(70) W. P. Jencks and J. Regenstein in "Handbook of Biochemistry", 1st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968.
(71) J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956).
(72) J. Hine and A. W. Kueppel, *J. Am. Chem. Soc.*, **96**, 2924 (1974).
(73) R. Shaw, *J. Chem. Eng. Data*, **14**, 461 (1969); S. W. Benson and G. D. Mendenhall, *J. Am. Chem. Soc.*, **98**, 2046 (1976).
(74) J. Hine and G. F. Koser, *J. Org. Chem.*, **36**, 1348 (1971).

# Poly(tertiary phosphines and arsines). 15. Some Polyphosphines with Terminal Dialkylamino and Alkoxy Groups[1]

**R. B. King* and W. F. Masler[2]**

*Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602.* *Received November 23, 1976*

**Abstract:** Reactions of $[(CH_3)_3N]_2PCl$ and $(C_2M_5)_2NPCl_2$ with vinylmagnesium bromide followed by hydrolysis with aqueous alkaline tetrasodium ethylenediamine tetraacetate give the vinylphosphorus derivatives $[(CH_3)_2N]_2PCH{=}CH_2$ and $(C_2H_5)_2NP(CH{=}CH_2)_2$, respectively. The additions of the secondary phosphines $R_2PH$ ($R = CH_3$ and $C_6H_5$) to $[(CH_3)_2N]_2PCH{=}CH_2$ catalyzed by KH give the corresponding diphosphines $R_2PCH_2CH_2P[N(CH_3)_2]_2$. The base-catalyzed additions of the primary phosphines $RPH_2$ ($R = CH_3$ and $C_6H_5$) to $[(CH_3)_2N]_2PCH{=}CH_2$ can be controlled to give either 1:1 adduct diphosphines $RP(H)CH_2CH_2P[N(CH_3)_2]_2$ or the 1:2 adduct triphosphines $RP[CH_2CH_2P[N(CH_3)_2]_2]_2$. Reaction of $KPH_2$ with $[(CH_3)_2N]_2PCH{=}CH_2$ followed by hydrolysis gives the tripod tetraphosphine $P[CH_2CH_2P[N(CH_3)_2]_2]_3$. Base-catalyzed additions of the secondary phosphines $R_2PH$ ($R = CH_3$ and $C_6H_5$) to $(C_2H_5)_2NP(CH{=}CH_2)_2$ can be controlled to give either the 1:1 adducts $(C_2H_5)_2NP(CH{=}CH_2)CH_2CH_2PR_2$ or the 2:1 adducts $(C_2H_5)_2NP(CH_2CH_2PR_2)_2$. Base-catalyzed addition of the primary phosphines $RPH_2$ ($R = C_6H_5$, $CH_2C_6H_5$, and $CH_2(C(CH_3)_3)_2$) to $(C_2H_5)_2NP(CH{=}CH_2)_2$ gives the corresponding 1,4-diphosphacyclohexane derivatives $(C_2H_5)_2NP(CH_2CH_2)_2PR$. Methanolysis of $[(CH_3)_2N]_2PCH{=}CH_2$ in boiling methanol gives $(CH_3O)_2PCH{=}CH_2$. Potassium hydride catalyzed additions of $(C_6H_5)_2PH$ and $C_6H_5PH_2$ to $(CH_3O)_2PCH{=}CH_2$ give the diphosphine $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ and the triphosphine $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$, respectively. The phosphines with terminal methoxy groups $R_2PCH_2CH_2P(OCH_3)_2$, $RP[CH_2CH_2P(OCH_3)_2]_2$ ($R = CH_3$ and $C_6H_5$), and $P[CH_2CH_2P(OCH_3)_2]_3$ can be obtained by methanolysis in boiling toluene of the corresponding phosphines with terminal dimethylamino groups. The base-catalyzed addition of $C_6H_5P(H)CH_2CH_2P[N(CH_3)_2]_2$ to $(CH_3O)_2PCH{=}CH_2$ gives $C_6H_5P[CH_2CH_2P(OCH_3)_2][CH_2CH_2P[N(CH_3)_2]_2]$. The proton, phosphorus-31, and carbon-13 NMR spectra of these new organophosphorus derivatives are described.

Previous papers of this series describe the preparation of poly(tertiary phosphines) in which the phosphorus atoms are linked by $-CH_2CH_2-$ bridges and the terminal positions on each phosphorus atom are occupied by hydrocarbon groups such as phenyl,[3] methyl,[4] or neopentyl[5] bonded to the phosphorus atoms through phosphorus–carbon bonds. We have also reported several polyphosphines containing terminal hydrogen atoms bonded to the trivalent phosphorus atoms through phosphorus–hydrogen bonds.[6] Related poly(tertiary phosphines) containing $PCH_2CH_2P$ structural units have also been studied by other research groups.[7-9]

This paper describes the first polyphosphines containing $PCH_2CH_2P$ structural units and dialkylamino or alkoxy terminal groups bonded to the trivalent phosphorus atoms through phosphorus–nitrogen and phosphorus–oxygen bonds, respectively. The polyphosphines containing terminal methoxy groups provide chelating ligands with stronger $\pi$-accepting properties than the previously available polyphosphines,[3-5] in which only carbon atoms are bonded to phosphorus. Furthermore, the relative susceptibilities of phosphorus–nitrogen and phosphorus–oxygen bonds toward cleavage under conditions where phosphorus–carbon bonds are stable suggests that the new polyphosphines described in this paper may be useful as intermediates for the preparation of a variety of potentially useful ligands in which various types of terminal groups are bonded to the trivalent phosphorus atoms of a network built from $PCH_2CH_2P$ structural units. Such interconversions of terminal groups in poly(tertiary phosphines) are demonstrated in this paper by syntheses of several poly(tertiary phosphines) containing terminal methoxy groups by methanolyses of the corresponding poly(tertiary phosphines) containing terminal dimethylamino groups.

## Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga., and Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Proton NMR spectra (Table I) were taken in $CDCl_3$ solution and were recorded either at 100 MHz on a Varian HA-100 spectrometer or at 60 MHz on a Perkin-Elmer Hitachi R-20 spectrometer. Phosphorus-31 (Table II) and carbon-13 (Table III) NMR spectra were taken in dichloromethane solutions unless otherwise indicated and recorded at 40.3 and 25.0336 MHz, respectively, on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton noise decoupling and a deuterium lock. Spectroscopic measurements on solutions of methyl poly(tertiary phosphines), $(C_2H_5)_2NP(CH{=}CH_2)_2$, $[(CH_3)_2N]_2PCH{=}CH_2$, and $C_6H_5P(H)CH_2CH_2P[N(CH_3)_2]_2$ in chlorinated solvents, particularly $CDCl_3$, must be done on freshly prepared solutions, since chlorinated solvents react slowly with these phosphines upon standing at room temperature.

All reactions were carried out in an efficient hood. For reactions using phosphine, methylphosphine, or dimethylphosphine two aqueous calcium hypochlorite traps in series were used to decompose the effluent vapors before passing them into the hood exhaust. A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions; (b) handling air-sensitive organophosphorus compounds; and (c) filling evacuated vessels containing potentially air-sensitive materials. When necessary a glove box was used to provide an inert atmosphere. High vacuum distillations were performed

Table I. Proton NMR Spectra of New Organophosphorus Derivatives Described in This Paper

