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Journal of Organometallic Chemistry 646 (2002) 230–238

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis of 1,2-bis[(diorgano)phosphino]ethanes via Michaelis–Arbuzov type rearrangements

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Received 1 August 2001; accepted 30 October 2001

Dedicated to Francois Mathey on the occasion of his ICMGC award

Abstract

A three-step process for the synthesis of the bis(diorganophosphino)ethanes $R_2PCH_2CH_2PR_2$ where R = Et, Ph, ^{i}Pr, Cy and ^{t}Bu was examined. In the first step, diorganochlorophosphines were allowed to react with ethylene glycol in the presence of triethylamine at room temperature in THF solution. For R = Ph, ^{i}Pr and Cy, the bisphosphinites $R_2POCH_2CH_2OPR_2$ were obtained in high yield. For R = Et, the bisphosphinite could not be isolated but may be formed in 80% mixtures with tetraethyldiphosphine, Et_2PPEt_2, as a minor component. The reaction of di-*t*-butylchlorophosphine with ethylene glycol occurs at temperatures greater than 130 °C giving di-*t*-butyl phosphine oxide, $^tBu_2PH(O)$, as the only phosphorus-containing product. Thermolysis of the bisphosphinites $R_2POCH_2CH_2OPR_2$ (R = Ph, ^{i}Pr and Cy) at 190–260 °C for 24 h gave the bisphosphine oxides, $R_2P(O)CH_2CH_2(O)PR_2$ in 9% (Ph), 90% (^{i}Pr) and 93% (Cy) yields. A DSC study of the thermal rearrangement of $Cy_2POCH_2CH_2OPCy_2$ to $Cy_2P(O)CH_2CH_2(O)PCy_2$ yielded an enthalpy of isomerization of -40.4 ± 0.6 kcal mol^{-1}. Reduction of the bisphosphine oxides, $R_2P(O)CH_2CH_2(O)PR_2$ (R = Ph, ^{i}Pr and Cy) with trichlorosilane gave the bisphosphines, $R_2PCH_2CH_2PR_2$ in 80–85% yield. The overall yields of the bisphosphines $R_2PCH_2CH_2PR_2$ (R = ^{i}Pr and Cy) in the three-step process were 61 and 75%, respectively, suggesting that this process should be an attractive synthetic pathway to these two bisphosphines.

Keywords: Bisphosphine; Chelating ligands; Homogeneous catalysis; Michaelis–Arbuzov rearrangements

1. Introduction

Metal complexes containing chelating bisphosphines as ligands have been employed in numerous catalytic processes [1,2]. A great advantage of these ligands is the potential tunability of catalyst reactivity by variation of molecular properties of the phosphine. Some of the properties that impact on catalysis include the bite angle of the chelate, the basicity and steric bulk of substituents on phosphorus, and the rigidity of the chelate backbone [2].

Catalysts containing bis(phosphino)ethanes have been employed successfully in hydrogenations [3,4], the copolymerization of ethylene and carbon monoxide [5–7], hydroformylation of open chain conjugated dienes [8] and the catalytic formation of 1,4-hexadiene, which is used as a comonomer in ethane–propene–diene elastomers [9]. However, there is a lack of simple and efficient preparations of bis(diorganophosphino)ethanes bearing alkyl substituents on the phosphorus. Development of more straightforward routes to these ligands could greatly advance their practical use in homogeneous catalytic systems.

There are three common ways of preparing bis(-diorganophosphino)ethanes, but all involve either difficult to prepare, difficult to handle, or in some cases, toxic starting materials. One method involves the reaction of alkali metal or magnesium phosphides with 1,2-dihaloethanes [10]. Typically, 1,2-dichloroethane is used since reactions with 1,2-dibromoethane are often complicated by β-elimination initiated by metal halogen exchange [10a]. Although moderate to good yields of ethylene bridged bisphosphines are obtained by this method, a major drawback is that the formation of the

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0022-328X/02/$ - see front matter
PII: S0022-328X(01)01431-0

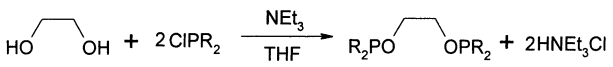
highly reactive metal phosphides often requires the use of toxic and/or pyrophoric reagents [11–15].

Synthesis of the bisphosphines may also be accomplished by the inverse reaction of 1,2 bis(dichlorophosphino)ethane with organoalkali metal or organomagnesium reagents [16]. The use of 1,2-bis(dichlorophosphino)ethane as the key starting material, however, requires a specialized stainless steel autoclave. The preparation entails reacting yellow phosphorus, phosphorus trichloride, and ethylene in an autoclave at 30 atm. and 200 °C for 6–16 h [16a,b]. The reported yield is only 50% of a product with 90% purity.

A more recent route to ethano-bridged bisphosphines involves the base or light catalyzed addition of a P–H bond, to a carbon–carbon double bond of a vinyl phosphine [17]. An obvious advantage of this route is the straightforward synthesis of non-symmetrical bisphosphines. However, this comes at the expense of additional synthetic steps in the independent preparation of the phosphine starting materials.

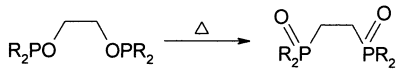
A three-step process has been developed by Brunner and Zettlmeier for the synthesis of some chiral 1,*n*-bis(-diphenylphosphino)alkanes which involves the initial reaction of diphenylchlorophosphine with 1,*n*-diols [18]. The essential P–C bond-forming step is a thermal Michaelis–Arbuzov rearrangement to give the bisphosphine oxide. Deoxygenation of the bisphosphine oxides by trichlorosilane gives bisphosphines in overall good yield.

