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Synthesis of New Bidentate Phosphine Ligands Containing Saturated Phosphorus Heterocycles

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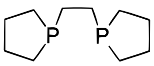
The synthesis of two ethylene-bridged bidentate phosphines is described. 1,2-Bis(1-phospholano)ethane ($(C_4H_8)PCH_2CH_2P(C_4H_8)$) was synthesized by the stepwise addition of 2,2-dioxo-1,3,2-dioxathiepane to $H_2PCH_2CH_2PH_2$. 1,2-Bis(1-phosphorinano)ethane ($(C_5H_{10})PCH_2CH_2P(C_5H_{10})$) was synthesized by the novel photochemical addition of 1,4-pentadiene to $H_2PCH_2CH_2PH_2$. These bis(phosphines) form two-to-one complexes of the form $Fe(PP)_2Cl_2$ when added to iron(II) chloride.

Introduction

The study of metal complexes of the ML_4X_2 type (M = Fe, Ru, Os; L = phosphine; X = halide, hydride) has been extensive, and the chemistry exhibited by such complexes depends to a large extent on the phosphine ligand(s) that they contain.[1] ML_4X_2 systems have been employed extensively in many types of reactions including intramolecular[2] and intermolecular[3] C−H activation and as catalysts in organic synthesis.[4] The most frequently studied ML_4X_2 systems have incorporated two bidentate ligands (*e.g.* $R_2PCH_2CH_2PR_2$, R = Ph,[5] Me,[2af,6,7] Et[8]). Tetradentate phosphine ligands ($P((CH_2)_nPR_2)$, $n = 2, 3$; R = Ph,[9] Me,[3g,10] Cy[11]) have been used to control the stereochemistry of octahedral complexes by constraining the phosphine donors to adjacent coordination sites.

In this paper we report the synthesis of two new bidentate bis(phosphine) ligands 1,2-bis(1-phospholano)ethane (BPE5) **(1)** and 1,2-bis(1-phosphorinano)ethane (BPE6) **(2)**. BPE5 **(1)** was synthesized using a procedure based on the reported synthesis of 1,2-bis((2*R*,5*R*)-2,5-dimethylphospholano)ethane,[12] and BPE6 **(2)** was synthesized by the novel photochemical addition of 1,4-pentadiene to $H_2PCH_2CH_2PH_2$ (DHPE).



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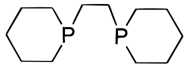

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Results and Discussion

Syntheses of saturated heterocycles containing phosphorus have been known for many years.[13,14] The construction of the phospholane ring system has usually been accomplished by α,ω-cyclization substitution reactions. Phospholanes were first synthesized by Gruttner *et al.*[13a] in the reaction between dichloroalkylphosphines and the bis(Grignard reagents) formed from 1,4-dihalobutanes. Other successful heterocyclizations to form phospholanes include (i) reaction of 1,4-dihalobutanes with metalated phosphines,[15] (ii) reduction of phospholane oxides[16] and phospholenes,[17] and (iii) the intramolecular addition of the P−H group across a terminal olefin.[18]

The incorporation of saturated phosphorus heterocyclic groups into polydentate phosphine ligand systems has been explored far less. Recently, Brunner[19] and Burk[20,21] reported multistep syntheses of chiral bidentate phospholane compounds, and subsequently, Emrich[22] reported a one-step synthesis of the simpler 1,4-bis(1-phospholano)butane. To our knowledge, no simple bidentate phospholanoethanes have yet been reported.

Synthesis of 1,2-Bis(1-phospholano)ethane (1). The direct reaction between thionyl chloride and 1,4-butanediol afforded 2-oxo-1,3,2-dioxathiepane **(3)** in good yield. Oxidation of **3** to 2,2-dioxo-1,3,2-dioxathiepane **(4)** was effected using $RuCl_3$ and $NaIO_4$ in acetonitrile/water,[23] and this was a significantly cleaner and higher yielding reaction than oxidation with acidic $KMnO_4$. The direct one-pot synthesis of cyclic sulfates described by Sharpless[23] gave lower yields than this two-step procedure.

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(1) Mayer, H. A.; Kaska, W. C. *Chem. Rev.* **1994**, 1239.

