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Preparation and Reactions of Functionalized Chlorodiorganophosphine-Borane Complexes Using Organozinc Reagents

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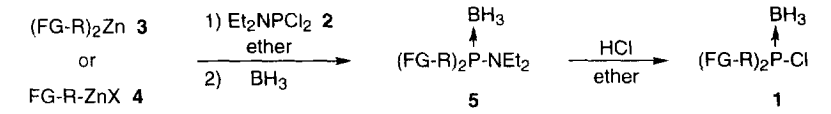
Abstract: A new efficient preparation of borane protected and free polyfunctional chlorodiorganophosphines using zinc organometallics is described. These chlorophosphine derivatives have been used for the preparation of several new chiral diphosphines of interest as ligands for transition metal catalysts.

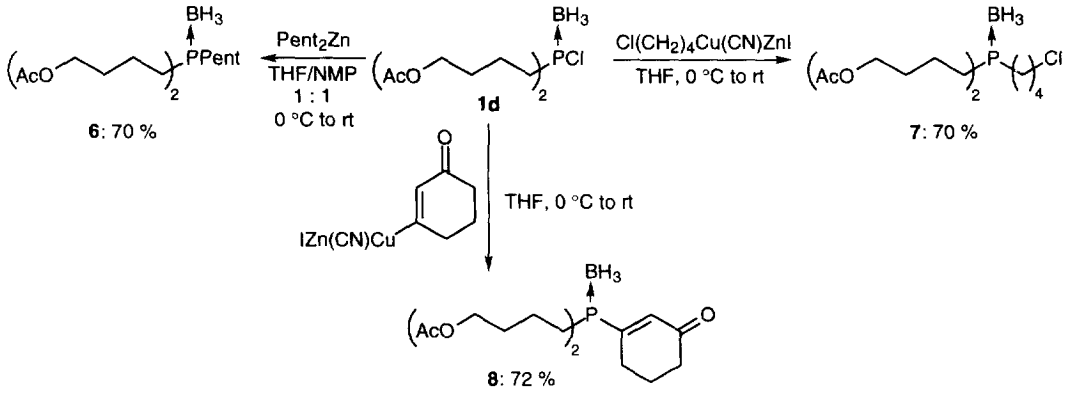
Polyfunctional phosphines and chiral phosphines are important target molecules since these compounds have found extensive applications as ligands of various transition metal catalysts.[1] Recently, we have shown that organozincs are effective organometallics for the preparation of polyfunctional triorganophosphines.[2] Herein, we wish to report an efficient synthesis of chlorodiorganophosphine-borane complexes $(FG\text{-}R)_2PCl{\cdot}BH_3$ of type **1** using zinc organometallics. Whereas the direct addition of organozinc halides (2 equiv) to PCl_3 is not selective and furnishes mixtures of chloroorganophosphines, the reaction of diethylaminodichlorophosphine[3] (**2**) with various diorganozincs[4] ($(FG\text{-}R)_2Zn$) of type **3** or organozinc halides (FG-R-ZnX) of type **4** furnishes after protection with borane,[5] air and water stable diethylaminodiorganophosphine-borane complexes **5** in 70-80 % yield (Scheme 1 and Table 1). Importantly, these compounds can be *conveniently purified* by standard flash chromatography and are readily converted by treatment with an ether solution of HCl[3,6] to the corresponding chlorodiorganophosphine-borane complexes **1**.

