*Inorganica Chimica Acta*, *115* (1986) L29–L30

# Borane and Monoiodoborane Derivatives of Bis(diphenylphosphino)methane

DONALD R. MARTIN, CAROLYN M. MERKEL and JOSE P. RUIZ

*Department of Chemistry, The University of Texas at Arlington, Arlington, Tex. 76019-0065, U.S.A.*

Received December 9, 1985

Previous research in this laboratory has been concerned with studies to elucidate factors affecting the Lewis base–boron bond in adducts. Several studies have been completed [1, 2] in which the electron environment around the donor atom or the boron atom has been changed by replacement of hydrogen atoms with alkyl, amino, halo and/or pseudohalo substituents.

Recently, a series of borane adducts and monoiodoborane salts of bis(diphenylphosphino) alkanes, $(C_6H_5)_2P{-}(CH_2)_n{-}P(C_6H_5)_2$, with $n$ having values from 2 to 4, have been synthesized and characterized [3].

In this study, the products of the reaction of borane and of monoiodoborane with bis(diphenylphosphino)methane have been isolated and characterized.

## Experimental

All reactions and transfers were performed under an atmosphere of dry nitrogen. Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer using samples prepared as Nujol mulls and placed between sodium chloride plates or as potassium bromide pellets. The proton NMR spectra were recorded on a Varian T-60 or Nicolet NT-200 wide bore spectrometer, using tetramethylsilane (TMS) as an internal standard. The $^{11}B$ NMR spectra were recorded on a Nicolet NT-200 wide bore spectrometer at 64.2 MHz using trimethoxyborane as an external standard. Melting points were determined on samples sealed under nitrogen in capillary tubes. Elemental analyses were determined in this laboratory using an F and M Model 185 carbon, hydrogen and nitrogen analyzer. A YSI Model 31 conductivity bridge was used to determine conductance of 1.0 mM solutions of the products in acetonitrile at 25 °C.

The bis(diphenylphosphino)methane was obtained from Strem Chemicals, Inc., Newburyport, Mass., and was used without further purification. Sodium borohydride (Fisher Scientific Company, Pittsburgh, Pa.) and $(CH_3)_2S{\cdot}BH_3$ (10.0 M in $BH_3$ from Aldrich Chemical Company, Milwaukee, Wis.) also were used as received. Benzene and ethyleneglycol dimethylether (glyme) (Aldrich Chemical Company) were distilled from sodium metal and benzophenone, respectively. Hexane was dried over Drierite. Acetonitrile was distilled from $P_4O_{10}$. All solvents were stored under dry nitrogen.

The compounds were prepared using procedures similar to those described previously [3–5].

### *Bis(diphenylphosphino)methane Borane*

In a typical preparation, 0.64 g (2.5 mmol) of $I_2$ in 40 ml of glyme was added dropwise with stirring to a solution of 0.38 (10 mmol) of $NaBH_4$ and 1.92 g (5 mmol) of bis(diphenylphosphino)methane in 40 ml of glyme [4]. A white precipitate of sodium iodide formed immediately. Stirring was continued for 1 h after which the solvent was removed under vacuum. The resulting solid was suspended in *ca.* 80 ml of benzene and then filtered to remove NaI. The filtrate was reduced to about 20 ml under vacuum and 200 ml of dry hexane added. The resulting precipitate was collected on a filter and dried overnight under a vacuum.

A 75.4% yield of a white solid (melting point 92–94 °C (decomposition)) was obtained. *Anal.* Calc. for $[(C_6H_5)_2P]_2CH_2{\cdot}BH_3$: C, 75.39; H, 6.34. Found: C, 75.81; H, 6.54%. IR Spectrum follows: 2420(w), 2370(m), 2350(w), 1440(w), 1310(w), 1100(m), 1050(m), 1000(m), 805(m), 790(m), 765(m), 740(m), 690(m), 620(m), 595(m) $cm^{-1}$.

### *Bis(diphenylphosphino)methaneboronium Iodide*

A solution of 1.0 ml (10 mmol) of $CH_3{\cdot}S{\cdot}BH_3$ and 1.27 g (5 mmol) of $I_2$ in 30 ml benzene was stirred overnight at room temperature. Added to this was 1.92 g (5 mmol) of bis(diphenylphosphino)methane in 30 ml benzene [5]. A small amount of precipitate formed. After stirring for 1 h, the solid was collected on a filter, washed with benzene and dried under vacuum to yield 0.44 g (16.8% yield) of a white solid (m.p. 128.5 (decomposition)). *Anal.* Calc. for $\{[(C_6H_5)_2P]_2CH_2BH_2\}^+I^-$: C, 57.28; H, 4.62. Found: C, 60.63; H, 6.77%. IR Spectrum follows: 2470(m), 2420(m), 1590(m), 1435(s), 1415(m), 1310(w), 1112(s), 998(m), 810(m), 745(m), 730(m), 690(s), 670(m), 620(w), 540(m).

