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A Facile Route to Phosphanylborohydrides: Synthesis, Crystal Structure and Spectroscopic Properties of 1,2-Bis(Diphenylphosphinoborane)Ethane

Leyla Tatar Yildirim[1], **Mehdi Masjedi**[2], **Saim Özkar**[2]

[1]Department of Engineering Physics, Hacettepe University, Ankara, Turkey;
[2]Department of Chemistry, Middle East Technical University, Ankara, Turkey
E-mail:[1]tatar@hacettepe.edu.tr, [2]mehdimasjedi@yahoo.com, [3]sozkar@metu.edu.tr

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ABSTRACT

A novel and simple synthetic way using $NaBH_4$ *in the mixture of* H_2O-*THF was applied to prepare* 1,2-*bis*(*diphenylphosphinoborane*)*ethane, dppe*(BH_3)$_2$, *in high yield and purity. The phosphanylborohydride compound dppe*(BH_3)$_2$ *was isolated in the form of colorless crystals and characterized by single crystal X-ray diffraction,* ^1H, ^{13}C, ^{31}P *and* ^{11}B *NMR spectroscopy. Prismatic colorless crystals of dppe*(BH_3)$_2$ *were obtained in monoclinic crystal system and space group* $P2_1$ *with two asymmetric units in the unit cell. Lattice parameters were:* a = 11.657(2), b = 17.237(2), c = 12.764(2) *Å*, β = 98.735(14)°, 2535.0(7) *Å*^{3}.

Keywords: *Crystal Structure*, *Synthesis*, *Phosphinoborane*, *Sodium Borohydride*, *Phosphanylborohydride*, *X-Ray Diffraction*

1. Introduction

A recent study [1] has reported the catalytic activity of ruthenium (III) acetylacetonate in the presence of different phosphorus compounds such as 1,2-bis(diphenylphosphino)ethane, dppe, in the hydrolysis of sodium borohydride. At the end of catalytic reaction, in addition to the unreacted dppe, unexpectedly we isolated a new species which contains two BH_3 molecules coordinated to dppe. Obviously, in this catalytic reaction, $NaBH_4$ acts not only as a substrate to generate hydrogen, but also as a BH_3 supplier in forming phosphanylborohydrides such as 1,2-bis(diphenylphosphinoborane)ethane, dppe(BH_3)$_2$. In literature, phosphanylborohydrides have been prepared by using the mixture of sodium borohydride and iodine in monoglyme [2] or using the other borane sources: dppe(BH_3)$_2$ by complexation of dppe with $BH_3\cdot S(CH_3)_2$ [3], rac/meso-[$HP(BH_3)(Ph)CH_2$]$_2$ from the reaction of BH_3.thf [4] or reaction of phosphine oxides with diborane [5], from the reaction of trialkylphosphines with bromoboranes or bromochloroboranes [6]. In addition following phosphanylborohydrides have been reported: tertiary mono and diphosphine-borane complexes [7-9], cyclic phosphine-boranes [10], phosphine-carborane clusters [11], phosphinyl-borane radicals [12] and phosphine alkylene boranes [13]. It is noteworthy that the phosphanylborohydride [$P(BH_3)Ph_2$]$^-$ forms dative bonds of higher p character and establish more stable σ adducts towards the acceptor orbital of the Lewis acid in comparison with its neutral counterpart $P(CH_3)Ph_2$ [14]. A similar phenomenon was observed in the study of chalcogenated phosphanylborohydrides K[$EP(BH_3)R_2$] (E: O, S, Se, Te; R: Ph, *t*-Bu) with a certain degree of E=P multiple bond character [15]. Borane complexes of phosphorus compounds, a very common oxidation free relay for catalytic ligands (phosphines, phosphites or phosphinites) can be easily deprotected by treatment with polymer- supported piperazine, N-methylpiperazine [16] or pyrrol derivatives [3]. Phosphanylborohydrides supported by amines such as polypyrroles, are very useful for homogeneous catalysis due to more efficient recovery and purification [3]. Despite the known examples given above, the chemistry of phosphanylborohydrides is still largely undeveloped [17-22]. Herein we report a new and simple synthetic way using $NaBH_4$ in an homogeneous aqueous-organic solution to yield

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1,2-bis(diphenylphosphinoborane)ethane, dppe$(BH_3)_2$, and its characterization by single crystal X-ray diffraction, ^{1}H, ^{13}C, ^{31}P and ^{11}B NMR spectroscopy.