Scheme 1



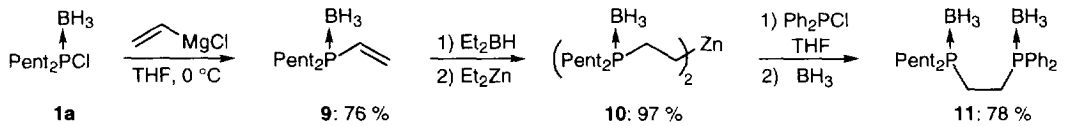
The phosphine derivatives **1** are versatile building blocks for the preparation of various polyfunctional phosphorus compounds. They react selectively with a range of Li, Mg and Zn organometallic reagents in good to excellent yields. As expected,[2] the reaction of organozinc reagents with $(FG\text{-}R)_2PCl{\cdot}BH_3$ (**1**) proceeds smoothly, although we have noticed that the free chlorodiorganophosphines ($(FG\text{-}R)_2PCl$) display a significantly higher reactivity. A solvent effect was observed in the substitution reactions and $Pent_2PCl{\cdot}BH_3$ reacts slowly with Et_2Zn in ether (0 °C to rt, 24 h) affording $Pent_2PEt{\cdot}BH_3$ (72 % yield), whereas a faster reaction was observed in THF (0 °C to rt, 2 h) furnishing $Pent_2PEt{\cdot}BH_3$ in 80 % yield. In general, the use of a polar solvent system is required for a substitution with less reactive zinc reagents than Et_2Zn. Thus, the reaction of the chlorodiorganophosphine-borane complex **1d** with dipentylzinc is best performed in a 1:1 mixture of THF:NMP (0 °C to rt, 12 h) leading to the phosphine-borane complex **6** in 70 % yield. Alternatively, **1d** reacts with the copper reagent $Cl(CH_2)_4Cu(CN)ZnI$ prepared by transmetallation using the THF soluble copper salt CuCN·2LiCl. It affords the mixed polyfunctional phosphine-borane complex **7** in 70 % yield (Scheme 2). This method allows the preparation of phosphine-borane complexes like **8** containing a carbonyl group which is usually reduced by diborane (Scheme 2).

Scheme 2

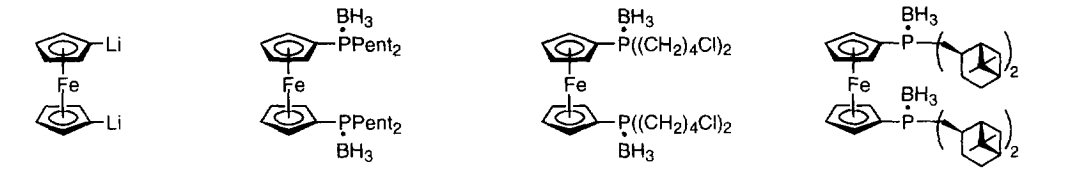


Excellent results are also obtained with organomagnesium halides. The reaction of **1a** with vinylmagnesium chloride provides the unsaturated phosphine-borane **9** in 76 % yield (Scheme 3). This phosphine can be hydroborated with Et_2BH leading to an intermediate borane which upon treatment with Et_2Zn undergoes a clean boron-zinc exchange[7] affording the new diorganozinc **10** which reacts with Ph_2PCl affording the mixed[8] chelating diphosphine **11** in 78 % yield.

Scheme 3

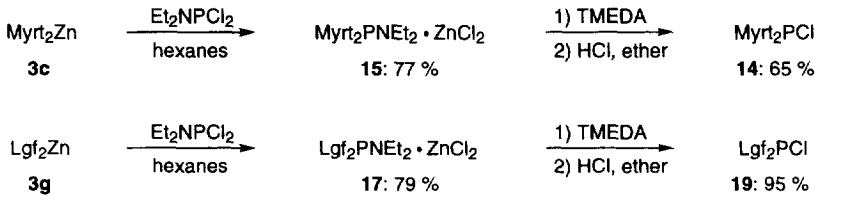


Ferrocenyldiphosphines are important ligands for various transition metal catalysts.[9] Several compounds of this class can be readily prepared by the reaction of a chlorodiorganophosphine-borane complex of type **1** with the dilithiated ferrocene[10] **12** leading to the expected borane protected ferrocenyldiphosphines **13a-c** in 30-96 % yield.

