Synthesis of New Tetradentate Oligophosphine Ligands

Nick Bampos, Leslie D. Field,* Barbara A. Messerle, and Ronald J. Smernik

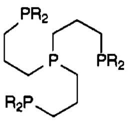
Department of Organic Chemistry, University of Sydney, Sydney 2006, NSW, Australia

Received April 6, 1993

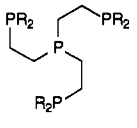
The synthesis of a series of symmetrical and unsymmetrical tripodal tetradentate alkylphosphine ligands is described. $Me_2PCH_2CH_2P(CH_2CH_2CH_2PMe_2)_2$ was synthesized by the photochemical reaction of (2-(dimethylphosphino)-ethyl)phosphine with excess allyldimethylphosphine, and $Me_2PCH_2CH_2CH_2P(CH_2CH_2PMe_2)_2$ was synthesized by the photochemical reaction of (3-(dimethylphosphino)propyl)phosphine with excess dimethylvinylphosphine. The known ligand $P(CH_2CH_2PMe_2)_3$ was synthesized in a one-step reaction by the photochemical addition of dimethylphosphine (3 equiv) to trivinylphosphine. The tetradentate ligands form one-to-one complexes $Fe(PP_3)Cl_2$ with iron by displacement of weaker phosphine ligands.

Introduction

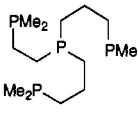
A number of symmetrical tetradentate tetraphosphine ligands including $P(CH_2CH_2CH_2PMe_2)_3$[1] (**1a**), $P(CH_2CH_2CH_2P(CH_2CH_3)_2)_3$[1] (**1c**), $P(CH_2CH_2PMe_2)_3$ (**2a**),[2] and $P(CH_2CH_2PPh_2)_3$ (**2b**)[3] have been synthesized and employed as ligands for transition metal complexation. The ligands with methyl substituents on the terminal phosphorus atoms have a relatively small Tolman cone angle about the terminal phosphorus atom, and these ligands should bind exceptionally well to a wide variety of transition metals.[4] In this paper we report an improved synthesis of the ligand **2a** and the synthesis and properties of the less symmetrical ligand systems **3** and **4**, where the radial alkyl chains are not all equivalent. Removing the symmetry of the tetradentate ligands will provide additional information regarding the stereochemistry of the metal complexes they form.



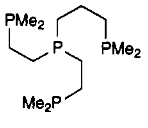
1 **a** R = Me
b R = Ph
c R = Et



2 **a** R = Me
b R = Ph



3



4

Experimental Section

General Data. All manipulations were carried out using standard Schlenk or vacuum line methods or in an argon-filled drybox. NMR spectra were obtained on a Bruker AMX400 spectrometer. ^{31}P NMR spectra (162.0 MHz) were referenced to external, neat trimethyl phosphite, taken as 140.85 ppm at the temperature quoted. ^1H NMR spectra (400.1 MHz) and ^{13}C NMR spectra (100.6 MHz) were referenced to residual solvent resonances. Mass spectra were recorded on an AEI Model MS902 double-focusing mass spectrometer with an accelerating voltage of 8000 V and using electron impact (EI) ionization with an electron energy of 70 eV and are quoted in the form *x* (*y*), where *x* is the mass to charge ratio and *y* is the percentage abundance relative to the base peak. IR spectra were recorded on a Biorad FT S20/80 spectrometer. Elemental analyses were performed by the National Analytical Laboratories, Ferntree Gully, Victoria, Australia. Nitrogen (>99.5%) and argon (>99.5%) were purchased from CIGHYTEC (Australia) and used as obtained. Pentane, tetrahydrofuran (THF), benzene, and diethyl ether were stored over sodium benzophenone ketyl under a dry nitrogen atmosphere and distilled immediately prior to use. NMR solvents (Merck) were used as received without further purification.

Dimethylphosphine[5] was prepared by reaction of tetramethyldiphosphine disulfide[6] with tri-*n*-butylphosphine in the presence of water. Dimethylphosphine is extremely air sensitive and pyrophoric and must be handled carefully under an atmosphere of argon or nitrogen. Tris-[3-(dimethylphosphino)propyl]phosphine[1] (**1a**) was prepared by the photochemical addition of dimethylphosphine to triallylphosphine.[7] Dimethylthiophosphinic bromide was prepared by the cleavage of tetramethyldiphosphine disulfide with bromine.[8] Dimethylvinylphosphine sulfide was prepared following the procedure of King *et al.*[2]

Preparation of Tris[2-(dimethylphosphino)ethyl]phosphine, $P(CH_2CH_2PMe_2)_3$ (2a). (i) Preparation of Trivinylphosphine, $(CH_2{=}CH)_3P$. Trivinylphosphine was prepared by the reaction of vinylmagnesium bromide with trimethyl phosphite. Vinyl bromide (45 g, 0.42 mol) was condensed into THF (200 mL), and the resulting solution was added dropwise to a stirred suspension of magnesium turnings (12.0 g, 0.49 mol) in degassed THF (300 mL). The reaction was initiated with a crystal of iodine and 1,2-dibromoethane (0.5 mL). On completion of the addition, the mixture was refluxed for 15 min, stirred for 1 h, and filtered under nitrogen to give a yellow-brown solution of vinylmagnesium bromide. A solution of trimethyl phosphite (14.7 g, 0.12 mol) in dry, deaerated ether (100 mL) was added dropwise to the stirred solution of vinylmagnesium bromide at 0 °C. A saturated, deaerated aqueous solution of ammonium chloride was added slowly, and the mixture extracted with dry, deaerated ether (2 × 200 mL, 2 × 100 mL). The combined ether extracts were concentrated by distillation under 150 mL of a solution of trivinylphosphine (approximately 0.12 mol) remained. This solution was used directly in the next step without further purification. $^{31}P\{^1H\}$ NMR (THF/ether): δ −20.6 (1P, s) ppm.

(ii) Preparation of Tris[2-(dimethylphosphino)ethyl]phosphine, $P(CH_2CH_2PMe_2)_3$ (2a). A solution of trivinylphosphine (approximately 0.12 mol) and dimethylphosphine (37.2 g, 0.60 mol) in ether/THF (300 mL) containing AIBN (100 mg) was irradiated with a medium-pressure mercury vapor lamp (125 W) through a quartz immersion well. The entire apparatus was immersed in ethanol cooled to 0–10 °C throughout the experiment. A dry ice condenser (cooled to −78 °C) was fitted to the reaction vessel to prevent the escape of volatile dimethylphosphine. The solution was maintained under an atmosphere of nitrogen, with nitrogen occasionally bubbled through to provide mixing. The solution was irradiated for 24 h by which time there was no trivinylphosphine remaining (by ^{31}P NMR). Excess dimethylphosphine and most of the ether/THF was removed by distillation, and the remaining ether removed under vacuum, leaving tris[2-(dimethylphosphino)ethyl]phosphine, (**2a**), as a white crystalline solid (32.0 g, 0.107 mol, 89%), mp 45–46 °C (lit.[2] mp 45–46 °C). $^{31}P\{^1H\}$ NMR (benzene): δ −48.6 (3P, d, $^3J_{P-P}$ = 20.7 Hz, 3 × $-P(CH_3)_2$), −19.8 (1P, q, $P(CH_2CH_2P(CH_3)_2)$) ppm.

---

(1) Antberg, M.; Prengel, C.; Dahlenburg, L. *Inorg. Chem.* **1984**, *23*, 4170.
(2) King, R. B.; Cloyd, J. C., Jr. *J. Am. Chem. Soc.* **1974**, *97*, 53.
(3) King, R. B.; Kapoor, R. N.; Saran, M. S.; Kapoor, P. N. *Inorg. Chem.* **1971**, *10*, 1851.
(4) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(5) Trenkle, A.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1987**, *34B*, 642.
(6) Parshall, G. W. *Org. Synth.* **1965**, *45*, 102.
(7) (a) Jones, W. J.; Davies, W. C.; Bowden, S. T.; Edwards, C.; Davies, V. E.; Thomas, L. H. *J. Chem. Soc.* **1947**, 1446. (b) Bampos, N.; Field, L. D.; Hambley, T. W. *Polyhedron* **1992**, *11*, 1213.
(8) Schmutzler, R. *Inorg. Synth.* **1970**, *12*, 287.