2. Experimental

2.1. Materials

Sodium borohydride, $NaBH_4$ (98%) and 1,2-bis(diphenylphosphino)ethane, dppe, were purchased from Aldrich. Tetrahydrofuran, THF and dichloromethane, CH_2Cl_2 were purchased from Merck. All glassware and Teflon-coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying at 150˚C in oven for a few hours.

2.2. Equipment

All reactions involving air sensitive compounds were performed under argon or nitrogen atmospheres. ^{1}H, ^{13}C, ^{31}P and ^{11}B NMR spectra were recorded on Bruker Avance DPX 400 MHz spectrometer (400.1 MHz for ^{1}H; 100.6 MHz for ^{13}C; 161.3 MHz for ^{31}P; 128.2 MHz for ^{11}B). TMS was used as internal reference for ^{1}H and ^{13}C NMR chemical shifts. $BF_3 \cdot (C_2H_5)_2O$ was used as external reference for ^{11}B NMR chemical shifts. H_3PO_4 (85% in glass capillary) was used as reference for ^{31}P NMR. Positive ion mass spectrometry data was obtained on a Bruker Micro TOF-LC/ESI/Ms system.

The experimental setup consists of a 75 mL jacketed reaction flask containing a Teflon-coated stir bar placed on a magnetic stirrer (Heidolph MR-301) which can be thermostated to 25.0˚C by circulating water through its jacket from a constant temperature bath (RL6 LAUDA water bath). Note that hydrogen liberated during hydrolysis of sodium borohydride was released from the flask through a bubbler.

2.3. Synthesis of 1,2-Bis(Diphenylphosphinoborane)Ethane, DPPE$(BH_3)_2$

For the preparation of 1,2-bis(diphenylphosphinoborane) ethane, dppe$(BH_3)_2$, 140 mg (0.35 mmol) of 1,2-bis(diphenylphospino)ethane, dppe, was dissolved in 10 mL of THF by vigorous stirring. Then, the solution was transferred into a 75 mL jacketed reaction flask containing 30 mg (0.79 mmol) $NaBH_4$ dissolved in 40 mL water and thermostated at 25.0˚C. The reaction was started by turning on the magnetic stirrer (Heidolph MR-301) at 1000 rpm under inert atmosphere (argon or nitrogen). After 3 h stirring, the mixture was extracted with dichloromethane and the combined organic extracts were cooled in order to precipitate out traces of sodium borohydride or metaborate remaining in organic extracts. Then, the solution was dried over magnesium sulfate, filtered and evaporated in vacuum giving 144 mg of pure dppe$(BH_3)_2$ complex (96% yield). Colorless crystals of dppe$(BH_3)_2$ were obtained by crystallization from the hexane-dichloromethane solution at 0˚C after one week, which were separated by filtration. $[Ph_2P(BH_3)CH_2]_2$: ^{1}H NMR (CD_2Cl_2, ppm): δ 1.99 (t, 6H, $J_{P\text{-}H}$ = 4.8 Hz, $2BH_3$), 2.15 (br d, 2H, $J_{P\text{-}H}$ = 6.4 Hz, CH_2), 2.38 (br d, $J_{P\text{-}H}$ = 2.8 Hz, 2H, CH_2), 7.38 (m, 12H, H-m,p), 7.54(m, 4H, H-o), 7.61 (m, 4H, H-o). ^{13}C {^{1}H} NMR (CD_2Cl_2, ppm): δ 22.93, 127.81, 129.87, 131.85, 137.59. ^{31}P {^{1}H} NMR (CD_2Cl_2, ppm): δ –12.5. ^{11}B {^{1}H} NMR (CD_2Cl_2, ppm): δ –40.06.

