ways of bonding either tetra(tertiary phosphine) (X or XI) to metal atoms have been prepared. Four of the ten possible ways of bonding the tripod tetra(tertiary phosphine) $P(-Pf)_3$ (X) to metal atoms are known as exemplified by the following complexes:[19] (1) biligate monometallic: $P(-Pf)_3PtCl_2$, $P(-Pf)_3M(CO)_4$ (M = Cr and Mo), $CH_3COMn(CO)_3P(-Pf)_3$, $[C_5H_5Mn(NO)$-$P(-Pf)_3][PF_6]$, and $[C_5H_5Fe(CO)P(-Pf)_3]I$; (2) triligate monometallic: $P(-Pf)_3MCl_3$ (M = Rh and Re), $P(-Pf)_3M(CO)_3$ (M = Cr and Mo), $CH_3Mn(CO)_2P$-$(-Pf)_3$, and $P(-Pf)_3Mn(CO)_2Br$; (3) tetraligate monometallic: $[P(-Pf)_3MCl]^+$ (M = Ni, Co, and Fe) and $P(-Pf)_3M(CO)_2$ (M = Mo and W); (4) tetraligate tetrametallic: $P(-Pf)_3[Mo(CO)_2(COCH_3)(C_5H_5)]_4$ and $P(-Pf)_3[Fe_2(CO)_2(C_5H_5)_2]_2$.

Six of the ten possible ways of bonding the linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf (XI) to metal atoms are known as exemplified by the following complexes:[19] (1) monoligate monometallic: CH_3COFe-$(CO)(Pf-Pf-Pf-Pf)(C_5H_5)$; (2) biligate monometallic: $(Pf-Pf-Pf-Pf)M(CO)_4$ (M = Cr and Mo), CH_3Mn-$(CO)_3(Pf-Pf-Pf-Pf)$, $[C_5H_5Mo(CO)_2(Pf-Pf-Pf-Pf)]Cl$, $C_5H_5Mn(CO)(Pf-Pf-Pf-Pf)$; (3) triligate monometallic: $(Pf-Pf-Pf-Pf)MCl_3$ (M = Rh and Re), $(Pf-Pf-Pf-Pf)M(CO)_3$ (M = Cr and Mo), $(Pf-Pf-Pf-Pf)$-$Mn(CO)_2Br$, and $[C_5H_5Fe(Pf-Pf-Pf-Pf)]^+$; (4) tetraligate monometallic: $[(Pf-Pf-Pf-Pf)M]^{2+}$ (M = Ni, Pd, and Pt), $[(Pf-Pf-Pf-Pf)CoCl]^+$, and $[(Pf-Pf-Pf-Pf)Rh]^+$; (5) triligate bimetallic: $[(C_5H_5)_2Mn_2(CO)$-$(NO)_2(Pf-Pf-Pf-Pf)][PF_6]_2$; (6) tetraligate tetrametallic: $(Pf-Pf-Pf-Pf)[Mo(CO)_2(COCH_3)(C_5H_5)]_4$ and $(Pf-Pf-Pf-Pf)[Fe_2(CO)_2(C_5H_5)_2]_2$.

Most of the gaps in the known ways of bonding of the tetra(tertiary phosphines) X and XI to metal atoms occur in the cases where one tetra(tertiary phosphine) unit is bonded to two or three metal atoms. In many of these cases it is difficult to conceive of a transition metal system that will possess the correct number of readily generated coordination positions so that two or three rather than one or four metal atoms will bond to each tetra(tertiary phosphine) unit.