One potentially great advantage of this non-organometallic strategy for the synthesis of 1,2-bis(dialkylphosphino)ethanes is the ready availability and low cost of many 1,2-diols and simple chlorophosphines. In this report, the potential synthesis of some simple bis(diorganophosphino)ethanes, beginning from the reaction of ethylene glycol with diorganochlorophosphines (Eqs. (1–3)), has been investigated. For the case of $R_2PCH_2CH_2PR_2$ (R = cyclohexyl, isopropyl), a simple and high yield three-step laboratory synthesis using $ClPR_2$, and the inexpensive and readily available reagents $HSiCl_3$, NEt_3 and ethylene glycol was found.



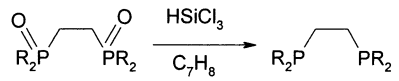
(1)

1a : R= Cy
1b : R= ^{i}Pr
1c : R= Ph
1d : R= Et



(2)

2a : R= Cy
2b : R= ^{i}Pr
2c : R= Ph



(3)

3a : R= Cy
3b : R= ^{i}Pr
3c : R= Ph

2. Experimental

2.1. General

Glassware was oven dried at 150 °C prior to use. All reactions were performed under dry nitrogen using standard Schlenk techniques. THF and benzene were distilled over sodium benzophenone ketyl under a blanket of nitrogen. Toluene and pentane were distilled from CaH_2 under nitrogen. Cy_2PCl, Et_2PCl, Ph_2PCl, $^tBu_2PCl$, and $^iPr_2PCl$ were used as received from Aldrich. Ethylene glycol was dried and distilled from BaO, under nitrogen, then redistilled from sodium metal under nitrogen. Triethylamine was dried using KOH then distilled from BaO under nitrogen. $HSiCl_3$ was distilled from Mg metal under nitrogen. $^{31}P\{^1H\}$-, $^{13}C\{^1H\}$- and ^1H-NMR data were recorded on a GE OMEGA-400 NMR spectrometer. ^1H-NMR chemical shifts were referenced to residual solvent peaks. $^{31}P\{^1H\}$-NMR chemical shifts are relative to 85% H_3PO_4. Infrared spectra were recorded on a Buck Scientific Model 500 infrared spectrophotometer. Mass spectral analyses were performed by David Bostwick's laboratory at the Georgia Institute of Technology, Atlanta, GA using a VG Instruments model 70-SE mass spectrometer. DSC data were recorded on TA Instruments 2920 differential scanning calorimeter with a cell constant of 1.1233. Samples were placed in aluminum pans and sealed hermetically. The samples were heated from 50 to 330 °C at 5.00 °C/min under a 74-cm^3 min^{-1} flow of argon. Analysis was done using the TA instruments thermal analyst 3100. Heat of isomerization was determined by integration of the area under the curve above the interpolated baseline of the DSC plot [19].

2.1.1. $Cy_2POCH_2CH_2OPCy_2$ (**1a**)

Cy_2PCl (5.5 g, 0.0236 mol) was placed into a 100-ml Schlenk flask fitted with a 25-ml addition funnel. Triethylamine (6.6 ml, $d = 0.728$ g ml^{-1}, 0.0474 mol) was syringed into the flask, followed by 40 ml of dry THF. Ethylene glycol (0.6 ml, $d = 1.113$ g ml^{-1}, 0.0107 mol) was syringed into the addition funnel, followed by 10 ml of THF. The 100-ml flask was next placed into an ice bath for 15 min. The ethylene glycol solution was added dropwise over 20 min with stirring. The ice bath was removed after 2 h of stirring. Stirring was continued for three days at room temperature (r.t.), after

which the solvent was removed in vacuo. Benzene (30 ml) was then syringed into the flask and the solution was filtered under nitrogen. Removal of solvent from the filtrate in vacuo yielded 4.89 g of a white solid. Yield: 98.7%; m.p.: 78.0–78.5 °C; ^{1}H-NMR (δ, d_6-benzene): 3.84 (m, 4H), 2.0-1.0 (m, 44H, -cyclohexyl); ^{31}P{^{1}H}-NMR (δ, d_6-benzene): 149.7; ^{13}C{^{1}H}-NMR (δ, d_6-benzene): 72.9 (dd, $^2J_{PC} = 20.7$ Hz, $^3J_{PC} = 7.6$ Hz, OCH_2CH_2O), 38.0(d, Cy), 28.1(d, Cy), (27.23, 27.18, 27.10, 27.08, 27.00, 26.74, Cy); IR (benzene, cm^{-1}): 931.68, 916.2 (broad m, *P*–O–C), 883.27 (m, P–O–*C*); MS (CI, isobutane) *m*/*z*: 455.4 [$M^+ + 1$, 29.24%]; 371.3 [$M^+ - Cy$, 96.26%]; 289.1 [$M + 1 - 2Cy$, 38.25%]; 241.2 (100%); 215.2 (54.86%); HRMS: (CI, isobutane, [M^{+1}]) $C_{26}H_{49}O_2P_2$, Calc.: 455.32078. Found: 455.32122.