| Compd[a] | Proton NMR spectrum,[b] $\tau$<br>$PCH_2CH_2P$ | OMe | $NR_2$ | RP |
|---|---|---|---|---|
| $(Me_2N)_2PVi$ | | | Me: 7.45 d (9) | Vi: 3.52-4.98 m |
| $Et_2NPVi_2$ | | | Et: 7.06 qd (7, 10), 8.95 t (7) | Vi: 3.35-4.93 m |
| $Ph_2PCH_2CH_2P(NMe_2)_2$ | 7.75-8.62 m | | Me: 7.46 d (9) | Ph: 2.50-2.97 m |
| $PhP[CH_2CH_2P(NMe_2)_2]_2$ | 8.35 t (4) | | Me: 7.45 d (9), 7.49 d (9) | Ph: 2.45-2.95 m |
| $PhP(H)CH_2CH_2P(NMe_2)_2$[c] | 8.15-8.45 m | | Me: 7.43 d (9) | Ph: 2.55-3.00 m |
| $Me_2PCH_2CH_2P(NMe_2)_2$ | 8.05-8.75 m | | Me: 7.50 d (9) | Me: 9.00 d (2.5) |
| $MeP[CH_2CH_2P(NMe_2)_2]_2$ | 8.13-8.87 m | | Me: 7.42 d (8) | Me: 8.99 d (3) |
| $MeP(H)CH_2CH_2P(NMe_2)_2$ | 8.05-8.87 m | | Me: 7.37 d (9) | Me: 8.97 d (2) |
| $P[CH_2CH_2P(NMe_2)_2]_3$ | 8.02-8.85 m | | Me: 7.42 d (8) | |
| $Et_2NP(Vi)CH_2CH_2PMe_2$ | 8.35-8.7 m | | Et: 7.08 qd (7, 9), 8.97 t (7) | Me: 8.96<br>Vi: 3.35-4.95 m |
| $Et_2NP(CH_2CH_2PMe_2)_2$ | 8.2-8.8 m | | Et: 7.15 m, 9.00 t (7) | Me: 9.00 |
| $Et_2NP(Vi)CH_2CH_2PPh_2$ | 7.6-8.65 m | | Et: 7.12 qd (7, 9), 9.01 t (7) | Ph: 2.50-3.05 m<br>Vi: 3.45-5.05 m |
| $Et_2NP(CH_2CH_2PPh_2)_2$ | 7.7-8.8 m | | Et: 7.23 qd (7, 9), 9.07 t (7) | Ph: 2.7-2.95 m |
| $Et_2NP(CH_2CH_2)_2PPh$ | 7.7-8.4 m | | Et: $\sim$7.1 m, 9.00 t (7) | Ph: 2.8-2.95 m |
| $Et_2NP(CH_2CH_2)_2PCH_2Ph$ | 7.9-8.6 m | | Et: 7.1-7.4 m, 9.03 td (7, 4) | $PhCH_2$: 3.06 s, 7.1-7.4 m |
| $Et_2NP(CH_2CH_2)_2PCH_2CMe_3$ | 8.0-8.8 m | | Et: 7.15 m, 9.05 t (7) | $Me_3CCH_2$: $CH_2$?, Me: 9.05 s |
| $MeOPVi_2$ | | 6.50 d (10) | | Vi: 3.50-4.65 m |
| $Ph_2PCH_2CH_2P(OMe)_2$ | 7.6-8.8 m | 6.56 d (11) | | Ph: 2.45-3.0 m |
| $PhP[CH_2CH_2P(OMe)_2]_2$ | 8.2-8.7 m | 6.54 d (11), 6.56 d (11) | | Ph: 2.5-3.0 m |
| $Me_2PCH_2CH_2P(OMe)_2$ | 8.1-8.7 m | 6.48 d (11) | | Me: 9.00 d (3) |
| $MeP[CH_2CH_2P(OMe)_2]_2$ | 8.3-8.6 m | 6.50 d (11) | | Me: 9.00 d (3) |
| $P[CH_2CH_2P(OMe)_2]_3$ | 8.3-8.7 m | 6.50 d (11) | | |
| $PhP[CH_2CH_2P(NMe_2)_2]$-$[CH_2CH_2P(OMe)_2]_2$ | 8.0-8.5 m | 6.54 d (11), 6.55 d (11) | Me: 7.47 d (9), 7.49 d (9) | Ph: 2.5-3.0 m |

[a] Me = methyl, Et = ethyl, Vi = vinyl, Ph = phenyl. [b] d = doublet, t = triplet, qd = doublet of quartets, m = ill-defined multiplet; coupling constants (Hz) in parentheses. [c] The lower half of the P-H doublet appears as a hump at $\tau$ 4.15. The upper half of this doublet is hidden under other resonances.

Table II. Proton-Decoupled Phosphorus-31 NMR Spectra of New Organophosphorus Derivatives Described in This Paper

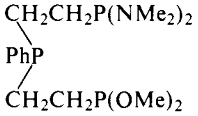
| Compd[a] | Phosphorus-31 NMR spectrum,[b] $\delta$<br>$PC_3$ or $PC_2H$ | $PCN_2$ or $PC_2N$ | $PCO_2$ |
|---|---|---|---|
| $(Me_2N)_2PVi$ | | -93.6 s | |
| $Ph_2PCH_2CH_2P(NMe_2)_2$ | 13.0 d (37) | -94.8 d (37) | |
| $PhP[CH_2CH_2P(NMe_2)_2]_2$ | 16.5 t (32) | -95.0 d (32) | |
| $PhP(H)CH_2CH_2P(NMe_2)_2$ | 46.5 d (25) | -93.6 d (25) | |
| $Me_2PCH_2CH_2P(NMe_2)_2$ | 47.8 d (29) | -95.3 d (29) | |
| $MeP[CH_2CH_2P(NMe_2)_2]_2$ | 33.3 t (29) | -95.2 d (29) | |
| $MeP(H)CH_2CH_2P(NMe_2)_2$ | 47.7 d (29) | -95.0 d (29) | |
| $P[CH_2CH_2P(NMe_2)_2]_3$ | 18.0 q (28) | -95.6 d (28) | |
| $Et_2NPVi_2$ | | -52.9 s | |
| $Et_2NP(Vi)CH_2CH_2PMe_2$ | 47.5 d (28) | -55.4 d (28) | |
| $Et_2NP(CH_2CH_2PMe_2)_2$ | 47.6 d (26) | -59.9 t (26) | |
| $Et_2NP(Vi)CH_2CH_2PPh_2$ | 12.8 d (34) | -55.4 d (34) | |
| $Et_2NP(CH_2CH_2PPh_2)_2$ | 12.8 d (31) | -60.5 t (31) | |
| $Et_2NP(CH_2CH_2)_2PPh$ Isomer A ($\sim$30%) | 26.9 s | -47.5 s | |
| Isomer B ($\sim$70%) | 29.2 d (17) | -48.2 d (17) | |
| $Et_2NP(CH_2CH_2)_2PCH_2Ph$ Isomer A ($\sim$40%) | 34.2 s | -45.2 s | |
| Isomer B ($\sim$60%) | 29.2 d (17) | -48.1 d (17) | |
| $MeOPVi_2$ | | | -164.5 s |
| $Ph_2PCH_2CH_2P(OMe)_2$ | 13.0 d (30) | | -183.9 d (30) |
| $PhP[CH_2CH_2P(OMe)_2]_2$ | 16.7 t (26) | | -184.2 d (26) |
| $Me_2PCH_2CH_2P(OMe)_2$ | 47.0 d (26) | | -184.6 d (26) |
| $MeP[CH_2CH_2P(OMe)_2]_2$ | 32.8 t (27) | | -184.4 d (27) |
| $P[CH_2CH_2P(OMe)_2]_3$ | 18.4 q (23) | | -184.7 d (23) |
| $PhP[CH_2CH_2P(NMe_2)_2][CH_2CH_2P(OMe)_2]_2$ | 16.7 t (29) | -94.7 d (32) | -184.7 d (27) |

[a] Me = methyl, Et = ethyl, Vi = vinyl, Ph = phenyl. [b] s = singlet, d = doublet, t = triplet, q = quartet; coupling constants (Hz) in parentheses.

using a diffusion pump in addition to the usual mechanical oil pump to minimize thermal decomposition at the boiling point.

Tetrahydrofuran and diethyl ether were purified by distillation under nitrogen from $LiAlH_4$ immediately before use. Dioxane was dried over molecular sieves before use. Methanol was dried by distillation under nitrogen from magnesium methoxide and was stored over

