Boron chelate complexes with some enaminones and diketones containing the pyridine fragment and their mutual transformations in solutions

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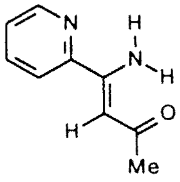
The interaction of Ph_2BOBu with 4-amino-4-(2-pyridyl)-3-buten-2-one, 3-amino-1-(2-pyridyl)-2-buten-1-one, and 1-(2-pyridyl)butan-1,3-dione was investigated. The 5- or 6-membered chelates with *N,O*- or *N,N*-coordination of boron are formed depending on the pyridine-containing ligand structure. These complexes are capable of mutual transformation in solutions.

Key words: 2-cyanopyridine, acetylacetone, catalysis, 4-amino-4-(2-pyridyl)-3-buten-2-one, 3-amino-1-(2-pyridyl)-2-buten-1-one, and 1-(2-pyridyl)butan-1,3-dione, diphenylboron chelates, dynamic equilibrium in solutions, nuclear Overhauser effect.

The synthetic potential of reagents capable of forming complexes can be enhanced significantly through the use of their chelates. In particular, original schemes of construction of different functionalized heterocycles have been elaborated on the basis of diphenylboron chelates of β-diketones and aminovinyl ketones.[1–4]

The present work deals with the interaction of butoxydiphenylborane with 4-amino-4-(2-pyridyl)-3-buten-2-one (**1**), 3-amino-1-(2-pyridyl)-2-buten-1-one (**2**), and 1-(2-pyridyl)-butan-1,3-dione (**3**) with the aim of obtaining the corresponding diphenylboron chelates that serve as new reagents for heterocyclic synthesis. The presence of a pyridine fragment in enaminones **1**, **2**, and diketone **3** is responsible for the variety of coordination interactions with the participation of these ligands (formation of cyclic complexes with chelate nodes C_2BN_2, C_2BNO or C_2BO_2).



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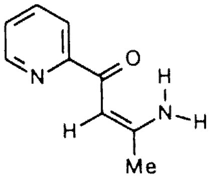

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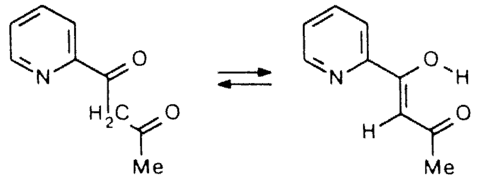

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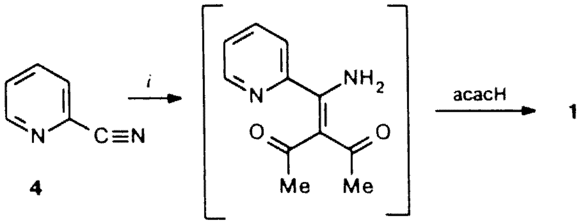
β-Diketone **3** and enaminone **2**, which is obtained from the former under the action of ammonia, have been described earlier in the literature.[5,6] However, it is impossible to transform β-diketone **3** into enaminone **1**, which is an isomer of compound **2**. That was the reason why we synthesized ligand **1** (see the preliminary report[7]) *via* the reaction of acetylacetone (acacH) with 2-cyanopyridine (**4**) in the presence of catalytic amounts of $Ni(acac)_2$ (*cf.*, for example, the $Ni(acac)_2$-promoted addition of methylene-active β-diketones to activated nitriles, Cl_3CCN,[8] F_3CCN,[9] 3-amino-4-cyanofurazan,[10] *etc.*). In this case, the process is accompanied by the deacetylation of the adduct formed (probably, under the action of an excess of acacH). Crystalline enaminone **1** was isolated in 40 % yield.



i. acacH, 110—120 °C, 10 mol. % $Ni(acac)_2$

The structure of compound **1** was confirmed by the data of ^1H (Table 1) and ^{13}C (Table 2) NMR spectra. The peak of the molecular ion (m/z = 162) was registered in its mass spectrum. The IR spectrum of enaminone **1** ($CHCl_3$) contains bands at 3452 and 3276 cm^{-1}, which may be attributed to free and associated NH bonds, respectively. The data of ^1H NMR in $CDCl_3$ also suggest the nonequivalence of protons in the amino

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 710—714, March, 1996.