3. Crystal Structure Analysis

X-ray diffraction measurements were performed with MoK_α radiation on an Enraf-Nonius CAD4 diffractometer [23] equipped with a graphite monochromator. Intensity data were collected by $\omega/2\theta$ scan mode. The cell parameters were determined from a least-squares refinement of 18 centered reflections in the range of $10.12^\circ \le \theta \le 18.03^\circ$. Cell refinement was carried out using CAD-4 EXPRESS. Data reduction was carried out using XCAD4 [24]. The structures were solved by Patterson methods and refined using the program SHELX [25]. A full-matrix least-squares refinement on F^2 was done. For all non-hydrogen atoms anisotropic displacement parameters were refined. Borane(BH_3) and phenyl ring hydrogen's of the compound were placed geometrically and a riding model was used with $U_{iso}(H) = 1.5U_{eq}(C)$ and $U_{iso}(H) = 1.2U_{eq}(C)$, respectively. Methylene hydrogen's were taken from a difference Fourier map and refined. Single crystal X-ray diffraction analysis of the colorless crystal shows the crystallization in monoclinic system with space group $P2_1$ and two asymmetric units with a formula of $C_{26}H_{30}B_2P_2$ and four molecules per unit cell. **Table 1** shows the crystal data and crystal refinement of dppe$(BH_3)_2$. The atomic coordinates and isotropic displacement parameters are listed in **Table 2**. Selected bond lengths and angles are given in **Table 3**. ORTEP [26] drawing of the dppe$(BH_3)_2$ complex with the atomic numbering scheme is given in **Figure 1**. The unit cell of the structure as shown in **Figure 2**. The conformations of molecules and molecular packing geometry were analyzed using PLATON [27]. The structure includes several pi-ring interactions between two asymmetric moieties. Details of the pi-ring interaction geometry are given in **Table 4**.

4. Results and Discussion

When an aqueous solution of sodium borohydride is added to a solution of 1,2-bis(diphenylphospino)ethane, dppe, in tetrahydrofurane under vigorous stirring in inert atmosphere at 25.0˚C, a reaction occurs, along with the

Table 1. Crystal data and structure refinement for dppe $(BH_3)_2$.

Chemical Formula	$C_{26}H_{30}B_2P_2$
Formula weight [g/mol]	426.06
Crystal colour and shape	prism, colorless
Crystal size (mm)	0.3 × 0.3 × 0.3
Temperature (K)	295(2)
Crystal system, Space group	monoclinic, $P2_1$
a (Å)	11.657(2)
b (Å)	17.237(2)
c (Å)	12.764(2)
β (˚)	98.735(14)
Cell volume (Å^3)	2535.0(7)
Z, calculated density (g/cm^3)	4, 1.116
Absorption coefficient (mm^{-1})	0.182
F (000)	904
θ-range for data collection (°)	2.21-26.29
Limiting indices	$-14 \le h \le 0, 0 \le k \le 21, -15 \le l \le 15$
Reflections collected / Unique	5542/5286 [R_{int}= 0.0492]
Data/restrains/parameters	5286/553/4
Goodness-of-fit on F^2	1.001
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0558$, $wR_2 = 0.1301$
Largest diff. peak and hole (e/Å^3)	0.519 and –0.303

Further details on the structural investigation are available on request from the Cambridge Crystallographica Data Centre, quoting the depository number CCDC 752883.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for dppe(BH_3).