**Table III.** Proton-Decoupled Carbon-13 NMR Spectra of Polyphosphines with Terminal Dialkylamino and Methoxy Groups

| | Carbon-13 NMR spectrum, δ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $R_2PCH_2CH_2PR_2'$ | | | | $R_2PCH_2$ | | $CH_2PR_2'$ | | |
| Compd[a] | $R_2$ | $R_2'$ | $R_2PCH_2$ | $CH_2PR_2'$ | $^1J$(C-P) | $^2J$(C-P) | $^1J$(C-P) | $^2J$(C-P) | Terminal groups[a,b] |
| $Ph_2PCH_2CH_2P(NMe_2)_2$ | $Ph_2$ | $(NMe_2)_2$ | 22.9 | 23.5 | 23 | 14 | ~15 | 6 | Ph: 139.0 (15), 132.9 (8)<br>128.7 (0), 128.6 (~5)<br>$Me_2N$: 40.9 (12) |
| $PhP[CH_2CH_2P(NMe_2)_2]_2$ | Ph, $C_2H_4$ | $(NMe_2)_2$ | 22.8 | 23.3 | 20 | 15 | 14 | 6 | Ph: 139.0 (16), 132.6 (18)<br>128.8 (0), 128.4 (6)<br>$Me_2N$: 40.8 (13) |
| $PhP(H)CH_2CH_2P(NMe_2)_2$ | Ph, H | $(NMe_2)_2$ | 18.2 | 25.6 | 21 | 12 | 7 | 7 | Ph: 135.3 t (12), 133.6 (15)<br>128.2 (7), 128.1 (0)<br>$Me_2N$: 40.7 (12) |
| $Me_2PCH_2CH_2P(NMe_2)_2$ | $Me_2$ | $(NMe_2)_2$ | 26.6 | 23.1 | 19 | 12 | 12 | 6 | Me: 14.1 (15)<br>$Me_2N$: 40.7 (13) |
| $MeP[CH_2CH_2P(NMe_2)_2]_2$ | Me, $C_2H_4$ | $(NMe_2)_2$ | 24.2 | 23.1 | 19 | 13 | 11 | 6 | Me: 11.5 (17)<br>$Me_2N$: 40.8 (13) |
| $MeP(H)CH_2CH_2P(NMe_2)_2$ | Me, H | $(NMe_2)_2$ | 26.2 | 22.8 | 20 | 11 | 12 | 6 | Me: 13.9 (14)<br>$Me_2N$: 40.7 (12) |
| $P[CH_2CH_2P(NMe_2)_2]_3$ | $C_2H_4$, $C_2H_4$ | $(NMe_2)_2$ | 21.3 | 23.2 | 20 | 16 | 12 | 6 | $Me_2N$: 40.8 (13) |
| $Et_2NP[CH_2CH_2PPh_2]_2$ | $Et_2N$, $C_2H_4$ | $Ph_2$ | 23.0 | 22.9 | 12 | 6 | ~21 | ~21 | Ph: 138.6 (15), 132.5 (18)<br>128.3 (0), 128.2 (6)<br>$Et_2N$: 42.8 (15), 15.4 (10) |
| $Et_2NP[CH_2CH_2PMe_2]_2$ | $Et_2N$, $C_2H_4$ | $Me_2$ | 25.4 | 27.3 | 17 | 11 | 14 | 12 | Me: 13.8 (14)<br>$Et_2N$: 42.8 (14), 15.4 |
| $Ph_2PCH_2CH_2P(OMe)_2$ | $Ph_2$ | $(OMe)_2$ | 19.8 | 29.5 | 15 | 15 | 22 | 13 | Ph: 138.8 (15), 132.8 (18),<br>128.7 (0), 128.5 (7)<br>OMe: 53.7 (10) |
| $PhP[CH_2CH_2P(OMe)_2]_2$ | Ph, $C_2H_4$ | $(OMe)_2$ | 19.5 | 29.1 | 15 | 15 | 22 | 11 | Ph: 137.4 (16), 132.4 (18)<br>128.9 (0), 128.4 (6)<br>OMe: 53.7 (12) |
| $Me_2PCH_2CH_2P(OMe)_2$ | $Me_2$ | $(OMe)_2$ | 23.1 | 29.0 | 13 | 13 | 20 | 9 | Me: 13.7 (13)<br>OMe: 53.7 (12) |
| $MeP[CH_2CH_2P(OMe)_2]_2$ | Me, $C_2H_4$ | $(OMe)_2$ | 20.5 | 28.9 | 14 | 14 | 21 | 10 | Me: 11.0 (17)<br>OMe: 53.7 (9) |
| $P[CH_2CH_2P(OMe)_2]_3$ | $C_2H_4$, $C_2H_4$ | $(OMe)_2$ | 17.6 | 28.8 | 16 | 16 | 21 | 10 | OMe: 53.7 (12) |
|  $PhP[CH_2CH_2P(NMe_2)_2][CH_2CH_2P(OMe)_2]$ | Ph, $C_2H_4$ | $(NMe_2)_2$ | 22.3 | 22.9 | 23 | 14 | 13 | 6 | Ph: 137.8 (17), 132.3 (18)<br>128.8 (0), 128.2 (6) |
| | Ph, $C_2H_4$ | $(OMe)_2$ | 19.6 | 29.1 | 25 | 15 | 21 | 10 | $Me_2N$: 40.6 (13)<br>OMe: 53.5 (11) |
| $Et_2NP(Vi)CH_2CH_2PPh_2$ | $Et_2N$, Vi | $Ph_2$ | 24.0 | 24.7 | 25 | 15 | 32 | 15 | Ph: 139.2 (15), 132.8 (20)<br>128.7 (0), 128.6 (6)<br>Vi: 141.3 (21), 123.1 (16)<br>$Et_2N$: 43.7 (15), 15.4 |

[a] Me = methyl, Et = ethyl, Vi = vinyl, Ph = phenyl. [b] Coupling constants (Hz) are given in parentheses. Unless otherwise indicated the terminal group resonances are doublets (t = triplet).

4A molecular sieves. Dimethyl sulfoxide was distilled at reduced pressure from barium oxide and was stored over 4A molecular sieves.

Lithium aluminum hydride and potassium hydride were purchased from the Alfa Division of Ventron, Beverly, Mass. Before use as a catalyst the potassium hydride was washed free of oil with dry diethyl ether. Fresh oil-free potassium hydride was pyrophoric. However, upon standing at room temperature in a screw-capped vial, the oil-free potassium hydride became coated with a layer of potassium hydroxide and/or carbonate, rendering it nonpyrophoric but still catalytically active. The amounts of the potassium hydride catalyst were estimated by the volume on the tip of a spatula to avoid weighing and possible exposure to hydrolysis. The potassium hydride was transferred rapidly in air to a reaction vessel through which nitrogen was being passed.

Vinyl bromide, dimethylamine, and phosphine were purchased from Matheson, Inc., Morrow, Ga. Dimethyl methylphosphonate was purchased from the Aldrich Chemical Co., Milwaukee, Wis. Tetramethylbiphosphine disulfide,[10] diphenylphosphine,[11] phenylphosphine,[11,12] benzylphosphine,[13] tris(dimethylamino)phosphine,[14] and diethylaminodichlorophosphine[15] were prepared by the cited published procedures.

**Preparation of Bis(dimethylamino)vinylphosphine.** Phosphorus trichloride (91.5 g, 0.66 mol) was added at room temperature with mechanical stirring to 217 g (1.33 mol) of tris(dimethylamino)phosphine. A vigorous exothermic reaction occurred with the production of some white fumes. The mixture was then heated at 100 °C for 20 min. The resulting $[(CH_3)_2N]_2PCl$ was cooled to room temperature and then diluted with approximately 2500 mL of dry diethyl ether. The resulting diethyl ether solution was treated at −78 °C with a solution of 2.0 mol of vinylmagnesium bromide in ~1500 mL of tetrahydrofuran over 2 h. The reaction mixture was allowed to warm slowly to room temperature and then stirred overnight at room temperature.

The reaction mixture was hydrolyzed by pouring during a period of 5 min into a vigorously stirred ice cold deoxygenated solution of 642 g (2.2 mol) of ethylenediaminetetraacetic acid (EDTA) and 370 g (9.25 mol) of sodium hydroxide in 4000 mL of water. The mixture was stirred for several minutes. After separation of the diethyl ether layer, the aqueous layer was extracted with an additional 1000 mL of diethyl ether. The combined diethyl ether solutions were dried over potassium carbonate, filtered, and concentrated at ∼25 °C (40 mm) to give a light yellow liquid. Distillation of this liquid gave 175 g (60% yield) of clear, colorless liquid bis(dimethylamino)vinylphosphine, $[(CH_3)_2N]_2PCH{=}CH_2$, bp 75-79 °C (28 mm): $^{13}$C NMR δ 139.5 (s), 124.4 (d, 15 Hz), and 41.3 (d, 15 Hz).

Anal. Calcd for $C_6H_{15}N_2P$: C, 49.3; H, 10.3; N, 19.2. Found: C, 49.2; H, 10.4; N, 19.1.

**Preparation of Diethylaminodivinylphosphine.** A solution of 1.0 mol of vinylmagnesium bromide in 750 mL of dry tetrahydrofuran was added over ∼1 h to a vigorously stirred solution of 87 g (0.5 mol) of $(C_2H_5)_2NPCl_2$ in 800 mL of dry diethyl ether cooled to −78 °C. The mixture was then allowed to warm slowly to room temperature and stirred overnight at room temperature. The reaction mixture was then poured during a period of 5 min into a vigorously stirred mixture of 321 g (1.1 mol) of EDTA, 184 g (4.6 mol) of sodium hydroxide, 1500 mL of deoxygenated water, and 1000 mL of diethyl ether held at room temperature. The resulting mixture was stirred for several minutes. The two layers were then separated. The organic layer was washed with saturated aqueous sodium chloride. The aqueous layer was extracted once with 250 mL of diethyl ether. The combined organic layers were dried over potassium carbonate, filtered, and concentrated at ∼25 °C (40 mm) to give an orange liquid. Distillation of this liquid gave 39.6 g (50% yield) of clear colorless diethylaminodivinylphosphine, $(C_2H_5)_2NP(CH{=}CH_2)_2$, bp 64-65 °C (15 mm): $^{13}$C NMR δ 139.8 (d, 20 Hz), 124.0 (d, 20 Hz), 44.1 (d, 15 Hz), and 15.2 (d, 3 Hz).

Anal. Calcd for $C_8H_{16}NP$: C, 61.1; H, 10.3; N, 8.9. Found: C, 61.4; H, 10.3; N, 8.9.

**Preparation of $(C_6H_5)_2PCH_2CH_2P[N(CH_3)_2]_2$.** A solution of 18.6 g (0.1 mol) of diphenylphosphine in 125 mL of dry tetrahydrofuran was treated with potassium hydride (4 spatula tips, ∼0.1 g). The resulting deep red solution was treated with 14.6 g (16.3 mL, 0.1 mol) of bis(dimethylamino)vinylphosphine. The reaction mixture was boiled under reflux for 4 days. The reaction mixture remained deep red, but showed no ν(PH) frequencies in its infrared spectrum. Concentration of the reaction mixture at ∼25 °C (40 mm) gave a red liquid which was purified by short-path high-vacuum distillation to give 30.9 g (93% yield) of thick, clear, colorless liquid $(C_6H_5)_2PCH_2CH_2P[N(CH_3)_2]_2$, bp 146-158 °C (0.005 mm).

Anal. Calcd for $C_{18}H_{26}N_2P_2$: C, 65.0; H, 7.9; N, 8.4. Found: C, 65.2; H, 7.9; N, 8.3.