Table 1. ^{1}H NMR spectra of compounds **1**—**3** and **5**—**9** (δ, *J*/Hz) in $CDCl_3$[a]

Compound	CH_3	=CH	H(3) (pyridine)	H(4)	H(5)	H(6)	NH	OH
1	2.21	5.82	7.78	7.78	7.38	8.65	7.1, 7.7	—
2	2.07	6.40	8.07	7.77	7.32	8.60	5.7, 10.2	—
3[b]	2.09	6.70	7.93	7.68	7.26	8.52	—	15.52
5	2.26	5.80[c]	7.77	7.85	7.38	8.73	9.05	—
6	2.21	5.81	8.02	8.18	7.65	8.60	10.1	—
7	2.29	6.56[c]	8.26	7.84	7.38	8.64	7.1	—
8[d]	2.72 (2.44)	5.95 (7.04)	7.99 (8.40)	8.20 (7.94)	7.69[f]	8.61 (8.72)	—	—
8[e]	2.52	6.18	8.58	8.47	8.95	9.05	—	—

[a] Chemical shifts of protons 2Ph = 7.1—7.6. [b] The content of compound **3** in the solution is equal to 90 %. [c] $^4J_{\mathrm{H,NH}}$ = 2.1—2.4. [d] Chemical shifts of the signals of isomer **9** (~7 %) are given in parentheses. [e] The data are given for the DMSO-d_6 solution (the signals of isomer **9** are absent). [f] The chemical shift of H(5) of isomer **9** is not determined.

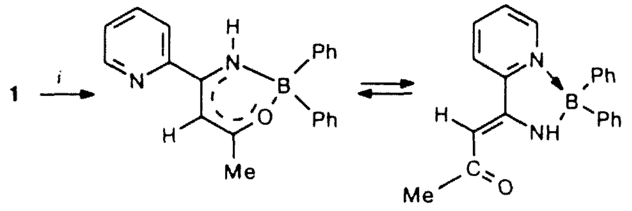
Table 2. ^{13}C NMR spectra of compounds **1**—**3** and **5**—**8** (δ, *J*/Hz)

Compound	Solvent	Me	=CH	C(2)[a] pyridine	C(3)[a]	C(4)[a]	C(5)[a]	C(6)[a]	NC=	MeCO	2Ph	CO
1	DMSO-d_6	29.87	92.30 (159)	151.43	120.19	136.75	124.95	148.92 (179)	155.45	197.41	—	—
2	$CDCl_3$	22.76	91.53 (163)	156.11	121.64	136.88	125.33	148.44 (182)	165.05	—	—	187.20
3	$CDCl_3$	25.76	90.06 (167)	151.89	121.64	136.79	126.03	149.06	—	194.67	—	180.80
5	$CDCl_3$	24.32	91.58	161.46	121.73	137.47	126.74	149.72 (182)	147.71	181.64	126.18 127.23 131.75 [b]	—
6	DMSO-d_6	29.27	88.72	154.06	121.13	143.24	127.28	143.12 (180)	150.66	194.94	126.48 127.47 130.04 [b]	—
7	$CDCl_3$	23.70	94.68 (172)	151.80	122.18	136.97	125.66	148.94 (179)	171.11	—	126.16 127.17 131.59 150	169.88
8	$CDCl_3$	31.50	103.00 (157)	151.03	120.73	142.02	126.37	141.65	—	198.95	127.40 127.79 132.12 145.7	160.77
8	DMSO-d_6	31.14	101.72 (160)	148.96	121.50	143.44	127.80	142.13 (188)	—	196.37	126.80 127.43 131.62 146.0	160.79

[a] Py atoms. [b] A very broad signal C—B.

group. Apparently, molecule **1** has an intramolecular hydrogen bonding N—H· · ·O and therefore exists in solution in the *Z*-form (with respect to a C=C bond).

We found that the interaction of ligand **1** and Ph_2BOBu resulted in the formation of two isomeric compounds, six-membered chelate **5** with *O,N*-coordination of boron and five-membered chelate **6** with *N,N*-coordination. When the reaction was carried out in ether, chelates **5** and **6** were separated successfully because of the poor solubility of the latter, and both isomers were isolated in the pure state in 31 and 68 % yields, respectively.