Atom	x	y	z	U_{eq}	**Atom**	x	y	z	U_{eq}
Molecule **I**					Molecule **II**				
B1	0.4854(7)	0.1328(6)	0.9091(8)	0.076(3)	**B1'**	0.1375(10)	0.3864(7)	0.4564(7)	0.098(4)
B2	0.8379(9)	0.1832(6)	1.2510(7)	0.085(3)	**B2'**	0.6106(9)	0.4078(8)	0.7863(8)	0.102(4)
P1	0.62838(14)	0.08831(10)	0.89049(14)	0.0544(5)	**P1'**	0.19495(15)	0.34115(11)	0.58949(14)	0.0597(5)
P2	0.86384(15)	0.22715(10)	1.12275(14)	0.0534(5)	**P2'**	0.54049(16)	0.45444(12)	0.65608(15)	0.0629(5)
C1	0.6261(6)	–0.0166(4)	0.8938(5)	0.0554(19)	**C1'**	0.1708(6)	0.2379(4)	0.5901(5)	0.0593(18)
C2	0.6967(6)	–0.0625(5)	0.8385(6)	0.071(2)	**C2'**	0.2342(7)	0.1881(5)	0.6624(6)	0.071(2)
C3	0.6936(8)	–0.1412(5)	0.8464(7)	0.089(3)	**C3'**	0.2160(7)	0.1088(5)	0.6572(7)	0.081(2)
C4	0.6239(8)	–0.1750(5)	0.9098(7)	0.084(3)	**C4'**	0.1320(7)	0.0775(5)	0.5804(7)	0.084(2)
C5	0.5550(7)	–0.1319(6)	0.9644(7)	0.083(2)	**C5'**	0.0685(7)	0.1260(5)	0.5095(7)	0.081(2)
C6	0.5572(6)	–0.0527(5)	0.9566(6)	0.073(2)	**C6'**	0.0858(6)	0.2057(5)	0.5135(6)	0.071(2)
C7	0.6817(6)	0.1161(4)	0.7718(6)	0.0621(19)	**C7'**	0.1323(6)	0.3814(4)	0.6979(6)	0.0596(18)
C8	0.6033(8)	0.1336(5)	0.6817(7)	0.092(3)	**C8'**	0.0241(7)	0.4146(6)	0.6764(8)	0.103(3)
C9	0.6447(15)	0.1521(7)	0.5869(9)	0.131(4)	**C9'**	–0.0286(9)	0.4421(7)	0.7604(12)	0.127(4)
C10	0.7593(17)	0.1524(8)	0.5842(11)	0.137(5)	**C10'**	0.0270(12)	0.4403(7)	0.8622(11)	0.122(4)
C11	0.8375(11)	0.1368(7)	0.6693(10)	0.126(4)	**C11'**	0.1327(11)	0.4088(6)	0.8823(8)	0.103(3)
C12	0.7993(7)	0.1182(5)	0.7641(7)	0.087(2)	**C12'**	0.1867(7)	0.3789(5)	0.8012(6)	0.083(2)
C13	0.7410(6)	0.1148(4)	1.0009(6)	0.0588(19)	**C13'**	0.3526(6)	0.3535(5)	0.6246(8)	0.071(2)
C14	0.7504(7)	0.2023(4)	1.0154(7)	0.062(2)	**C14'**	0.3843(6)	0.4399(5)	0.6297(8)	0.074(2)
C15	0.9964(8)	0.1979(6)	1.0806(10)	0.1055(16)	**C15'**	0.5950(6)	0.4217(4)	0.5387(5)	0.0599(18)
C16	1.0228(8)	0.2233(6)	0.9836(9)	0.1055(16)	**C16'**	0.5452(7)	0.4447(5)	0.4389(6)	0.081(2)
C17	1.1287(8)	0.2001(5)	0.9498(9)	0.1055(16)	**C17'**	0.5935(9)	0.4216(6)	0.3511(7)	0.094(3)
C18	1.2024(8)	0.1564(6)	1.0190(9)	0.1055(16)	**C18'**	0.6882(9)	0.3766(6)	0.3618(8)	0.094(3)
C19	1.1808(8)	0.1314(5)	1.1106(9)	0.1055(16)	**C19'**	0.7410(8)	0.3524(6)	0.4595(8)	0.093(3)
C20	1.0748(7)	0.1514(5)	1.1433(8)	0.097(3)	**C20'**	0.6922(7)	0.3747(5)	0.5480(7)	0.081(2)
C21	0.8710(5)	0.3316(4)	1.1266(5)	0.0498(17)	**C21'**	0.5562(6)	0.5580(4)	0.6561(5)	0.062(2)
C22	0.7938(7)	0.3779(5)	1.0625(6)	0.069(2)	**C22'**	0.4858(7)	0.6070(5)	0.7037(7)	0.089(3)
C23	0.8033(7)	0.4581(5)	1.0697(7)	0.084(2)	**C23'**	0.5003(9)	0.6864(6)	0.7041(8)	0.107(3)
C24	0.8903(8)	0.4909(5)	1.1428(7)	0.080(2)	**C24'**	0.5826(10)	0.7187(6)	0.6564(8)	0.100(3)