2.1.2. $^iPr_2POCH_2CH_2OP^iPr_2$ (1b)

^{i}Pr$_2$PCl (5.0 ml, $d = 0.959$ g ml^{-1}, 0.031 mol) and 30 ml of THF was placed into a 250-ml Schlenk flask attached to a 250-ml pressure equalizing funnel. NEt_3 (9.5 ml, $d = 1.113$ g ml^{-1}, 0.068 mol) followed by 30 ml of THF was then syringed into the flask. The addition funnel was next charged with 0.8 ml ($d = 1.113$ g ml^{-1}, 0.014 mol) of ethylene glycol and 30 ml of THF. The flask was placed into a −7 °C bath and allowed to stir for 20 min. The ethylene glycol solution was then added dropwise with stirring over a period of 50 min. The flask was removed from the bath and the reaction mixture was allowed to warm to r.t. and stirred overnight. The THF was removed via distillation and 60 ml of benzene was introduced. The resultant mixture was filtered in an inert atmosphere. The benzene was removed from the filtrate via distillation. The resulting clear oil was then transferred to a 10-ml round-bottom flask in a nitrogen filled glove box. Distillation of this oil at 98–100 °C/0.5 mm afforded 3.7 g of a clear liquid. Yield: 87.6%; ^{1}H-NMR (δ, d_6-benzene): 3.79 (m, 4H, $-CH_2CH_2-$), 1.6 (m, 4H, $-CH(CH_3)_2$), 1.08 (m, 12H, $-CH(CH_3)_2$), 0.94 (m, 12H, $-CH(CH_3)_2$); ^{31}P{^{1}H}-NMR (δ, d_6-benzene): 154.6 (s); ^{13}C{^{1}H}-NMR (δ, d_6-benzene): 77.3 (dd, $^2J_{PC} = 20.1$ Hz, $^3J_{PC} = 7.3$ Hz, $-OCH_2CH_2O-$), 28.0 (m), 17.6 (m), 16.7 (m); IR (benzene, cm^{-1}): 919.4 (m, *P*–O–C), 877.6 (s, P–O–*C*); MS (FAB, mnba) *m*/*z*: 295.2 [$M^+ + 1$, 5.08%]; [$M^+ - {}^i$Pr, 100%]; 161.3 [$M^+ - OP^iPr_2$, 34.95%].

2.1.3. $Ph_2POCH_2CH_2OPPh_2$ (1c)

Ph_2PCl (5 ml, $d = 1.229$ g ml^{-1}, 0.027 mol), NEt_3 (12.0 ml, 0.082 mol), and THF (60 ml) were placed into a 250-ml Schlenk flask equipped with an addition funnel. A mixture of 30 ml of THF and 0.71 ml (0.013 mol) of ethylene glycol was added to the addition funnel. The flask was cooled in an ice bath for 10 min, then the glycol solution was added dropwise with stirring over 1.5 h. The reaction mixture was allowed to stir in the ice bath for 1 h, after which the bath was removed. The solvent and triethylamine were distilled off and 60 ml of benzene was introduced. ^{31}P{^{1}H}-NMR analysis showed that 75% of the phosphorus containing product was the bisphosphinite **1c**. The solution was filtered under nitrogen using a fritted Schlenk flask. The filtrate was collected and the solvent and most impurities were removed via distillation under reduced pressure (0.2 mmHg). This gave a viscous oil pure enough for ^{1}H- and ^{31}P-NMR analysis. ^{1}H- and ^{31}P-NMR chemical shifts were identical to literature values [20]. This sample was used in subsequent steps without further purification. Yield: 75%; ^{1}H-NMR (δ, d_6-benzene): 7.54 (t, 8H, Ph), 7.00–6.95 (m, 12H, Ph), 3.77 (m, 4H, $-CH_2CH_2-$); ^{31}P{^{1}H}-NMR (δ, d_6-benzene): s, 115.8.

2.1.4. Attempted synthesis of $Et_2POCH_2CH_2OPEt_2$ (1d)

Et_2PCl (5.4 g, 0.043 mol), NEt_3 (13.0 ml, 0.093 mol) and 60 ml of THF were added to a 250-ml Schlenk flask fitted with a 250-ml addition funnel. Ethylene glycol (1.1 ml, $d = 1.113$ g ml^{-1}, 0.020 mol) and 40 ml of THF were added to the addition funnel. The contents of the flask were allowed to cool in a −7 °C bath and were stirred for 20 min. The ethylene glycol solution was then added dropwise with stirring, over a period of 2.5 h. The solution was allowed to warm to r.t. and was stirred overnight. The THF was removed via distillation. Benzene (60 ml) was introduced and the solution was filtered under an inert atmosphere. The benzene was subsequently removed by distillation. The resulting clear oil was then transferred in the glove box, into a 10-ml round bottom flask. Three products—as indicated by three phosphorus resonances—were not isolable via short path distillation. The compounds that corresponded to ^{31}P-NMR resonances at 141.6 and −32.41 ppm could be purified enough for spectroscopic identification (each ∼90% pure). The other ^{31}P-NMR resonance was at −6.61 ppm. The peak at −32.41 is assigned as Et_2PPEt_2. B.p. 27–30 °C/0.3 mm, lit. [21] 55–60 °C/1 mm; ^{1}H-NMR (δ, d_6-benzene): 1.42 (m, 8H, $-CH_2-$), 1.05 (q, 12H, $-CH_3$), lit. [21] 1.42 (m, CH_2), 1.07 (q, CH_3); ^{31}P-NMR (δ, d_6-benzene): −32.41, lit. [19] −32.70. The compound with the ^{31}P resonance at 141.6 ppm was assigned as $Et_2POCH_2CH_2OPEt_2$; b.p. 54–85 °C/1.4 mm; ^{31}P-NMR (δ, d_6-benzene): 141.6 ppm.