## Results and Discussion

The products of the reaction of borane with $[(C_6H_5)_2P]_2CH_2$ depend upon the stoichiometry used. The bis(borane) adduct was isolated and reported previously [4]. In this study, it was found if an excess of base is used, a monoborane adduct is isolable. This result is not observed in the reactions

0020-1693/86/$3.50

TABLE I. NMR Data for Products

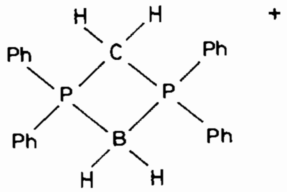
| Compound | $^1H$ Resonance | | $^{11}B$ Resonance[a] | |
|---|---|---|---|---|
| | Proton | δ (ppm) | δ (ppm) | $J_{B-P}$ |
| $[(C_6H_5)_2P]_2CH_2\,2BH_3$[b] | $CH_2$ | 3.27 | −55.4 | – |
| | $C_6H_5$ | 7.46 | | |
| $[(C_6H_5)_2P]_2CH_2BH_3$ | $CH_2$ | 2.97 | −56.4 | 38.9 Hz |
| | $C_6H_5$ | 7.32 | | |
| $\{[(C_6H_5)_2P]_2CH_2BH_2\}^+I^-$ | $CH_2$ | 5.30 | −55.31 | 40.0 Hz |
| | $C_6H_5$ | 7.45 | | |

[a] Reference $B(OCH_3)_3$. [b] Compound and data previously reported [4].

of borane with $[(C_6H_5)_2P]_2(CH_2)_n$ ($n = 2$ to 4), in which a bis(borane) adduct is obtained regardless of the stoichiometry between the base and the borane [3].

The infrared spectrum for the borane adduct shows three characteristic bands due to B–H symmetric and asymmetric stretching at 2330–2420 $cm^{-1}$. In addition, a band at 590–595 $cm^{-1}$ resulting from the B–P stretching is observed.

The reaction of monoiodoborane with $[(C_6H_5)_2P]_2CH_2$ produces a boronium iodide salt. It is proposed that a four-coordinate boronium cation forms containing a 4-membered ring:



The infrared spectrum of the monoiodoboronium salt shows two bands at 2415–2430 $cm^{-1}$ and 2470–2495 $cm^{-1}$, which are characteristic for a $BH_2$ group and correspond to the symmetric and asymmetric H–B–H stretching [6]. In addition, the relative complexity of the spectrum between 2000–2500 $cm^{-1}$ indicates an ionic rather than a neutral species.

The formation of the boronium iodide upon reaction of the phosphine with monoiodoborane is further confirmed by the observed molar conductivity in an acetonitrile solution of $\Lambda = 0.0140\ \Omega^{-1}\ mol^{-1}\ m^2$ and is an indication of the presence of 2 ions [5].

The $^1H$ proton NMR spectrum of the boronium iodide shows the aliphatic proton resonances greatly shifted downfield compared to those of the corresponding borane adduct (both mono and bis) (Table I) and shifts larger than observed in the boronium salts of $[(C_6H_5)_2P](CH_2)_n$ ($n = 2$–4) [3].

The $^{11}B$ NMR data (Table I) show that there is a little more shielding in the monoborane adduct than in the bis(borane) adduct. For the boronium iodide, on the other hand, the $^{11}B$ resonance is downfield indicating less electron density around the four coordinate boronium cation.

In conclusion, the synthesis of a borane adduct of bis(diphenylphosphino)methane is controlled by the stoichiometry used whereas with the bis(diphenylphosphino)alkanes, $[(C_6H_5)_2P]_2(CH_2)_n$ in which $n$ has values of 2–4, only the bis(borane) adducts could be isolated. With $BH_2I$, only a boronium iodide is obtained in which $n$ has a value of 1–4.

## Acknowledgement

The support of The Robert A. Welch Foundation is gratefully acknowledged.

## References

1 C. M. Merkel and D. R. Martin, *Inorg. Chim. Acta, 96,* L59 (1985).
2 D. R. Martin, C. M. Merkel, J. U. Mondal and C. R. Rushing, *Inorg. Chim. Acta, 99,* 81 (1985).
3 D. R. Martin, C. M. Merkel, J. P. Ruiz and J. U. Mondal, *Inorg. Chim. Acta, 100,* 293 (1985).
4 K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem., 8,* 2671 (1969).
5 B. T. Pennington, M. A. Chuisano, D. J. Dye, E. D. Martin and D. R. Martin, *J. Inorg. Nucl. Chem., 40,* 389 (1978).
6 P. J. Bratt, M. P. Brown and K. R. Seddon, *J. Inorg. Nucl. Chem., 37,* 887 (1975).