**Preparation of $C_6H_5P[CH_2CH_2P[N(CH_3)_2]_2]_2$.** A solution of 5.0 g (0.0454 mol) of phenylphosphine in 100 mL of dry tetrahydrofuran was treated with potassium hydride (4 spatula tips, 0.1 g). The resulting bright yellow solution was treated with 13.3 g (14.8 mL, 0.908 mol) of bis(dimethylamino)vinylphosphine and then boiled under reflux. The yellow mixture first turned red-orange, then deep yellow, and finally gradually became colorless. After 4 days at the boiling point the infrared spectrum indicated the absence of ν(PH) frequencies. Solvent was removed first at ∼25 °C (30 mm) and then at ∼25 °C (0.1 mm) to give 17.4 g (95% yield) of viscous yellow liquid $C_6H_5P[CH_2CH_2P[N(CH_3)_2]_2]_2$, which crystallized upon standing at −10 °C. This product was purified by short-path high-vacuum distillation to give 10.1 g (55% yield) of clear, colorless, viscous $C_6H_5P[CH_2CH_2P[N(CH_3)_2]_2]_2$, bp 155-162 °C (0.005 mm), which crystallized upon standing, mp 38-40 °C.

Anal. Calcd for $C_{18}H_{37}N_4P_3$: C, 53.7; H, 9.3; N, 13.9. Found: C, 51.8; H, 8.9; N, 13.4.

**Preparation of $C_6H_5P(H)CH_2CH_2P[N(CH_3)_2]_2$.** A mixture of 11.0 g (11.0 mL, 0.10 mol) of phenylphosphine, 14.6 g (16.3 mL, 0.10 mol) of bis(dimethylamino)vinylphosphine, and ∼0.1 g of potassium hydride was boiled under reflux in 100 mL of dry tetrahydrofuran for 4 days in a procedure similar to that used for the preparation of $C_6H_5P[CH_2CH_2P[N(CH_3)_2]_2]_2$ described above. Solvent was then removed under vacuum at room temperature after addition of 0.5 mL of methanol. Short-path high-vacuum distillation of the liquid residue gave 13.65 g (53% yield) of $C_6H_5P(H)CH_2CH_2P[N(CH_3)_2]_2$, bp 105-110 °C (0.005 mm), IR ν(PH) 2290 cm$^{-1}$.

Anal. Calcd for $C_{12}H_{22}N_2P_2$: C, 56.2; H, 8.6; N, 10.9. Found: C, 56.2; H, 8.4; N, 10.9.

**Preparation of $(CH_3)_2PCH_2CH_2P[N(CH_3)_2]_2$.** The dimethylphosphine (∼0.3 mol) prepared from 27.9 g (0.15 mol) of tetramethylbiphosphine disulfide[10] and 8.50 g (0.225 mol) of $LiAlH_4$ in 150 mL of dry dioxane by the published procedure[16] was distilled into 150 mL of tetrahydrofuran containing ∼0.2 g of potassium hydride and cooled to −78 °C. At the end of the dimethylphosphine distillation, the distillation head was removed and 32.8 g (36.6 mL, 0.225 mol) of bis(dimethylamino)vinylphosphine was added through a syringe. The mixture was boiled under reflux for 8 h using a −78 °C condenser and then for the remainder of 4 days using a normal water-cooled condenser. After cooling the reaction mixture to room temperature a yellow solution containing a black precipitate was observed. Solvent was removed at 25 °C (40 mm) to give a yellow liquid, which was separated from the black precipitate by centrifugation and decantation. High-vacuum distillation of the yellow liquid gave 40.2 g (86% yield) of clear colorless liquid $(CH_3)_2PCH_2CH_2P[N(CH_3)_2]_2$, bp 40-45 °C (0.007 mm).

Anal. Calcd for $C_8H_{22}N_2P_2$: C, 47.1; H, 10.6; N, 13.4. Found: C, 47.3; H, 10.9; N, 13.5.

**Preparation of $CH_3P[CH_2CH_2P[N(CH_3)_2]_2]_2$.** The methylphosphine (0.1 mol) generated by the dropwise addition of a solution of 12.4 g (10.8 mL, 0.1 mol) of dimethyl methylphosphonate in 25 mL of dry dioxane to a stirred suspension of 5.5 g (0.145 mol) of $LiAlH_4$ in 100 mL of dry dioxane was passed into a stirred mixture of 14.6 g (16.3 mL, 0.1 mol) of bis(dimethylamino)vinylphosphine, ∼0.1 g (4 spatula tips) of potassium hydride, and 50 mL of dry tetrahydrofuran cooled to −78 °C. The resulting mixture was boiled under reflux for 4 days using a −78 °C condenser for the first 10 h of refluxing. Solvent was removed from the resulting brown mixture at ∼25 °C (40 mm). The residue was taken up in 75 mL of dichloromethane and hydrolyzed with 3 drops of water. The solution was then dried immediately over magnesium sulfate and filtered, and the solvent removed from the filtrate at ∼25 °C (40 mm) to give a brown oil which solidified upon standing. High-vacuum distillation of this crude product gave 13.1 g (77% yield) of clear, colorless liquid $CH_3P[CH_2CH_2P[N(CH_3)_2]_2]_2$, bp 130-133 °C (0.005 mm), which crystallized upon standing in the freezer.

Anal. Calcd for $C_{13}H_{35}N_4P_2$: C, 45.9; H, 10.4; N, 16.5. Found C, 45.8; H, 10.4; N, 16.6.

**Preparation of $CH_3P(H)CH_2CH_2P[N(CH_3)_2]_2$.** The methylphosphine generated over 1.5 h by the dropwise addition of 24.8 g (21.6 mL, 0.2 mol) of dimethyl methylphosphonate to 11.0 g (0.29 mol) of $LiAlH_4$ in 200 mL of dry dioxane was passed into a stirred mixture of 14.6 g (16.3 mL, 0.1 mol) of bis(dimethylamino)vinylphosphine, ∼0.1 g of potassium hydride, and 100 mL of dry tetrahydrofuran. The resulting mixture was boiled under reflux for 4 days using a −78 °C condenser for the first 8 h of the heating period. After addition of 5 drops of water, solvent was removed from the reaction mixture first at ∼25 °C (40 mm) and then at ∼25 °C (0.05 mm). Distillation of the resulting oil gave 1.5 g (7.7% yield) of $CH_3P(H)CH_2CH_2P[N(CH_3)_2]_2$, bp 60-65 °C (0.02 mm).

Anal. Calcd for $C_7H_{20}N_2P$: C, 43.3; H, 10.4; N, 14.4. Found: C, 42.7; H, 9.9; N, 14.0.

After removal of the $CH_3P(H)CH_2CH_2P[N(CH_3)_2]_2$ further high vacuum distillation of the liquid residue gave 7.8 g (46% yield) of $CH_3P[CH_2CH_2P[N(CH_3)_2]_2]_2$, bp 103-130 °C (0.005 mm).

**Preparation of $P[CH_2CH_2P[N(CH_3)_2]_2]_3$.** A solution of potassium phosphide in liquid ammonia was prepared by passing phosphine through the blue solution of 3.9 g (0.1 g-atom) of potassium metal in 300 mL of liquid ammonia until the blue color became bright yellow. The ammonia was then allowed to evaporate. The residue was treated with a mixture of 125 mL of tetrahydrofuran and 125 mL of dimethyl sulfoxide followed by 43.8 g (48.8 mL, 0.3 mol) of bis(dimethylamino)vinylphosphine. The resulting mixture was then boiled under reflux for 40 h. The original canary yellow reaction mixture first became dark yellow and then gradually became paler to give a very pale yellow, opaque mixture at the end of the reaction period. The final reaction mixture was cooled to room temperature and then transferred under nitrogen to a separatory funnel. The residue in the reaction flask was washed into the separatory funnel with 500 mL of diethyl ether. The combined diethyl ether solutions were then washed quickly with five 100-mL portions of deoxygenated water. The water washings were extracted with 150 mL of diethyl ether. The resulting ether extract was washed with three 50-mL portions of water. The combined diethyl ether solutions were dried over magnesium sulfate. Solvent was removed from the filtrate at ∼25 °C (40 mm) to give 27.9 g (59% yield) of $P[CH_2CH_2P[N(CH_3)_2]_2]_3$ as a slightly cloudy colorless oil. A small analytical sample of this product was purified further by short-path high-vacuum distillation, bp 190 °C (0.05 mm).

Anal. Calcd for $C_{18}H_{48}N_6P_4$: C, 45.7; H, 10.2; N, 17.8. Found: C, 45.9; H, 10.2; N, 17.5.

**Reaction of $(CH_3)_2PH$ with $(C_2H_5)_2NP(CH{=}CH_2)_2$.** The dimethylphosphine prepared from 9.3 g (0.05 mol) of tetramethylbiphosphine disulfide and 2.83 g (0.075 mol) of $LiAlH_4$ in 75 mL of dry dioxane was distilled into 50 mL of dry tetrahydrofuran containing ~0.1 g of potassium hydride kept at −78 °C. After addition of 5.5 g (0.035 mol) of diethylaminodivinylphosphine, the reaction mixture was boiled under reflux for 4 days using a −78 °C condenser for the first 10 h. By the end of the reaction period the reaction mixture had turned from yellow to red-brown. Solvent was removed at ~25 °C (0.1 mm) to give a dark oil. Fractional distillation of this oil gave first 1.0 g (13% yield) of $(C_2H_5)_2NP(CH{=}CH_2)CH_2CH_2P(CH_3)_2$, bp 55-65 °C (0.01 mm), then 1.0 g of a mixture of $(C_2H_5)_2NP(CH{=}CH_2)CH_2CH_2P(CH_3)_2$ and $(C_2H_5)_2NP[CH_2CH_2P(CH_3)_2]_2$, and finally 2.2 g (22% yield) of pure $(C_2H_5)_2NP[CH_2CH_2P(CH_3)_2]_2$, bp 80-95 °C (0.01 mm).