The two tetra(tertiary phosphines) X and XI represent an unusual isomeric pair of ligands with the same types of bridges (CH_2CH_2) between each pair of trivalent phosphorus atoms and with the same groups (C_6H_5) to fill each nonbridging position of the trivalent phosphorus atoms. They differ only in the relative arrangements of the phosphorus atoms and the bridging CH_2CH_2 groups. Indeed, the relationship between the linear tetra(tertiary phosphine) $(C_6H_5)_2PCH_2CH_2P$-$(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (Pf-Pf-Pf-Pf, XI) and the tripod tetra(tertiary phosphine) $P[CH_2CH_2P(C_6H_5)_2]_3$ ($P(-Pf)_3$, X) resembles the relationship between the isomeric hydrocarbons n-butane, $CH_3CH_2CH_2CH_3$, and isobutane, $HC(CH_3)_3$. For these reasons, a comparison of the complexing behaviors of the linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf (XI) and the tripod tetra(tertiary phosphine) $P(-Pf)_3$ (X) was of particular interest.

The following transition metal systems were found to form different types of metal complexes with the linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf (XI) than with the tripod tetra(tertiary phosphine) $P(-Pf)_3$ (X).[19] (1) The linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf (XI) reacts with nickel(II) chloride in boiling ethanol to form brown to yellow square-planar nickel(II) derivatives (e.g., $(Pf-Pf-Pf-Pf)NiCl_2$ and $[(Pf-Pf-Pf-Pf)Ni][PF_6]_2$, whereas the tripod tetra(tertiary phosphine) $P(-Pf)_3$ (X) reacts with nickel(II) chloride under similar conditions to give blue to violet five-coordinate nickel(II) derivatives (e.g., $[P(-Pf)_3NiCl][PF_6]$). (2) The linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf (XI) does not react with ferrous chloride in boiling ethanol. However, the tripod tetra(tertiary phosphine) $P(-Pf)_3$ (X) reacts with ferrous chloride under these conditions

to give the violet five-coordinate derivative [P(–Pf)₃-FeCl]⁺. (3) The linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf (I) reacts with [C₅H₅Mn(CO)₂NO][PF₆] to form the triligate bimetallic derivative [(C₅H₅)₂Mn₂-(CO)(NO)₂(Pf-Pf-Pf-Pf)][PF₆] whereas the tripod tetra(tertiary phosphine) P(–Pf)₃ reacts with [C₅H₅Mn-(CO)₂NO][PF₆] under the same conditions, including mole ratios of reactants, to give the biligate monometallic derivative [C₅H₅Mn(NO)P(–Pf)₃][PF₆].

These results suggest that among the two tetra(tertiary phosphine) ligands X and XI the tripod tetra(tertiary phosphine) P(–Pf)₃ (X) is the better "chelating agent" (i.e., better at forming complexes with several phosphorus atoms all bonded to a single metal atom). However, the linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf (XI) is better at forming polymetallic complexes (i.e., complexes with two or more metal atoms bonded to a single tetra(tertiary phosphine) ligand) presumably because of the greater possible maximum phosphorus–phosphorus distance in Pf-Pf-Pf-Pf (XI) than in P(–Pf)₃ (X). The greater possible maximum phosphorus–phosphorus distance in the linear tetra(tertiary phosphine) ligand Pf-Pf-Pf-Pf (XI) relative to the tripod tetra(tertiary phosphine) ligand P(–Pf)₃ (X) arises from the fact that the two end phosphorus atoms in Pf-Pf-Pf-Pf (XI) are separated by three CH₂CH₂ bridges and two middle phosphorus atoms, whereas no pair of phosphorus atoms in P(–Pf)₃ (X) is separated by more than two CH₂CH₂ bridges and one middle phosphorus atom.

The Hexa(tertiary phosphine) XII. The coordination chemistry of the hexa(tertiary phosphine) [(C₆H₅)₂-PCH₂CH₂]₂PCH₂CH₂P[CH₂CH₂P(C₆H₅)₂]₂ (XII; abbreviated as P₂(–Pf)₄) is of interest because of the general similarity of the relative positions of the six donor phosphorus atoms in XII as compared with those of the six donor oxygen and nitrogen atoms in the analytically important ethylenediaminetetraacetic acid (EDTA).[5] However, investigation of the reactions of the hexa(tertiary phosphine) P₂(–Pf)₄ (XII) with a wide variety of transition metal systems failed to reveal any cases where the hexa(tertiary phosphine) unambiguously acted as a hexadentate (hexaligate monometallic) ligand (XXVII).[23] This contrasts with the behavior of EDTA which forms hexadentate metal complexes very easily.[5] Apparently, it is difficult to bend the five CH₂CH₂ bridges in the hexa(tertiary phosphine)