(2) (a) Jones, W. D.; Foster, G. P.; Putinas, J. M. *Inorg. Chem.* **1987**, *26*, 2120. (b) Antberg, M.; Dahlenberg, L. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 260.

(3) (a) Jones, W. D.; Feher, F. *Organometallics* **1983**, *2*, 562. (b) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433. (c) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7436. (d) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1987**, *109*, 2825. (e) Antberg, M.; Dahlenberg, L.; Frosin, K. M.; Höck, N. *Chem. Ber.* **1988**, *121*, 859. (f) Field, L. D.; George, A. V.; Messerle, B. A. *J. Chem. Soc. Chem. Commun.* **1991**, *19*, 1339. (g) Bampos, N.; Field, L. D.; Messerle, B. A. *Organometallics* **1993**, *12*, 2529.

(4) (a) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (b) Hsu, G. C.; Kosar, W. P.; Jones, W. D. *Organometallics* **1994**, *13*, 385.

(5) Hata, G.; Kondo, H.; Miyake, A. *J. Am. Chem. Soc.* **1968**, *90*, 2278.

(6) Chatt, J.; Watson, H. R. *J. Chem. Soc.* **1962**, 2545.

(7) Burn, M. J.; Fickes, M. G.; Hollander F. J.; Bergman, R. G. *Organometallics* **1995**, *14*, 137.

(8) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 5507.

(9) (a) Bianchini, C.; Perruzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19. (b) Bianchini, C.; Perruzini, M.; Polo, A.; Vacca, A.; Zanobini, F. *Gazz. Chim. Ital.* **1991**, *121*, 543. (c) Bianchini, C.; Perez, P. J.; Perruzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279.

(10) (a) Bampos, N.; Field, L. D. *Inorg. Chem.* **1990**, *29*, 587. (b) Bampos, N.; Field, L. D.; Messerle, B. A. *Magn. Reson. Chem.* **1991**, *29*, 36.

(11) Jia, G.; Drouin, S. D.; Jessop, P. G.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 906.

(12) Burk, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 8518.

(13) (a) Gruttner, G.; Wiernik, M. *Chem. Ber.* **1915**, *48*, 1473. (b) Gruttner, G.; Krause, E. *Chem. Ber.* **1916**, *49*, 437.

(14) Kosoapoff, G. H.; Struck, R. F. *J. Chem. Soc.* **1957**, 3739.

(15) Issleib, K.; Häusler, S. *Chem. Ber.* **1961**, *94*, 113.

(16) (a) Quin, L. D.; Somers, J. H.; Prince, R. H. *J. Org. Chem.* **1969**, *34*, 3700. (b) Marsi, K. L. *J. Org. Chem.* **1974**, *39*, 265.

(17) Hasserodt, U.; Hunger, K.; Korte, F. *Tetrahedron* **1963**, *19*, 1563.

(18) (a) Issleib, K.; Hohlfeld, G. *Z. Anorg. Allg. Chem.* **1961**, *312*, 169. (b) Davies, J. H.; Downer, J. D.; Kirby, P. J. *J. Chem. Soc. C.* **1966**, 245.

(19) Brunner, H.; Sieve, R. *J. Organomet. Chem.* **1987**, *328*, 71.

(20) (a) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Organometallics* **1990**, *9*, 2653. (b) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Tetrahedron Asymm.* **1991**, *2*, 569.

(21) Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125.

(22) Emrich, R.; Jolly, P. W. *Synthesis* **1993**, 39.

(23) Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538.

