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Syntheses and Spectroscopic Studies of Diphenylphosphinato Derivatives of Boron

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Summary. 2-Diphenylphosphinato-1,3,2-dioxaborolanes and -borinanes of the type $\overline{\mathrm{O}G\mathrm{OB}}\mathrm{OP(O)Ph_2}$ (where G = $-CH_2CHMe-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CHMe-$, $-CMe_2CMe_2-$, $-CMe_2CH_2CHMe-$, $-CH_2CMe_2CH_2-$, $-CH_2CEt_2CH_2-$, and $-C_6H_4-$) are obtained by the reaction of diphenylphosphinic acid with the corresponding 2,2′-oxo-*bis*-1,3,2-dioxaborolanes and -borinanes. The products are white crystalline solids, which have sharp melting points and are hydrolytically stable. They have been characterized by elemental analysis, IR and multinuclear NMR (^{11}B, ^{31}P, and ^{119}Sn) studies. The data suggest structures with monodentate phosphinato moieties and 3-coordinated boron atoms.

Keywords. Boron; Diphenylphosphinato; IR; NMR; B-11; P-31; Sn-119.

Synthesen und spektroskopische Untersuchungen von Diphenylphosphinatoderivaten von Bor

Zusammenfassung. 2-Diphenylphosphinato-1,3,2-dioxaborolane und -borinane des Typs $\underline{\mathrm{O}G\mathrm{OP}}\mathrm{OP(O)Ph_2}$ (mit G = $-CH_2CHMe-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CHMe-$, $-CMe_2CMe_2-$, $-CMe_2CH_2CHMe-$, $-CH_2CMe_2CH_2-$, $-CH_2CEt_2CH_2-$ und C_6H_4) erhält man durch Reaktion von Diphenylphosphinsäure mit den entsprechenden 2,2′-Oxo-*bis*-1,3,2-dioxaborolanen und -borinanen. Die Produkte sind weiße, kristalline, hydrolyseunempfindliche Festkörper. Sie wurden mittels Elementaranalyse, IR-Spektroskopie und multinuklearer NMR-Spektroskopie (^{11}B, ^{31}P und ^{119}Sn) charakterisiert. Die Resultate legen Strukturen mit monodentaten Phosphinatoeinheiten und dreifach koordinierten Boratomen nahe.

Introduction

A survey of the literature shows that dialkylphosphinato and -phosphonato derivatives of a number of metals and organometallic species, both from non-transition (Al, Ga, In, Sn) [1–4] as well as transition elements (Ti, Zr, Cr) [5–7] have been isolated and characterized in detail. In almost all of these cases the dialkyl phosphinato moieties behave as bridging bidentate ligands, thus giving rise to oligomeric or polymeric species. The reactivity of boron as an electrophilic centre in a variety of 1,3-dioxa-2-borins has been studied. It has been reported that 1,3,2-dixoaborolanes and -borinanes behave in the same way as trialkoxy boranes [8–11]. However, phosphinato derivatives of boron have not been investigated so far. In view of their interesting coordination chemistry as well as the utility of such types of complexes (solvent extraction [12], biocidal activity [13], models in a search for industrially useful coordination polymers [14]), it seemed worthwhile to synthesize the 2-diphenylphosphinato-1,3,2-dioxaborolanes and -borinanes and characterize them by various physico-chemical techniques.

Experimental Part

Two types of compounds (boron *tris*(diphenylphosphinate), $B[OP(O)Ph_2]_3$, and 2-diphenylphosphinato-1,3,2-dioxaborolanes and -borinanes) have been synthesized during the present investigations.

Boron *tris*(diphenylphosphinate) has been obtained by the reaction of boric acid with diphenylphospinic acid in 1:3 molar ratio in refluxing benzene with azeotropic removal of the liberated water

$$B(OH)_3 + 3Ph_2P(O)OH \rightarrow B[OP(O)Ph_2]_3 + 3H_2O.$$

Boron *tris*(diphenylphosphinate) is a white solid, which melts at 178 °C and is insoluble in common organic solvents but shows some solubility in hot benzene and methanol. Unlike the corresponding *tris*(dibutyl-) and (-diphenylphosphato) derivatives, it is resistant to atmospheric moisture.

