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UNSYMMETRICAL BIS-PHOSPHORUS LIGANDS

VIII*. SYNTHESIS OF AN ω-DIPHENYLPHOSPHINOALKYL GRIGNARD REAGENT, ITS PRECURSOR AND NOVEL DERIVATIVES

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Summary

Syntheses of the chloroalkyldiphenylphosphines, $Cl(CH_2)_nP(C_6H_5)_2$ (n = 1, 2, or 3) in high yields are reported. Reaction of magnesium with $Cl(CH_2)_2P(C_6H_5)_2$ is followed by β-elimination to produce C_2H_4 and $(C_6H_5)_2P^-$. However, formation of the Grignard reagent from $Cl(CH_2)_3P(C_6H_5)_2$ occurs normally. This Grignard reagent reacts in the expected manner with CO_2, $(C_6H_5)_3SnCl$ and $(CH_3)_2PCl$, the latter forming an unsymmetrical bis-tertiary phosphine ligand $(C_6H_5)_2P(CH_2)_3P(CH_3)_2$. Other unsymmetrical bis-tertiary phosphine ligands of the series, $(C_6H_5)_2P(CH_2)_3P(C_6H_5)R$, where R = CH_3, C_2H_5, and i-C_3H_7, were prepared from $R(C_6H_5)PLi$ and the 3-chloropropyldiphenylphosphine.

Introduction

We report a straight forward synthesis, in high yield, of the useful intermediates, ω-chloroalkyldiphenylphosphines, $(C_6H_5)_2P(CH_2)_nCl$ (n = 1, 2, or 3); the first reported example of a phosphinoalkyl Grignard reagent, viz. $(C_6H_5)_2P(CH_2)_3MgCl$; and a new series of unsymmetrical bis-tertiary phosphine chelating ligands, $(C_6H_5)_2P(CH_2)_3PR^1R^2$ (R^1 = C_6H_5, R^2 = CH_3, C_2H_5, and i-C_3H_7; R^1 = R^2 = CH_3), prepared via the above compounds.

Two of the chloralkyldiphenylphosphines, $(C_6H_5)_2PCH_2Cl$ [1] and $(C_6H_5)_2P(CH_2)_2Cl$, [2,3] were previously prepared in poor yield (10 and 9%, respectively). Cloyd and Meek [4] reported a higher yield (80%) of the chloroethyl compound but were unable to isolate it. Similar compounds of arsenic have been reported, e.g., $(C_6H_5)_2As(CH_2)_2Cl$ [5], $(C_6H_5)_2AsCH{=}CHCl$ [6], and $(CH_3)_2As(CH_2)_3Cl$ [7]; the Grignard reagent of the latter has been used to synthesize a variety of multidentate ligands [7,8].

* For part VII see ref. 20.

Results and discussion

The three homologous chlorides, $(C_6H_5)_2P(CH_2)_nCl$ (n = 1, 2, and 3) can be synthesized in good yield by the following sequence of reactions:

$$(C_6H_5)_3P + Na \xrightarrow[-78°C]{NH_3} (C_6H_5)_2PNa + NaC_6H_5$$

$$NaC_6H_5 + NH_4Cl \rightarrow NaCl + NH_3 + C_6H_6$$

$$(C_6H_5)_2PNa + Cl(CH_2)_nCl \xrightarrow[-78°C]{} (C_6H_5)_2P(CH_2)_nCl$$

In the case of dichloromethane, the $NaP(C_6H_5)_2$ is poured, in approximately 25 ml aliquots (ca. 0.5 M), into a large excess (200/1) of CH_2Cl_2. The product is formed in about 80% yield (based on ^{31}P NMR data for the crude reaction mixture) but was not isolated as a pure compound. It rapidly decomposes by quaternization or oxidation during various manipulations such as warming or attempted vacuum concentration. The product was identified and characterized by conversion to the known oxide [9] and the previously unreported sulfide $(C_6H_5)_2P(E)CH_2Cl$ (E = O or S).