P₂(–Pf)₄ (XII) around so that all six phosphorus atoms in P₂(–Pf)₄ can bond to a single metal atom as in structure XXVII.
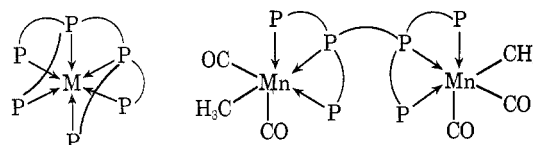
The hexa(tertiary phosphine) P₂(–Pf)₄ (XII) reacts with metal(II) chloride derivatives of the nickel, palladium, and platinum triad to form the diamagnetic metal(II) cations [P₂(–Pf)₄M]²⁺ where the hexa(tertiary phosphine) acts as a tetradentate (tetraligate monometallic) ligand as in structure XXVIII. The complexes of the type [P₂(–Pf)₄M]²⁺ resemble the corresponding tetraligate monometallic complexes [(Pf-Pf-Pf-Pf)M]²⁺ obtained from the same metal chloride derivatives and the linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf (XI). The hexa(tertiary phosphine) P₂(–Pf)₄ (XII) reacts with metal chloride derivatives of cobalt, rhodium, and ruthenium to form the metal(III) cations [P₂(–Pf)₄MCl₂]⁺ in which the hexa(tertiary phosphine) XII acts as a tetradentate (tetraligate monometallic) ligand as in structure XXIX. The cobalt and rhodium derivatives of type XXIX exhibit the expected diamagnetism for these metals in the +3 oxidation state whereas the ruthenium derivative of type XXIX exhibits the expected paramagnetism corresponding to one unpaired electron. The cobalt(III) derivative [P₂(–Pf)₄CoCl₂]Cl is formed by reaction of cobalt(II) chloride with the hexa(tertiary phosphine) P₂(–Pf)₄ (XII); since this reaction was carried out in a nitrogen atmosphere, the source of the oxidation from cobalt(II) to cobalt(III) is not clear.

Our work with the hexa(tertiary phosphine) P₂(–Pf)₄ (XII) has failed to yield any complexes with all six phosphorus atoms bonded to a single metal atom. However, bimetallic complexes of P₂(–Pf)₄ were prepared in which all six phosphorus atoms are bonded to metal atoms.[23] The most distinctive complexes of this type are the derivatives P₂(–Pf)₄[M(CO)₃]₂ (XXX, M = Cr, Mo, and W), which are readily prepared by heating the hexa(tertiary phosphine) P₂(–Pf)₄ (XII) with excess of the metal hexacarbonyl in boiling xylene. A similar complex, P₂(–Pf)₄[Mn(CO)₂CH₃]₂ (XXXI), can be prepared by heating CH₃Mn(CO)₅ with the hexa(tertiary phosphine) P₂(–Pf)₄ (XII) in at least a 2:1 metal:ligand ratio in boiling mesitylene. However, if the mole ratio of CH₃Mn(CO)₅ to P₂(–Pf)₄ (XII) is only 1:1 and the reaction is carried out in boiling xylene rather than boiling mesitylene, the product is the
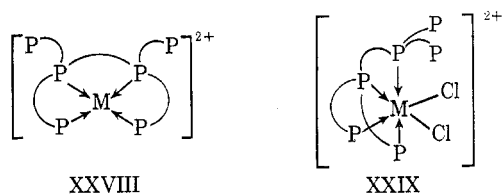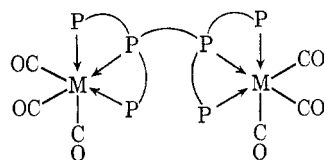