2-Diphenylphosphinato-1,3,2-dioxaborolanes and -borinanes have been synthesized by the condensation of diphenylphosphinic acid with the corresponding 2,2′-oxo-bis-1,3,2-dioxaborolanes and -borinanes in a 2:1 molar ratio:

$$2Ph_2P(O)OH + (\overline{OGOB})_2O \longrightarrow 2Ph_2P(O)O\overline{BOGO} + H_2O$$

$$G = -CH_2CHMe-, -CH_2CH_2CH_2-, -CH_2CH_2CHMe-, -CMe_2CMe_2-$$

$$-CH_2CMe_2CH_2-, -CH_2CEt_2CH_2-, -CMe_2CH_2CHMe-, -C_6H_4-.$$

The above reactions were carried out in refluxing benzene in a *Dean-Stark* apparatus with continuous removal of water from the reaction mixture. The products are white crystalline solids which have sharp melting points and are quite stable towards atmospheric moisture. They are sparingly soluble in benzene, but insoluble in other organic solvents.

Moisture was carefully excluded throughout the experimental manipulations. The IR spectra were recorded on a Perkin Elmer-577 spectrophotometer using KBr pellets. Multinuclear NMR spectra were recorded on a JEOL FX 90Q spectrophotometer using $Et_2O \cdot BF_3$ (for ^{11}B), H_3PO_4 (for ^{31}P) and Me_4Sn (for ^{119}Sn) as external references.

Reaction of diphenylphosphinic acid with 2,2′-oxo-bis-(4-methyl-1,3,2-dioxaborolane) in 2:1 molar ratio

A mixture of diphenylphosphinic acid (1.40 g) and 2,2′-oxo-*bis*-(4-methyl-1,3,2-dioxaborolane) (0.60 g) in benzene (*ca.* 40 ml) was refluxed in a *Dean-Stark* apparatus with simultaneous removal of water as the diphenylphosphinic acid dissolved slowly *ca.* 5 hrs.) and a clear solution as obtained after the completion of the reaction. On cooling the reaction mixture to room temperature, the product crystallized (1.70 g, 87.6%) as a white solid. Anal.: Found: C, 60.02; H, 5.38; B, 3.49%. Calcd. for $C_{15}H_{16}BO_4P$: C, 59.64; H, 5.34, B, 3.58%.

The above procedures was utilized to prepare various other 2-diphenylphosphinato-1,3,2-dioxaborolanes and -borinanes as summarized in Table 1.

Results and Discussion

IR Spectra

In the IR spectrum of *tris*(diphenylphosphinato)boron, the bands observed at 1320 and 1215 cm^{-1} have been assigned to ν_{B-O} [15] and $\nu_{P=O}$ [16] frequencies, respectively. A strong intensity band at 775 cm^{-1} has been assigned as ν_{P-O} [16] absorption.

Table 1. Synthetic and analytical data for diphenylphosphinato derivatives of boron

Reactant			Product	Analyses (%)		
	$Ph_2P(O)OH$	$[\overline{BOGO}]$ *G*		B found (calcd.)	C found (calcd.)	H found (calcd.)
1	1.40 g	$-CH_2CHMe-$ 0.60 g	$Ph_2P(O)O\overline{BOCH_2CHMeO}$ 1.70 g 87.6%	3.49 (3.58)	60.02 (59.64)	5.38 (5.34)
2	1.10 g	$-CH_2CH_2CH_2-$ 0.47 g	$Ph_2P(O)O\overline{BOCH_2CH_2CH_2O}$ 1.50 g 98.7%	3.32 (3.58)	59.80 (59.64)	5.41 (5.34)
3	2.05g	$-CH_2CH_2CHMe-$ 1.00 g	$Ph_2P(O)O\overline{BOCH_2CH_2CHMeO}$ 2.65 g 89.2%	3.52 (3.42)	60.69 (60.80)	5.61 (5.74)
4	0.50 g	$-CMe_2CMe_2-$ 0.31 g	$Ph_2P(O)O\overline{BOCMe_2CMe_2O}$ 0.77 g 97.5%	2.97 (3.14)	62.49 (62.82)	6.37 (6.44)
5	0.69 g	$-CMe_2CH_2CHMe-$ 0.43 g	$Ph_2P(O)O\overline{BOCMe_2CH_2CHMeO}$ 1.05 g 96.3%	3.05 (3.14)	62.66 (62.82)	6.37 (6.44)
6	0.76 g	$-CH_2CMe_2CH_2-$ 0.42 g	$Ph_2P(O)O\overline{BOCH_2CMe_2CH_2O}$ 1.07 g 93.0%	3.20 (3.27)	61.55 (61.85)	6.17 (6.11)
7	2.15 g	$-CH_2CEt_2CH_2-$ 1.47 g	$Ph_2P(O)O\overline{BOCH_2CEt_2CH_2O}$ 3.25 g 92.1%	2.91 (3.02)	63.30 (63.71)	6.65 (6.75)
8	0.50 g	$-C_6H_4-$ 0.29 g	$Ph_2P(O)O\overline{BOC_6H_4O}$ 0.71 g 92.2%	3.45 (3.53)	69.89 (70.66)	4.41 (4.61)