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C25	0.9654(7)	0.4449(5)	1.2062(6)	0.081(2)	**C25'**	0.6512(10)	0.6726(7)	0.6109(9)	0.118(4)
C26	0.9546(6)	0.3663(4)	1.1979(6)	0.069(2)	**C26'**	0.6405(8)	0.5929(5)	0.6082(7)	0.092(3)

Table 3. Selected bond length [Å] and angles [˚] for two asymmetric units of dppe(BH$_3$)$_2$.

Molecule **I**		Molecule **II**	
B1 – P1	1.882(8)	B1' – P1'	1.896(9)
B2 – P2	1.870(9)	B2' – P2'	1.914(10)
P1 – C1	1.809(7)	P1' – C1'	1.802(8)
P1 – C7	1.788(7)	P1' – C7'	1.799(7)
P1 – C13	1.832(7)	P1' – C13'	1.837(8)
P2 – C14	1.805(7)	P2' – C14'	1.818(8)
P2 – C15	1.784(9)	P2' – C15'	1.805(7)
P2 – C21	1.803(7)	P2' – C21'	1.794(8)
C13 – C14	1.521(9)	C13' – C14'	1.533(11)
B1 – P1 – C1	112.8(4)	B1' – P1' – C1'	112.1(4)
B1 – P1 – C7	115.3(4)	B1'– P1' – C7'	113.6(5)
B1 – P1 – C13	110.2(4)	B1' – P1' – C13'	112.0(5)
B2 – P2 – C14	111.8(5)	B2' – P2' – C14'	112.7(5)
B2 – P2 – C15	114.3(5)	B2' – P2' – C15'	115.6(5)
B2 – P2 – C21	113.2(4)	B2' – P2' – C21'	112.8(5)
C1 – P1 – C7	107.2(3)	C1' – P1' – C7'	107.2(3)
C1 – P1 – C13	104.0(3)	C1' – P1' – C13'	105.3(4)
C7 – P1 – C13	106.5(3)	C7' – P1' – C13'	106.0(4)
C14 – P2 – C15	105.8(5)	C14' – P2' – C15'	105.8(4)
C14 – P2 – C21	106.5(3)	C14' – P2' – C21'	103.7(4)
C15 – P2 – C21	104.6(4)	C15' – P2' – C21'	105.2(3)
P1 – C13 – C14	111.8(5)	P1' – C13' – C14'	110.4(5)
P2 – C14 – C13	111.0(5)	P2' – C14' – C13'	111.7(5)

Table 4. Structural parameters of pi-ring interaction geometry (Å,˚) for the title compound.