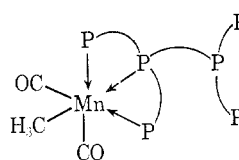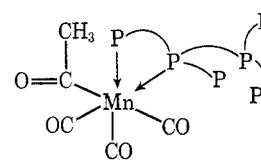XXVIII   XXIX   XXVII   XXXI

XXX   XXXII   XXXIII

triligate monometallic derivative $P_2(-Pf)_4Mn(CO)_2CH_3$ (XXXII) in which only half of the hexa(tertiary phosphine) XII is involved in bonding to the metal atom. If the reaction between $CH_3Mn(CO)_5$ and $P_2(-Pf)_4$ (XII) is carried out under milder conditions in the polar solvent tetrahydrofuran, one of the liberated molecules of carbon monoxide inserts into the methyl–manganese bond to form the biligate monometallic acetyl derivative $CH_3COMn(CO)_3P_2(-Pf)_4$ (XXXIII).

One of the most unusual metal complexes of the hexa(tertiary phosphine) $P_2(-Pf)_4$ (XII) is the hexaligate hexametallic derivative $P_2(-Pf)_4[Mo(CO)_2-(COCH_3)(C_5H_5)]_6$ which is formed as a yellow precipitate upon reaction of $CH_3Mo(CO)_3C_5H_5$ with the hexa(tertiary phosphine) $P_2(-Pf)_4$ (XII) in acetonitrile solution. This reaction demonstrates dramatically the great ease of generating from $CH_3Mo(CO)_3C_5H_5$ in acetonitrile solution one vacant coordination position which is so reactive that it exhaustively seeks out all available uncomplexed trivalent phosphorus atoms.

Conclusion

This work has shown that numerous poly(tertiary phosphines, arsines, and phosphine–arsines) can be prepared by the base-catalyzed additions of phosphorus–hydrogen bonds or arsenic–hydrogen bonds to the vinyl bonds of vinylphosphines. Other trivalent phosphorus derivatives of interest can be prepared by similar base-catalyzed additions of phosphorus–hydrogen bonds to other unsaturated compounds such as vinyl isocyanide and diethyl vinylphosphonate. The potential for the synthesis of additional organophosphorus compounds by techniques related to those summarized in this Account is very large for the following reasons. (1) Phosphorus–hydrogen bonds can be added to a large variety of appropriate unsaturated compounds particularly those known to undergo Michael addition[32] reactions. (2) Compounds with "active hydrogen" other than those with phosphorus–hydrogen or arsenic–hydrogen bonds can be added to the carbon–carbon

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

multiple bonds in vinylphosphorus or ethynylphosphorus derivatives. (3) Compounds can be prepared where the "extra" coordination positions of the trivalent phosphorus atoms are occupied by groups other than phenyl. Phenylphosphorus derivatives were used in the work summarized in this article for two reasons: (a) they are readily available as compared with analogous organophosphorus derivatives in which the phenyl groups are replaced by other organic groups; (b) related aliphatic alkylphosphorus derivatives are more toxic and air-sensitive and also are more likely to form less readily characterized liquid products rather than crystalline poly(tertiary phosphines) when subjected to reactions analogous to those summarized in this Account.

The new poly(tertiary phosphines) prepared during the course of this research are interesting to coordination chemists because they form a wide variety of metal complexes. Thus complexes of the tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ were prepared in which the tri(tertiary phosphine) ligand is bonded to metal atoms in each of the six possible fundamentally different ways. The variety of unusual poly(tertiary phosphine) types that can be prepared by these new synthetic methods and the variety of transition metal systems which form tertiary phosphine complexes make the coordination chemistry of the poly(tertiary phosphines) and related compounds a nearly limitless field. Furthermore, studies on the coordination chemistry of poly(tertiary phosphines) are likely to lead eventually to major contributions to areas of practical importance such as nitrogen fixation, fuel cell technology, homogenous hydrogenation, and new catalytic processes for the synthesis of useful organic chemicals.