The chloroethyl compound was prepared in the same manner (cf., Cloyd and Meek, [4] who used $KPPh_2$ in tetrahydrofuran). However, in this case, an excellent isolated yield (91%) of crystalline product, m.p. 40-42°C (lit. [2], 40-41°C), was obtained by crystallization of the concentrated crude reaction product from hot ethanol.

The chloropropyl derivative, a new compound, was prepared from $NaPPh_2$ and 1,3-dichloropropane (2 fold excess) dissolved in toluene at −78°C. The product is an oil which was converted to the oxide, $(C_6H_5)_2P(O)(CH_2)_3Cl$, for further characterization. The chloroethyl and chloropropyl compounds react with lithium diorganophosphides to produce unsymmetrical bis-tertiary phosphine chelate ligands, e.g.:

$$(C_6H_5)_2PCH_2CH_2Cl + LiP(C_6H_5)(CH_3) \rightarrow (C_6H_5)_2PCH_2CH_2P(C_6H_5)(CH_3)$$

This gives ready access by a two step synthesis to ligands which previously have been prepared only by a rather tedious route [10,11] for ethylene bridged ligands and not at all for the three carbon analogues.

Probably the most important observation is the synthesis of a Grignard reagent from the chloropropyl compound:

$$(C_6H_5)_2P(CH_2)_3Cl + Mg \xrightarrow[\text{or THF}]{Et_2O} (C_6H_5)_2P(CH_2)_3MgCl$$

We believe this represents the first instance of a Grignard reagent of a phosphinoalkyl compound. The few compounds reported which are most similar to this Grignard reagent include $Ph_2PC{\equiv}CMgBr$, prepared by Gilman and Brown [12], $Ph_2PC_6H_4MgX$-*o* prepared by Hart [13] and the previously mentioned $(CH_3)_2As(CH_2)_3MgCl$ [7,8].

The reaction is best initiated via a small amount of reacting $BrCH_2CH_2Br/Mg$ in THF, ideally when the reactants are present in >1M concentration and the reaction mixture is heated at reflux.

The Grignard reagent was characterized by reaction with CO_2/H^+, $(C_6H_5)_3SnCl$, and $(CH_3)_2PCl$ to give $(C_6H_5)_2P(CH_2)_3COOH$, m.p. 92-93°C (lit. [14], 97-98°C), 17%; $(C_6H_5)_2P(CH_2)_3Sn(C_6H_5)_3$, m.p. 74-75°C, 54%; and $(C_6H_5)_2P(CH_2)_3P(CH_3)_2$, an oil, ca. 50% respectively. The latter was identified as the disulfide $(C_6H_5)_2P(S)(CH_2)_3P(S)(CH_3)_2$, m.p. 126-127°C.

The reaction of $(C_6H_5)_2P(CH_2)_2Cl$ with Mg in THF visually appears to occur, however, the Grignard reagent could not be identified, presumably because of its facile β-elimination:

$$(C_6H_5)_2PCH_2CH_2MgCl \rightarrow (C_6H_5)_2P^- + CH_2{=}CH_2 + MgCl^+$$

Evidence for this is given by isolation of large amounts of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (diphos), m.p. 139-142°C (lit. [15], 141°C), from the reaction of $(C_6H_5)_2P^-$ with the starting chloroethyl compound. Also, the ^{31}P spectrum of the hydrolyzed reaction mixture always contained, in addition to the diphos peak at 13 ppm (lit. [16], 12.5), a doublet at δ 40.1 ppm, $J(PH) = 192$ Hz, (lit. [9], $\delta = 41.1$, $J(PH) = 214$) due to substantial amounts of diphenylphosphine from the hydrolysis of $(C_6H_5)_2P^-$.

Finally, as indicated above, the unsymmetrical bis-tertiary phosphines, $(C_6H_5)_2P(CH_2)_3PR^1R^2$, can be prepared by two routes: reaction of the chloropropylphosphine with lithium diorganophosphides; or, by reaction of the Grignard reagent with diorganochlorophosphines. The former is more convenient because of the easier accessibility of the lithium phosphides [17] over the phosphinous chlorides. However, the Grignard reagent should prove useful for incorporating other functional groups into the phosphino compound. Coordination studies of these novel ligands are in progress.

