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Pyrazole complexes of acyloxydialkylboranes

Marek Dąbrowski, Tomasz Kliś, Sergiusz Luliński, Izabela Madura, Janusz Serwatowski *, Janusz Zachara

Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

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Abstract

The reaction of $Me_3CCOOBEt_2$ with pyrazole led to the formation of the stable addition complex **1**, which was found to be monomeric in solution. The reaction of 9-H-9-borabicyclo[3.3.1]nonane $(9\text{-H-9-BBN})_2$ with pyrazole and pivalic acid yielded a similar complex $Me_3CCOO(9\text{-BBN})\text{-pzH}$ **2**. Crystallographic analysis of **2** revealed a dimeric structure due to the strong hydrogen bonding between azole hydrogen and carbonyl oxygen. The one boron–carbon bond of compound **1** cleaves readily with triethylborane at 20°C with the evolution of ethane, giving a species $Me_3CCOO(BEt_2)_2pz$ **3** with a seven-membered heterocyclic ring as the main structural feature. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Acyloxyboranes; Pyrazaboles; Pyrazole; Crystal structure; NMR spectroscopy

1. Introduction

The substitution of acidic hydrogen in a pyrazole molecule (pzH) with a dialkylboryl group leads to the formation of the so-called tetraalkylpyrazaboles [1] which exist usually as very stable dimers with a six-membered B_2N_4 ring. Standard syntheses of tetraalkylpyrazaboles involve non-catalyzed reactions of pzH with trialkylboranes or tetraalkyldiboranes(6) [2] or, more recently, alkylation of B-halogenated pyrazaboles with lithium or magnesium alkyls [3]. The former require elevated temperatures, usually 130–150°C, due to the great stability of the boron–carbon bond. Carboxylic acids are well-known reagents which readily cleave B–C bonds of trialkylboranes. The mechanism of this cleavage was proposed earlier by Brown [4] and Dessy [5,6]. Pivalic acid and/or its borylated derivatives $Me_3CCOOBR_2$ have been widely used for many years as active catalysts in protolysis of trialkylboranes [7,8]. The mechanism of this catalysis depends on the type of the protolytic reagent and is thought to be simple in the case of water and alcohols and more complicated in the case of primary amines. The formation of stable addition complexes of $Me_3C{-}COOBEt_2$ with ammonia and primary amines was proved by Köster et al. [9].

We have found that pivalic acid or $Me_3CCOOBEt_2$ act as a catalysts also in the synthesis of 4,4,8,8-tetraethylpyrazabole (TEP) from Et_3B and pzH. In this paper we report the preparation and structural characterization of addition complexes of $Me_3CCOOBR_2$ ($R = Et$ (**1**), $R_2 = 1,5$-cyclooctandiyl (**2**)) with pyrazole. We suppose that **1** as well as its derivative $Me_3CCOO(BEt_2)_2pz$ **3** are intermediates in the catalytic cycle leading to the formation of TEP.

2. Results and discussion

The reaction of $Me_3C{-}COOBEt_2$ with pyrazole in the molar ratio 1:1 afforded the addition complex **1** as an oily liquid, according to Eq. 1 (Scheme 1).

The presence of the hydrogen bond in the molecule of **1** has been confirmed by the solution infrared spec-

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* Corresponding author. Fax: +48 22 6282741; e-mail: serwat@ch.pw.edu.pl

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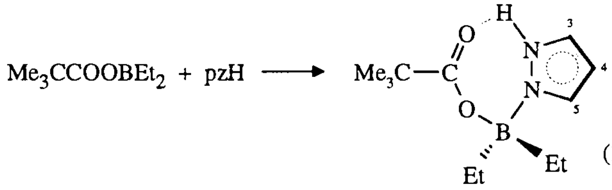


(1)

Scheme 1.

trum which exhibits a broad band of the associated NH group in the range of 3300–2300 cm^{-1}. The molecular weight determination of **1** in benzene, points to a monomeric structure in solution. These results allowed to conclude that the additional stabilization of the molecule is reached owing to the intramolecular hydrogen bonding and the formation of the seven-membered ring structure. This observation can also be supported by the fact that our attempts to obtain the corresponding complex of type **1** with imidazole were unsuccessful. In the ^{13}C-NMR spectrum of **1**, three signals of the three non-equivalent carbon atoms of the pyrazole ring are observed, which is in agreement with the structure proposed for **1.** However, the ^{1}H-NMR spectrum shows that complex **1** has a dynamic character (on the ^{1}H-NMR time scale). As a result two hydrogen atoms H3 and H5 bound to carbon atoms C3 and C5 become equivalent and give, at room temperature, one broadened signal. The process is slowed down below 0°C where two well resolved doublets appear in the spectrum. The nature of this process is somewhat unclear and it could be explained in different ways. One possibility is the slow dissociation of **1** with subsequent exchange of pyrazole. However, flipping of the pyrazole ring in a molecule of **1** cannot be completely excluded although it would involve a transfer of azole hydrogen to carbonyl oxygen. Complex **1** is stable and can be stored at room temperature during several weeks without decomposition. It is also stable during several hours at 60°C in $CDCl_3$. Neat **1** decomposes rapidly only above 100°C to give TEP and pivalic acid.