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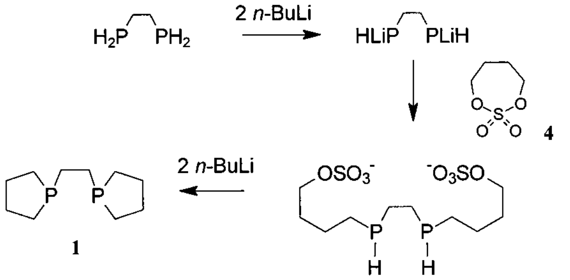
Scheme 1



1,2-Bis(1-phospholano)ethane **(1)** was synthesized from DHPE (Scheme 1). Treatment of an ether solution of DHPE sequentially with 2 equiv of *n*-BuLi, 2 equiv of **4**, and a further 2 equiv of *n*-BuLi afforded **1** in good yield. The *n*-BuLi deprotonates each $-PH_2$ fragment to give the lithium phosphide $-PHLi$; secondary metalation does not occur when only 1 equiv of base is used per $-PH_2$ group.[24] Each phosphide attacks the cyclic sulfate, forming a P−C bond, and treatment of the intermediate with a second equivalent of *n*-BuLi (without isolation or purification) deprotonates the remaining −PH fragments and closes the five-membered rings.

^{31}P NMR spectroscopy indicated that **1** was the only product formed. Attempts to use 1,4-dibromobutane instead of the cyclic sulfate **(4)** were unsuccessful and resulted in a complex mixture of products, some presumably polymeric. The clean cyclization using cyclic sulfate substrates has been attributed by Burk[21] to the fact that the anionic sulfate leaving group is kinetically less reactive than the initial substrate.

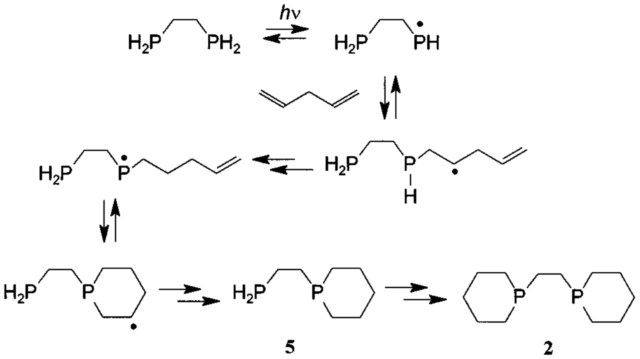
Photochemical Synthesis of Phosphorinanes. The base-catalyzed[25] and photochemical[26] addition of a P−H group to an olefin has proved a useful synthetic method in the synthesis of complex phosphines and has been used in the intramolecular addition of a P−H fragment to a terminal olefin.[18] Both approaches give anti-Markovnikov addition products with the phosphorus attached to the terminal carbon atoms of the original olefin.

In an extension to this approach, we have investigated the photochemical addition of α,ω-dienes to the primary phosphines ($R-PH_2$) as an approach to saturated heterocycles containing phosphorus. DHPE was irradiated in the presence of various α,ω-dienes. The dienes were usually present in a slight excess. The addition of a radical initiator (AIBN) had no effect on the outcome of the photochemical reactions.

(i) 1,4-Pentadiene. Irradiation of DHPE with 1,4-pentadiene (1:2 ratio) at ambient temperature and pressure afforded a mixture of the difunctionalized 1,2-bis(1-phosphorinano)ethane **(2)** and the monofunctionalized 2-phosphino-1-(1-phosphorinano)ethane **(5)**. In the presence of excess 1,4-pentadiene, **2** was the sole product, and in the presence of 1 equiv of olefin, this procedure was found to be suitable for the synthesis of **5**.

The mechanism of radical addition by the −PH fragment to olefins has been well described by Dahlenburg *et al.*[26a] The formation of the phosphorinane ring(s) in **2** and **5** is a sequential double addition of the PH_2 fragment to each terminal olefin of 1,4-pentadiene in an anti-Markovnikov mode. ^{31}P NMR spectroscopy revealed that there were no significantly long-lived secondary phosphine products, indicating that ring closure is rapid as compared to the initial addition of the P−H to the olefin.

Scheme 2



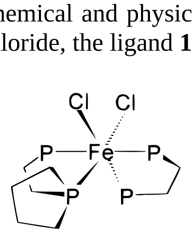
(ii) 1,5-Hexadiene. In contrast to the facile reaction of DHPE with 1,4-pentadiene, irradiation of DHPE with 1,5-hexadiene at ambient temperature and pressure *does not* cleanly produce 1,2-bis(phospholano)ethane. ^{31}P NMR spectroscopy showed that a mixture of products formed and the product mixture contained asymmetrically functionalized PCH_2CH_2P units and secondary phosphines (R_1R_2PH), the latter evident by resonances in the ^{31}P spectrum with large $^{1}J_{P-H}$ couplings. No symmetrically functionalized bis(phosphine) products were evident in this reaction, and it appears that the formation of oligomeric and polymeric products predominates over ring closure in attempts to prepare the seven-membered heterocycles.