Experimental

^{31}P spectra were recorded on a Varian DP-60 Spectrometer at 24.3 MHz and are referenced to 85% H_3PO_4 (positive values are upfield from H_3PO_4). Elemental analyses were performed by Dr. Franz Kasler of this Department. All reactions were carried out under nitrogen.

Synthesis of $(C_6H_5)_2PCH_2Cl$ and derivatives

NH_3 (1l) was condensed at —78°C into a 2 l, 3-necked round bottomed flask fitted with a mechanical stirrer. To the flask was added with stirring 23 g (2.0 mol) of freshly cut sodium which had been washed in benzene. The intensely blue solution which formed immediately was stirred for 1 h to dissolve all the sodium. Triphenylphosphine (131 g, 0.50 mol) was then added over a 15 min period and the deep red solution was stirred for 1 h. Treatment with 25 g (0.47 mol) of NH_4Cl (dried overnight at 120°C) destroyed the C_6H_5Na formed as a cleavage product and after stirring for another hour an orange solution was obtained. This solution was then poured in approximately 25 ml portions over a period of 1 h into a cooled (—78°C) flask containing 600 ml CH_2Cl_2. The resulting cream colored solution was stirred overnight to effect evaporation of the ammonia. After washing with 400 ml of degased water, the organic layer was then dried over Na_2SO_4. The decanted clear liquid was warmed to 50°C under vacuum for one hour to remove excess CH_2Cl_2 *. The

* Caution: Maintenance of low pressure for extended periods results in decomposition.

resulting oil, approximately 75% yield based on ^{31}P peak areas (the remaining impurity was apparently oxide, see below), was refrigerated to prevent quaternerization and/or oxidation. The ^{31}P chemical shift of $(C_6H_5)_2PCH_2Cl$ is 9.6 ppm.

The oxide, $(C_6H_5)_2P(O)CH_2Cl$, was obtained from the above by stirring in acetone overnight at room temperature in an open flask. The ^{31}P chemical shift is —30.2 ppm (lit. [9], —30.4). The PMR spectrum had a small phenyl multiplet at δ 7.7-8.1 characteristic of phenyl groups attached to phosphoryl or thiophosphoryl groups [18], the remainder of the phenyl signal at δ 7.1-7.6 and the methylene doublet at δ 4.03 ppm (^2J(PH) = 5.0 Hz).

The sulfide, $(C_6H_5)_2P(S)CH_2Cl$ was precipitated from the phosphine by stirring in THF overnight with a slight excess of sulfur. Recrystallization from hot absolute ethanol resulted in a white powder, m.p. 58-59°C, δ(P) —42.7 ppm. Anal. Found: C, 59.35; H, 4.73. $C_{13}H_{12}ClPS$ calcd.: C, 58.54; H, 4.54%. The PMR spectrum displayed a phenyl multiplet at δ 7.4-8.2 and a doublet at δ 4.20 ppm (^2J(PH) = 6.0) for the methylene protons.

Synthesis of $(C_6H_5)_2P(CH_2)_2Cl$ and derivatives

Sodium diphenylphosphide (0.5 mol), prepared as above, was poured into a degassed solution of 100 ml (1.3 fold excess) of $ClCH_2CH_2Cl$ and 100 ml toluene at —78°C. Following overnight evaporation of the NH_3, 200 ml toluene was added to the mixture and it was then washed twice with 150 ml of degassed water. The organic layer was dried for 30 min over Na_2SO_4 and the solvents removed with a rotary evaporator at 100°C (water vacuum). A ^{31}P NMR spectrum of the clear solution showed peaks at 13 and 20 ppm of relative intensities 1/15 representing $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and $(C_6H_5)_2PCH_2CH_2Cl$ respectively. Addition of 400 ml of hot absolute ethanol and subsequent slow cooling gave a white precipitate which upon successive recrystallization from ethanol gave 98 g (79% yield) of pure $(C_6H_5)_2PCH_2CH_2Cl$, m.p. 40-41°C (lit. [2], 41-42°C), δ(P) = 19.8 ppm. PMR peaks are at δ 7.2-7.5 for phenyl, a complex multiplet at δ 3.4-3.8 due to the chloromethylene group and an unsymmetrical triplet of equal intensity due to the phosphinomethylene group at δ 2.5 ppm. Anal. Found: C, 68.06; H, 5.99; P, 12.43. $C_{14}H_{14}ClP$ calcd.: C, 67.61; H, 5.67; P, 12.47%.