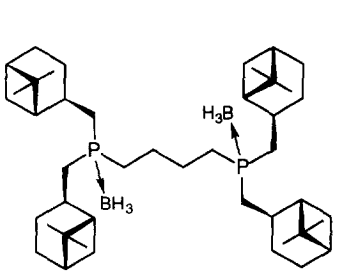


The preparation of chiral diphosphines can be achieved by reacting 1,4-diorganozinc reagents[11] with chlorodiorganophosphines. Extensive experimentation showed that the borane-free chlorodimyrtanylphosphine (**14**) is required for this synthesis. This compound is obtained by treating *bis*-myrtanylzinc[2,7] (**3c**, $Myrt_2Zn$) with **2** resulting in the formation of the aminodiorganophosphine·$ZnCl_2$ complex **15** in 77 % yield. The reaction of **15** with TMEDA (5 equiv) in CH_2Cl_2 leads to the precipitation of $ZnCl_2$·TMEDA and to the production of salt free $Myrt_2PNEt_2$ (**16**, 81 % yield). The treatment of **16** with an ether solution of HCl produces $Myrt_2PCl$ (**14**, 80 % yield). The same procedure was performed with *bis*-longifolylzinc (**3g**, Lgf_2Zn) affording Lgf_2PNEt_2· $ZnCl_2$ (**17**), Lgf_2PNEt_2 (**18**) and finally Lgf_2PCl (**19**) in respectively 79 %, 97 % and 97 % yield (Scheme 4).

Scheme 4

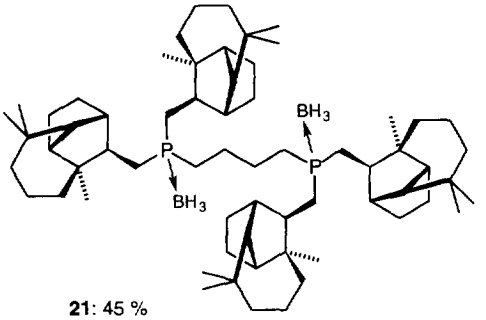


The reaction of **14** and **19** with $IZn(CH_2)_4ZnI$[11] produces, after borane protection, the new chiral chelating 1,4-diphosphines (**20** and **21**) in respectively 70 % and 45 % yield.



20: 70 %

$[\alpha]_D^{22}$ = -20.9 ($CHCl_3$, c=0.77)



21: 45 %

$[\alpha]_D^{22}$ = -23.8 ($CHCl_3$, c=2.85)

Table 1. Diethylaminodiorganophosphine-borane (**5a-f**) obtained by the reaction of Et_2NPCl_2 (**2**) with zinc organometallics (**3a-c** and **4a-c**) and chlorodiorganophosphine-borane complexes (**1a-f**).

Entry	$(FG\text{-}R)_2Zn$ **3** or FG-R-ZnX **4**		Product **5**		Yield (%)[a]	Product **1**		Yield (%)[a]
1	$Pent_2Zn$	**3a**	$Pent_2PNEt_2{\cdot}BH_3$	**5a**	79	$Pent_2PCl{\cdot}BH_3$	**1a**	97
2	Oct_2Zn	**3b**	$Oct_2PNEt_2{\cdot}BH_3$	**5b**	80	$Oct_2PCl{\cdot}BH_3$	**1b**	96
3	$Myrt_2Zn$	**3c**	$Myrt_2PNEt_2{\cdot}BH_3$	**5c**	77	$Myrt_2PCl{\cdot}BH_3$	**1c**	89
4	$AcO(CH_2)_4ZnI$	**4a**	$(AcO(CH_2)_4)_2PNEt_2{\cdot}BH_3$	**5d**	72	$(AcO(CH_2)_4)_2PCl{\cdot}BH_3$	**1d**	80
5	$Cl(CH_2)_4ZnI$	**4b**	$(Cl(CH_2)_4)_2PNEt_2{\cdot}BH_3$	**5e**	78	$(Cl(CH_2)_4)_2PCl{\cdot}BH_3$	**1e**	70
6	$NC(CH_2)_3ZnI$	**4c**	$(NC(CH_2)_3)_2PNEt_2{\cdot}BH_3$	**5f**	71	$(NC(CH_2)_3)_2PCl{\cdot}BH_3$	**1f**	70

[a]Isolated yield of spectroscopically pure compounds (^1H, ^{13}C and ^{31}P NMR)

In summary we have developed a new preparation[12] of polyfunctional chlorodiorganophosphines and their borane complexes. We have demonstrated that these phosphine derivatives are important building blocks for the preparation of a range of polyfunctional and chiral phosphines and diphosphines. The catalytic activity and enantioselectivity of metal complexes prepared from these phosphines is currently being evaluated in our laboratories.