(iii) 1,3-Butadiene. Irradiation of DHPE with 1,3-butadiene was carried out at ambient pressure and temperature using a cold finger condenser (−78 °C) to contain the volatile diene. No reaction was observed, despite prolonged irradiation times, and the starting diene and DHPE were recovered unchanged.

The failure of the reaction between DHPE and 1,3-butadiene to yield a phospholane ring and/or other polymeric products is surprising in light of the reported synthesis of a phospholane ring from 3-but-3-enylphenylphosphine.[18] The failure of the primary phosphine to give products with the butadiene could be a result of the formation of a relatively stable conjugated radical intermediate which fails to undergo further reaction and reverts to starting materials. Other similar photochemical additions where the initial radical intermediate can be resonance stabilized have also shown no reaction.[27]

Sulfurization of Phosphines 1 and 2. 1,2-Bis(1-phospholano)ethane *P,P′*-Disulfide ((BPE5)S$_2$) (6) and 1,2-Bis(1-phosphorinano)ethane *P,P′*-disulfide ((BPE6)S$_2$) (7). Reaction of **1** and **2** with 2 equiv of sulfur gave **6** and **7**, respectively, as pure white air-stable solids. The disulfide **6** has been synthesized previously by an independent method.[28]

Metal Complexes. The ligands **1** and **2** form two-to-one complexes with iron but with significantly different geometries and chemical and physical properties. On reaction with iron(II) chloride, the ligand **1** forms *cis*-Fe(BPE5)$_2$Cl$_2$ **(8)** as a dark maroon crystalline solid and **2** forms *trans*-Fe(BPE6)$_2$Cl$_2$ **(9)** as a pale green microcrystalline solid. Full characterization and properties of these complexes will be reported elsewhere.



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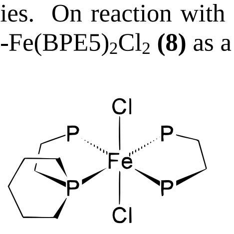

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[24] Issleib, K.; Thorausch, P. *Phosphorus Sulfur Relat. Elem.* **1977**, *3*, 203.

[25] (a) King, R. B.; Cloyd, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 53. (b) King, R. B.; Cloyd, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 46.

[26] (a) Antberg, M.; Prengel, C.; Dahlenberg, L. *Inorg. Chem.* **1984**, *23*, 4170. (b) Bampos, N.; Field, L. D.; Messerle, B. A.; Smernik, R. J. *Inorg. Chem.* **1993**, *32*, 4089.

[27] Stiles, A. R.; Vaughan, W. E.; Rust, F. F. *J. Am. Chem. Soc.* **1958**, *80*, 714.

[28] Schmutzler, R. *Inorg. Chem.* **1964**, *3*, 421.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk or vacuum methods or in a nitrogen-filled drybox. NMR spectra were obtained on a Bruker AMX400 spectrometer. ^{1}H NMR spectra (400.1 MHz) and ^{13}C NMR spectra (100.6 MHz) were referenced to residual solvent resonances. ^{31}P NMR spectra (162.0 MHz) were referenced to external neat trimethyl phosphite taken as 140.85 ppm at 300 K. 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/charge ratio and *y* is the percentage abundance relative to the base peak. Irradiations were performed in a quartz 250 mL round-bottom flask using an Oriel 350 W high-pressure mercury arc lamp. Nitrogen ($>$99.5%) was purchased from BOC-HYTEC Australia and used as obtained. Pentane, tetrahydrofuran (THF), and diethyl ether were stored over sodium benzophenone ketyl under a dry nitrogen atmosphere and distilled prior to use. Dichloromethane, acetonitrile, and NMR solvents (Merck) were used as supplied without further purification.