The synthesis of **1** was also accomplished starting from the triethylborane-pyrazole complex and pivalic acid. This reaction proceeds rapidly at room temperature with ethane evolution. It is well-known that complexes of Et_3B with nitrogen donors have generally a significant dynamic character [10] and we have also proved this for Et_3B*pzH complex by ^{11}B-NMR experiments which showed the dependence of the chemical shift on the Et_3B:pzH molar ratio. The mode of formation of complex **1** remains essentially the same as described above. Nevertheless, it should be stressed that the protolysis of Et_3B with pivalic acid in the system Et_3B/pzH, i.e. the formation of $Me_3CCOOBEt_2$, is slowed down by the competition of the much stronger base pzH (rapid cleavage of Et_3B by pivalic acid in the absence of pzH is observed at 0°C [8]).

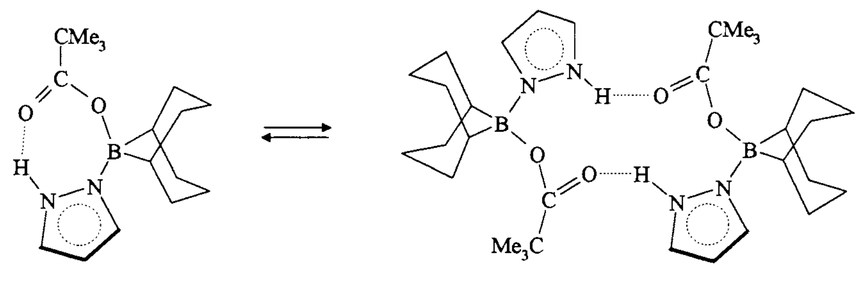
Another species of type **1** was synthesized in a one-pot reaction from $(9\text{-H-9-BBN})_2$, pyrazole and pivalic acid, as is shown below (Eq. (2)):

$$\mathrm{Me_3CCOOH + pzH + 1/2(9\text{-}H\text{-}9\text{-}BBN)_2} \rightarrow \mathrm{Me_3CCOO(9\text{-}BBN)\text{-}pzH} \qquad (2)$$

Compound **2** is a crystalline solid moderately air-stable (slow decomposition after several days was observed). **2** in comparison with **1**, is more stable, which is confirmed by its ^{1}H-NMR spectrum, where two doublets of two hydrogen atoms: H3 and H5 are observed (at room temperature). Molecular weight measurements revealed that **2** exists in solution as a monomer (Scheme 2). The solution infrared spectrum of **2** suggests the existence of an intramolecular hydrogen bond N–H–O (the broad band with a maximum at 3125 cm^{-1}).

The X-ray structure analysis of **2** shows that there are two independent dimers in the unit cell located over crystallographic centres of symmetry as shown in Fig. 1. The molecular structure of one of these dimers is presented in Fig. 2. Both dimers are chemically identical as confirmed by precise geometry analyses; the bond lengths (Table 1) are the same within 3σ, but this is not the case for some angles, e.g. B(1)–O(11)–C(31) and B(2)–O(21)–C(81), suggesting slight differences in the geometry of these dimers.

The comparison of adequate torsion angles (Table 5) leads to a conclusion that there are two different conformers, possibly due to crystal packing. The biggest



in solution (monomeric)

in solid state (dimeric)

Scheme 2.

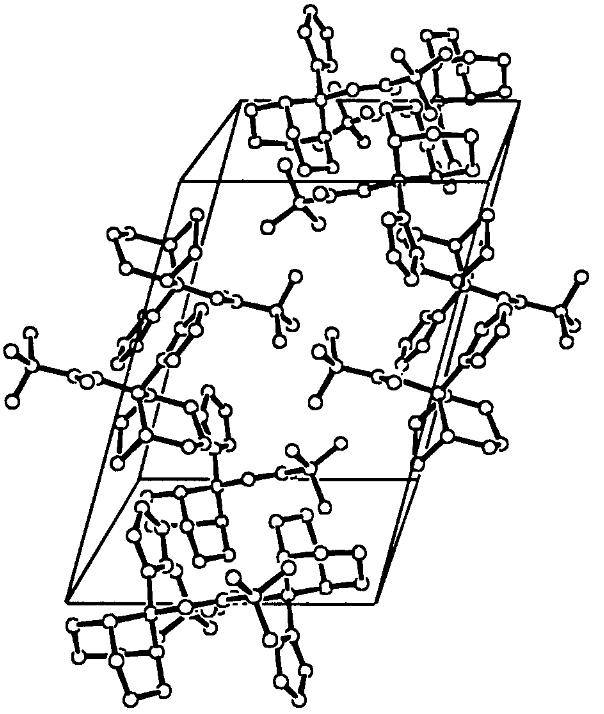


Fig. 1. Packing diagram of **2**.