0020-1669/93/1332-4084$04.00/0

Preparation of (2-(Dimethylphosphino)ethyl)bis[3-(dimethylphosphino)propyl]phosphine, $\mathbf{Me_2PCH_2CH_2P(CH_2CH_2CH_2PMe_2)_2}$ (3). (i) Preparation of Diethyl (2-Bromoethyl)phosphonate, $\mathbf{BrCH_2CH_2PO(OEt)_2}$ (6). A solution of triethyl phosphite (83.1 g, 0.5 mol) in 1,2-dibromoethane (2817 g, 15.0 mol) was refluxed for 8 h. Excess dibromoethane was removed by distillation, and the residue was fractionally distilled under reduced pressure. Diethyl (2-bromoethyl)phosphonate (**6**) (111.0 g, 0.46 mol, 91%) was collected as a colorless liquid in the fraction 80–140 °C/2 mmHg. IR ν_{max} ($CHCl_3$): 1442 m, 1411 w, 1393 m, 1370 w, 1284 s, 1270 s, 1164 m, 1097 m, 1028 s, 971 s, 589 m cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.3 (1P, s). ^1H NMR ($CDCl_3$): δ 1.34 (6H, t, $^3J_{H-H} = 6.6$ Hz, 2 × $-\mathrm{OCH_2C}H_3$), 2.39 (2H, dm, $^2J_{P-H} = 18.9$ Hz, $-\mathrm{C}H_2\mathrm{P(O)}-$), 3.54 (2H, dm, $^3J_{P-H} = 8.5$ Hz, $-\mathrm{CH_2C}H_2\mathrm{Br}$), 4.13 (4H, m, 2 × $-\mathrm{OC}H_2\mathrm{CH_3}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.3 (2C, d, $^3J_{C-P} = 5.7$ Hz, 2 × $-\mathrm{OCH_2}C\mathrm{H_3}$), 24.7 (1C, s, $-C\mathrm{H_2Br}$), 31.7 (1C, d, $^1J_{C-P} = 113.4$ Hz, $-C\mathrm{H_2P(O)}-$), 62.9 (2C, d, $^2J_{C-P} = 7.8$ Hz, 2 × $-\mathrm{O}C\mathrm{H_2CH_3}$) ppm. MS (EI) *m/z* 245 (M, ^{81}Br, 0.5%), 243 (M, ^{79}Br, 0.5%), 219 (14), 217 (14), 191 (25), 189 (25), 173 (21), 171 (21), 165 (71), 138 (62), 109 (100), 93 (22), 91 (28), 82 (33), 81 (71), 65 (39). High-resolution MS: Calcd for $C_6H_{14}PO_3{}^{81}Br$, *m/z* 245.9799; found, *m/z* 245.9794.

(ii) Preparation of Diethyl Vinylphosphonate, $\mathbf{CH_2{=}CHPO(OEt)_2}$ (8). Triethylamine (183 g, 1.81 mol) was added to a solution of diethyl (2-bromoethyl)phosphonate (111 g, 0.46 mol) in benzene (180 mL), and the mixture was refluxed for 9 h. The reaction mixture was filtered to remove precipitated salts, and excess triethylamine and benzene were removed under vacuum. The residue was distilled under reduced pressure. Diethyl vinylphosphonate (**8**) was obtained as a colorless liquid (65.0 g, 0.40 mol, 88%) bp 60–70 °C/0.1–0.2 mmHg. IR ν_{max} ($CHCl_3$): 1442 m, 1399 m, 1164 m, 1053 s, 1028 s, 973 s, 597 w cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.3 (1P, s). ^1H NMR ($CDCl_3$): δ 1.36 (6H, t, $^3J_{H-H} = 7.1$ Hz, 2 × $-\mathrm{OCH_2C}H_3$), 4.1 (4H, dq, $^3J_{P-H} = 7.5$ Hz, 2 × $-\mathrm{OC}H_2\mathrm{CH_3}$), 6.0–6.35 (3H, overlapping multiplets, $-\mathrm{C}H{=}\mathrm{C}H_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.8 (2C, d, $^3J_{C-P} = 6.4$ Hz, 2 × $-\mathrm{OCH_2}C\mathrm{H_3}$), 62.2 (2C, $^2J_{C-P} = 5.6$ Hz, 2 × $-\mathrm{O}C\mathrm{H_2CH_3}$), 126.5 (1C, d, $^2J_{C-P} = 183.9$ Hz, $-\mathrm{CH}C\mathrm{H_2}$), 135.7 (1C, d, $^1J_{C-P} < 2$ Hz, $-C\mathrm{HCH_2}$) ppm. MS (EI) *m/z* 164 (M, 0.5%), 163 (4), 137 (44), 136 (31), 120 (15), 119 (18), 109 (81), 93 (16), 92 (30), 91 (100), 82 (23), 81 (31), 65 (54). High-resolution MS: Calcd for $C_6H_{13}PO_3$, *m/z* 164.0602; found, *m/z* 164.0523.

(iii) Preparation of Diethyl (2-(Dimethylphosphino)ethyl)phosphonate, $\mathbf{Me_2PCH_2CH_2PO(OEt)_2}$ (7). A solution of dimethylphosphine (5.0 g, 81 mmol), diethyl vinylphosphonate (10.0 g, 61 mmol), and AIBN (*ca.* 100 mg) in ether (130 mL) was irradiated for 24 h with a medium-pressure mercury vapor lamp (125 W) using a cooled quartz immersion well fitted with a dry ice condenser. The temperature of the reaction vessel was maintained at 0–10 °C during the irradiation. Ether and excess dimethylphosphine were removed under vacuum (*ca.* 0.1 mmHg), to give crude diethyl (2-(dimethylphosphino)ethyl)phosphonate, (**7**), as a colorless air-sensitive oil (13.5 g). The purity of the material was >98% by NMR spectroscopy, and it was used without further purification for the preparation of (2-(dimethylphosphino)ethyl)phosphine. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ –48.1 (1P, d, $^3J_{P-P} = 50.4$ Hz, $-P\mathrm{(CH_3)_2}$), 30.8 (1P, d, $-P\mathrm{(O)}-$). ^1H NMR (benzene-d_6): δ 0.96 (6H, d, $^2J_{P-H} = 2.8$ Hz, $-\mathrm{P(C}H_3\mathrm{)_2}$), 1.30 (6H, t, $^3J_{H-H} = 7.1$ Hz, 2 × $-\mathrm{OCH_2C}H_3$), 1.83 (2H, m, $-\mathrm{C}H_2\mathrm{P(CH_3)_2}$), 1.97 (2H, m, $-\mathrm{C}H_2\mathrm{P(O)}-$), 4.17 (4H, m, 2 × $-\mathrm{OC}H_2\mathrm{CH_3}$) ppm. $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 14.1 (2C, d, $^1J_{P-C} = 15.3$ Hz, $-\mathrm{P(}C\mathrm{H_3)_2}$), 17.3 (2C, d, $^3J_{P-C} = 3.2$ Hz, 2 × $-\mathrm{OCH_2}C\mathrm{H_3}$), 23.2 (1C, dd, $^1J_{P-C} = 140.6$, $^2J_{P-C} = 13.9$ Hz, $-C\mathrm{H_2P(O)}-$), 24.9 (1C, dd, $^1J_{P-C} = 13.7$, $^2J_{P-C} = 6.8$ Hz, $-C\mathrm{H_2P(CH_3)_2}$), 62.0 (2C, d, $^2J_{P-C} = 6.5$ Hz, 2 × $-\mathrm{O}C\mathrm{H_2CH_3}$) ppm.