1,2-Bis(phosphino)ethane (DHPE) was prepared by reaction of 1,2-bis(diethoxyoxophosphoranyl)ethane, $((\mathrm{EtO})_2(\mathrm{O})\mathrm{P})\mathrm{CH_2CH_2}(\mathrm{P}(\mathrm{O})(\mathrm{OEt})_2)$, in ether with $\mathrm{LiAlH_4}$.[29] DHPE was extracted into ether and the concentration of the solution calibrated by ^{31}P NMR spectroscopy against a known concentration of $\mathrm{PhP(O)(OMe)_2}$. In all reactions, DHPE was used as an ethereal solution without further purification.

Synthesis of 1,2-Bis(1-phospholano)ethane (1). (i) 2-Oxo-1,3,2-dioxathiepane (3). 1,4-Butanediol (49.6 g, 48.7 mL, 550 mmol) and a solution of thionyl chloride (88.0 g, 54.6 mL, 738 mmol) in dichloromethane (150 mL) were added simultaneously to dichloromethane (200 mL) at 0 °C. The reaction mixture was maintained at 0 °C and left to warm to room temperature after addition was complete. The dichloromethane solution was washed with water (3 × 200 mL), saturated $\mathrm{NaHCO_3}$ solution (2 × 100 mL), and water (1 × 100 mL). The organic solution was dried over anhydrous $\mathrm{MgSO_4}$ and the solvent removed *in vacuo*. The residue was distilled under reduced pressure to give **3** as a clear colorless liquid, bp 35−45 °C/1.0−1.5 mmHg (lit.[30] bp 35 °C/1.0 mmHg). Yield: 54.3 g (72%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.80 (complex m, 4H, $\mathrm{C}H_2\mathrm{C}H_2$), 3.91 (complex m, 2H, $\mathrm{CH}H\mathrm{O}$), 4.37 (complex m, 2H, $\mathrm{C}H\mathrm{HO}$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$): δ 25.4 ($C\mathrm{H_2CH_2O}$), 64.2 ($C\mathrm{H_2O}$) ppm. MS (EI) *m/z*: 137 ((M + 1)$^+$, 51%), 136 (M$^+$, 1%), 106 (10), 73 (32), 71 (25), 55 (71), 44 (26), 43 (21), 42 (100), 41 (31).

(ii) 2,2-Dioxo-1,3,2-dioxathiepane (4). Ruthenium(III) chloride (430 mg, 2.07×10^{-3} mmol) was added to a solution of **3** (42.5 g, 310 mmol) in a mixture of carbon tetrachloride (200 mL), acetonitrile (200 mL), and water (300 mL) at 0 °C. Once a homogeneous dark brown solution had formed (approximately 2 min), sodium periodate (136 g, 636 mmol) was added. The reaction solution was allowed to warm to room temperature over 1.5 h, during which time the color of the mixture gradually turned orange. The reaction mixture was diluted with water (250 mL) and extracted with ether (4 × 200 mL). The ethereal solution was filtered through a plug of silica to remove flocculant green ruthenium salts. The solvent was removed *in vacuo* to give **4** as an impure oil, which was taken up in a minimum quantity of ether, and hexane was added until crystallization occurred. 2,2-Dioxo-1,3,2-dioxathiepane **(4)** was obtained as translucent crystalline needles, mp 45−47 °C (lit.[30] mp 41−42 °C). Yield: 31.0 g (67%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 3.37 (complex m, 4H, $\mathrm{C}H_2\mathrm{C}H_2$), 5.72 (complex m, 4H, $\mathrm{C}H_2\mathrm{O}$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$): δ 28.1 ($C\mathrm{H_2}$-$\mathrm{CH_2O}$), 72.5 ($C\mathrm{H_2O}$) ppm. MS (EI) *m/z*: 152 (M$^+$, 5%), 123 (10), 71 (53), 54 (71), 43 (37), 42 (100), 41 (78), 40 (16), 39 (15).