2.1.5. Attempted synthesis of $^tBu_2POCH_2CH_2OP^tBu_2$

^{t}Bu$_2$PCl (5 ml, $d = 0.951$ g ml^{-1}, 0.028 mol) was syringed into a 100-ml Schlenk flask attached to a pressure equalizing funnel. NEt_3 (7.3 ml, $d = 0.728$ g ml^{-1}, 0.053 mol) was then syringed into the flask followed by 40 ml of THF. Ethylene glycol (0.67 ml,

$d = 1.113$ g ml^{-1}, 0.012 mol) followed by 10 ml of THF was then introduced into the addition funnel. The flask was placed into an ice bath and the reaction mixture allowed to cool with magnetic stirring for 15 min. The ethylene glycol solution was added dropwise over a period of 10 min and the reaction mixture was allowed to stir for an additional one h at 0 °C. The bath was removed and the solution was stirred for an additional 24 h. At this point no reaction had occurred. The solution was further heated to 70 °C for 5 h and still there was no reaction. Finally, the flask was heated at 130 °C for 9–12 h (the NEt_3 and THF had boiled off). A tan oil with a solid precipitate resulted. The sample was put under vacuum to remove any remaining volatiles. A white waxy oil resulted. Hexane was added and the solid was filtered. The solid was washed with hexane and dried on the frit. We assigned this solid as $^tBu_2P(O)H$ on the basis of ^{31}P-NMR, ^{1}H-NMR, and mass spectral analysis. Yield: 1.4 g (31%) ^{1}H-NMR (δ, $CDCl_3$): 1.25 (d, $^3J_{PH} = 15.2$ Hz, 2^{t}Bu), 6.05 (d, $^1J_{PH} =$ 428 Hz); ^{31}P-NMR (δ, $CDCl_3$): 67.4 (s); MS (EI, 70 eV) m/z 162 [M^+], 106 [$M^+ -$ butylene], 57 (^{t}Bu, 100%).

2.1.6. $Cy_2P(O)CH_2CH_2(O)PCy_2$ (2a)

$Cy_2POCH_2CH_2OPCy_2$ (4.89 g, 0.011 mol) was placed into a 100-ml Schlenk flask under N_2 and, with stirring, was heated at 250 °C for 14 h. Upon cooling, a white solid had formed. The solid was washed and sonicated with wet benzene and deionized H_2O, and then filtered on a medium frit in the atmosphere. Drying at 45 °C/0.06 mm for 10 h gave 4.56 g of the white solid product. Yield: 93.3%; m.p.: 194–195 °C; ^{1}H-NMR (δ, d_6-benzene): 2.20–0.85 (broad multiplet), 2.02 (s, $-CH_2CH_2-$); $^{31}P\{^1H\}$-NMR (δ, $CDCl_3$): 51.9 (s); $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$): 37.2–36.2 (m, P–CH_2), 26.5 (t, cyclohexyl), 26.9 (d, cyclohexyl), 25.6 (s, cyclohexyl), 16.0–15.0 (m, P–C–$H_{cyclohexyl}$); IR (benzene, cm^{-1}): 2936.3 (s), 2858.7 (s), 1447.6 (w), 1265.2 (m), 1153.0 (w), 854.86 (m), 824.85 (w), 735.88 (s), 705.22 (s); MS (EI, 70 eV) m/z: 454.3 [M^+, 9.62%], 371.2 [$M^+ -$ Cy, 87.98%], 290.1(39.8), 289.1(100.00%), 241.2 [$M^+ - OPCy_2$, 81.71%], 207.1 (16.21%); HRMS: $C_{26}H_{48}O_2P_2$, Calc.: 454.3130. Found: 454.3117.

2.1.7. $^iPr_2P(O)CH_2CH_2(O)P^iPr_2$ (2b)

$^iPr_2POCH_2CH_2OP^iPr_2$ (1.27 g, 0.0043 mol) was placed into a 25-ml Schlenk flask with a magnetic stirring bar under nitrogen. The product was heated with stirring at 245 °C overnight. The resulting oily solid was crystallized from benzene/pentane to yield 1.1 g of a white fluffy solid. Yield: 87%; m.p.: 105.5–106.2 °C; ^{1}H-NMR (δ, d_6-benzene): 1.84 (d, 4H, $-CH_2CH_2-$), 1.60– 1.45 (br m, 4H, $-CH(CH_3)_2$), 1.0–0.8 (two multiplets, 12H, $-CH_3$); $^{31}P\{^1H\}$-NMR (δ, d_6–benzene): 53.3 (d); $^{13}C\{^1H\}$-NMR (δ, d_6-benzene): 26.5–25.4 (m, $-CH_2CH_2-$), 16.0–14.5 (m, ^{i}Pr); IR (benzene, cm^{-1}): 2964.3 (s), 2938.6 (m), 2899.9 (m), 2876.1 (s), 1462.7 (w), 1452.2 (w), 1415.2 (w), 1385.6 (w), 1367.9 (w), 1261.2 (w), 1188.1 (m), 1157.3 (w), 926.88 (w), 882.77 (s), 740.48 (s); MS (EI, 70 eV) m/z: 294.2 [M^+, 8.82%]; 251.2 [$M^+ -$ ^{i}Pr, 100%]; 209.1 (95.66%); 161.1 [$M^+ - OP^iPr_2$, 97.15]; HRMS: $C_{14}H_{32}O_2P_2$, Calc.: 294.1878. Found: 294.1891.

2.1.8. $Ph_2P(O)CH_2CH_2(O)PPh_2$ (2c)

$Ph_2POCH_2CH_2OPPh_2$ was heated overnight, with stirring, in a 100-ml Schlenk flask at 250 °C under nitrogen. The resulting oily solid was dissolved in CH_2Cl_2. Addition of pentane precipitated 0.5 g of a white fluffy solid. Yield: 9.1%; m.p.: 263–264 °C; ^{1}H-NMR (δ, $CDCl_3$): 7.71 (m, 8H, C–$H_{aromatic}$), 7.51 (t, 4H, C–$H_{aromatic}$), 7.43 (t, 8H, C–$H_{aromatic}$), 2.53 (d, 4H, $-CH_2CH_2-$); $^{31}P\{^1H\}$-NMR (δ, $CDCl_3$): 33.5 (s); $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$): 132.0 (s, phenyl), 130.8 (m, phenyl), 128.8 (m, phenyl), 22.4–21.2 (m, $-CH_2CH_2-$); MS (EI, 70 eV) m/z: 429.1(2.38), 354.1(40.43), 353.1(100.00), 337.1(25.85), 229.1(72.78), 201.1(34.61); HRMS: $C_{26}H_{24}O_2P_2$, Calc.: 430.1252. Found: 430.1252.