5 **6**

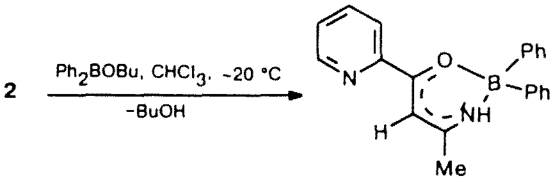
i. Ph_2BOBu, Et_2O, -20 °C, -BuOH

The structure of compounds **5** and **6** was established using ^{13}C NMR spectra (Table 2). Thus, a significant downfield shift of a CO signal (δ 181.6) in comparison with a free ligand **1** (δ 197.4) and chelate **6** (δ 194.9) is observed there. This suggests the participation of the acetyl fragment of ligand **1** in the coordination with boron (*cf.* data[4,11,12] published by us earlier for boron chelates with aminovinylcarbonyl compounds). In addition, the spectrum of chelate **6**, compared to the spectra of compounds **1** and **5**, contains an upfield shift signal for the C(4) atom of the pyridine ring and a downfield shift signal for the C(6) atom (see Table 1). Such an effect is characteristic of chelates in which the boron atom is directly bonded to the pyridine ring.[13,14]

It was necessary to establish the positions of the substituents of chelate **6** relative to a C=C bond, and this was performed on the basis of the data of nuclear Overhauser effect (NOE). When the proton of the =CH group is saturated, the ^1H NMR spectrum of the solution in DMSO-d_6 shows a 17 ± 0.5 % NOE on the H(3) proton of the pyridine ring. Analogously, the saturation of the H(3) proton results in a 20 ± 0.5 % NOE on the proton of the =CH group. Hence, the structure of *Z*-isomer should be attributed to compound **6**.

The study of the complex formation of compound **1** with Ph_2BOBu using ^1H NMR spectra in $CDCl_3$ (in an ampoule) showed that initially isomer **5** was formed and only after 3—4 h did the signals of compound **6** appear in the spectrum of the reaction mixture. The concentrations of chelates **5** and **6** gradually become equal, and when dynamic equilibrium is attained (after 3 days), their ratio is equal to 1 : 2.3. When the interaction of compound **1** with Ph_2BOBu takes place in DMSO-d_6, the formation of complexes **5** and **6** proceeds, initially, at the same rate, but in the end (after 3 days) the solution contains almost the same ratio between the isomers as with $CDCl_3$. When crystalline, compounds **5** and **6** remain unchanged with time, but in the course of dissolving, their mutual transformations into each other occurs until dynamic equilibrium is attained (2—3 days).

In contrast to enaminone **1**, its isomer **2** reacts with Ph_2BOBu in chloroform to give only one chelate complex **7**, which was isolated in a 79 % yield.



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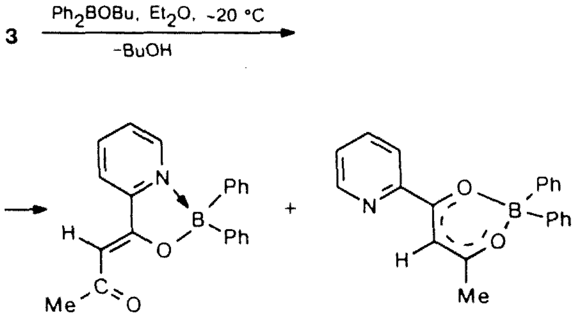
The data of ^{13}C NMR spectra of compound **7** (Table 2) bear witness to the fact that the pyridine ring does not participate in coordination with the B atom. The structure of compound **7** was also confirmed by IR, ^1H NMR, and mass spectra. Thus, for the IR spectrum of compound **7** in $CHCl_3$, as with chelate **5**, the most intense bands at 1625 and 1535 cm^{-1} are characteristic, which refer to the delocalized system of the multiple bonds of the chelate ring formed by aminovinylcarbonyl ligand. One narrow band at 3310 cm^{-1} is observed within the range of the stretching vibrations of the NH group. The ^1H NMR spectrum of compound **7** in $CDCl_3$ remains unchanged for 4 days, as well as when the solution is heated up to 65 °C (1 h). Thus, no traces of an isomer with a five-membered chelate ring were found.

When the interaction of β-diketone **3** with Ph_2BOBu occurs, a chelate complex (yield 95 %) was obtained, which unexpectedly had the structure **8** with a five-membered ring (*O,N*-coordination of boron), instead of the β-diketonate structure (**9**).



8 **9**

The data of the ^{13}C NMR spectra in $CDCl_3$ and DMSO-d_6 favor the structure **8** (*cf.* the data for chelate **6** in Table 2 and corresponding arguments given above to prove its structure). The IR spectrum of compound **8** in $CDCl_3$ differs significantly from the spectra of boron β-diketonates (*cf.* the data in Refs. 15 and 16) and, in part, by the absence of intense bands within the 1500—1600 cm^{-1} range, which is typical for the latter.