The phosphino phosphonate (**7**) was characterized fully as its phosphine sulfide derivative. Sulfur powder (44 mg, 1.4 mmol) was added to a stirred solution of diethyl (2-(dimethylphosphino)ethyl)phosphonate (269 mg, 1.38 mmol) in THF (5 mL). The resulting clear solution was filtered and the solvent removed under vacuum to give diethyl (2-(dimethylthiophosphino)ethyl)phosphonate as a colorless oil (291 mg, 1.29 mmol, 93%). IR ν_{max} ($CHCl_3$): 1443 w, 1413 m, 1370 w, 1290 m, 1164 m, 1098 m, 1031 s, 970 s, 946 s, 577 w cm^{-1}. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 30.5 (1P, bs, $W_{1/2} = 185$ Hz, $-P\mathrm{(S)(CH_3)_2}$), 37.0 (1P, d, $^3J_{P-P} = 66.7$ Hz, $-P\mathrm{(O)}-$). ^1H NMR (benzene-d_6): δ 1.30 (6H, t, $^3J_{P-H} = 7.0$ Hz, 2 × $-\mathrm{OCH_2C}H_3$), 1.44 (6H, br m, $-\mathrm{P(S)(C}H_3\mathrm{)_2}$), 2.22 (2H, br m, $-\mathrm{C}H_2\mathrm{P(S)(CH_3)_2}$), 2.36 (2H, m, $-\mathrm{C}H_2\mathrm{P(O)}-$), 4.16 (4H, m, 2 × $-\mathrm{OC}H_2\mathrm{CH_3}$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 17.2 (2C, d, $^3J_{C-P} = 5.9$ Hz, 2 × $-\mathrm{OCH_2}C\mathrm{H_3}$), 19.8 (1C, dd, $^1J_{C-P} = 143.1$, $^2J_{C-P} = 2.7$ Hz, $-C\mathrm{H_2P(O)}-$), 21.0 (2C, d, $^1J_{C-P} = 54.6$ Hz, $-\mathrm{P(S)(}C\mathrm{H_3)_2}$), 28.4 (1C, dd, $^1J_{C-P} = 52.5$, $^2J_{C-P} = 4.8$ Hz, $-C\mathrm{H_2P(S)(CH_3)_2}$), 62.9 (2C, d, $^2J_{C-P} = 6.3$ Hz, 2 × $-\mathrm{O}C\mathrm{H_2CH_3}$) ppm. MS (EI) *m/z*: 258 (M, 53%), 243 (29), 212 (13), 211 (14), 185 (19), 165 (100), 137 (36), 121 (38), 111 (43), 109 (83), 94 (53), 93 (87), 81 (25), 79 (29), 77 (20), 65 (47), 63 (21). High-resolution MS: Calcd for $C_8H_{20}O_3P_2S$, *m/z* 258.0608; found, *m/z* 258.0650.

(iv) Preparation of (2-(Dimethylphosphino)ethyl)phosphine), $\mathbf{Me_2PCH_2CH_2PH_2}$ (5). A solution of diethyl (2-(dimethylphosphino)ethyl)phosphonate (**7**) (11.0 g, 56.4 mmol) in dry ether (50 mL) was added dropwise to a suspension of powdered lithium aluminum hydride (7.0 g, 0.12 mol) in ether (200 mL) while the solution temperature was maintained in the range 0–10 °C. The mixture was stirred at room temperature (48 h) and hydrolyzed by the successive addition of deaerated water (15 mL), deaerated aqueous sodium hydroxide solution (15%, 10 mL), and deaerated water (15 mL). The resulting slurry was filtered under nitrogen, and the volume was reduced under vacuum to approximately 80 mL. The solution of (2-(dimethylphosphino)ethyl)phosphine was used without further purification in subsequent reactions. ^{31}P NMR (ether): δ –49.7 (1P, d, $^3J_{P-P} = 15.0$ Hz, $\mathrm{(CH_3)_2}P\mathrm{(CH_2)_2PH_2}$), –130.5 (1P, dt, $\mathrm{(CH_3)_2P(CH_2)_2}P\mathrm{H_2}$, $^1J_{P-H} = 180$ Hz) ppm.

(v) Preparation of Allyldimethylphosphine Sulfide. A solution of allyl bromide (67.0 g, 0.55 mol) in ether (100 mL) was added dropwise to a stirred suspension of magnesium turnings (20.0 g, 0.82 mol) in dry ether (100 mL). The reaction was initiated with a crystal of iodine, and the rate of addition was such that the reaction mixture maintained a gentle reflux during the addition. After the addition was complete, the mixture was filtered under nitrogen to remove excess magnesium. The solution was cooled (0–10 °C), and a solution of dimethylthiophosphinic bromide (48.0 g, 0.27 mol) in ether (60 mL) was added slowly, maintaining the low temperature. The resulting gray slurry was stirred overnight at room temperature and a saturated aqueous solution of ammonium chloride was added carefully, while the solution temperature was maintained below 10 °C until all solids had dissolved. The ether layer was removed and dried (anhydrous sodium sulfate). The aqueous layer was further extracted with ether (3 × 60 mL). The combined ether extracts were filtered, and the solvent was removed under vacuum to give the crude product which was recrystallized from hexane. Allyldimethylphosphine sulfide was obtained as a white fibrous solid (33.0 g, 0.25 mol, 89%), mp 41–44 °C. IR ν_{max} 1636 m, 1302 m, 1288 m, 1220 w, 1196 m, 1072 m, 992 m, 953 s, 932 s, 917 s, 862 m, 805 m, 755 m, 610 s cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.3 (1P, s). ^1H NMR ($CDCl_3$): δ 1.70 (6H, d, $^2J_{P-Me} = 12.7$ Hz, $-\mathrm{P(S)(C}H_3\mathrm{)_2}$), 2.77 (2H1, dddd, $^2J_{P-CH1} = 15.3$, $^3J_{H1-H4} = 7.6$, $^4J_{H1-H2} = 1.4$, $^3J_{H1-H3} = 0.9$ Hz, $-\mathrm{C}H_2\mathrm{P(S)(CH_3)_2}$), 5.23 (1H2, dddd, $^4J_{P-H2} = 5.5$, $^3J_{H2-H4(trans)} = 17.0$, $^2J_{H2-H3(gem)} = 1.4$ Hz, $-\mathrm{CH_2CH{=}C}H\mathrm{H}$), 5.30 (1H3, dddd, $^4J_{P-H3} = 4.8$, $^3J_{H3-H4(cis)} = 10.1$ Hz, $-\mathrm{CH_2CH{=}CH}H$), 5.89 (1H4, dddt, $^3P_{P-H4} = 5.6$ Hz, $-\mathrm{CH_2C}H\mathrm{{=}CHH}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.7 (2C, d, $^1J_{P-Me} = 55.2$ Hz, $-\mathrm{P(S)(}C\mathrm{H_3)_2}$), 42.0 (1C, d, $^1J_{P-CH2} = 50.0$ Hz, $-C\mathrm{H_2P(CH_3)_2}$), 121.3 (1C, d, $^3J_{P-CH2} < 5.0$ Hz, $-\mathrm{CH_2CH{=}}C\mathrm{H_2}$), 129.0 (1C, d, $^2J_{P-CH} = 8.5$ Hz, $-\mathrm{CH_2}C\mathrm{H{=}CH_2}$) ppm. Anal. Calcd for $C_5H_{11}PS$: C, 44.76; H, 8.26. Found: C, 44.8; H, 8.0.