(iii) 1,2-Bis(1-phospholano)ethane (1). *n*-Butyllithium (33.4 mL, 2 equiv, 2.14 M solution in hexane) was added dropwise to an ether/THF (400 mL, 1:1) solution of DHPE (35.7 mmol). The cream-colored slurry was stirred for 90 min before dropwise addition of **5** (12.6 g, 71.4 mmol, 2 equiv) as a THF solution (100 mL), whereupon the solution decolorized. The solution was stirred for 2 h, after which *n*-butyllithium (100 mL, 6 equiv) was added dropwise until the solution remained cream in color. The reaction was quenched by addition of NaOH solution (approximately 200 mL, 4 M). The organic layer was removed and the aqueous layer extracted with ether (2 × 100 mL). The combined organic extracts were dried over anhydrous $\mathrm{MgSO_4}$, and the solvent was removed by distillation. Distillation afforded **1** as a clear colorless liquid, bp 100−110 °C/0.1 mmHg. Yield: 3.62 g (50%). ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6): δ −21.9 (s) ppm. ^{1}H NMR (400 MHz, benzene-d_6): δ 1.49 (apparent t, splitting = 4.0 Hz, 4H, $\mathrm{PC}H_2\mathrm{C}H_2\mathrm{P}$), 1.52, 1.67, 1.80 (complex multiplets, 2 × 4H, 1 × 8H, $\overline{\mathrm{P(C}H_2)_3\mathrm{C}}H_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6): δ 26.9 (apparent d, splitting = 5.2 Hz), 27.0 (apparent d, splitting = 5.2 Hz), 28.7 (apparent t, splitting = 1.9 Hz) ppm.

(iv) 1,2-Bis(1-phospholano)ethane *P,P′*-disulfide ($(\mathbf{BPE5})\mathbf{S_2}$) (6). A solution of **1** (100 mg, 0.495 mmol) in THF (2 mL) was added to a slurry of sulfur (31 mg, 97 mmol) in THF (1 mL). A white precipitate formed immediately. The solid was isolated and washed with *n*-hexane to yield **6**, mp 175−177 °C (lit.[28] mp 185 °C). Yield: 82 mg (63%). ^{31}P{^{1}H} NMR (162 MHz, methanol-d_4): δ 69.4 (s) ppm. ^{1}H NMR (400 MHz, methanol-d_4): δ 1.90 (complex m, 8H), 2.05 (complex m, 4H), 2.28 (complex m, 8H) ppm. ^{13}C{^{1}H} NMR (100 MHz, methanol-d_4): δ 27.2 (apparent t, splitting = 3.5 Hz), 28.0 (apparent dd, splittings = 20.1 Hz, 21.5 Hz), 34.1 (apparent dd, splittings = 25.0 Hz, 27.1 Hz) ppm. MS (EI) *m/z*: 267 ((M + 1)$^+$, 14%), 266 (M$^+$, 65%), 233 (13), 178 (15), 149 (13), 148 (15), 147 (100), 120 (15), 119 (32), 105 (11), 63 (31), 55 (10). High-resolution MS *m/z*: found 266.0478, $\mathrm{C_{10}H_{20}P_2S_2}$ requires 266.0482.