D – H ··· Cg	D–H	Cg···H	D······Cg	D–H···Cg
C9 –H9···Cg4'	0.93	2.81	3.685(14)	158
C11′–H11′···Cg1i	0.93	2.79	3.634(12)	151
C25′ –H25′···Cg1′ii	0.93	2.91	3.662(12)	138

Symmetry codes [i: x, y, 1 + z and ii: 1 – x, ½ + y,1 – z]

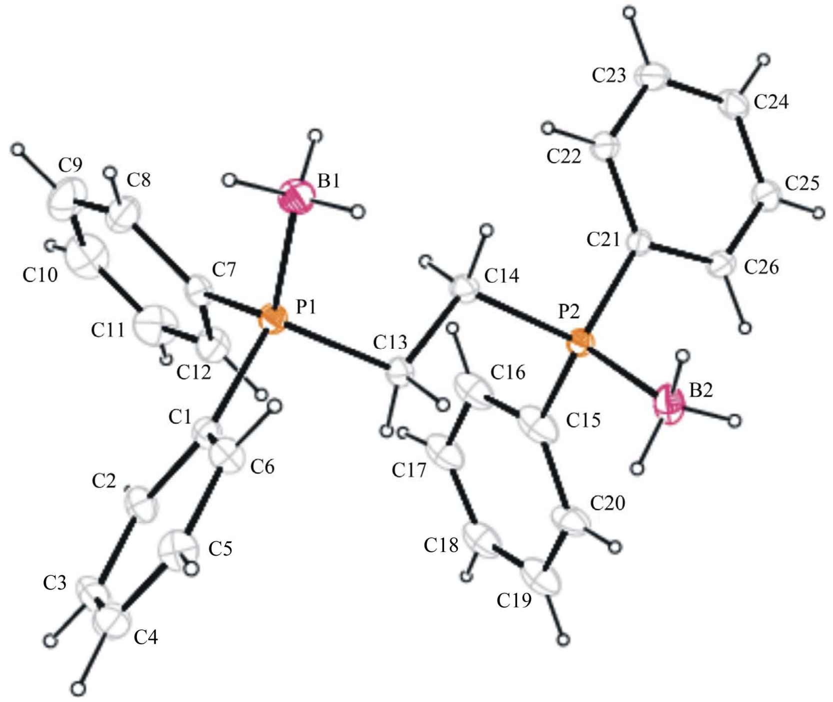

Figure 1. ORTEP drawing for the dppe$(BH_3)_2$ complex with the atomic numbering scheme.

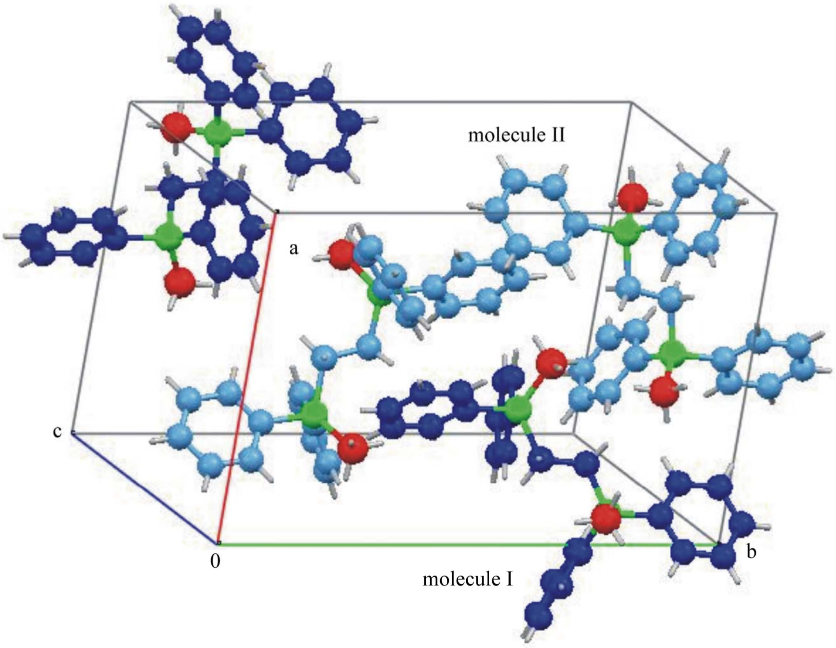

Figure 2. The unit cell of dppe$(BH_3)_2$.

hydrogen evolution, yielding 1,2-bis(diphenylphosphinoborane)ethane, dppe$(BH_3)_2$, which can be isolated by extraction in dichloromethane. Colorless crystals of dppe$(BH_3)_2$ obtained by crystallization from the hexane-dichloromethane solution were used for the single crystal diffraction determination.