2.1.9. $Cy_2PCH_2CH_2PCy_2$ (3a)

$Cy_2P(O)CH_2CH_2(O)PCy_2$ (6.13 g, 0.013 mol) was placed into a 500-ml Schlenk flask equipped with a reflux condenser. Xylene (250 ml) was syringed into the flask, followed by $HSiCl_3$ (13.6 ml, $d = 1.3417$ g ml^{-1}, 0.13 mol). The mixture was heated at 155 °C for 18 h. The xylene was removed via distillation and the flask was heated at 120 °C for 10–20 min in vacuo. Approximately 90 ml of benzene was syringed into the flask. The mixture was cooled in a NaCl/ice bath and stirred for 15 min. A degassed 20% NaOH solution (50 ml) was then introduced via syringe. The bath was removed and the mixture was stirred for an additional 6 h at r.t. Two layers had formed. The benzene layer was cannulated into a dry Schlenk flask containing $MgSO_4$. The mixture was stirred at r.t. for 6–12 h. The solution was then filtered and the solvent removed in vacuo yielding 5.12 g of a crude white solid. Sublimation at 135 °C/0.06 mm gave 4.61 g of a pure white product. Yield: 81%; m.p.: 96–97 °C lit. [16a] 96–97 °C; ^{1}H-NMR (δ, d_6-benzene) 2.0–1.0 (broad m); $^{31}P\{^1H\}$-NMR (δ, d_6-benzene) 1.84 (s).

2.1.10. $^iPr_2PCH_2CH_2P^iPr_2$ (3b)

A 250-ml Schlenk flask, with a coiled reflux condenser attached, was charged with 1.0 g (0.0034 mol) of $^iPr_2(O)PCH_2CH_2(O)P^iPr_2$ in a nitrogen-filled dry box. A magnetic stirring bar was placed into the flask. The setup was then connected to a Schlenk line under nitrogen. Toluene (50 ml) was then syringed into the flask followed by $HSiCl_3$ (5.0 ml, $d = 1.3417$ g ml^{-1}, 0.050 mol). The solution was stirred 34 h at 130 °C in an oil bath. The reaction flask was then cooled in an ice

bath and 75 ml of 20% aqueous NaOH was syringed into the flask slowly. The resulting mixture was stirred at r.t. for 10 h. The toluene layer was decanted via a cannula into a 100-ml Schlenk flask. The aqueous layer was washed with two 20-ml aliquots of benzene. Each portion of benzene was cannulated into the toluene solution. The solvent was removed via distillation yielding a clear liquid. This liquid was transferred in a nitrogen filled glove box, into a 25 ml round bottom flask and fractionally distilled at 91.5 °C (0.5 mmHg) to yield 0.71 g of a clear liquid product. Yield: 80%; ^{1}H-NMR (δ, d_6-benzene) 1.54 (m, 8H, $-CH_2CH_2-$ and 4P–C–*H*), 0.97 (m, 24H, $8CH_3$), lit. [16d] (δ, d_6-benzene) 1.65 septet, 1.62 (d (second-order)), 1.10 dd, 1.07 dd; ^{31}P-NMR (δ, d_6-benzene) 9.87 (s), lit. [16d] (δ, d_6-benzene) 8.7 (s) relative to $P(OMe)_3$ at 141.0 ppm.

2.1.11. $Ph_2PCH_2CH_2PPh_2$ (**3c**)

$Ph_2(O)PCH_2CH_2(O)PPh_2$ (0.4 g, 0.001 mol)), $HSiCl_3$ (1.0 ml, $d = 1.3417$ g mol^{-1}, 0.010 mol), and 30 ml of toluene were added to a 50-ml Schlenk flask equipped with a coiled reflux condenser. The suspension was heated for 12 h at 145 °C. The flask was next placed into an ice bath. The solution was then quenched with 30 ml of 20% aqueous NaOH and allowed to stir overnight. The organic layer was cannulated into a 50-ml Schlenk flask containing $MgSO_4$. Filtration followed by removal of solvent yields 0.31g (84%) white solid. Yield: 84%; m.p.: 144–146 °C lit. [22] 143–144 °C; ^{1}H-NMR (δ, d_6-benzene) 7.30–7.23 (broad m, 8H), 6.97–6.93 (m, 12H), 2.16 (s, 4H); ^{31}P-NMR (δ, d_6-benzene) -12.00(s).

3. Results and discussion

3.1. Reaction of ethylene glycol with chlorophosphines

Typically, alkoxyphosphines can be easily prepared by reacting a chlorophosphine with an alcohol in the presence of a base [23]. Correspondingly, the synthesis of bisphosphinites **1a**–**d** (Eq. (1)) was attempted from the addition of ethylene glycol to the corresponding diorganochlorophosphine in the presence of triethylamine. In most cases, the addition of ethylene glycol was performed at 0 °C and the reaction mixture was subsequently allowed to warm to room temperature. Results are summarized in Table 1.

The bisphosphinites **1a**–**d** were produced in good spectroscopic yields, although only **1a** and **1b** could be obtained as analytically pure materials. No reaction occurs when the bulky di-*t*-butylchlorophosphine is employed at temperatures between 0 and 70 °C. When heated at temperatures greater than 130 °C (in the absence of base-NEt_3 boils at 89 °C), ^{t}Bu$_2$PCl is converted, not to the bisphosphinite, but to ^{t}Bu$_2$P(O)H.

