Synthesis and properties of 1-diphenylboryl-2-diphenylphosphino-1,2-diphenylethene

A. S. Balueva and G. N. Nikonov*

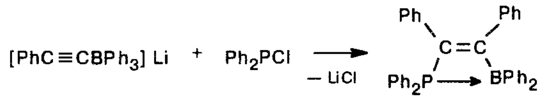
A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.
Fax: +7 (843) 275 2253

Consecutive interaction of lithium phenylacetylide with triphenylborane and diphenylchlorophosphine gave 1-diphenylboryl-2-diphenylphosphino-1,2-diphenylethene, which is less reactive than dialkylborylphosphinoethenes.

Key words: 1-diphenylboryl-2-diphenylphosphino-1,2-diphenylethene, reactivity.

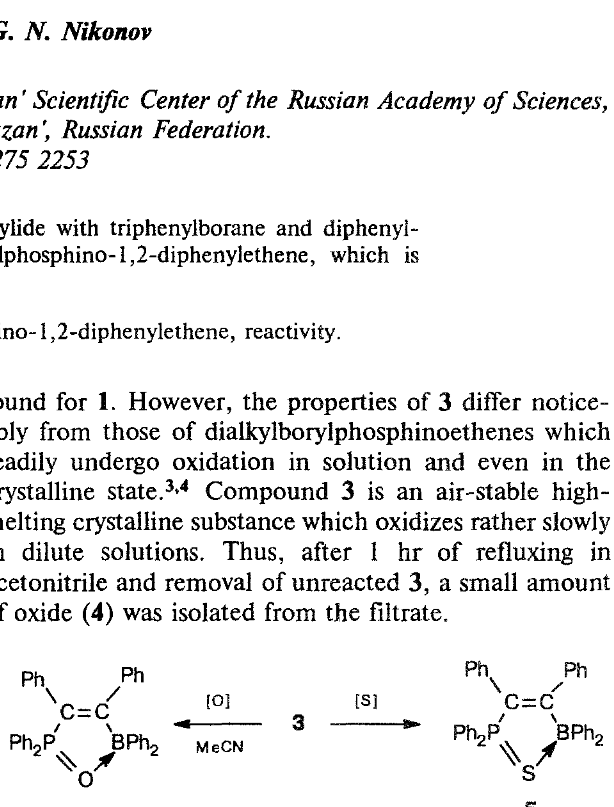
The chemical properties of 1-boryl-2-phosphinoethenes are determined to a great extent by the strength of intramolecular coordination of the $P\rightarrow B$ bond. The energy of interaction between the heteroatoms depends, in turn, on the molecular geometry parameters which are essential for orbital overlap, and on the donor-acceptor characteristics of the phosphorus and boron atoms. According to the X-ray analysis data of 1-diphenylboryl-2-diphenylphosphino-1-trimethylsilyl-2-phenylethene[1] and 1-butyl-1-dibutylboryl-2-diphenylphosphino-2-phenylethene[2] (**1**), the principal geometric parameters of the molecule — the length of the P—B bond and the values of the torsional angles — remain practically unaffected by the variation of the substituents at the boron atom. Also, a comparison of the reactivity of compound **1** with that of 1-butyl-1-dibutylboryl-2-ethylphosphino-2-phenylethene (**2**) revealed no serious differences caused by changing the substituents at the phosphorus atom.[3] In this connection, it was of interest to define the influence of the substituents at the boron atom on the behavior of borylphosphinoethenes.

For this purpose, 1-diphenylboryl-2-diphenylphosphino-1,2-diphenylethene (**3**) was prepared by a procedure[2,3] used for the synthesis of **1** and **2**.



3

In the ^{31}P NMR spectrum of compound **3** a signal at δ 6.9, typical of borylphosphinoethenes,[2,3] points to the existence of intramolecular $P\rightarrow B$ bonding. The molecular mass, determined ebullioscopically in C_6H_6, amounts to 550, which is close to the calculated value (528). The dipole moment of **3** is 4.24 D*, which is close to that found for **1**. However, the properties of **3** differ noticeably from those of dialkylborylphosphinoethenes which readily undergo oxidation in solution and even in the crystalline state.[3,4] Compound **3** is an air-stable high-melting crystalline substance which oxidizes rather slowly in dilute solutions. Thus, after 1 hr of refluxing in acetonitrile and removal of unreacted **3**, a small amount of oxide (**4**) was isolated from the filtrate.



4 **5**

It should be noted that the oxidation of dialkylborylphosphinoethenes primarily affects the B—C bonds.[4] Also, the addition of elemental sulfur to **3** proceeds under more severe conditions than in the case of compound **1**, for which the reaction in CS_2 is completed within several minutes at room temperature. The formation of sulfide (**5**) requires refluxing in toluene for 2 h. Thus, in comparison with dialkylborylphosphinoethene **1**, compound **3** is more inert in reactions involving the phosphorus atom.