Table 2. Some relevant IR spectral data (cm^{-1}) for 2-(diphenylphosphinato)dioxaborolanes and -borinanes

Compound	$\nu_{(B)-O-C}$	$\nu_{P=O}$	$\nu_{(B)-O-P}$	ν_{B-O}	Vibrations due to monosubstituted benzene rings		
					I	II	III
1 $Ph_2P(O)O\overline{BOCH_2CHMeO}$	1022 m	1256 m	802 m	1300 w	755 w	720 s	690 w
2 $Ph_2P(O)O\overline{BOCMe_2CMe_2O}$	1033w	1260 m	854 s	1325 w	755 s	722 s	696 s
3 $Ph_2P(O)O\overline{BOCMe_2CH_2CHMeO}$	1010 br	1280 m	815 m	1315 s	760 s	725 m	698 s
4 $Ph_2P(O)O\overline{BOCH_2CMe_2CH_2O}$	967 s	1257 m	811 w	1301 m	750 m	720 s	690 m
5 $Ph_2P(O)O\overline{BOCH_2CEt_2CH_2O}$	965 s	1265 m	805 m	1340 m	755 s	722 s	690 s
6 $Ph_2P(O)O\overline{BOC_6H_4O}$	1010 w	1250 s	800 s	1385 s	756 s	728 s	696 s

In the IR spectra of 2-diphenylphosphinato-1,3,2-dioxaborolanes and -borinanes, a medium intensity band is observed in the region between 1280–1256 cm^{-1} which may be assigned to $\nu_{P=O}$ vibrations. The position of this band is indicative of the absence of a coordination between phosphoryl oxygen and boron atoms.

NMR Spectra

Due to the insolubility in a suitable solvent, no ^{1}H NMR spectra of the compounds could be recorded.

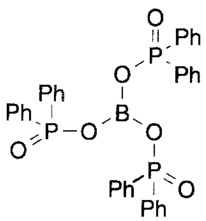
The ^{11}B NMR spectrum of *tris*(diphenylphosphinato)boron shows the chemical shift of ^{11}B at 19.5 ppm in C_6H_6 which is comparable to the ^{11}B chemical shift for $B(OH)_3$ (18.0 ppm) in water and is indicative of tricoordinated boron.

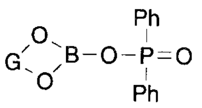
The ^{11}B NMR spectra of 2-diphenylphosphinato-1,3,2-dioxaborolanes and -borinanes show chemical shift values in the range of 18.0–23.2 ppm, which is clearly indicative of tricoordinated boron. As expected, there is a small but noticeable difference between the chemical shift values of 5-membered borolane and 6-membered borinane derivatives. The latter have resonances between 18.5–20.0 ppm, while the former show δ-values of *ca.* 23 ppm.

The ^{31}P NMR spectrum of *tris*(diphenylphosphinato)boron shows only one resonance signal at 33.7 ppm, which is indicative of monodentate diphenylphosphinato moieties.