The pure bisphosphinites **1a** and **1b** are soluble in typical organic solvents including ether, THF, and benzene. Both compounds are also very sensitive to moisture and oxygen: the liquid isopropyl (**1b**) derivative has a strong stench and will ignite paper in the presence of oxygen. Spectroscopic data are completely consistent with the ascribed structures. The IR data assignment is based on IR data for monophosphites. The range of frequencies for the monophosphites [24] is $\nu_{((P)-O-C)} = 1050–960$ cm^{-1} and $\nu_{(P-O-(C))} = 805–775$ cm^{-1}. The dicyclohexyl- (931.68, 916.2 and 883.27 cm^{-1}) and diisopropyl bisphosphinite (919.4 and 877.6 cm^{-1}) frequencies are towards the middle of the two ranges.

The nature of the reaction between ethylene glycol and the chlorophosphine is greatly dependent on the substituents on the chlorophosphine. In particular, the steric bulk of the phosphine significantly affects both the rate of reaction as well as the product distribution. As expected, chlorophosphines with larger organic substituents tended to react slower than those containing less sterically hindering groups. The overall rate of reaction of R_2PCl with $HOCH_2CH_2OH$ in the presence of triethylamine follows the order Et > ^{i}Pr ≈ Ph > Cy > ^{t}Bu (no phosphinite formed).

The reaction of ethylene glycol with diethylchlorophosphine resulted in the immediate formation of three

Table 1
Reaction of ethylene glycol with chlorophosphines

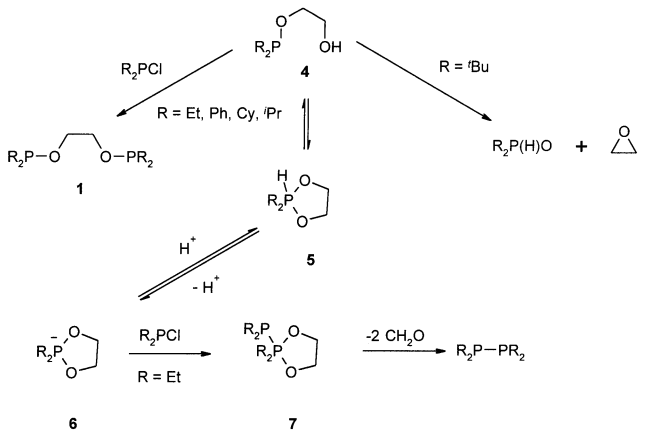
R	Conditions (reaction time, initial → final temperature)	Products	^{31}P-NMR (C_6D_6, δ, ppm relative to 85% H_3PO_4)	Isolated yield (%)
tert-Butyl	8–24 h, >130 °C	^{t}Bu$_2$P(O)H (major)	67.2	31
Cyclohexyl	24–36 h, −78 → 25 °C	$Cy_2POCH_2CH_2OPCy_2$ (**1a**)	149.7	98.7
Phenyl	8–24 h, −78 → 25 °C	$Ph_2POCH_2CH_2OPPh_2$ (**2a**)	115.8	75 [a]
Isopropyl	8–24 h, −78 → 25 °C	$^i Pr_2POCH_2CH_2OP^iPr_2$ (**3a**)	154.6	87.6
Ethyl	2–4 h, −78 → 25 °C	$Et_2POCH_2CH_2OPEt_2$ (**4a**)	141.6	NA [b]
		Et_2PPEt_2	−32.4	
		Unidentified product	−6.6	

[a] Not isolated. The yield of the phenyl derivative was obtained by ^{31}P{^{1}H}-NMR.
[b] Not applicable. Unable to isolate as a pure material. ^{31}P{^{1}H}-NMR yield was variable.

major products (^{31}P-NMR resonances at 141.6, −6.61 and −32.4 ppm, relative to H_3PO_4). These compounds could not be separated satisfactorily by distillation although fractions could be obtained which were enriched (>90%) in either the 141.6 ppm or the −32.4 ppm component. We assign the resonance at 141.6 ppm to the bisphosphinite **1d** on the basis of its ^{31}P-NMR chemical shift value which is very similar to the values of the isolated derivatives **1a** (149.7 ppm) and **1b** (154.6 ppm). The resonance at −32.4 ppm is assigned to Et_2PPEt_2 on the basis of physical properties and ^{31}P- and ^{1}H-NMR spectroscopy of a purified (>90%) fraction (comparison with literature data are shown in Section 2) [21]. The compound corresponding to the ^{31}P resonance at −6.61 ppm, which is not directly coupled to a proton, has not yet been definitively assigned.

The ratio of products depends upon the relative concentration of Et_2PCl and ethylene glycol during the reaction as well as the rate of addition. When there is an excess of Et_2PCl and ethylene glycol is added slowly (~1–2 h), the major product (>80% by ^{31}P-NMR) is $Et_2POCH_2CH_2OPEt_2$. The other two products are always present with Et_2PPEt_2 being from two to ten times more prevalent than the −6.61ppm product. If the addition order is reversed and an equimolar amount of Et_2PCl is added to ethylene glycol, Et_2PPEt_2 now becomes the major product (from 60 to 75%). The −6.61 ppm species is present as 25–30% of the phosphorus-containing product while less than 10% is $Et_2POCH_2CH_2OPEt_2$.

A general explanation of the product distribution resulting from the reaction of ethylene glycol with chlorophosphines is summarized in Scheme 1. In all cases, we believe that the initial reaction step is the condensation of one equivalent of chlorophosphine with ethylene glycol to give the corresponding monophosphinite (**4**). The fate of this key intermediate is expected to be strongly dependent on the steric bulk of the reacting chlorophosphine. For instance, the monophosphinite (**4**) may further react with chlorophosphine in the presence of NEt_3 to afford the expected bisphosphinite (**1**) or, alternatively, may undergo an intramolecular cyclization to give the σ^5,λ^5-1,3,2-dioxaphospholane (**5**). In the presence of triethylamine, the dioxaphospholane **5** is probably in equilibrium with its conjugate base (**6**).