The characteristic signal in the ^{31}P NMR spectrum of compound **4** is observed at δ 62.85. Taken together with the low-frequency shift of the band of the phosphoryl group in the IR spectrum (ν 1118 cm^{-1}), this indicates the existence of an intramolecular coordination bond $O\rightarrow B$ (cf.[4]). In the case of sulfide **5**, similar speculations lead to the conclusion that interaction occurs between the sulfur atom and the boryl moiety, since the closest structural analog of **5**, diphenyl(vinyl)phosphinesulfide, displays a signal in the ^{31}P NMR spectrum at δ 37.5.[5]

An even larger difference is observed in the reactivities of diphenyl- and dialkylborylphosphinoethenes towards

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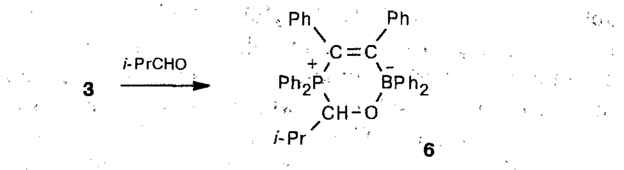
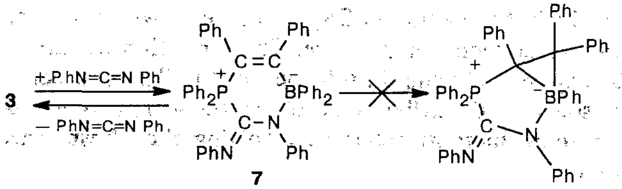
nucleophilic reagents. Compound **1** forms a complex with pyridine which exists in solution and may be detected by means of ^{31}P NMR spectroscopy.[2] On dissolving **3** in pyridine, the chemical shift in the ^{31}P NMR spectrum remains unaffected. This indicates the absence of complexing, although the phenyl substituents at the boron atom should be expected to enhance the stability of complexes of boranes with aromatic amines.[6] Oxide **4** also forms no complex with pyridine.

Compound **3** is also less reactive towards compounds with multiple polar bonds. For instance, thiocyanates, which readily form [4+2] adducts with dialkylborylphosphinoethenes, do not react with **3**. The reaction of **3** with isobutanal to give the corresponding 1-oxa-5-phosphonia-2-boratacyclohex-3-ene (**6**) is completed in 3 h, whereas the similar transformation of **1** takes only a few minutes.



The reactions involving heterocumulenes were of particular interest because earlier it was found that the initially formed [4+2] adducts with carbodiimides and phenyl isocyanate underwent 1,2-migration of the butyl group from the boron atom to give 2-aza-4-phosphonia-1-boratabicyclo[3.1.0]hexanes; in the case of carbodiimides, the intermediate cyclic adduct could not be detected.[7,8]

We found that phenyl isocyanate and phenyl isothiocyanate do not react with **3**. The reaction of **3** with diphenyl carbodiimide comes to completion only in 5 days, resulting in a cyclic betaine (**7**).



Compound **7** is a yellowish crystalline substance. Its IR spectrum displays an absorption band at ν 1566 cm^{-1} characteristic of a C=N bond. A signal at δ –4.2 (in C_6H_6), characteristic of cyclic betaines of similar structure, is observed in its ^{31}P NMR spectrum. The δ values for the signals of P in the bicyclic rearrangement products are known to range from 4.7 to 12.[7,8]

Against expectations, no anionotropic rearrangement was observed at higher temperatures. Instead, a reverse reaction occurred. The signal of **3** appeared in the ^{31}P NMR spectra after heating **7** in benzene for only a few minutes. The ready dissociation of **7** to give **3** presents extra evidence of high stability of the latter.

Thus, replacement of alkyl substituents at the boron atom with phenyl groups brings about a noticeable decrease in the reactivity of borylphosphinoethene, possibly due to the strengthening of the intramolecular donor-acceptor interaction.

Experimental

The ^{31}P NMR spectra were recorded on a Bruker WM-250 spectrometer at 101 MHz and 34.5°C, with 85 % H_3PO_4 as external reference. IR spectra were recorded on a Specord M-80 spectrometer in vaseline oil mulls.

The synthesis of compounds 1 and 2 has been described earlier.[2,3]

1-Diphenylboryl-2-diphenylphosphino-1,2-diphenylethene (3). A solution of phenyl lithium (2.39 g, 28.5 mmol) in 30 mL of Et_2O was added dropwise at 0°C under N_2 atmosphere to a stirred solution of phenyl acetylene (2.9 g, 28.5 mmol) in 3 mL of Et_2O. After stirring at 20°C for 0.5 h, a solution of triphenylborane (6.9 g, 28.5 mmol) in 15 mL of THF was added dropwise at 0°C, and the mixture was stirred for 1 h at 20°C. Then, a solution of diphenylchlorophosphine (5.28 g, 28.5 mmol) in 5 mL of Et_2O was added, and the reaction mixture was refluxed for 2.5 h. A precipitate, consisting of **3** and lithium chloride, was filtered on the next day. Another portion of **3** was obtained on evaporation of the filtrate. The precipitates were combined and recrystallized from DMF—MeCN (10:1, v/v) to afford 3.33 g (22.3 %) of compound **3**, mp 244—246°C. Found (%): C 86.81; H 5.94; P 6.49. $C_{38}H_{30}BP$. Calculated (%): C 86.36; H 5.68; P 5.87. ^{31}P NMR spectrum (C_6H_6), δ: 6.9.