Anal. (A) $(C_2H_5)_2NP(CH{=}CH_2)CH_2CH_2P(CH_3)_2$. Calcd for $C_{10}H_{23}NP_2$: C, 54.8; H, 10.6; N, 6.4. Found: C, 54.8; H, 10.9; N, 6.2. (B) $(C_2H_5)_2NP[CH_2CH_2P(CH_3)_2]_2$. Calcd for $C_{12}H_{30}NP_3$: C, 51.2; H, 10.8; N, 5.0. Found: C, 51.3; H, 10.8; N, 4.7.

**Preparation of $(C_2H_5)_2NP[CH_2CH_2P(C_6H_5)_2]_2$.** A mixture of 11.8 g (0.0636 mol) of diphenylphosphine, 5.0 g (0.0318 mol) of diethylaminodivinylphosphine, a base catalyst (6 mL (0.003 mol) of 0.5 M lithium dimethylamide in tetrahydrofuran or ~0.1 g of potassium hydride), and 100 mL of dry tetrahydrofuran was boiled under reflux for 5 days. The reaction mixture was diluted with 100 mL of diethyl ether and then washed with three 25-mL portions of water. The ether layer was dried over anhydrous magnesium sulfate. Solvent was removed from the filtered ether solution at ~25 °C (40 mm) to give 15.1 g (93% yield) of clear viscous liquid $(C_2H_5)_2NP[CH_2CH_2P(C_6H_5)_2]_2$, which crystallized upon standing, mp 49-51 °C.

Anal. Calcd for $C_{32}H_{38}NP_3$: C, 72.6; H, 7.2; N, 2.6. Found: C, 72.3; H, 7.2; N, 2.5.

**Preparation of $(C_2H_5)_2NP(CH{=}CH_2)CH_2CH_2P(C_6H_5)_2$.** A solution of 9.3 g (8.65 mL, 0.05 mol) of diphenylphosphine in 50 mL of dry tetrahydrofuran was treated with ~0.1 g of potassium hydride. Then 7.85 g (0.05 mol) of diethylaminodivinylphosphine was added. The resulting mixture was boiled under reflux for 3 days. After removal of the solvent at ~25 °C (0.1 mm), high-vacuum distillation of the oily residue gave 10.8 g (63% yield) of $(C_2H_5)_2NP(CH{=}CH_2)CH_2CH_2P(C_6H_5)_2$ as a clear, slightly yellow liquid, bp 139-147 °C (0.005 mm).

Anal. Calcd for $C_{20}H_{27}NP_2$: C, 70.0; H, 7.9; N, 4.1. Found: C, 69.9; H, 7.9; N, 4.1.

**Preparation of 1-Diethylamino-4-phenyl-1,4-diphosphacyclohexane.** A mixture of 4.7 g (0.03 mol) of diethylaminodivinylphosphine, 3.3 g (0.03 mol) of phenylphosphine, 0.1 g of potassium hydride, and 60 mL of tetrahydrofuran was boiled under reflux for 4 days. Removal of solvent first at ~25 °C (40 mm) and finally at ~25 °C (0.1 mm) followed by high-vacuum distillation of the oily residue gave 3.8 g (48% yield) of $(C_2H_5)_2NP(CH_2CH_2)_2PC_6H_5$ as a clear colorless liquid, bp 100-108 °C (0.004 mm).

Anal. Calcd for $C_{14}H_{23}NP_2$: C, 62.9; H, 8.7; N, 5.2; P, 23.2; mol wt, 267. Found: C, 62.6; H, 8.6; N, 5.3; P, 23.5; mol wt, 264 in benzene.

**Preparation of 1-Diethylamino-4-benzyl-1,4-diphosphacyclohexane.** A mixture of 4.7 g (0.03 mol) of diethylaminodivinylphosphine, 3.7 g (0.03 mol) of benzylphosphine, 0.1 g of potassium hydride, and 150 mL of tetrahydrofuran was boiled under reflux for 7 days. Removal of solvent under vacuum followed by high-vacuum distillation of the residue gave 1.6 g (19% yield) of $(C_2H_5)_2NP(CH_2CH_2)_2PCH_2C_6H_5$, bp 122-135 °C (0.026 mm).

Anal. Calcd for $C_{15}H_{25}NP_2$: C, 64.1; H, 8.9; N, 5.0; P, 22.1. Found: C, 64.0; H, 9.0; N, 5.0; P, 22.7.

**Preparation of 1-Diethylamino-4-neopentyl-1,4-diphosphacyclohexane.** A mixture of 3.1 g (0.02 mol) of diethylaminodivinylphosphine, 2.1 g (0.02 mol) of neopentylphosphine,[5] 0.05 g of potassium hydride, and 50 mL of tetrahydrofuran was boiled under reflux for 4 days. Removal of solvent under vacuum followed by high-vacuum distillation of the residue gave 1.0 g (19% yield) of $(C_2H_5)_2NP(CH_2CH_2)_2PCH_2C(CH_3)_3$, bp 78-88 °C (0.026 mm).

Anal. Calcd for $C_{13}H_{29}NP_2$: C, 59.8; H, 11.1; N, 5.4; P, 23.7; mol wt, 261. Found: C, 60.0; H, 11.1; N, 4.4; P, 22.8; mol wt, 283 in acetonitrile.

**Preparation of Dimethoxyvinylphosphine.** A mixture of 38 g (0.26 mol) of bis(dimethylamino)vinylphosphine and 17.4 g (22 mL, 0.544 mol) of dry methanol was boiled under reflux for 5 h. Distillation of the resulting reaction mixture gave a small forerun of methanol followed by 27.9 g (89% yield) of clear, colorless liquid dimethoxyvinylphosphine, $(CH_3O)_2PCH{=}CH_2$, bp 68 °C (158 mm): $^{13}C$ NMR $\delta$ 141.2 (d, 26 Hz), 128.6 (d, 30 Hz), and 52.5 (d, 8 Hz).

Anal. Calcd for $C_4H_9O_2P$: C, 40.0; H, 7.6. Found: C, 40.0; H, 7.6.

**Preparation of $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$. (a) By Addition of $(C_6H_5)_2PH$ to $CH_2{=}CHP(OCH_3)_2$.** A solution of 6.2 g (5.75 mL, 0.033 mol) of diphenylphosphine in 50 mL of dry tetrahydrofuran was treated with ~0.1 g of potassium hydride. Hydrogen evolution occurred with the production of an orange color. Then 4.0 g (0.033 mol) of dimethoxyvinylphosphine was added all in one portion. The orange color disappeared almost immediately, so additional potassium hydride (~0.1 g) was added until the color reappeared. The resulting mixture was boiled under reflux for 4 days. After this reaction period, the infrared spectrum showed no $\nu$(P–H) frequency. The solution was decanted away from a small amount of insoluble solid. Removal of solvent at ~25 °C (40 mm) followed by short-path high-vacuum distillation gave 5.9 g (58% yield) of $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ as a clear, colorless liquid, bp 133-137 °C (0.005 mm).

Anal. Calcd for $C_{16}H_{20}O_2P_2$: C, 62.7; H, 6.6; P, 20.2. Found: C, 62.9; H, 6.6; P, 19.7.

**(b) By Methanolysis of $(C_6H_5)_2PCH_2CH_2P[N(CH_3)_2]_2$.** A mixture of 5.0 g (0.015 mol) of $(C_6H_5)_2PCH_2CH_2P[N(CH_3)_2]_2$, 1.06 g (1.34 mL, 0.033 mol) of dry methanol, and 20 mL of dry toluene was boiled under reflux for 16 h. Removal of solvent at ~25 °C (0.1 mm) followed by high-vacuum distillation gave 4.35 g (95% yield) of $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ as a clear, colorless liquid, bp 130-140 °C (0.012 mm), identified by its proton and phosphorus-31 NMR spectra.

**Preparation of $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$. (a) By Addition of $C_6H_5PH_2$ to $CH_2{=}CHP(OCH_3)_2$.** A mixture of 1.10 g (0.01 mol) of phenylphosphine, 2.52 g (0.021 mol) of dimethoxyvinylphosphine, 0.05 g of potassium hydride, and 50 mL of dry tetrahydrofuran was boiled under reflux for 5 days, adding an additional 0.5 g (0.0042 mol) of dimethoxyvinylphosphine after 2 days of heating. Removal of solvent at 25 °C (40 mm) followed by short-path high-vacuum distillation gave 1.3 g (37% yield) of clear, colorless liquid $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$, bp 130-136 °C (0.004 mm).

Anal. Calcd for $C_{14}M_{25}O_4P_3$: C, 48.0; H, 7.2; P, 26.5. Found C, 48.2; H, 7.3; P, 26.2.

**(b) By Methanolysis of $C_6H_5P[CH_2CH_2P[N(CH_3)_2]_2]_2$.** A solution of 5.0 g (0.0124 mol) of $C_6H_5P[CH_2CH_2P[N(CH_3)_2]_2]_2$, 1.75 g (2.22 mL, 0.0547 mol) of dry methanol, and 20 mL of dry toluene was boiled under reflux for ~16 h. Removal of solvent at ~25 °C (0.1 mm) followed by high-vacuum distillation gave 2.5 g (57% yield) of colorless liquid $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$, bp 143-148 °C (0.008 mm).