difference for torsion angles are within conformation of the boron atom, pz and the carboxylic group. The boron atom for dimer **2B** lies on the opposite side of the pz plane than the O(21) atom. This is confirmed by different sign of the torsion angles for B(1)–N(11)–N(12)–C(23) and B(2)–N(21)–N(22)–C(73), respectively. The distance of boron atoms from pz planes for dimer **2A** is 0.131(3) and 0.051(3) Å for dimer **2B** [11]. Centrosymmetric dimers are formed due to the relatively strong hydrogen bonding resulting in the formation of the 14-membered heterocyclic ring (Fig. 2).

The N...O′ distance of 2.722(2) Å observed for pair **2A**–**2A**′ is slightly shorter than that for the pair **2A**–**2A**′ (2.784(3) Å), where typical N...O distances lie within 2.79–2.68 Å [12] (Tables 2 and 3).

Complex **1** reacts rapidly with triethylborane in heptane at room temperature with ethane evolution. The product obtained was as an oily liquid, after evaporation of the solvent. Spectroscopic data and molecular weight determination indicated that the borylation of **1** resulted in the formation of a new heterocyclic system **3**, consisting of seven-membered $CO_2B_2N_2$ and pyrazole fused rings, according to Eq. 3 (Scheme 3).

Compound **3** represents a new type of a pyrazolylborane adduct, although similar species where the carboxyl group is replaced by hydrogen, -OH as well as -SH groups were reported [2,13]. On the other hand, species possessing a six-membered CO_2B_2N ring, where the pz ring is replaced by the bridging -NH_2 group, are also known. [9,14]. The ^{11}B-NMR spectrum of **3** shows one signal at 10.3 ppm in the region typical for the tetracoordinated boron atom bonded to one oxygen, one nitrogen and two carbon atoms. The ^{1}H- and ^{13}C-NMR spectra point to a symmetrical arrangement of the pyrazole ring. In the infrared spectrum an absorption band of the C=O group at 1590 cm^{-1} is most noteworthy as it occurs in the range typical for the carbonyl group coordinating the boron atom [9,15]. Compound **3** is stable and decomposes rapidly only above 100°C to give TEP and $Me_3C–COOBEt_2$. **3** can be also synthesized by borylation of **1** with $Me_3C–COOBEt_2$. However, the best method which yielded the desired product free of impurities was the one-pot synthesis from 1 equivalent of pivalic acid, 1 equivalent of pzH and 2 equivalents of Et_3B. Probably an important role in the $Et_2B^{\oplus}/H^{\oplus}$ exchange is played by the carbonyl group, which coordinates the boron atom analogously as it was proved in the reaction of carboxylic acids with R_3B. Unfortunately, we were unable to synthesize a crystalline compound of type **3** in order to confirm the proposed structure by X-ray diffraction. The attempt to obtain a similar compound from **2** and 9-H-9-BBN failed due to side reactions. Finally, the treatment of 1 equivalent of benzoic acid and 1 equivalent of 3,5-dimethylpyrazole with 2 equivalents of Et_3B resulted in the evolution of only 1 equivalent of ethane and a crystalline complex of $PhCOOBEt_2$ with 3,5-dimethylpyrazole **4** was isolated. This complex was found to be inert in the protolysis of Et_3B, even at elevated temperature, which can clearly be explained by the steric influence of methyl groups. The question whether the methyl group in the *ortho* position to the NH bond hinders the coordination of the Et_3B molecule by the carbonyl group sufficiently to prevent subsequent protolysis or rather the formation of the appropriate rotamer in which the distance between carbonyl and NH groups is small, remains open.

In conclusion, pyrazole complexes of $Me_3C–COOBEt_2$ were found to have interesting structural properties in the liquid as well as in the solid state. The specific arrangement of NH and carbonyl groups in the molecule of **1** is responsible for the much higher activity of the azole hydrogen in the cleavage of the boron–carbon bond in the molecule of triethylborane than it is observed in the case of pyrazole. The role of complexes of type **1** and **3** in the catalyzed synthesis of tetraalkylpyrazaboles will be investigated.