(vi) Preparation of Allyldimethylphosphine (9). Allyldimethylphosphine sulfide (32.0 g, 0.24 mol) was suspended in tri-*n*-butylphosphine (48 g, 0.24 mol), and the mixture was warmed gently (oil bath, 100 °C) while stirring. The solution became homogeneous, and the mixture was heated further (220–260 °C). Allyldimethylphosphine (**9**) distilled from the mixture and was collected under nitrogen as a colorless air-sensitive liquid (17.3 g, 0.17 mol, 71%). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ –53.8 (1P, s). ^1H NMR (toluene-d_8): δ 0.95 (6H, d, $^2J_{P-H} = 3.4$ Hz, $-\mathrm{P(S)(C}H_3\mathrm{)_2}$), 2.12 (2H1, dddd, $^2J_{P-H1} < 2$, $^3J_{H1-H4} = 7.7$, $^4J_{H1-H2} = 1.4$, $^3J_{H1-H3} = 0.9$ Hz, $-\mathrm{C}H_2\mathrm{P(S)(CH_3)_2}$), 5.04 (1H2, dddd, $^4J_{P-H2} = 3.32$, $^3J_{H2-H4(trans)} = 17.0$, $^2J_{H2-H3(gem)} = 2.1$ Hz, $-\mathrm{CH_2CH{=}C}H\mathrm{H}$), 5.10 (1H3, dddd, $^4J_{P-H3} = 3.0$, $^3J_{H3-H4(cis)} = 10.2$ Hz, $-\mathrm{CH_2CH{=}CH}H$), 5.84 (1H4, dddt, $^3J_{P-H4} = 4.7$ Hz, $-\mathrm{CH_2C}H\mathrm{{=}CHH}$). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 13.8 (2C, d, $^1J_{P-C} = 10.0$ Hz, $\mathrm{P(S)(}C\mathrm{H_3)_2}$), 37.6 (1C, d, $^1J_{P-C} = 12.6$ Hz, $-C\mathrm{H_2P(CH_3)_2}$), 116.7 (1C, d, $^3J_{P-C} = 4.6$ Hz, $-\mathrm{CH_2CH{=}}C\mathrm{H_2}$), 134.6 (1C, d, $^2J_{P-C} < 2$ Hz, $-\mathrm{CH_2}C\mathrm{H{=}CH_2}$) ppm.

(vii) Preparation of (2-(Dimethylphosphino)ethyl)bis[3-(dimethylphosphino)propyl]phosphine, $\mathbf{Me_2PCH_2CH_2P(CH_2CH_2CH_2PMe_2)_2}$ (3). The concentration of an ethereal solution of (2-(dimethylphosphino)ethyl)phosphine was determined by integration of its ^{31}P NMR spectrum against an internal standard. Allyldimethylphosphine (**9**) (9.8 g, 0.157 mol) and AIBN (*ca.* 100 mg) were added to a solution of (2-(dimethylphosphino)ethyl)phosphine (**5**) (2.0 g, 14.6 mmol) in ether (80 mL). The solution was irradiated for 50 h with a medium-pressure mercury vapor lamp through a quartz immersion well. The apparatus was fitted with a dry ice condenser, and the reaction well was cooled to 0–10 °C throughout the experiment. The solution was maintained under an atmosphere of nitrogen, with nitrogen occasionally bubbled through to provide mixing. When the reaction was complete (^{31}P NMR), the solvent was removed under vacuum (*ca.* 0.1 mmHg). Excess allyldimethylphosphine was separated by distillation under reduced pressure (80–100 °C, 0.5 mmHg) leaving (2-(dimethylphosphino)ethyl)bis[3-(dimethylphosphino)propyl]phosphine (**3**) as a colorless oil (4.5 g, 12.4 mmol, 92%). By ^{31}P NMR spectroscopy, the residue contains only (2-(dimethylphosphino)ethyl)bis[3-(dimethylphosphino)propyl]phosphine, and this was used directly in subsequent reaction steps without further purification. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (benzene-d_6): δ −54.0 (2P, s, 2 × $-\mathrm{CH_2CH_2CH_2}P(\mathrm{CH_3})_2$), −48.6 (1P, d, $^3J_{\mathrm{P-P}} = 19.8$ Hz, $-\mathrm{PCH_2CH_2}P(\mathrm{CH_3})_2$), −29.1 (1P, d, $-P\mathrm{CH_2CH_2P(CH_3)_2}$). ^{1}H NMR (benzene-$d_6$): δ 1.05 (24H, overlapping m, 3 × $-\mathrm{P(C}H_3)_2$), 1.4–1.9 (16H, overlapping m, 8 × $-\mathrm{C}H_2-$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-d_6): δ 14.8 (2C, d, $^1J_{\mathrm{C-P}} = 16.4$ Hz, $-\mathrm{PCH_2CH_2P(}C\mathrm{H_3)_2}$), 15.0 (2C, d, $^1J_{\mathrm{C-P}} = 13.0$ Hz, $-\mathrm{PCH_2CH_2CH_2P(}C\mathrm{H_3)_2}$), 23.5 (1C, dd, $^1J_{\mathrm{C-P}} \approx {}^3J_{\mathrm{C-P}} = 15.6$ Hz, $-\mathrm{PCH_2CH_2}C\mathrm{H_2P(CH_3)_2}$), 23.8 (2C, dd, $^1J_{\mathrm{C-P}} = 16.7$, $^2J_{\mathrm{C-P}} = 12.2$ Hz, $-\mathrm{P(CH_2}C\mathrm{H_2P(CH_3)_2)_2}$), 28.8 (2C, dd, $^1J_{\mathrm{C-P}} = 11.2$, $^2J_{\mathrm{C-P}} = 12.0$ Hz, $-\mathrm{P(}C\mathrm{H_2CH_2P(CH_3)_2)_2}$), 29.9 (1C, dd, $^1J_{\mathrm{C-P}} = 15.1$, $^3J_{\mathrm{C-P}} = 11.6$ Hz, $-\mathrm{P}C\mathrm{H_2CH_2CH_2P(CH_3)_2}$), 35.0 (1C, dd, $^2J_{\mathrm{C-P}} \approx {}^2J_{\mathrm{C-P}} = 10.9$ Hz, $-\mathrm{PCH_2}C\mathrm{H_2CH_2P(CH_3)_2}$) ppm.

The tetraphosphine (**3**) was characterized fully as its sulfurized derivative. Sulfur powder (72.7 mg, 2.27 mmol) was added to a solution of **3** (185 mg, 0.57 mmol) in THF (5 mL). A white precipitate formed instantaneously. The suspension was stirred overnight and filtered, and the residue was recrystallized from hot chloroform.

(2-(Dimethylphosphino)ethyl)bis[3-(dimethylphosphino)propyl]phosphine tetrasulfide was obtained as a white solid (240 mg, 52.8 mmol, 93%), mp 176–183 °C. IR ν_{max} (KBr) 1458 w, 1412 m, 1290 m, 1232 w, 1193 w, 1105 w, 981 s, 944 s, 910 s, 854 w, 744 s cm^{-1}. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (TFA-d_1): δ 43.4 (2P, s, $-\mathrm{CH_2CH_2CH_2}P\mathrm{(S)(CH_3)_2}$), 45.1 (2P, d, $^3J_{\mathrm{P-P}} = 53.4$ Hz, $-\mathrm{P(S)(CH_2CH_2}P\mathrm{(S)(CH_3)_2)_2}$), 53.5 (1P, d, $-P\mathrm{(S)(CH_2CH_2P(S)(CH_3)_2)_2}$). ^{1}H NMR (TFA-$d_1$): δ 1.68–1.79 (18H, overlapping multiplets, $(\mathrm{C}H_3)_2\mathrm{PCH_2CH_2CH_2P(CH_2CH_2P(C}H_3)_2)_2$), 1.93–2.45 (14H, overlapping multiplets, $\mathrm{(CH_3)_2PC}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{P(C}H_2\mathrm{C}H_2\mathrm{P(CH_3)_2)_2}$). MS (EI) *m/z*: 454 (M, 18%), 360 (24), 348 (30), 334 (8), 287 (34), 267 (19), 199 (20), 181 (48), 167 (8), 135 (90), 121 (31), 93 (100), 75 (19), 63 (20). High-resolution MS: Calcd for $\mathrm{C_{14}H_{34}P_4S_4}$, *m/z* 454.0494; found, *m/z* 454.0440.