The $(C_6H_5)_2P(CH_2)_2Cl$ in C_6H_6 solution was quaternized with excess CH_3Br in a pressure bottle. The resulting salt, $[(C_6H_5)_2(CH_3)P(CH_2)_2Cl]Br$, has a ^{31}P chemical shift at —23.0 ppm, which is in the expected region for phosphonium salts [19]. The methyl group appears as a doublet at δ 3.05 (^2J(PH) = 13.8 Hz) in the PMR spectrum. The methylene (δ 3.5-4.5 ppm) and phenyl (δ 7.5-8.2 ppm) regions are complex. The bromide was converted to the tetraphenylborate, $[(C_6H_5)_2(CH_3)P(CH_2)_2Cl][B(C_6H_5)_4]$, m.p. 146-5-148°C, by metathesis in CH_3OH. Anal. Found: C, 80.07; H, 6.65; P, 5.40; Cl, 6.04. $C_{39}H_{37}BClP$ calcd.: C, 80.35; H, 6.40; P, 5.31; Cl, 6.08%.

Synthesis of $(C_6H_5)_2P(CH_2)_2P(C_6H_5)(CH_3)$

Lithium methylphenylphosphide was prepared from 12 g (0.06 mol) of $(C_6H_5)_2PCH_3$ in 50 ml of THF by the published procedure [17]. This solution was added dropwise with stirring to a solution of 12.5 g (0.05 mol) of $(C_6H_5)_2P(CH_2)_2Cl$ in 100 ml of THF at room temperature. The red lithium phosphide

solution decolorized rapidly upon addition and therefore addition was stopped when the first permanent reddish orange color remained. The solution was washed with 150 ml of degassed H_2O, dried over Na_2SO_4 for 1 h, and concentrated by evaporation to a light tan oil, which contained no phosphorus impurities observable in the ^{31}P NMR spectrum. The product has chemical shifts of 13.5 and 31.7 ppm (lit. [10], 13.0 and 31.4).

Synthesis of $(C_6H_5)_2P(CH_2)_3Cl$ and derivatives

The propyl analog was synthesized in a manner similar to that described for the chloromethyl and chloroethyl phosphines; however, the $(C_6H_5)_2PNa$ (0.25 mol) was added to a cooled, degassed solution of 200 ml toluene and 60 g (0.53 mol) of $ClCH_2CH_2CH_2Cl$. Workup as before gave 60 g (93%) of a light yellow viscous oil of good purity as evidenced by PMR and NMR spectra. The ^{31}P chemical shift is 17.5 ppm. The PMR spectrum has a phenyl multiplet at δ 7.1-7.6, a sharp triplet (intensity 2) at δ 3.42 (^3J(HH) = 6.1 Hz) due to $—CH_2Cl$ and a multiplet at δ 1.5-2.3 ppm of intensity 4 due to the remaining methylene groups.

The oxide $(C_6H_5)_2P(O)CH_2CH_2CH_2Cl$ formed as a precipitate of large clear crystals from a batch of the above phosphine which had been allowed to stand for several months. The ^{31}P NMR chemical shift (—38.2 ppm) is in the normal region for tertiary phosphine oxides. The PMR spectrum has phenyl peaks at δ 7.7-8.2 and δ7.2 to 7.7 and the methylenes all appear indistinguishably at about δ 3.3 ppm. Anal. Found: C, 65.25; H, 5.78. $C_{15}H_{16}ClOP$ calcd.: C, 64.64; H, 5.79%.