The ^1H NMR spectrum of compound **8** in DMSO-d_6 contains one set of signals, whereas in $CDCl_3$ the signals of compound **8** are accompanied by signals of low intensity, which may be attributed to isomer **9** (Table 1). However, the content of the latter does not exceed 7 %. The spectrum of the mixture remains unchanged for 3 days, as well as on heating the solution up to 60 °C (1 h). Unfortunately, we failed to record the signals of all the carbon atoms in the ^{13}C NMR spectrum because of the low percentage of β-diketonate **9**.

According to experimental data concerning the measurements of NOE, chelate **8**, like complex **6**, has the *Z*-configuration relative to a C=C bond. The saturation of the proton of the =CH group in the ^1H NMR spectrum of the solution of compound **8** in $CDCl_3$ gives a 14±0.5 % NOE on the H(3) proton of the pyridine ring, and the saturation of the H(3) proton gave a 13±0.5 % NOE on =CH.

When ammonia acts on chelate 8, substitution of O atom for NH group occurs to give complex 7.

$$\mathbf{8} \xrightarrow{NH_3,\ THF,\ -20\ ^\circ C} \mathbf{7}$$

The final results of the chelation of ligands **1—3** with Ph_2BOBu are evidently determined by the thermodynamic stabilities of the complexes formed. An important factor contributing to the strong donor-acceptor interaction in a chelate system is the delocalization of π-electrons of β-diketonate type (six π-electrons on the orbitals of the five-atom fragment of a six-membered boron-containing ring[17]).

Consequently, it was easy to suppose that the reactions of ligands **1—3** with Ph_2BOBu would lead to the formation of chelates **5**, **7**, and **9** of similar type. However, considering the ability of compound **3** for complex formation, it is also necessary to take into account the fact that nitrogen has, as is well known, stronger electron-donor properties than oxygen. In fact, this factor defines the formation of five-membered chelate **8** with *O,N*-coordination of boron from diketone **3**. As for complex **7**, which is obtained from enaminone **2** and stabilized both by the participation of nitrogen in a donor-acceptor interaction and by the presence of a delocalized system of π-electrons, an alternative five-membered chelate structure does not have any advantages in this case. Finally, enaminone **1** characteristically forms both six-membered chelate **5** (with *O,N*-coordination of boron) and five-membered chelate **6** (with *N,N*-coordination), the yield of the latter and its content in the equilibrium mixture in the solutions being higher.

The ability of the five- and six-membered cyclic four-coordinated boron compounds to mutually transform in solutions should be taken into account when studying their chemical properties.

Experimental

^1H NMR spectra were recorded on a Bruker WM-250 (250.13 MHz) instrument, and ^{13}C NMR spectra were recorded on a Bruker AM-300 (75.47 MHz). Chemical shifts are given relative to TMS. Experiments on the nuclear Overhauser effect (NOE) were performed on a Bruker WM-250 spectrometer according to the NOE MULT procedure of the firm Bruker in difference variant, in DMSO-d_6 for chelate **6** and in $CDCl_3$ for chelate **8**. IR spectra were obtained with a Perkin-Elmer-577 device, and mass spectra were obtained with a Varian MAT 311A spectrometer.

3-Amino-1-(2-pyridyl)-2-buten-1-one (**2**) and 1-(2-pyridyl)-butan-1,3-dione (**3**) were synthesized according to the procedure of Refs. 6 and 5, respectively. All manipulations concerning the synthesis of diphenylboron complexes were carried out in a nitrogen atmosphere.

4-Amino-4-(2-pyridyl)-3-buten-2-one (1). A mixture of 2-cyanopyridine (1.7 g, 16 mmol), acetylacetone (6.0 g, 60 mmol), and $Ni(acac)_2$ (0.46 g, 1.8 mmol) was heated at 110—120 °C for 15 h (monitored by TLC and IR). Highly volatile substances were removed *in vacuo*, and the rest (3.65 g) was purified on a column with SiO_2 (C_6H_6—$CHCl_3$ as the eluent). Ligand **1** (2.1 g) was isolated and purified by sublimation *in vacuo* (1—2 Torr) at ~100 °C. 1.04 g (40 %) of compound **1** was obtained, m.p. 74—76 °C. Found (%): C, 66.75; H, 6.28; N, 17.20. $C_9H_{10}N_2O$. Calculated (%): C, 66.65; H, 6.21; N, 17.27. IR-spectrum ($CHCl_3$, ν/cm^{-1}): 3452, 3276 (NH), 1632, 1587, 1570, 1538. MS (*m/z*): 162 $[M]^{+\cdot}$. The ^1H NMR and ^{13}C NMR of enaminone **1** and the other compounds synthesized are given in Tables 1, 2.