Preparation of Bis[2-(dimethylphosphino)ethyl](3-(dimethylphosphino)propyl)phosphine, $\mathrm{Me_2PCH_2CH_2CH_2P(CH_2CH_2PMe_2)_2}$ (4). (i) Diethyl Allylphosphonate, $\mathrm{CH_2{=}CHCH_2P(O)(OCH_2CH_3)_2}$ (13). A mixture of triethyl phosphite (40.0 g, 0.24 mol) and allyl bromide (43.7 g, 0.36 mol) was refluxed for 18 h, after which excess allyl bromide was removed by distillation. Diethyl allylphosphonate (**13**) was purified by distillation under vacuum (63–67 °C/0.01 mmHg) and obtained as a colorless liquid (39.8 g, 0.22 mol, 93%). IR ν_{max} (CHCl$_3$): 1443 w, 1367 w, 1163 m, 1096 m, 1051 s, 1029 s, 991 w, 969 s cm^{-1}. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (CDCl$_3$): δ 26.7 (1P, s). ^{1}H NMR (CDCl$_3$): δ 1.34 (6H, m, 2 × $-\mathrm{OCH_2C}H_3$), 2.63 (2H, m, $-\mathrm{C}H_2\mathrm{CH{=}CH_2}$), 4.13 (4H, m, 2 × $-\mathrm{OC}H_2\mathrm{CH_3}$), 5.24 (2H, m, $-\mathrm{CH_2CH{=}C}H_2$), 5.82 (1H, m, $-\mathrm{CH_2C}H\mathrm{{=}CH_2}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (CDCl$_3$): δ 16.9 (2C, d, $^3J_{\mathrm{P-H}} = 3.7$ Hz, 2 × $-\mathrm{OCH_2}C\mathrm{H_3}$), 32.3 (1C, d, $^1J_{\mathrm{P-H}} = 138.4$ Hz, $-C\mathrm{H_2CH{=}CH_2}$), 62.4 (2C, d, $^2J_{\mathrm{C-H}} = 6.5$ Hz, 2 × $-\mathrm{O}C\mathrm{H_2CH_3}$), 120.3 (1C, d, $^3J_{\mathrm{C-P}} = 14.2$ Hz, $-\mathrm{CH_2CH{=}}C\mathrm{H_2}$), 128.1 (1C, d, $^2J_{\mathrm{C-P}} = 12.0$ Hz, $-\mathrm{CH_2}C\mathrm{H{=}CH_2}$) ppm. MS (EI) *m/z*: 178 (M, 10%), 151 (11), 137 (12), 124 (9), 109 (100), 81 (83), 65 (22). High-resolution MS: Calcd for $\mathrm{C_7H_{15}O_3P}$, *m/z* 178.0759; found, *m/z* 178.0753.

(ii) Diethyl (3-(Dimethylphosphino)propyl)phosphonate, $\mathrm{(CH_3)_2PCH_2CH_2CH_2P(O)(OCH_2CH_3)_2}$ (14). A solution of diethyl allylphosphonate (**13**) (24.2 g, 0.14 mol), dimethylphosphine (8.67 g, 0.14 mol), and AIBN (*ca.* 100 mg) in ether (150 mL) was irradiated with a medium-pressure mercury vapor lamp (125 W) in a cooled (0–10 °C) quartz photolysis immersion well, fitted with a dry ice condenser for 28 h. The reaction was followed by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy, and when starting materials were no longer present, the solvent and all volatile phosphines were removed under vacuum (*ca.* 0.1 mmHg) to give diethyl (3-(dimethylphosphino)propyl)phosphonate (**14**) as a colorless oil (30.3 g, 0.13 mol, 93%). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (benzene-d_6): δ −54.2 (1P, s, $-P\mathrm{(CH_3)_2}$), 30.7 (1P, s, $-P\mathrm{(O)}-$). ^{1}H NMR (benzene-d_6): δ 1.00 (6H, d, $^2J_{\mathrm{P-H}} = 2.0$ Hz, $-\mathrm{P(C}H_3)_2$), 1.29 (6H, t, $^3J_{\mathrm{H-H}} = 7.0$ Hz, 2 × $-\mathrm{OCH_2C}H_3$), 1.43 (2H, m, $-\mathrm{C}H_2\mathrm{P(CH_3)_2}$), 1.98 (2H, m, $-\mathrm{CH_2C}H_2\mathrm{CH_2}-$), 1.98 (2H, m, $-\mathrm{C}H_2\mathrm{P(O)}-$), 4.17 (4H, m, 2 × $-\mathrm{OC}H_2\mathrm{CH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-d_6): δ 14.6 (2C, d, $^1J_{\mathrm{C-P}} = 14.5$ Hz, $-\mathrm{P(}C\mathrm{H_3)_2}$), 17.3 (2C, d, $^3J_{\mathrm{C-P}} = 3.4$ Hz, 2 × $-\mathrm{OCH_2}C\mathrm{H_3}$), 20.3 (1C, dd, $^1J_{\mathrm{C-P}} = 16.0$, $^3J_{\mathrm{C-P}} = 4.4$ Hz, $-C\mathrm{H_2P(CH_3)_2}$), 29.5 (1C, dd, $^1J_{\mathrm{C-P}} = 139.8$, $^3J_{\mathrm{C-P}} = 11.4$ Hz, $-C\mathrm{H_2P(O)}-$), 34.0 (1C, dd, $^2J_{\mathrm{C-P}} = 11.6$, $^2J_{\mathrm{C-P}} = 14.8$ Hz, $-\mathrm{CH_2}C\mathrm{H_2CH_2}-$), 61.7 (2C, d, $^2J_{\mathrm{C-P}} = 6.4$ Hz, 2 × $-\mathrm{O}C\mathrm{H_2CH_3}$) ppm.

The phosphino phosphonate (**14**) was characterized fully as its sulfurized derivative. Diethyl (3-(dimethylphosphino)propyl)phosphonate (**14**) (315.0 mg, 1.31 mmol) was dissolved in THF (4 mL) and sulfur powder (42.1 mg, 1.31 mmol) added while stirring. The resulting clear solution was filtered and the solvent removed under vacuum to give diethyl (3-(dimethylthiophosphino)propyl)phosphonate as a colorless oil (341 mg, 1.26 mmol, 96%). IR ν_{max} (CHCl$_3$): 1442 w, 1413 m, 1369 w, 1303 w, 1290 m, 1164 m, 1096 m, 1056 s, 1028 s, 981 s, 964 s, 941 s, 912 s, 575 m cm^{-1}. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (benzene-d_6): δ 29.9 (1P, d, $^4J_{\mathrm{P-P}} = 4.0$ Hz, $-P\mathrm{(O)}-$), 34.2 (1P, d, $-P\mathrm{(S)(CH_3)_2}$). ^{1}H NMR (benzene-d_6): δ 1.33 (6H, t, $^3J_{\mathrm{H-H}} = 7.1$ Hz, 2 × $-\mathrm{OCH_2C}H_3$), 1.45 (6H, br d, $^2J_{\mathrm{P-H}} = 12.7$ Hz, $-\mathrm{P(S)(C}H_3)_2$), 1.88 (2H, m, $-\mathrm{C}H_2\mathrm{P(S)}-$), 1.93 (2H, td, $^2J_{\mathrm{P-H}} = 17.9$, $^3J_{\mathrm{H-H}} = 7.7$ Hz, $-\mathrm{C}H_2\mathrm{P(O)}-$), 2.20 (2H, m, $-\mathrm{CH_2C}H_2\mathrm{CH_2}-$), 4.18 (4H, m, 2 × $-\mathrm{OC}H_2\mathrm{CH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-d_6): δ 17.3 (2C, d, $^3J_{\mathrm{C-P}} = 5.7$ Hz, 2 × $-\mathrm{OCH_2}C\mathrm{H_3}$), 17.4 (1C, dd, $^2J_{\mathrm{C-P}} = 4.8$, $^2J_{\mathrm{C-P}} = 2.3$ Hz, $-\mathrm{CH_2}C\mathrm{H_2CH_2}-$), 21.5 (2C, d, $^1J_{\mathrm{C-P}} = 54.3$ Hz, $-\mathrm{P(S)(}C\mathrm{H_3)_2}$), 27.3 (1C, dd, $^1J_{\mathrm{C-P}} = 140.2$, $^3J_{\mathrm{C-P}} = 15.2$ Hz, $-C\mathrm{H_2P(O)}-$), 35.5 (1C, dd, $^2J_{\mathrm{C-P}} = 53.3$, $^2J_{\mathrm{C-P}} = 13.4$ Hz, $-C\mathrm{H_2P(S)}-$), 62.2 (2C, d, $^2J_{\mathrm{C-P}} = 6.3$ Hz, 2 × $-\mathrm{O}C\mathrm{H_2CH_3}$) ppm. MS (EI) *m/z*: 272 (M, 9%), 225 (7), 199 (8), 179 (100), 151 (23), 123 (53), 109 (13), 93 (21). High-resolution MS: Calcd for $\mathrm{C_9H_{22}O_3P_2S}$, *m/z* 272.0765; found, *m/z* 272.0739.