The methyl quaternary salt $[(C_6H_5)_2(CH_3)P(CH_2)_3Cl]Br$, ($\delta$(P) = —24.5 ppm) was made as described above and converted to the tetraphenyl borate, $[(C_6H_5)_2(CH_3)P(CH_2)_3Cl]\,[B(C_6H_5)_4]$, m.p. 156-158°C. Anal. Found: C, 79.80; H, 6.65. $C_{40}H_{39}BClP$ calcd.: C, 80.48; H, 6.61%.

Synthesis of $(C_6H_5)_2P(CH_2)_3P(C_6H_5)(CH_3)$ and analogues

3-Chloropropyldiphenylphosphine (13 g, 0.05 mol) in 50 ml of THF was added dropwise with stirring at room temperature to $LiP(C_6H_5)(CH_3)$ in 200 ml of THF [prepared from Li and 0.05 mol of $(C_6H_5)_2(CH_3)P$]. The solution was washed with degassed water, dried over Na_2SO_4, and concentrated to a clear oil on a rotary evaporator. The crude product (28% yield) has ^{31}P NMR chemical shifts at 17.6 and 34.2 ppm, corresponding to the diphenylphosphino and methylphenylphosphino groups respectively.

Also prepared in this manner from $LiP(C_6H_5)(C_2H_5)$ and $LiP(C_6H_5)$ (i-C_3H_7) were $(C_6H_5)_2P(CH_2)_3P(C_6H_5)(C_2H_5)$ (41%, δ(P) = 17.4 and 21.8 ppm) and $(C_6H_5)_2P(CH_2)_3P(C_6H_5)$(i-$C_3H_7$) (65%, δ(P) = 18.0 and 9.5 ppm), respectively.

Synthesis of $(C_6H_5)_2P(CH_2)_3MgCl$ and its reactions

Magnesium (2.6 g, 0.11 mol) and 26.2 g (0.11 mol) of $(C_6H_5)_2P(CH_2)_3Cl$ were mixed in 100 ml of THF. The reaction mixture was heated to reflux and initiated with a small amount of reacting $BrCH_2CH_2Br$/Mg. Heating and stirring were continued for 1 h. The resulting red solution had a ^{31}P chemical shift of 17.0 ppm.

Reaction of the Grignard reagent with solid CO_2 gave after hydrolysis, acidification, and purification, $(C_6H_5)_2P(CH_2)_3COOH$, m.p. 92-93°C (lit. [14], 97-98°C), in 17% yield. The ^{31}P NMR chemical shift is 17.3 ppm.

Reaction of the Grignard reagent with $(C_6H_5)_3SnCl$ gave the expected product, $(C_6H_5)_2P(CH_2)_3Sn(C_6H_5)_3$, m.p. 74-75°, in 54% yield. It has a ^{31}P NMR chemical shift of 17.3 ppm. Anal. Found: C, 68.50; H, 5.42; P, 5.08. $C_{33}H_{31}PSn$ calcd.: C, 68.66; H, 5.41; P, 5.37%.

The Grignard reagent also reacted with $(CH_3)_2PCl$ by addition of the phosphinous chloride in THF to the Grignard reagent until the reddish color of the Grignard just disappeared. The solution was hydrolyzed with degassed water, dried over Na_2SO_4, and concentrated with a rotary evaporator to give a clear oil, $(C_6H_5)_2P(CH_2)_3P(CH_3)_2$, $\delta(P) = 16.9$ and 52.9 ppm. For further characterization, the oil was stirred with excess S overnight in THF. The white precipitate of $(C_6H_5)_2P(S)(CH_2)_3P(S)(CH_3)_2$, m.p. 126-127°C, $\delta(P) = -40.2$ (diphenyl) and −36.0 (dimethyl) ppm, weighed 11 g, and corresponded to a 38% yield of the ditertiary phosphine, assuming 100% conversion to the disulfide. The proton spectrum has a methyl doublet at δ 1.68 ($^2J(PH) = 13.1$ Hz), complex methylene multiplets at δ 1.9-3.1, and phenyl multiplets at δ 7.4-8.2 ppm. Anal. Found: C, 57.95; H, 6.53; P, 17.85. $C_{17}H_{22}P_2S_2$ calcd.: C, 57.93; H, 6.29; P, 17.58%.

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