Diphenylboron complexes of 4-amino-4-(2-pyridyl)-3-buten-2-one (5,6). Enaminone **1** (0.145 g, 0.89 mmol) in ether (7 mL) was added to a solution of Ph_2BOBu (0.27 g, 1.13 mmol) in ether (3 mL), and this mixture was left to stand for 3 days. The crystals formed were filtered off and washed with hexane (5×5 mL), and chelate **6** (0.2 g, 68 %) was obtained, m.p. 183—184 °C (in a sealed capillary under N_2). Found (%): C, 77.33; H, 5.80; B, 3.31; N, 7.71. $C_{21}H_{19}BN_2O$. Calculated (%): C, 77.30; H, 5.83; B, 3.31, N, 8.59. IR spectrum ($CHCl_3$, ν/cm^{-1}): 3422 (NH), 1692 (C=O), 1628, 1540. The filtrate was concentrated *in vacuo*, then hexane (10 mL) was added, and the mixture obtained was left to stand in a refrigerator. The precipitate formed was filtered off and washed with pentane, and complex **5** (0.09 g, 30.8 %) was obtained, m.p. 202—203 °C (in a capillary under N_2). Found (%): C, 77.58; H, 6.04; B, 3.28; N, 8.36. $C_{21}H_{19}BN_2O$. Calculated (%): C, 77.30; H, 5.83; B, 3.31; N, 8.59. IR spectrum ($CHCl_3$, ν/cm^{-1}): 3310 (NH), 1625 pl., 1618, 1582, 1574, 1535.

Diphenylboron complex of 1-(2-pyridyl)butan-1,3-dione (8). A solution of β-diketone **3** (3.0 g, 18.4 mmol) and Ph_2BOBu (4.76 g, 20 mmol) in ether (15 mL) was stirred for 2 h, then the precipitate formed was filtered off and washed with pentane. Chelate **8** (5.72 g, 95 %) was obtained, m.p. 229—230 °C. Found (%): C, 76.57; H, 5.22; B, 3.48. $C_{21}H_{18}BNO_2$. Calculated (%): C, 77.11; H, 5.51; B, 3.31. IR spectrum ($CHCl_3$, ν/cm^{-1}): 1640, 1618.

Diphenylboron complex of 3-amino-1-(2-pyridyl)-2-buten-1-one (7). **a.** A mixture of enaminone **2** (0.120 g, 0.74 mmol) and Ph_2BOBu (0.220 g, 0.92 mmol) in $CHCl_3$ (15 mL) was left to stand at –20 °C for 3 days, then the solvent and *n*-butanol formed were removed *in vacuo*, pentane (15 mL) was added, and the mixture was left to stand at –5 °C for 12 h. The precipitate was filtered off and washed with pentane. Chelate **7** (0.190 g, 79 %) was obtained, m.p. 154—155 °C. Found (%): C, 77.18; H, 5.85; B, 3.16; N, 9.04. $C_{21}H_{19}BN_2O$. Calculated (%): C, 77.35; H, 5.83; B, 3.32; N, 8.59. IR spectrum ($CHCl_3$, ν/cm^{-1}): 3370 (NH), 1627, 1525. MS (*m/z*): 326 $[M]^{+\cdot}$; 249 $[M-Ph]^+$.

b. An excess of ammonia was passed through a solution of complex **8** (1.2 g, 7.4 mmol) in THF (10 mL), and the mixture was left to stand for 12 h. The solvent was removed *in vacuo*, pentane (50 mL) was added to the residual viscous yellow mass, and the mixture was left to stand for 12 h. The precipitate formed was filtered off and washed with pentane. Impure chelate **7** (1.17 g) was obtained, which was purified on a column with SiO_2 (C_6H_6 as the eluent). 0.9 g (75 %) of compound **7** was isolated, m.p. 154—155 °C.

This work was carried out with financial support from the International Science Foundation (Grant M5Q 300) and the Russian Foundation for Basic Research (Project No. 94-03-08964).

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Received September 19, 1995