(iii) (3-(Dimethylphosphino)propyl)phosphine, $\mathrm{(CH_3)_2PCH_2CH_2CH_2PH_2}$ (11). A solution of diethyl (3-(dimethylphosphino)propyl)phosphonate (**14**) (20.0 g, 83.3 mmol) in dry ether (70 mL) was added dropwise to a suspension of powdered lithium aluminum hydride (12.0 g, 0.33 mol) in dry ether (200 mL) while the solution temperature was maintained in the range 0–10 °C. The mixture was stirred at room temperature (48 h) and hydrolyzed by the successive addition of deaerated water (25 mL), deaerated aqueous sodium hydroxide solution (15%, 20 mL), and deaerated water (25 mL). The resulting slurry was filtered under nitrogen. By ^{31}P NMR spectroscopy, the ethereal solution contained only (3-(dimethylphosphino)propyl)phosphine (>98%), and this solution was used directly in subsequent reaction steps without further purification. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (benzene-d_6): δ −139.4 (1P, s, $-P\mathrm{H_2}$), −53.7 (1P, s, $-P\mathrm{(CH_3)_2}$). ^{1}H NMR (benzene-d_6): δ 1.03 (6H, d, $^2J_{\mathrm{P-H}} = 1.0$ Hz, $-\mathrm{P(C}H_3)_2$), 1.36 (2H, m, $-\mathrm{C}H_2\mathrm{P(CH_3)_2}$), 1.52 (2H, m, $-\mathrm{C}H_2\mathrm{PH_2}$), 1.67 (2H, m, $-\mathrm{CH_2C}H_2\mathrm{CH_2}-$), 2.84 (2H, dm, $^1J_{\mathrm{P-H}} = 190.5$ Hz, $-\mathrm{P}H_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-d_6): δ 14.9 (2C, d, $^1J_{\mathrm{C-P}} = 14.9$ Hz, $-\mathrm{P(}C\mathrm{H_3)_2}$), 16.4 (1C, dd, $^1J_{\mathrm{C-P}} = 12.0$, $^3J_{\mathrm{C-P}} = 9.5$ Hz, $-C\mathrm{H_2P(CH_3)_2}$), 30.3 (1C, dd, $^1J_{\mathrm{C-P}} = 14.3$, $^3J_{\mathrm{C-P}} = 3.1$ Hz, $-C\mathrm{H_2PH_2}$), 34.2 (1C, dd, $^2J_{\mathrm{C-P}} = 10.9$, $^2J_{\mathrm{C-P}} = 3.9$ Hz, $-\mathrm{CH_2}C\mathrm{H_2CH_2}-$) ppm.

(iv) Preparation of Dimethylvinylphosphine Sulfide. Vinyl bromide (20.0 g, 0.15 mol) was condensed into dry THF (50 mL, kept at 0 °C). The solution was added dropwise to a stirred suspension of magnesium filings (3.8 g, 0.16 mol) in tetrahydrofuran (100 mL), to which a crystal of iodine and 1,2-dibromoethane (2 mL) was added, maintaining a gentle reflux throughout the addition. The resulting Grignard reagent was filtered under nitrogen to remove unreacted magnesium. The vinyl Grignard reagent had a tendency to solidify at room temperature and was warmed (40–50 °C) to ensure that the reagent remained in solution. The Grignard reagent was added, dropwise, to a solution of dimethylthiophosphinic bromide (32.0 g, 0.18 mol) in THF (50 mL) while the temperature of the solution was maintained below 5 °C throughout the addition. The resulting slurry was refluxed (30 min) and then cooled (0 °C), and a saturated solution of ammonium chloride was added carefully. The ether layer was removed and the aqueous layer washed with ether (4 × 50 mL). The combined ether extracts were dried (anhydrous sodium sulfate) and filtered, and the solvent was removed under vacuum to afford the crude product as a pale yellow solid, which was purified by sublimation (100 °C Kugelrohr, 0.1 mmHg). Dimethylvinylphosphine sulfide was obtained as a white crystalline solid (13.0 g, 0.11 mol, 58%), mp 47–51 °C. IR ν_{max} (Nujol): 1289 m, 1262 w, 1017 m, 917 s, 860 s, 734 s, 680 s cm^{-1}. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (CDCl$_3$): δ 29.1 (1P, s). ^{1}H NMR (CDCl$_3$): δ 1.71 (6H, d, $^2J_{\mathrm{P-Me}} = 13.1$ Hz, $-\mathrm{P(S)(C}H_3)_2$), 6.09 (1H, ddd, $^2J_{\mathrm{P-H}} = 45.5$, $^3J_{\mathrm{H-H}(trans)} = 10.8$, $^3J_{\mathrm{H-H}(gem)} = 2.3$ Hz, $-\mathrm{CH{=}C}H\mathrm{H}$), 6.25–6.39 (2H, unresolved multiplet, $-\mathrm{C}H\mathrm{{=}CH}H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (CDCl$_3$): δ 22.1 (2C, d, $^1J_{\mathrm{P-C}} = 58.3$ Hz, $-\mathrm{P(S)(}C\mathrm{H_3)_2}$), 133.3 (1C, d, $^2J_{\mathrm{C-P}} = 12.0$ Hz, $-\mathrm{CH{=}}C\mathrm{H_2}$), 133.4 (1C, s, $-C\mathrm{H{=}CH_2}$) ppm.

(v) Preparation of Dimethylvinylphosphine (12). Dimethylvinylphosphine sulfide (10.8 g, 89.9 mmol) was suspended in tri-*n*-butylphosphine (18.2 g, 90.0 mmol) and the mixture warmed gently (oil bath, 100 °C), with stirring. The soluton became homogeneous, and the mixture was heated further (160–200 °C). Dimethylvinylphosphine distilled from the mixture and was collected under nitrogen as a colorless air-sensitive liquid (bp 70–90 °C) (2.2 g, 25.0 mmol, 28%). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ −49.6 (1P, s). ^1H NMR (benzene-d_6): δ 1.12 (6H, d, $^2J_{P-Me}$ = 2.8 Hz, $-P(CH_3)_2$), 5.7 (1H, ddd, $^3J_{P-H}$ = 12.1, $^3J_{H-H(trans)}$ = 18.3, $^2J_{H-H(gem)}$ = 2.0 Hz, $-CH{=}CHH$), 5.72 (1H, ddd, $^3J_{P-H}$ = 25.7, $^3J_{H-H(cis)}$ = 11.9 Hz, $-CH{=}CHH$), 6.42 (1H, ddd, $^2J_{P-H}$ = 15.0 Hz, $-CH{=}CHH$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 14.2 (2C, d, $^1J_{C-P}$ = 13.1 Hz, $-P(CH_3)_2$), 123.9 (1C, d, $^2J_{C-P}$ = 15.7 Hz, $-CH{=}CH_2$), 144.1 (1C, d, $^1J_{C-P}$ = 17.6 Hz, $-CH{=}CH_2$) ppm.