Anal. Found: C, 48.1; H, 7.3; P, 26.5.

**Preparation of $(CH_3)_2PCH_2CH_2P(OCH_3)_2$.** A mixture of 5.0 g (0.024 mol) of $(CH_3)_2PCH_2CH_2P[N(CH_3)_2]_2$, 1.92 g (2.43 mL, 0.060 mol) of dry methanol, and 25 mL of dry toluene was boiled under reflux for 12 h. Removal of solvent at ~25 °C (20 mm) followed by vacuum distillation gave 3.95 g. (91% yield) of $(CH_3)_2PCH_2CH_2P(OCH_3)_2$ as a clear colorless liquid, bp 48 °C (0.4 mm).

Anal. Calcd for $C_6H_{16}O_2P_2$: C, 39.6; H, 8.8; P, 34.0. Found: C, 39.9; H, 8.6; P, 33.9.

**Preparation of $CH_3P[CH_2CH_2P(OCH_3)_2]_2$.** A mixture of 5.0 g (0.0147 mol) of $CH_3P[CH_2CH_2P[N(CH_3)_2]_2]_2$, 2.07 g (2.62 mL, 0.0647 mol) of dry methanol, and 20 mL of dry toluene was boiled under reflux for 16 h. Removal of solvent at ~25 °C (20 mm) followed by high-vacuum distillation gave 3.5 g (83% yield) of clear colorless liquid $CH_3P[CH_2CH_2P(OCH_3)_2]_2$, bp 102-112 °C (0.005 mm).

Anal. Calcd for $C_9H_{23}O_4P$: C, 37.5; H, 8.0; P, 32.2. Found: C, 37.2; H, 7.8; P, 31.9.

**Preparation of $P[CH_2CH_2P(OCH_3)_2]_3$.** A mixture of 5.7 g (0.0121 mol) of $P[CH_2CH_2P[N(CH_3)_2]_2]_3$, 2.56 g (3.24 mL, 0.080 mol) of methanol, and 25 mL of dry toluene was boiled under reflux for 16 h. Removal of solvent at ~25 °C (0.1 mm) followed by short-path high-vacuum distillation gave 2.1 g (44% yield) of colorless liquid $P[CH_2CH_2P(OCH_3)_2]_3$, bp 135-147 °C (0.03 mm).

Anal. Calcd for $C_{12}H_{30}O_6P_4$: C, 36.6; H, 7.7; P, 31.3. Found: C, 36.6, 36.9; H, 7.6, 7.7; P, 30.8, 31.0.

**Preparation of $C_6H_5P[CH_2CH_2P(OCH_3)_2][CH_2CH_2P[N(CH_3)_2]_2]$.** A mixture of 4.0 g (0.0156 mol) of $C_6H_5P(H)CH_2CH_2P[N(CH_3)_2]_2$, 1.88 g (0.0156 mol) of dimethoxyvinylphosphine, ~0.1 g of potassium hydride, and 20 mL of dry tetrahydrofuran was boiled under reflux for 5 days. Removal of solvent at 25 °C (0.2 mm) followed by vacuum distillation gave 3.1 g (53% yield) of $C_6H_5P[CH_2CH_2P(OCH_3)_2][CH_2CH_2P[N(CH_3)_2]_2]$, bp 152-160 °C (0.01 mm).

Anal. Calcd for $C_{16}H_{31}N_2O_2P_3$: C, 51.1; H, 8.3; N, 7.4; P, 24.7. Found: C, 51.3; H, 8.4; N, 7.6; P, 24.8.

## Results and Discussion

**A. Polyphosphines with Terminal Dialkylamino Groups.** The most generally applicable method for constructing polyphosphine structures containing $PCH_2CH_2P$ units is the base-catalyzed addition of phosphorus-hydrogen compounds to the carbon-carbon double bond of vinylphosphines.[3] This method for the preparation of polyphosphines containing terminal dialkylamino groups and $PCH_2CH_2P$ bridges requires either phosphorus-hydrogen compounds of the general type $(R_2N)_nPH_{3-n}$ ($n$ = 1 or 2) or vinylphosphorus compounds of the general type $(R_2N)_nP(CH{=}CH_2)_{3-n}$ ($n$ = 1 or 2). However, no phosphorus-hydrogen compounds of the type $(R_2N)_nPH_{3-n}$ ($n$ = 1 or 2) are known, although the borane adduct $[(CH_3)_2N]_2PH\cdot BH_3$ has been reported.[17] Attempts to prepare $(R_2N)_2PH$ derivatives (R = $CH_3$ and $C_2H_5$) by reductions of the corresponding $(R_2N)_2PCl$ derivatives with $LiAlH_4$ or $LiAlH[OC(CH_3)_3]_3$ were unsuccessful. The reactions with $LiAlH_4$ resulted in light yellow solutions which decomposed rapidly at room temperature to give nonvolatile black material. The reaction of $[(CH_3)_2N]_2PCl$ with $LiAlH[OC(CH_3)_3]_3$ gave $[(CH_3]_2N]_2POC(CH_3)_3$ rather than $[(CH_3)_2N]_2PH$.

The preparation of vinylphosphorus compounds of the type $(R_2N)_nP(CH{=}CH_2)_{3-n}$ was considerably more successful than the preparation of $(R_2N)_nPH_{3-n}$ derivatives. Treatment of $[(CH_3)_2N]_2PCl$ and $(C_2H_5)_2NPCl_2$ with vinylmagnesium bromide gave the desired vinylphosphorus derivatives $[(CH_3)_2N]_2PCH{=}CH_2$ and $(C_2H_5)_2NP(CH{=}CH_2)_2$, respectively. In the preparations of these vinylphosphorus compounds an aqueous alkaline tetrasodium ethylenediaminetetraacetate solution was used for the hydrolysis in order to prevent both acid cleavage of the dialkylamino-phosphorus bonds and precipitation of hydrous magnesium oxide. In attempted anhydrous workup of these reaction mixtures the yields of the desired vinylphosphorus compounds were low and quite variable (0 to 25%), clearly indicating the superiority of the workup with $Na_4EDTA$.

The choice of the base catalyst for the additions of various phosphorus-hydrogen compounds to $[(CH_3)_2N]_2PCH{=}CH_2$ and $(C_2H_5)_2NP(CH{=}CH_2)_2$ appeared somewhat critical in order to avoid exchange of some of the terminal dialkylamino groups by groups derived from the base catalyst. In the initial experiments the corresponding lithium dialkylamides $LiNR_2$ prepared from R′Li (R′ = $n$-$C_4H_9$, etc.) and $R_2NH$ were used as the base catalysts. However, the commercially available potassium hydride was found to be a suitable and more convenient base catalyst for these addition reactions. No evidence for the substitution of terminal dialkylamino groups with hydrogen atoms was observed in any of the reactions carried out with the potassium hydride catalyst.

The potassium hydride catalyzed additions of the secondary phosphines $R_2PH$ (R = $CH_3$ and $C_6H_5$) to $[(CH_3)_2N]_2PCH{=}CH_2$ were found to be effective methods for preparing the diphosphines $R_2PCH_2CH_2P[N(CH_3)_2]_2$ according to the following equation:

$$\mathrm{R_2PH + CH_2{=}CHP[N(CH_3)_2]_2 \xrightarrow{KH} R_2PCH_2CH_2P[N(CH_3)_2]_2} \quad (1)$$

The corresponding additions of the primary phosphines $RPH_2$ (R = $CH_3$ and $C_6H_5$) to $[(CH_3)_2N]_2PCH{=}CH_2$ could be controlled to give either the tertiary-secondary diphosphine 1:1 adducts $RP(H)CH_2CH_2P[N(CH_3)_2]_2$ (eq 2) or the tri(tertiary phosphine) 1:2 adducts $RP[CH_2CH_2P[N(CH_3)_2]_2]_2$ (eq 3).

$$\mathrm{RPH_2 + CH_2{=}CHP[N(CH_3)_2]_2 \xrightarrow{KH} RP(H)CH_2CH_2P[N(CH_3)_2]_2} \quad (2)$$

$$\mathrm{RPH_2 + 2CH_2{=}CHP[N(CH_3)_2]_2 \xrightarrow{KH} RP[CH_2CH_2P[N(CH_3)_2]_2]_2} \quad (3)$$

Recently the base-catalyzed additions of the primary phosphines $RPH_2$ to the vinyl derivatives of tetracoordinate phosphorus $CH_2{=}CHP(O)(OR)_2$ (R = ethyl or isopropyl) and $CH_2{=}CHP(S)(CH_3)_2$ were likewise found to be controllable to give good yields of either the 1:1 adducts or the 1:2 adducts.[18]

The addition of $PH_3$ to 3 equiv of $[(CH_3)_2N]_2PCH{=}CH_2$ to give the tripod tetra(tertiary phosphine) $P[CH_2CH_2P[N(CH_3)_2]_2]_3$ was of interest, since the only terminal groups in the product are dimethylamino groups. In order to avoid handling the volatile $PH_3$ during this addition reaction, the $PH_3$ was first converted to the nonvolatile $KPH_2$ by using metallic potassium. Reaction of the $KPH_2$ with 3 equiv of $[(CH_3)_2N]_2PCH{=}CH_2$ followed by hydrolysis was found to give the tripod tetra(tertiary phosphine) $P[CH_2CH_2P[N(CH_3)_2]_2]_3$ in 60% yield:

$$\mathrm{KPH_2 + 3\,CH_2{=}CHP[N(CH_3)_2]_2 \rightarrow \xrightarrow{+H_2O} P[CH_2CH_2P[N(CH_3)_2]_2]_3 + K^+ + OH^-} \quad (4)$$