(2-Diphenylboryl-1,2-diphenylethenyl)diphenylphosphine oxide (4). Compound **3** (0.4 g, 0.75 mmol) was dissolved with heating in 5 mL of dry pyridine, and a flow of dry air was bubbled through the solution for 4 days. Pyridine was removed in a vacuum, and the residue was crystallized from MeCN and recrystallized from DMF—MeCN (2:1) to give 0.3 g (73 %) of compound **4**, mp 225—227°C. Found (%): C 83.32; H 5.96; P 5.47. $C_{38}H_{30}BOP$. Calculated (%): C 83.82; H 5.51; P 5.69. IR spectrum, ν (cm^{-1}): 1118 (P=O). ^{31}P NMR spectrum (C_6H_6), δ: 62.85.

(2-Diphenylboryl-1,2-diphenylethenyl)diphenylphosphine sulfide (5). A mixture of 0.8 g (1.5 mmol) of compound **3** and 0.1 g (3.1 mmol) of sulfur was dissolved in 7 mL of toluene and refluxed for 2 h. Toluene was removed in a vacuum, and the residue was crystallized from acetone—MeCN (1:1), and once again from MeCN to afford 0.41 g (48 %) of compound **5**. An analytical sample was obtained by recrystallization from benzene; mp 210—212°C. Found (%): C 79.82; H 5.31; P 4.89; S 6.19. $C_{38}H_{30}BPS$. Calculated (%): C 81.42; H 5.36; P 5.54; S 5.71. IR spectrum, ν (cm^{-1}): 624 (P=S). ^{31}P NMR spectrum (C_6H_6), δ: 60.1.

6-Isopropyl-2,2,3,4,5,5-hexaphenyl-1-oxa-5-phosphonia-2-borata-3-cyclohexene (6). Isobutanal (0.5 mL) was added to a solution of compound **3** (0.15 g, 0.28 mmol) in 5 mL of benzene. After 3 h, the reaction mixture was evaporated in a vacuum, and the residue was crystallized from MeCN to yield 0.08 g (47 %) of compound **6**, mp 245—246°C. Found (%): C 83.39; H 6.53; P 4.86. $C_{42}H_{38}BOP$. Calculated (%): C 84.00; H 6.33; P 5.17. ^{31}P NMR spectrum (C_6H_6), δ: –7.0.

1,2,2,3,4,5,5-Heptaphenyl-6-phenylimino-1-aza-5-phosphonia-2-borata-3-cyclohexene (7). Diphenylcarbodiimide (0.23 g, 1 mmol) was added to a solution of compound **3** (0.58 g, 1 mmol) in 15 mL of benzene. After 5 days, the solvent was removed in a vacuum, and the residue was crystallized from MeCN to give 0.35 g (44 %) of compound **7**, mp 166°C (dec). Found (%): C 84.26; H 5.83; N 3.26; P 3.95. $C_{51}H_{40}BN_2P$. Calculated (%): C 84.76; H 5.54; N 3.88; P 4.29. IR spectrum, ν (cm^{-1}): 1556 (C=N). ^{31}P NMR spectrum (C_6H_6), δ: −4.2.

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On the relationship between the mass spectral and structural indices of arylsilanes

Yu. S. Nekrasov*, E. E. Tepfer, and Yu. N. Sukharev

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085

A common informational approach has been employed to obtain a generalized description of molecular structures (based on the graph spectra) and that of the respective mass spectra. The approach is suitable for comparing these two characteristics on a scale with common dimensional representation. A series of 28 arylsilane derivatives was studied to demonstrate the correlation between the mass spectral and structural informational indices. This series is divided into three subsets which differ in their inherent regression lines and characteristic structural features. The results thus obtained can be used in designing compact data base retrieval systems for the structures and mass spectra of organosilicon compounds.

Key words: mass spectra; molecular graphs; mass spectral vs. structural indices correlations; arylsilanes; vertex eccentricity; vertex distance; graph distance.

Choosing the proper structural and spectral characteristics is of crucial importance for establishing spectrostructural correlations. A set of microfragments associated with a set of spectral lines is usually used to describe a molecular structure in data base and artificial intelligence systems.[1,2] An alternative approach is based on constructing some generalized numerical characteristics of a structure and of the respective mass-spectrum. The information-topological indices adequately depict the molecular structural features and are commonly used as structural invariants.[3,4] One way of constructing the mass spectral indices (that is, convoluting an entire mass-spectrum to a single number) is to calculate the information entropy of a mass spectrum using Shenon's equation:

$$H = -\sum_{i=1}^{N} p_i \log_2 p_i \,, \tag{1}$$

where $p_i = I_i / \Sigma I_i$ is the intensity of the i-th peak normalized to the total ionic current; N is the total number of

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