(vi) Preparation of Bis[2-(dimethylphosphino)ethyl](3-(dimethylphosphino)propyl)phosphine, $Me_2PCH_2CH_2CH_2P(CH_2CH_2PMe_2)_2$ (4). The concentration of an ethereal solution of (3-(dimethylphosphino)propyl)phosphine was determined by integration of its ^{31}P NMR spectrum against an internal standard. Dimethylvinylphosphine (**12**) (3.8 g, 43.1 mmol) and AIBN (*ca.* 100 mg) were added to a solution of (3-(dimethylphosphino)propyl)phosphine (**11**) (1.46 g, 10.8 mmol) in ether (50 mL). The solution was irradiated for 24 h with a medium-pressure mercury vapor lamp through a quartz immersion well. The apparatus was fitted with a dry ice condenser, and the reaction well was cooled to 0–10 °C throughout the experiment. The solution was maintained under an atmosphere of nitrogen, with nitrogen occasionally bubbled through to provide mixing. When the reaction was complete (^{31}P NMR), the solvent plus excess dimethylvinylphosphine were removed under vacuum (*ca.* 0.1 mmHg) leaving bis[2-(dimethylphosphino)ethyl](3-(dimethylphosphino)propyl)phosphine (**4**) as a colorless oil (3.1 g, 9.9 mmol, 94%). By ^{31}P NMR spectroscopy, the residue contains only bis[2-(dimethylphosphino)ethyl]-(3-(dimethylphosphino)propyl)phosphine (**4**), and this was used directly in subsequent reaction steps without further purification. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ −54.0 (1P, s, $-CH_2CH_2CH_2P(CH_3)_2$), −48.6 (2P, d, $^3J_{P-P}$ = 20.7 Hz, $-P(CH_2CH_2P(CH_3)_2)_2$), −24.4 (1P, t, $-P(CH_2CH_2P(CH_3)_2)_2$). ^1H NMR (benzene-d_6): δ 1.08 (6H, d, $^2J_{P-Me}$ = 2.6 Hz, $-CH_2CH_2CH_2P(CH_3)_2$), 1.08 (12H, d, $^2J_{P-Me}$ = 2.7 Hz, $-P(CH_2CH_2P(CH_3)_2)_2$), 1.53–1.89 (14H, overlapping m, $(CH_3)_2PCH_2CH_2CH_2P(CH_2CH_2P(CH_3)_2)_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 14.7 (4C, d, $^1J_{C-P}$ = 15.4 Hz, 2 × $-CH_2CH_2P(CH_3)_2$), 14.9 (2C, d, $^1J_{C-P}$ = 12.5 Hz, $-PCH_2CH_2CH_2P(CH_3)_2$), 23.5 (1C, dd, $^1J_{C-P} \approx {}^3J_{C-P}$ = 14.6 Hz, $-PCH_2CH_2CH_2P(CH_3)_2$), 23.7 (2C, dd, $^1J_{C-P}$ = 17.9, $^2J_{C-P}$ = 12.5 Hz, 2 × $-CH_2CH_2P(CH_3)_2$), 28.9 (2C, dd, $^1J_{C-P}$ = 11.9, $^2J_{C-P}$ = 12.0 Hz, 2 × $-CH_2CH_2P(CH_3)_2$), 29.6 (1C, dd, $^1J_{C-P}$ = 16.0, $^3J_{C-P}$ = 10.8 Hz, $-PCH_2CH_2CH_2P(CH_3)_2$), 35.2 (1C, dd, $^2J_{C-P} \approx {}^2J_{C-P}$ = 11.4 Hz, $-PCH_2CH_2CH_2P(CH_3)_2$).

The tetraphosphine (**4**) was characterized fully as its phosphine sulfide derivative. Sulfur powder (82.4 mg, 2.57 mmol) was added to a solution of **4** (200 mg, 0.64 mmol) in THF (5 mL). A white precipitate formed instantaneously. The suspension was stirred overnight and the precipitate collected by filtration.

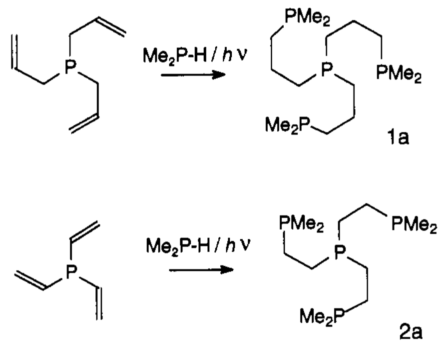
Bis[2-(dimethylphosphino)ethyl](3-(dimethylphosphino)propyl)phosphine tetrasulfide was obtained as a white solid (245 mg, 0.56 mmol, 87%), mp 155–160 °C. IR (KBr) ν_{max} 1522 w, 1413 m, 1290 m, 1196 m, 1136 s, 947 s, 858 w, 744 s cm^{-1}. $^{31}P\{^1H\}$ NMR (TFA-d_1): δ 47.8 (2P, s, 2 × $-CH_2CH_2CH_2P(S)(CH_3)_2$), 49.8 (1P, t, $^3J_{P-P}$ = 57.4 Hz, $-P(S)CH_2CH_2P(S)(CH_3)_2$), 60.5 (1P, d, $-P(S)CH_2CH_2P(S)(CH_3)_2$). ^1H NMR (TFA-d_1): δ 1.74–1.85 (24H, overlapping multiplets, 3 × $-P(S)(CH_3)_2$), 2.00–2.25 (16H, overlapping multiplets, $(CH_3)_2PCH_2CH_2P(CH_2CH_2CH_2P(CH_3)_2)_2$). MS (EI) *m/z*: 440 (M, 18%), 424 (4), 362 (12), 347 (13), 331 (8), 315 (5), 287 (20), 273 (31), 257 (10), 237 (19), 221 (32), 209 (27), 169 (25), 153 (30), 135 (32), 121 (60), 105 (78), 93 (72). High-resolution MS: Calcd for $C_{13}H_{32}P_4S_4$, *m/z* 440.0337; found, *m/z* 440.0323.

Results and Discussion

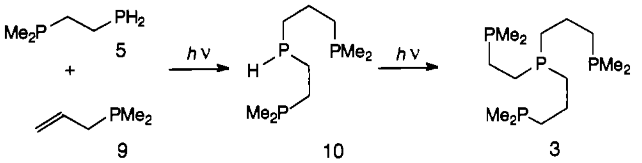
The photochemical addition of dimethylphosphine across the C═C bond of an alkene is a general synthetic strategy which has been used successfully to introduce the dimethylphosphinoethyl– fragment into organic compounds. The reaction between triallylphosphine and excess dimethylphosphine has been employed in the one-step assembly of $P(CH_2CH_2CH_2PMe_2)_3$[1] (**1a**). We have found that a similar reaction between trivinylphosphine and dimethylphosphine can be employed to synthesize the ethylene-bridged analogue $P(CH_2CH_2PMe_2)_3$ (**2a**) in high yield (Scheme I).

This synthetic approach to **2a** is a significant improvement on the previous multistep synthesis,[2] which involved stepwise construction of the tetraphosphine skeleton using a series of Michael-type additions of phosphides to vinylphosphine sulfides followed by desulfurization.[5]

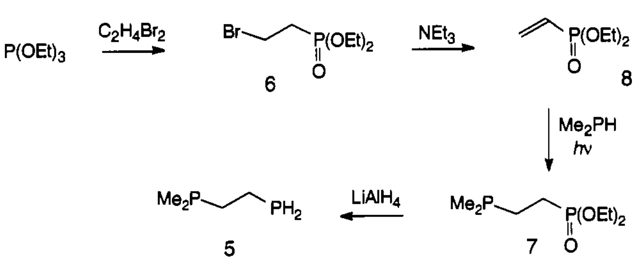
Scheme I



Scheme II



Scheme III



The tetradentate ligand **2a** was obtained as an air-sensitive low-melting white solid and exhibits two signals in the ^{31}P spectrum with the central P resonating at δ −19.8 ppm and the terminal phosphorus nuclei at δ −48.6 ppm. The nonequivalent phosphorus nuclei are coupled ($^3J_{P-P}$ = 20.7 Hz) resulting in quartet and doublet resonances, respectively. No such coupling is observed between the central and terminal P atoms of the analogous ligand **1a** with three CH_2 groups separating the phosphorus centers.

The unsymmetrical ligand systems **3** and **4** were synthesized by a related scheme but required the preliminary assembly of the appropriate primary phosphine and vinylphosphine fragments. The ligand (2-(dimethylphosphino)ethyl)bis[3-(dimethylphosphino)propyl]phosphine (**3**) was synthesized by the photochemical reaction of (2-(dimethylphosphino)ethyl)phosphine (**5**) with 2 equiv of allyldimethylphosphine (**9**) and obtained as a colorless air-sensitive oil. The reaction proceeds over a period of 24 h, and the intermediate compound (2-(dimethylphosphino)ethyl)(3-(dimethylphosphino)propyl)phosphine (**10**) is seen to accumulate in the early stages of the reaction by ^{31}P NMR spectroscopy[9] (Scheme II).