Scheme 1. Proposed mechanism for the reaction of chlorophosphines with ethylene glycol.

The nucleophilic dioxaphospholane anion (**6**) is likely responsible for P–P bond formation in the case where R = Et. The reaction of **6** with excess Et_2PCl would give the λ^3-λ^5-diphosphine phospholane (**7**). Similar reactions of pentacoordinate hydridophophoranes with chlorophosphines in the presence of triethyamine to give λ^3-λ^5 diphosphines have been reported previously [25].

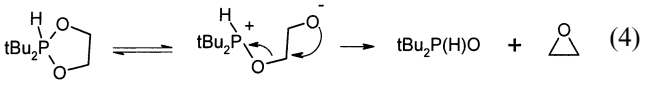
The formation of Et_2PPEt_2 is likely the result of a retrocyclic fragmentation of the dioxaphopholane ring to give two equivalents of formaldehyde along with the diphosphine. The reverse process is a common reaction of hexafluoroacetone with phosphines to give σ^5,λ^5-1,3,2-dioxaphospholanes [26]. Recently, the reaction of a diazaphosphorinone with hexafluoroacetone was found to be fully reversible at room temperature [27] Other similar retrocyclic processes have observed for perfluoropinacol orthosulfites [28] and the photochemical fragmentation of transition metal pinacolates [29].

Only for the case of R = Et does the bimolecular reaction of **4** to give **1** appear to be competitive with the pathway which ultimately leads to the diphosphine, Et_2PPEt_2. The existence of a competitive pathway is supported with the observation that at high Et_2PCl to ethylene glycol ratios, the bisphosphinite **1d** is favored whereas if the ratio is low, the formation Et_2PPEt_2 becomes the prominent process. For the case of larger substituents on phosphorus, only the bimolecular pathway is observed. This may be due to either the inability of the monophosphinite **5** to form the dioxaphospholane **6**, or possibly due to the attenuation of the P–P bond formation reaction **6**→**7**. The conversion of **6** to **7** should be particularly sensitive to the steric environment at phosphorus.

The formation of $^tBu_2P(O)H$ from the reaction of ethylene glycol with $^tBu_2PCl$ is also readily explainable from the phospholane intermediate, **4** (Scheme 1). In this case, the extreme bulkiness of the *t*-butyl group appears to shut down all bimolecular pathways in favor of a unimolecular elimination reaction at higher temperatures. Elimination of ethylene oxide from 2,2,2-triphenyl-1,3,2-dioxaphospholanes has been previously observed to afford phosphine oxides [30]. This elimination has been proposed to occur through the open chain betaine isomer of the dioxaphospholane. The reaction sequence shown in Eq. (4) is therefore likely responsible for the formation of the di-*t*-butylphosphine oxide.

Table 2
Formation of bisphosphine oxides from thermolysis of bisphosphinites

R	Conditions	M.p. (°C)	^{31}P-NMR (δ, ppm relative to 85% H_3PO_4)	Isolated yield (%)
Cyclohexyl (**2a**)	230–260 °C, 12–18 h	194–195	51.9 (d_6-benzene)	93.3
Phenyl (**2c**)	190 °C, 10–16 h	263–264	33.5 ($CDCl_3$)	9.1
Isopropyl (**2b**)	220–235 °C, 10–34 h	105.2–106.2	53.3 (d_6-benzene)	87.0



(4)

3.2. Isomerization of bisphosphinites to bisphosphine oxides

The Michaelis–Arbuzov rearrangement (P–O–C→P(=O)–C) of alkoxyphosphines is an excellent non-organometallic route for the formation of phosphorus–carbon bonds. The reactions occur at elevated temperatures and may be catalyzed by iodine or alkyl iodides. The iodine-catalyzed thermal rearrangement of aryl-substituted bisphosphinites to generate bisphosphine oxides has been reported to occur at temperatures between 150 and 160 °C. We have found that the isomerization of the bisphosphinites **1a** and **1b** to give **2a** and **2b**, respectively, efficiently occurs after heating the melt (without catalyst) at 190–260 °C for 24 h (Eq. (2)). Results are tabulated in Table 2.

Although the yields of **2a** and **2b** were high, the yield of the phenyl derivative **2c** was only 9.1%. Although we have no explanation for this difference, low yields have also been observed for similar isomerizations of diphenyl phosphinites. Brunner and Zettlmeir synthesized several bis(diphenylphosphine oxides) from the thermal isomerization of the corresponding bis(-diphenylphosphinites) using iodine as a catalyst [18]. Yields of only 31–39% were reported.

The cyclohexyl and phenyl derivatives are stable to air and moisture, while those with the diisopropyl group are quite reactive. All derivatives are soluble in methylene chloride and chloroform. The dialkyl derivatives **2a** and **2b** are also partially soluble in benzene.

The thermal isomerization of **1a** and **1b** was examined by differential scanning calorimetry (DSC). DSC curves for **1a** and **1b** are shown in Figs. 1 and 2, respectively. The DSC curve for the cyclohexyl derivative (**1a**) shows a sharp melting point at 78.2 °C and a broad exotherm with a peak maximum at 267.1 °C. This broad exotherm corresponds to the heat of isomerization, ΔH_{iso}, which was calculated to be -40.4 ± 0.6 kcal mol^{-1}. The DSC curve of the isopropyl derivative (**1b**) also shows a broad endotherm with a peak minimum at 101.0 °C. We speculate that this may be a boiling point at the unknown pressure in the container. The broad exotherm centered at 268.8 °C corresponds to the isomerization process. Quantitative determination of ΔH_{iso} for the liquid isopropyl derivative (**1b**) was not possible due to its volatility and unavoidable escape of vapor from the sample container.