Synthesis of 1,2-Bis(1-phosphorinano)ethane (2). (i) Irradiation of DHPE with 1,4-Pentadiene. An ether solution of DHPE (38.3 mmol) and 1,4-pentadiene (5.00 g, 73.5 mmol) was irradiated at room temperature. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy until no further reaction was observed. The solvent was removed by distillation. The crude product was found by ^{31}P{^{1}H} NMR spectroscopy to consist of 1,2-bis(1-phosphorinano)ethane **(2)** and 2-phosphino(1-phosphorinano)ethane **(5)**. Distillation of the crude mixture under reduced pressure gave 2-phosphino-1-(1-phosphorinano)ethane **(5)** [bp 140−150 °C/1−1.5 mmHg; yield 1.13 g (18%)] and 1,2-bis(1-phosphorinano)ethane **(2)** [bp 175−185 °C/1−1.5 mmHg]. On cooling, **2** crystallized as large translucent crystals, mp 17−18 °C. Yield: 1.89 g (21%). 2-Phosphino-1-(1-phosphorinano)ethane **(5)**: ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6) δ −40.5 (d, $^3J_{\mathrm{P-P}} = 16.3$ Hz, $(\mathrm{CH_2})_2P\mathrm{CH_2}$), −129.6 (d, $^3J_{\mathrm{P-P}} = 16.3$ Hz, $P\mathrm{H_2}$) ppm; ^{1}H NMR (400 MHz, benzene-d_6) δ 1.17−1.91 (complex m, 14H, $\mathrm{C}H_2$), 2.98 (d, $^1J_{\mathrm{P-H}} = 190$ Hz, 2H, $\mathrm{P}H_2$) ppm; ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6) δ 54.3 (dd, $^1J_{\mathrm{P-P}} = 17.0$ Hz, $^2J_{\mathrm{P-P}} = 9.5$ Hz, $\mathrm{P}C\mathrm{H_2CH_2PH_2}$), 67.4 (s, $C\mathrm{H_2CH_2CH_2P}$), 68.6 (d, $^1J_{\mathrm{P-P}} = 13.2$ Hz, $C\mathrm{H_2P}$), 72.0 (s, $C\mathrm{H_2CH_2P}$), 74.7 (dd, $^1J_{\mathrm{P-P}} = 17.3$ Hz, $^2J_{\mathrm{P-P}} = 3.4$ Hz, $\mathrm{PCH_2}C\mathrm{H_2PH_2}$) ppm. 1,2-Bis(1-phosphorinano)ethane **(2)**: ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6) δ −38.9 (s) ppm; ^{1}H NMR (400 MHz, benzene-d_6) δ 1.40 (complex m, 6H), 1.61 (complex m, 2H), 1.70−1.78 (complex m, 8H), 1.91 (complex m, 8H) ppm; ^{13}C{^{1}H} NMR (100 MHz, benzene-d_6) δ 67.1 (m, $\mathrm{P}C\mathrm{H_2}C\mathrm{H_2P}$), 67.4 (m, $C\mathrm{H_2CH_2P}$), 68.8 (dd, $^1J_{\mathrm{P-C}} = 8.1$ Hz, $^4J_{\mathrm{P-C}} = 8.1$ Hz $C\mathrm{H_2P}$), 72.1 (s, $C\mathrm{H_2CH_2CH_2P}$) ppm.

(ii) 1,2-Bis(1-phosphorinano)ethane *P,P′*-Disulfide ($(\mathbf{BPE6})\mathbf{S_2}$) (7). A solution of **2** (130 mg, 0.565 mmol) in THF (2 mL) was added to a slurry of sulfur (36 mg, 1.1 mmol) in THF (1 mL). A white precipitate formed immediately. The solid was isolated and washed with *n*-hexane to yield pure **7**, mp 207−208 °C. Yield: 82 mg (63%). ^{31}P{^{1}H} NMR (162 MHz, $\mathrm{CDCl_3}$): δ −39.9 ppm. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.70 (complex m, 6H), 1.94 (complex m, 6H), 2.14 (complex m, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$): δ 22.7 (apparent triplet, splitting = 3.1 Hz, $C\mathrm{H_2CH_2P}$), 24.0 (apparent triplet, splitting = 24.4 Hz, $\mathrm{P}C\mathrm{H_2}C\mathrm{H_2P}$), 26.9 (apparent triplet, splitting = 3.1 Hz, $C\mathrm{H_2CH_2}$-$\mathrm{CH_2P}$), 31.6 (apparent triplet, splitting = 24.1 Hz, $C\mathrm{H_2P}$). MS (EI) *m/z*: 296 ((M + 2)$^+$, 11%), 295 ((M + 1)$^+$, 22%), 294 (M$^+$, 84%), 262 (19), 261 (64), 225 (18), 192 (12), 163 (21), 162 (30), 161 (100), 134 (14), 133 (20), 129 (19), 101 (18), 100 (11), 99 (21), 73 (12), 67 (11), 63 (30), 41 (20). High-resolution MS *m/z*: found 294.0784, $\mathrm{C_{12}H_{24}P_2S_2}$ requires 294.0796.

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(29) Taylor, R. B.; Rhee, W. M. *Inorg. Chem.* **1978**, *17*, 2961.

(30) Berridge, M. S.; Franceschini, M. P.; Rosenfeld, E.; Tewson, T. J. *J. Org. Chem.* **1990**, *55*, 1211.