The base-catalyzed additions of various phosphorus-hydrogen compounds to the divinylphosphorus derivative $(C_2H_5)_2NP(CH{=}CH_2)_2$ give polyphosphines in which one phosphorus atom has a single dialkylamino substituent. The additions of the secondary phosphines $R_2PH$ (R = $CH_3$ and $C_2H_5$) to $(C_2H_5)_2NP(CH{=}CH_2)_2$ can be controlled to give either the diphosphine 1:1 adducts $R_2PCH_2CH_2P(CH{=}CH_2)[N(C_2H_5)_2]$ (eq 5) containing an unreacted vinyl group or the triphosphine 1:2 adducts $(C_2H_5)_2NP[CH_2CH_2PR_2]_2$ (eq 6):

$$\mathrm{(C_2H_5)_2NP(CH{=}CH_2)_2 + R_2PH \xrightarrow{KH} R_2PCH_2CH_2P(CH{=}CH_2)[N(C_2H_5)_2]} \quad (5)$$

$$\mathrm{(C_2H_5)_2NP(CH{=}CH_2)_2 + 2R_2PH \xrightarrow{KH} (C_2H_5)_2NP[CH_2CH_2PR_2]_2} \quad (6)$$

The preparations of the 1:1 adducts $R_2PCH_2CH_2P(CH{=}CH_2)[N(C_2H_5)_2]$ (R = $CH_3$ and $C_6H_5$) by eq 5 represent the first known examples of the selective addition of a phosphorus-hydrogen bond to only one of the two vinyl groups of a divinylphosphorus derivative.

The base-catalyzed 1:1 additions of primary phosphines $RPH_2$ to divinylphosphorus derivatives $(CH_2{=}CH)_2PR'$ might be expected to give either linear polymers or cyclic oligomers of the type $[-P(R)CH_2CH_2P(R')CH_2CH_2-]_n$. Previous attempts[3] to obtain identifiable products from the base-catalyzed 1:1 addition of $C_6H_5PH_2$ to $C_6H_5P(CH{=}CH_2)_2$ were unsuccessful. In the present work the base-catalyzed 1:1 additions of the primary phosphines $RPH_2$ (R = $C_6H_5$, $C_6H_5CH_2$, and $(CH_3)_3CCH_2$) to $(C_2H_5)_2NP(CH{=}CH_2)_2$ were found to give the 1,4-diphosphacyclohexane derivatives $(C_2H_5)_2NP(CH_2CH_2)_2PR$ as distillable liquids according to the equation:

$$(C_2H_5)_2NP(CH{=}CH_2)_2 + RPH_2 \xrightarrow{KH} (C_2H_5)_2NP(CH_2CH_2)_2PR \quad (7)$$

The 1,4-diphosphacyclohexane formulations of these products suggested by their volatilities are demonstrated by their monomeric molecular weights in benzene or acetonitrile solution. The 1,4-diphosphacyclohexane derivatives are the first known derivatives of this heterocyclic system containing different substituents on the two phosphorus atoms. Previously reported[19-21] 1,4-diphosphacyclohexanes have identical substituents on the two phosphorus atoms.

**B. Polyphosphines with Terminal Methoxy Groups.** The polyphosphines containing $PCH_2CH_2P$ structural units and terminal methoxy groups were of interest in providing a new class of chelating ligands with relatively strong $\pi$-acceptor properties. The following two approaches were used to prepare such polyphosphines: (1) base-catalyzed addition of various phosphorus-hydrogen compounds to $(CH_3O)_2PCH{=}CH_2$; (2) methanolysis of the corresponding polyphosphine containing terminal dimethylamino groups.

The $(CH_3O)_2PCH{=}CH_2$ required for the first of these methods was readily prepared in ~90% yield by the methanolysis of $[(CH_3)_2N]_2PCH{=}CH_2$. Additions of $(C_6H_5)_2PH$ and $C_6H_5PH_2$ to this $(CH_3O)_2PCH{=}CH_2$ provided satisfactory methods for the preparations of the diphosphine $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ and the triphosphine $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$, respectively.

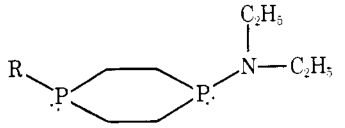
Since the preparation of $(CH_3O)_2PCH{=}CH_2$ involved the methanolysis of $[(CH_3)_2N]_2PCH{=}CH_2$, it appeared equally convenient first to use the $[(CH_3)_2N]_2PCH{=}CH_2$ to construct the desired polyphosphine structure containing terminal dimethylamino groups by appropriate addition reactions and then to methanolyze the terminal dimethylamino groups in the resulting polyphosphine to methoxy groups. This second approach provided syntheses of $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ and $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$ in higher yields. In addition, the compounds $(CH_3)_2PCH_2CH_2P(OCH_3)_2$, $CH_3P[CH_2CH_2P(OCH_3)_2]_2$, and $P[CH_2CH_2P(OCH_3)_2]_3$ were prepared by this method using the poly(tertiary phosphines) containing terminal dimethylamino groups described above.

The base-catalyzed addition of $C_6H_5P(H)CH_2CH_2P[N(CH_3)_2]_2$ to $(CH_3O)_2PCH{=}CH_2$ gives $C_6H_5P[CH_2CH_2P[N(CH_3)_2]_2][CH_2CH_2P(OCH_3)_2]$, which represents a novel example of a polyphosphine with terminal dimethylamino groups on one arm and terminal methoxy groups on the other arm. The ability to prepare such compounds in relatively good yields illustrates the flexibility of our synthetic methods.

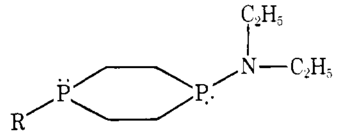
**C. NMR Spectra of the New Polyphosphines.** In addition to elemental analyses the new polyphosphines were characterized by their proton, phosphorus-31, and carbon-13 NMR spectra (Tables I, II, and III, respectively). In the proton NMR spectra (Table I) the relative intensities of the resonances in the $PCH_2CH_2P$, $NR_2$, $OCH_3$, and terminal methyl, phenyl, and/or vinyl regions by integration correspond to the proposed formulas. The fine structures of the phenyl and vinyl proton resonances in these compounds were found to be too complex for precise interpretation. Methyl resonances from $P[N(CH_3)_2]_2$ groups appear as doublets in the $\tau$ 7.3-7.5 region with 8-9 Hz splittings, methyl resonances from $P(OCH_3)_2$ groups appear as doublets in the $\tau$ 6.5-6.6 region with 10-11 Hz splittings, and methyl resonances from $P(CH_3)_2$ and $PCH_3$ groups appear as doublets around $\tau$ 9 with 2-3 Hz splittings.

Some of the new compounds containing $-CH_2CH_2P[N(CH_3)_2]_2$ and $-CH_2CH_2P(OCH_3)_2$ units exhibit a slight, but detectable, splitting of the methyl doublets in the proton NMR spectrum. This occurs in some cases where the two methyl groups in these units are diastereotopic[22] because the unit is bonded to a trivalent phosphorus atom in which the two remaining substituents are different. Compounds prepared in this study which exhibit this effect (Table I) include $C_6H_5P[CH_2CH_2P[N(CH_3)_2]_2]_2$ and $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$. In addition both types of arms in $C_6H_5P[CH_2CH_2P[N(CH_3)_2]_2][CH_2CH_2P(OCH_3)_2]$ exhibit this diastereotopic splitting of the methyl proton resonances. An apparent requirement for detectable splitting of the diastereotopic methyl resonances is bonding of the $-CH_2CH_2P[N(CH_3)_2]_2$ or $-CH_2CH_2P(OCH_3)_2$ unit to a trivalent phosphorus atom to which one of the remaining substituents is bonded through an $sp^3$ carbon atom and the other remaining substituent is bonded through an $sp^2$ carbon atom. Thus the methylphosphorus derivatives $CH_3P[CH_2CH_2P[N(CH_3)_2]_2]_2$ and $CH_3P[CH_2CH_2P(OCH_3)_2]_2$ do not exhibit this splitting of the diastereotopic methyl protons on the terminal groups attached to the outer phosphorus atoms, in contrast to the corresponding phenylphosphorus derivatives. Entirely similar effects were previously observed[4] in polyphosphines containing $-CH_2CH_2P(CH_3)_2$ structural units.