(2-(Dimethylphosphino)ethyl)phosphine (**5**) was synthesized in four steps from dibromoethane and triethyl phosphite (Scheme III). Diethyl vinylphosphonate (**8**) was synthesized by treatment of diethyl (2-bromoethyl)phosphonate (**6**) with base,[10] and photochemical addition of dimethylphosphine across the double bond afforded diethyl (2-(dimethylphosphino)ethyl)phosphonate (**7**). The phosphino phosphonate (**7**) has been synthesized previously by the base-catalyzed conjugate addition of dimethylphosphine to the double bond of **8**, under reflux conditions.[2,11] We have found the photochemical addition of dimethylphosphine

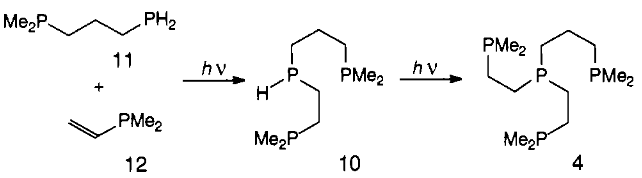
---

[9] ^{31}P NMR data for **10**: δ −64.7 (1P, dd, $^1J_{P-H}$ = 194 Hz, $^3J_{P-P}$ = 19.7 Hz, $-PH-$), −53.8 (1P, s, $-CH_2CH_2CH_2PMe_2$), −49.4 (1P, d, $-CH_2CH_2PMe_2$).

[10] Ford-Moore, A. H.; Williams, J. H. *J. Chem. Soc.* **1947**, 1465.

[11] King, R. B.; Cloyd, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 46.

Scheme IV



across a double bond to be an extremely effective and general method for introducing the Me_2P group.

The tetradentate ligand **3** exhibits three signals in the ^{31}P spectrum with the central phosphorus resonating at δ −29.1 ppm and the terminal phosphorus nuclei at δ −48.6 and −54.0 ppm. The phosphorus nuclei separated by an ethylene bridge exhibit a resolved ^{31}P–^{31}P coupling ($^2J_{P-P}$ = 19.8 Hz) resulting in two doublet resonances. No resolved coupling was observed between the phosphorus nuclei separated by the three-carbon bridge.

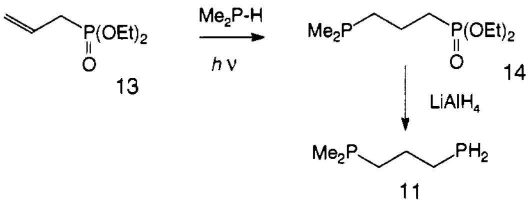
Bis[2-(dimethylphosphino)ethyl](3-(dimethylphosphino)propyl)phosphine (**4**) was synthesized by the photochemical reaction of (3-(dimethylphosphino)propyl)phosphine (**11**) with 2 equiv of dimethylvinylphosphine (**12**) (Scheme IV). The reaction proceeds over a period of 24 h, and as was observed in the synthesis of **3**, the intermediate compound (2-(dimethylphosphino)ethyl)(3-(dimethylphosphino)propyl)phosphine (**10**) is seen to accumulate in the early stages of the reaction by ^{31}P NMR spectroscopy[9] (Scheme IV).

The tetradentate ligand **4** exhibits three signals in the ^{31}P spectrum with the central phosphorus resonating at δ −24.4 ppm and the terminal phosphorus nuclei at δ −45.6 ppm and −54.1 ppm. Again, the phosphorus nuclei separated by an ethylene bridge exhibit well-resolved P–P coupling ($^2J_{P-P}$ = 20.7 Hz) resulting in triplet and doublet resonances, respectively. No coupling was observed between the phosphorus nuclei separated by the three-carbon bridge.

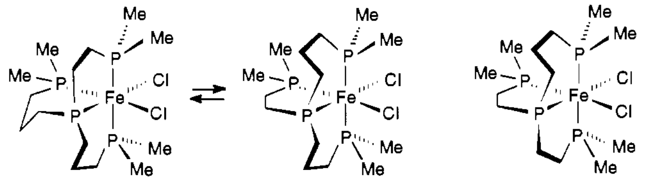
((Dimethylphosphino)propyl)phosphine (**11**) was synthesized by the photochemical addition of dimethylphosphine to diethyl allylphosphonate (**13**) followed by reduction of the ester **14** with lithium aluminum hydride (Scheme V).

All of the phosphines were characterized as their air-stable phosphine sulfide derivatives. Sulfurization was achieved by stirring the phosphine with a stoichiometric amount of elemental sulfur in THF. The polyphosphine ligands **3** and **4** resulted in tetrasulfide derivatives which were white, poorly soluble powders. The lower molecular weight phosphine sulfides (derivatives of the phosphino phosphonates **7** and **14**) were colorless viscous oils.

Scheme V



Metal Complexes. The symmetrical ligand **1a** forms one-to-one complexes with iron[12] and ruthenium,[13] and the metal centers adopt a pseudooctahedral coordination with the phosphorus donors constrained to four *cis* coordination sites. A five-coordinate nickel complex incorporating the ligand **2a** has also been reported.[3] The unsymmetrical ligands **3** and **4** form one-to-one complexes with iron. When mixed with $Fe(DPrPE)_2Cl_2$ [DPrPE = 1,2-bis(dipropylphosphino)ethane], **3** and **4** displace 2 equiv of DPrPE to give diamagnetic 6-coordinate complexes **15** and **16**, respectively.[14] The product complexes have not yet been fully characterized; however, **15** exists in solution as an equilibrating mixture of isomers (**15a**,**b**) whereas **16** exists as a single unsymmetrical isomer with the two shorter arms of the ligand in *cis* coordination sites. Full characterization and properties of these complexes will be reported elsewhere.



15a 15b 16

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Council, the Australian Government for an Australian Postgraduate Research Award (N.B., R.J.S.), and a Queen Elizabeth II Fellowship (B.A.M.).

---

(12) Antberg, M.; Dahlenberg, L. *Inorg. Chem. Acta* **1985**, *104*, 51.

(13) Antberg, M.; Dahlenburg, L. *Inorg. Chim. Acta* **1986**, *111*, 73.

(14) ^{31}P NMR data for **15a** (243 MHz, toluene-d_8, 300 K): δ 11.4 (1P, ddd, $^2J_{P(A)-P(B)}$ = 56.5, $^2J_{P(A)-P(C)}$ = 166.3, $^2J_{P(A)-P(D)}$ = 67.1 Hz, P_A), 32.5 (1P, ddd, $^2J_{P(B)-P(C)}$ = 45.8, $^2J_{P(B)-P(D)}$ = 56.5 Hz, P_B), 49.5 (1P, ddd, $^2J_{P(C)-P(D)}$ = 41.2 Hz, P_C), 75.6 (1P, ddd, P_D). ^{31}P NMR data for **15b** (243 MHz, toluene-d_8, 300 K): δ 8.2 (2P, dd, $^2J_{P(A)-P(B)}$ = 48.8, $^2J_{P(A)-P(C)}$ = 61.8 Hz, P_A), 67.1 (1P, dt, $^2J_{P(B)-P(C)}$ = 38.2 Hz, P_B), 76.4 (1P, dt, P_C). ^{31}P NMR data for **16** (162 MHz, toluene-d_8, 300 K): δ 14.6 (1P, ddd, $^2J_{P(A)-P(B)}$ = 171.2, $^2J_{P(A)-P(C)}$ = 50.0, $^2J_{P(A)-P(D)}$ = 58.3 Hz, P_A), 60.1 (1P, ddd, $^2J_{P(B)-P(C)}$ = 45.2, $^2J_{P(B)-P(D)}$ = 36.9 Hz, P_B), 76.9 (1P, ddd, $^2J_{P(C)-P(D)}$ = 36.9 Hz, P_C), 125.0 (1P, ddd, P_D).