In the crystal structure of the title compound, the monoclinic unit cell contains two molecules of $[C_{26}H_{30}B_2P_2]$ and four molecules per unit cell. All molecular properties of two asymmetric units of the molecule **I** are similar of the molecule **II** as given in **Table 3**.

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The average bond angles around phosphorus atoms are 112.9˚, 113.1˚, 105.8˚, and 105.5˚ for B-P-C, B'-P'-C', C-P-C and C'-P'-C', respectively. Study of the interactions between P atoms and contact atoms in coordination sphere with average distances (P-B: 1.876 Å for the molecule **I**, 1.905 Å for **II** and P-C 1.804 Å for **I**, 1.809 Å for **II**) reveals that the P atoms are surrounded by four atoms (one boron and three carbon atoms) in nearly ideal tetrahedral geometry.

Both molecules in an asymmetric unit have a similar three-dimensional conformation. Dihedral angles between the least square planes of phenyl rings in coordination sphere of P atoms are Cg1-Cg2 = 76.4(3) Å, Cg3-Cg4 = 88.2(3) Å for molecule **I** and Cg5-Cg6 = 71.2(3) Å, Cg7-Cg8 = 71.5(3) Å for molecule **II**. **Figure 2** shows the unit cell of dppe$(BH_3)_2$.

There is no classic hydrogen bond in the structure but the compound includes several pi-ring interactions between two asymmetric moieties. Rings are composed of atoms Cg1 = C1/C6, Cg2 = C7/C12, Cg3 = C15/C20, Cg4 = C21/C26, Cg1' = C1'/C6', Cg2' = C7'/C12', Cg3' = C15'/C20', Cg4' = C21'/C26'. Details of the pi-ring interaction geometry are given in **Table 4**.

The solution NMR data of 1,2-bis(diphenylphosphinoborane)ethane, dppe$(BH_3)_2$, are also in good agreement with the single crystal structure. It is noteworthy that the ^{1}H NMR spectrum gives two doublets at 2.15 and 2.38 ppm for the prochiral methylene groups [28] while the ^{13}C NMR spectrum exhibits only one signal at 22.93 ppm for the methylene carbons. Moreover, two separated multiplets at 7.54 and 7.61 ppm are observed for ortho-hydrogens of phenyl rings and similar to hydrogens of methylene groups, ortho-hydrogens of phenyl rings are not identical due to their different positions with respect to borane moieties. ^{31}P NMR spectrum shows a peak at –12.5 ppm which is about 10 ppm more shielded than corresponding peak of meso-$[HP(BH_3)(Ph)CH_2]_2$ complex [4], indicating that dppe$(BH_3)_2$ complex containing more phenyl rings has more electron-rich phosphorus atoms. However, ^{11}B NMR gives a peak at –40.06 ppm for borane groups comparable to the value of –41.6 ppm reported for meso-$[HP(BH_3)(Ph)CH_2]_2$ complex [4]. MS does not show the molecular ion peak expected at m/z = 425. Instead, it shows peaks at m/z = 429 or 431 due to oxidation of dppe$(BH_3)_2$ during the sampling/ionization whereby BH_3 groups are replaced by the oxo groups.

5. Conclusions

In conclusion, sodium borohydride is a facile BH_3 source in the synthesis of phosphanylborohydride compounds such as 1,2-bis(diphenylphosphinoborane)ethane, dppe$(BH_3)_2$, in high yield. Sodium borohydride and metaborate are easily separated by extraction with dichloromethane, providing an easy separation for the preparation of phosphanylborohydrides with high purity. The adduct dppe$(BH_3)_2$ crystallizes in monoclinic system with space group $P2_1$ and two asymmetric units containing nearly ideal tetrahedral phosphorus atoms.

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