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12. **Typical procedures:** a) Preparation of di(4-acetoxybutyl)diethylaminophosphine-borane complex (**5d**). 4-Acetoxybutylzinc iodide **4a** (ca. 12 mmol) prepared from 4-iodobutyl acetate (3.19 g, 13.2 mmol) and zinc dust (-325 mesh) in THF (5 mL) was added via syringe to a solution of diethylaminodichlorophosphine (**2**) (0.98 g, 5.63 mmol) in ether (5 mL) at 0 °C. The reaction mixture was stirred 2 h at 0 °C and 12 h at rt. It was cooled to 0 °C and a 1M solution of borane-methyl sulfide (5.6 mL) in CH_2Cl_2 was added. GC analysis of reaction aliquots indicates that the reaction was completed after 4 h. After the usual workup, the resulting oil obtained after evaporation of the solvents was purified by flash chromatography affording **5d** (1.40 g, 72 % yield) as a colorless oil.
    b) Preparation of di(4-acetoxybutyl)chlorophosphine-borane complex (**1d**). A saturated solution of HCl (4 mL of a ca. 1 M solution in ether) was added to a solution of the phosphine-borane complex **5d** (0.69 g, 2 mmol) in ether (2 mL) at 0 °C using methyl orange as an indicator. After 1 h of stirring the precipitate ($Et_2NH{\cdot}HCl$) was filtered off under argon. The solvent was removed under vacuum at rt affording the pure chlorophosphine-borane complex **1d** (0.49 g, 1.6 mmol, 80 % yield) as an colorless oil.
    c) Preparation of diethylaminodimyrtanylphosphine-zinc chloride complex (**15**). Diethylamino-dichlorophosphine (**2**) (3.48 g, 20 mmol, 1 equiv) was slowly added at 0°C to a solution of dimyrtanylzinc[2] (6.78 g, 20 mmol, 1 equiv) in ether (20 mL). The reaction mixture was stirred overnight at rt and diluted with hexanes (20 mL). The resulting white precipitate was filtered off, washed twice with hexanes (2 x 10 mL) and dried under vacuum providing pure **15** (7.89 g, 15.4 mmol, 77 % yield) as an air sensitive solid.
    d) Preparation of diethylaminodimyrtanylphosphine (**16**). The phosphine-zinc chloride complex **15** (7.30 g, 14.2 mmol) was dissolved in CH_2Cl_2 (20 mL) and TMEDA (10.7 mL, 8.25 g, 71 mmol) was added at 0 °C. The reaction mixture was stirred overnight at rt. The precipitate ($ZnCl_2{\cdot}$TMEDA) was filtered off and the solution was concentrated. The obtained residue was triturated with hexanes (10 mL), filtered again and the solvent was removed by vacuum resulting in the isolation of pure **16** (4.32 g, 11.4 mmol, 81 % yield) as a yellow oil.
    e) Preparation of chlorodimyrtanylphosphine (**14**). The previously prepared aminophosphine **16** (4.32 g, 11.4 mmol) was dissolved in ether (5 mL) and cooled to 0 °C. A saturated solution of HCl (15 mL, ca. 1M) in ether was added affording a thick precipitate which was filtered off after 1 h of stirring. The precipitate was washed twice with ether (2 x 10 mL). The combined ether solution was evaporated. The residue was dissolved in hexanes, filtered and the solvent was evaporated affording **14** as a colorless oil (3.12 g, 9.2 mmol, 80 %).
    f) Preparation of 1,4-*bis*(dimyrtanylphosphinyl)butane-*bis*-borane complex (**20**). Chlorodimyrtanylphosphine (3.12 g, 9.2 mmol; 2.3 equiv) was dissolved in NMP (3 mL) and a THF solution of $IZn(CH_2)_4ZnI$ (ca. 3.6 mmol, 1 equiv) prepared from 1,4-diiodobutane (1.24 g, 4.0 mmol) and zinc dust (20 mmol) was added. The reaction mixture was stirred for 3 h at rt and overnight at 55 °C. After cooling $BH_3{\cdot}Me_2S$ (0.68 g, 9 mmol, 2.3 equiv) was added and the reaction mixture was stirred for 3 h. The usual workup using hexane:CH_2Cl_2 (250 mL of a 1:1 mixture) and chromatographical purification of the residue using hexanes:CH_2Cl_2 (3:1) and 200 g of silica gel furnishes the desired product **20**. After recrystallization from ethyl acetate, **20** was obtained as white crystals (1.67 g, 2.4 mmol, 70 % yield; mp = 198-201 °C).

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