In the ^{31}P NMR spectra of 2-diphenylphosphinato-1,3,2-dioxaborolanes and -borinanes, only one resonance signal in each case was observed in the region of 32.0–33.6 ppm. The chemical shifts of these products are almost the same as those for alkyl diphenylphosphinates (*e.g.* $Ph_2P(O)OEt$: $\delta_{^{31}P} = 31.7$ ppm) and are indicative of monodentate ligands.

The molecular weights of the diphenylphosphinato derivatives of boron could not be determined due to the insolubility in suitable solvents. The spectroscopic data, however, show that the boron atoms are tricoordinate and the diphenylphosphinato moieties are unidentate in all cases. The compounds are therefore assumed to be monomeric and to have simple structure resembling those of boric acid esters and $\overline{\text{OGOB}}\text{OR}$.





Miscellaneous Reactions

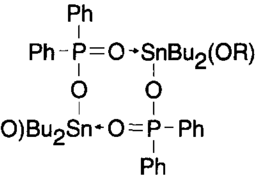
(*i*) Diphenylphosphinoxy groups can be conveniently transferred from boron to tin as indicated by the insertion reaction of dibutyltin oxide with 2-diphenylphosphinato-5-5′-dimethyl-1,3,2-dioxaborinane in 1:1 molar ratio.

$$\overline{\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OB}}\text{O(O)PPh}_2 + \text{Bu}_2\text{SnO} \longrightarrow \overline{\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OB}}\text{OSnBu}_2\text{O(O)PPh}_2.$$

Table 3. ^{11}B and ^{31}P NMR data for 2-(diphenylphosphinato)-1,3,2-dioxaborolanes and -borinanes in benzene (δ, ppm)

Compound		^{11}B	^{31}P
1	$\mathrm{Ph_2P(O)O\overline{BOCH_2CHMeO}}$	–	32.4
2	$\mathrm{Ph_2P(O)O\overline{BOCH_2CH_2CH_2O}}$	18.6	32.4
3	$\mathrm{Ph_2P(O)O\overline{BOCH_2CH_2CHMeO}}$	19.2	33.6
4	$\mathrm{Ph_2P(O)O\overline{BOCMe_2CMe_2O}}$	23.2	33.6
5	$\mathrm{Ph_2P(O)O\overline{BOCMe_2CH_2CHMeO}}$	18.5	33.6
6	$\mathrm{Ph_2P(O)O\overline{BOCH_2CMe_2CH_2O}}$	18.7	33.0
7	$\mathrm{Ph_2P(O)O\overline{BOCH_2CEt_2CH_2O}}$	19.9	32.0
8	$\mathrm{Ph_2P(O)O\overline{BOC_6H_4O}}$	18.5	33.6

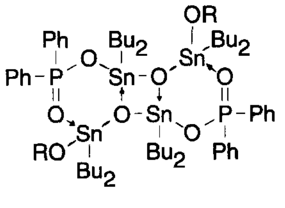
The completion of the above reaction, carried out in refluxing benzene, is indicated by the complete dissolution of dibutyltin oxide. The ^{31}P chemical shift of the product is 20.7 ppm, which is 9.3 ppm upfield from that of the starting boron compound. The ^{119}Sn chemical shift of the above dibutyltin phosphinato derivative is -250.9 ppm, which is indicative of pentacoordinate tin.

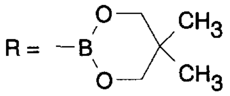


(*ii*) The insertion reaction of dibutyltin oxide with 2-diphenylphosphinato-5-5′-dimethyl-1,3,2-dioxaborlnane proceeds in a 2:1 molar ratio and yields a tetrabutyl distannoxane derivative.

$$\overline{\mathrm{OCH_2CMe_2CH_2OB}}\mathrm{O(O)PPh_2} + 2\mathrm{Bu_2SnO} \longrightarrow$$
$$\overline{\mathrm{OCH_2CMe_2CH_2OB}}\mathrm{OSnBu_2OSnBu_2O(O)PPh_2}.$$

The ^{119}Sn NMR spectrum of the product shows two peaks at -215.5 and -219.0 ppm (along with a law intensity peak at -250 ppm for the 1:1 derivative) in the pentacoordinate tin region. These values suggests an oligomeric structure:





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