The phosphorus-31 NMR spectra (Table II) of the new polyphosphines exhibit resonances at $\delta$ $-93$ to $-96$ for $-CH_2CH_2P[N(CH_3)_2]_2$ units, resonances at $\delta$ $-55$ to $-61$ for $(C_2H_5)_2NP(CH_2CH_2-)_2$ units, and $\delta$ $-183$ to $-185$ for $-CH_2CH_2P(OCH_3)_2$ units in addition to the resonances for the other phosphorus atoms in positions expected on the basis of previous work with alkylphosphines[23] and poly(tertiary phosphines).[3,4] The phosphorus-31 NMR spectra of the 1,4-diphosphacyclohexane derivatives $(C_2H_5)_2NP(CH_2CH_2)_2PR$ ($R = C_6H_5$ and $C_6H_5CH_2$) exhibit two pairs of phosphorus resonances. In each pair one resonance is in the expected region for a $(C_2H_5)_2NP(CH_2CH_2-)_2$ unit and the other resonance is in the expected region for a $RP(CH_2CH_2-)_2$ unit. This suggests that the actual products are mixtures of the cis and trans isomers Ia and Ib. Previous studies on other 1,4-diphosphacyclohexane derivatives[19,20] provide other evidence for pairs of cis and trans isomers in this ring system. In one of the stereoisomers of $(C_2H_5)_2NP(CH_2CH_2)_2PR$ ($R = C_6H_5$ and $C_6H_5CH_2$) the phosphorus-phosphorus coupling is appreciable (17 Hz), whereas in the other stereoisomer the phosphorus-phosphorus coupling is less than the 2 Hz resolution of the Fourier transform spectrometer. Heating the 1,4-diphosphacyclohexanes $(C_2H_5)_2NP(CH_2CH_2)_2PR$ ($R = C_6H_5$ and $C_6H_5CH_2$) up to 175 °C did not cause the phosphorus-31 resonances from the two isomers to coalesce even at the highest temperatures. This indicates a higher barrier to pyramidal inversion in the 1,4-diphosphacyclohexanes I ($R = C_6H_5$ and $C_6H_5CH_2$) than in simple acyclic tertiary phosphines of the type $(R)(R')(CH_3)P$ (R and R′ are hydrocarbon groups) which undergo pyramidal inversion[24] with loss of optical activity at around 130 °C.



Ia



Ib

The proton-decoupled carbon-13 NMR spectra of the new polyphosphines (Table III) are similar to those reported previously[25] for other polyphosphines containing $PCH_2CH_2P$ structural units. Terminal phenyl and vinyl groups exhibit the expected four and two resonances, respectively, with each resonance except for the *p*-phenyl carbon being a doublet from the carbon–phosphorus splitting. Methyl resonances from $P[N(CH_3)_2]_2$ groups appear as doublets at $\delta$ 40.8 ± 0.1 with 12–13 Hz splittings, methyl resonances from $P(OCH_3)_2$ groups appear as doublets at $\delta$ 53.6 ± 0.1 with 9–12 Hz splittings, and methyl resonances from $P(CH_3)_2$ groups appear as doublets at $\delta$ 13.9 ± 0.2 with 13–15 Hz. splittings. The assignments of the carbon resonances in the $PCH_2CH_2P$ bridges and the corresponding $|{}^1J(C-P)|$ and $|{}^2J(C-P)|$ are difficult and somewhat uncertain. However, the assignments presented for the $PCH_2CH_2P$ carbons in Table III appear to be self-consistent and are reasonable when compared with previous data.[25] Terminal dialkylamino and methoxy groups, like terminal hydrogen atoms but unlike terminal alkyl and aryl groups, lead to nonequivalence of the two couplings $|{}^1J(C-P)|$ and $|{}^2J(C-P)|$ for the $PCH_2CH_2P$ carbons so that these resonances appear as double doublets rather than triplets. For $-CH_2CH_2P(OCH_3)_2$ units the two $J(C-P)$ couplings are 21 ± 1 and 11 ± 2 Hz, whereas for $-CH_2CH_2P[N(CH_3)_2]_2$ units the two $J(C-P)$ couplings are 21 ± 2 and 14 ± 3 Hz. The carbon-13 NMR spectra of the terminal groups of the 1,4-diphosphacyclohexane derivatives $(C_2H_5)_2NP(CH_2CH_2)_2PR$ (R = $C_6H_5$ and $C_6H_5CH_2$) like their phosphorus-31 NMR spectra exhibit two sets of resonances, further demonstrating the presence of the two stereoisomers Ia and Ib. The carbon-13 NMR resonances from the $P(CH_2CH_2)_2P$ ring carbons appear as a very complex group of lines in the region $\delta$ 30–20. The complexity and overlapping of these resonances make it impossible to identify reliably individual ring carbon resonances in these 1,4-diphosphacyclohexane stereoisomers.

**Acknowledgment.** We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-75-2869. We are also indebted to the National Science Foundation for a major equipment grant to the University of Georgia chemistry department toward the purchase of the Jeolco PFT-100 pulsed Fourier transform NMR spectrometer used in this work.

## References and Notes

(1) (a) For part 14 of this series see R. B. King, J. C. Cloyd, Jr., and R. H. Reimann, *Inorg. Chem.*, **15**, 449 (1976). (b) Portions of this work were presented at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., September, 1976.
(2) Postdoctoral research associate, 1975–1976.
(3) R. B. King and P. N. Kapoor, *J. Am. Chem. Soc.*, **93**, 4158 (1971).
(4) R. B. King and J. C. Cloyd, Jr., *J. Am. Chem. Soc.*, **97**, 53 (1975).
(5) R. B. King, J. C. Cloyd, Jr., and R. H. Reimann, *J. Org. Chem.*, **41**, 972 (1976).
(6) R. B. King, J. C. Cloyd, Jr., and P. N. Kapoor, *J. Chem. Soc., Perkin Trans. 1*, 2226 (1973).
(7) S. O. Grim, R. P. Molenda, and R. L. Keiter, *Chem. Ind. (London)*, 1378 (1970).
(8) S. O. Grim, J. Del Gaudio, R. P. Molenda, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 3416 (1974).
(9) L. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, W. E. Hill, J. V. Quagliano, and L. M. Vallarino, *J. Chem. Soc., Chem. Commun.*, 999 (1974).
(10) G. W. Parshall, *Org. Synth.*, **45**, 102 (1965).
(11) W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2871 (1958).
(12) W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2296 (1958); R. C. Taylor, R. Kolodny, and D. B. Walters, *Synth. Inorg. Met.-Org. Chem.*, **3**, 175 (1958).
(13) L. Horner, H. Hoffmann, and P. Beck, *Chem. Ber.*, **91**, 1583 (1958).
(14) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).
(15) K. Issleib and W. Seidel, *Chem. Ber.*, **92**, 2681 (1959).
(16) G. W. Parshall, *Inorg. Synth.*, **11**, 157 (1968).
(17) H. Nöth and H. J. Vetter, *Chem. Ber.*, **96**, 1298 (1963).
(18) R. B. King and J. C. Cloyd, Jr., *J. Am. Chem. Soc.*, **97**, 46 (1975).
(19) K. Issleib and K. Standtke, *Chem. Ber.*, **96**, 279 (1963).
(20) K. Issleib and G. Döll, *Chem. Ber.*, **96**, 1544 (1963).
(21) K. Issleib and H. Weichmann, *Chem. Ber.*, **101**, 2197 (1968).
(22) K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).
(23) S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, **32**, 781 (1967).
(24) R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **92**, 3090 (1970).
(25) R. B. King and C. Cloyd, Jr., *J. Chem. Soc., Perkin Trans. 2*, 938 (1975).

---

# Tetracarbon Metallocarboranes. 1. Iron, Nickel, and Molybdenum Complexes Derived from $(CH_3)_4C_4B_8H_8$. Crystal Structure of $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$

**William M. Maxwell, Robert F. Bryan, and Russell N. Grimes***

*Contribution from the Department of Chemistry, University of Virginia,*
*Charlottesville, Virginia 22901.* *Received December 9, 1976*

**Abstract:** Reduction of the carborane $(CH_3)_4C_4B_8H_8$ with sodium in tetrahydrofuran produces the apparent $(CH_3)_4C_4B_8H_8{}^{2-}$ dianion, which in turn reacts with $FeCl_2$ and $NaC_5H_5$ to generate a series of iron tetracarbon metallocarboranes. These include four isomers of a 14-vertex system, $(\eta^5\text{-}C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$, and one isomer of a nido 12-vertex species, $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$. The latter complex was structurally characterized by x-ray diffraction and was shown to contain an open face with a bridging B–H–B hydrogen atom. The four skeletal carbon atoms occupy three-, four-, four-, and five-coordinate vertices, three of them on the open face. The reaction of dichloro-1,2-bis(diphenylphosphine)ethanenickel(II) with $(CH_3)_4C_4B_8H_8{}^{2-}$ ion produces two isomers of the 12-vertex system $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_7H_7$ and three isomers of a 13-vertex system, $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$. Direct reaction of $Mo(CO)_6$ and of $W(CO)_6$ with the neutral species $(CH_3)_4C_4B_8H_8$ produces the 13-vertex species $(CO)_3M(CH_3)_4C_4B_8H_8$ (M = Mo or W). Crystal data for $(C_5H_5)Fe(CH_3)_4C_4B_7H_8$: space group $P2_1/c$, $Z = 4$, $a = 9.492(2)$, $b = 13.476(2)$, $c = 15.176(2)$ Å, $\beta = 124.01(1)°$, $V = 1609.2$ Å$^3$, $R = 3.8\%$ for 2370 reflections.

Carboranes containing more than two carbon atoms in the same polyhedral cage are rare. The only known tricarbon systems, all prepared in this laboratory, are $C_3B_3H_7$ (as methyl derivatives),[1] $C_3B_5H_7$,[2] and $(CO)_3MnCH_3C_3B_3H_5$.[3] The single example of a tetracarbon species[4] prior to this work is the pentagonal pyramidal molecule $C_4B_2H_6$, which has been synthesized by several different methods in parent[6,7] or peralkylated[8] form and structurally confirmed by microwave[9] and