Thermal analysis of the isomerization of simple monophosphinites has been reported previously [31]. The temperature at which isomerization begins (approximately 220 and 230 °C for cyclohexyl and isopropyl derivatives, respectively) is nearly the same as that (230–250 °C) of monophosphinites [31a]. No determination of the enthalpy of isomerization of the monophosphinites was reported.

The DSC data do not distinguish between a concerted isomerization process involving both phosphorus centers simultaneously and a fast stepwise process that gives overlapping DSC peaks.

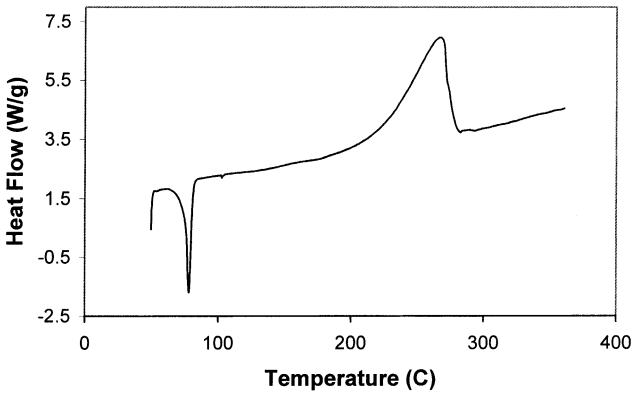


Fig. 1. DSC for the isomerization of $Cy_2POCH_2CH_2OPCy_2$. Heat flow (vertical axis) is expressed in terms of W g^{-1}.

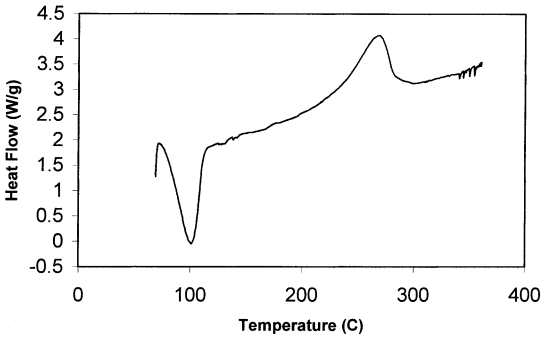


Fig. 2. DSC analysis for the isomerization of $^{i}Pr_2POCH_2CH_2OP^{i}Pr_2$. Heat flow (vertical axis) is expressed in terms of W g^{-1}.

3.3. Reduction of bisphosphine oxides with trichlorosilane

The reduction of phosphine oxides with trichlorosilane is a well-established method of generating phosphines [32]. Usually these reductions are done in the presence of a base, generally triethylamine or pyridine. We have found that the use of these bases results in a more difficult work-up and lower product yield, therefore trichlorosilane was used without a base. Under these conditions, yields between 80 and 84% were obtained for **3a**–**3c**.

A special workup of **3a** and **3c** was necessary to ensure high yields. Before quenching with aqueous NaOH, toluene was removed by distillation and the mixture was consequently heated under vacuum to remove any remaining volatile silanes or siloxanes. When this reduced pressure step was not included, a 30–60% drop in yield occurred. This reduced pressure step was not necessary for the isopropyl derivative, **3b**. As a consequence, 1,2-bis(diisopropylphosphino)ethane (**3b**) could be distilled directly from the impurities after quenching and removal of solvent. Attemped reduction of the bisphosphine oxides with $LiAlH_4$ [33] and $PhSiH_3$ [34] were unsuccessful due to the apparent inertness of the bisphosphine oxides to these reagents.

4. Conclusions

A potential three-step synthesis of symmetric chelating bis(phosphino)ethane ligands was examined. The first step involves the reaction of ethylene glycol with a dialkylchlorophosphine to give a bisphosphinite; the second step, a thermal Michaelis–Arbuzov rearrangement of the bisphosphinite to give a bisphosphine oxide; and finally, the reduction of the bisphosphine oxide by trichlorosilane to give the bisphosphine. In the first step, the reactivity of R_2PCl to ethylene glycol was directly related to the steric bulk of the alkyl group and follows the expected order $R = Et > Ph \cong {}^{i}Pr > Cy > {}^{t}Bu$. Most importantly, the yield of the expected bisphosphinite was highly dependent on the nature of the alkyl group. For the smallest alkyl group examined (Et), a competitive reaction gives Et_2PPEt_2 as an ubiquitous side-product. For the largest alkyl group (^{t}Bu), an elimination reaction to give $^{t}Bu_2P(O)H$ was found to predominate. Only for organic groups of intermediate size (R = Ph, ^{i}Pr, Cy) was the expected bisphosphinite formed in good yields.

Thermolysis of the three bisphosphinites (R = Ph, ^{i}Pr, Cy) gave high yields of the bisphosphine oxide only for the case of the alkyl-substituted derivatives. Reduction of all three bisphosphine oxides, however, proceeded smoothly to give the corresponding bisphosphines.

The synthetic procedure described in this paper, although very sensitive to the substituent on phosphorous, nevertheless gave very good overall yields for 1,2-bis(diisopropylphosphino)ethane (61%) and 1,2-bis(dicyclohexylphosphino)ethane (75%). For these bisphosphine ligands, this procedure offers an extremely attractive alternative to previously reported synthetic methods.

Acknowledgements

The Tulane Center for Bioenvironmental Research (DSWA) is gratefully acknowledged for financial support of this work. We also thank Aldrich Chemical for gifts of phosphines, and David Bostwick and Sarah Shealy of Georgia Institute of Technology for their assistance with mass spectrometry.

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