3. Experimental section

^{1}H-, ^{13}C-, ^{11}B-NMR as well as IR spectra were recorded at room temperature (unless otherwise noted). Chemical shifts are given in ppm relative to TMS in ^{1}H- and ^{13}C-NMR spectra and relative to Et_2O*BF_3 in ^{11}B-NMR spectra. The solvent was $CDCl_3$ (NMR spec-

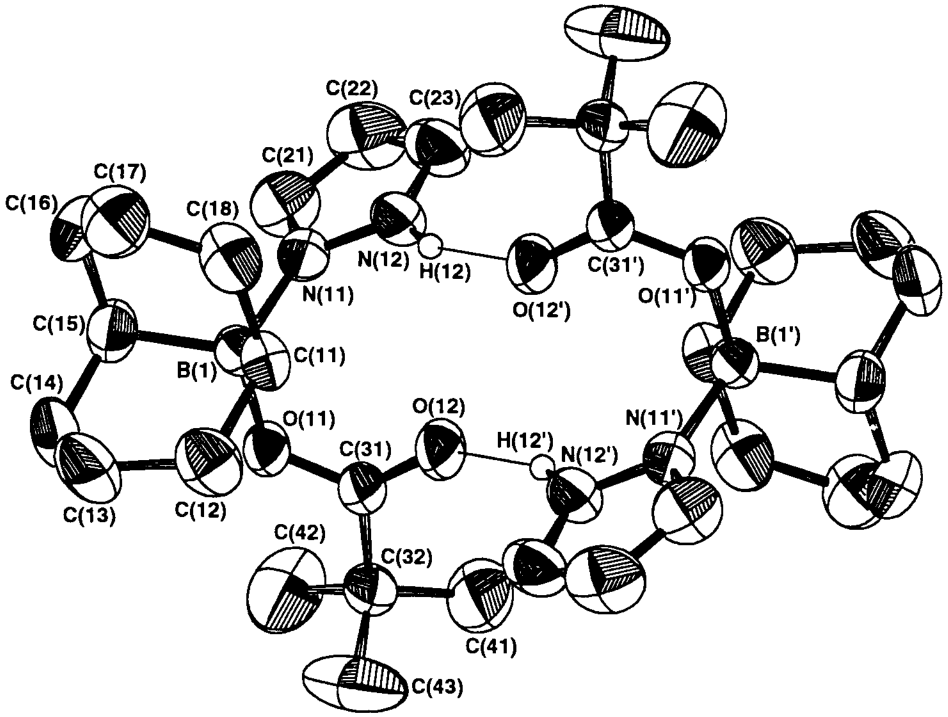


Fig. 2. ORTEP [18] plot of the molecular structure of one of the independent centrosymmetric dimers of Me_3CCOO(9-BBN)-pzH **2**. Thermal ellipsoids are drawn at 50% probability level; the hydrogen atoms, except NH groups, are omitted for clarity.

tra). Molecular weight determinations were performed cryoscopically in benzene. Triethylborane, 98%, was received from MPI für Kohlenforschung, Mülheim/Ruhr. Pyrazole and pivalic acid were received from Aldrich, and were laboratory grade. (2,2-Dimethyl)propanoiloxydiethylborane was synthesized as described in the literature [8]. All reactions were carried out under dry argon using standard Schlenk techniques. Pyrazole and benzoic acid were dried in vacuo prior to use. Solvents were dried by conventional methods. Other reagents were used without purification.

3.1. Preparation of the Et_3B_*pzH complex

Et_3B (31.0 g, 0.32 mol) was added to a suspension of pyrazole (21.1 g, 0.31 mol) in heptane (100 ml). The rate of dropping in was adjusted to maintain the temperature below 15°C. After the addition of Et_3B the solvent and the excess of Et_3B were evaporated off under reduced pressure. The product (51.0 g, yield 99%) was obtained as a colourless oily liquid.

Table 1
Selected bond lengths (Å)

O(11)–C(31)	1.300(2)	O(21)–C(81)	1.304(3)
O(11)–B(1)	1.521(3)	O(21)–B(2)	1.524(3)
O(12)–C(31)	1.221(2)	O(22)–C(81)	1.219(3)
N(11)–N(12)	1.338(2)	N(21)–N(22)	1.343(2)
N(11)–B(1)	1.600(3)	N(21)–B(2)	1.603(3)
N(12)–H(1)	0.89(2)	N(22)–H(2)	0.84(2)

^{1}H-NMR (300 MHz) δ: 10.1 (br, 1H, NH), 7.64 (d, 2H, CH), 6.45 (t, 1H, CH), 0.65 (t, 9H, CH_3), 0.42 (q, 6H, CH_2); ^{11}B-NMR (96.24 MHz) δ: 0.0; IR (CCl_4): 3450 cm^{-1} (sharp, N–H).

*3.2. Preparation of the addition complex of Me_3C–$COOBEt_2$ with pzH (**1**)*

A solution of pyrazole (2.26 g, 33.2 mmol) in chloroform (10 ml) was dropped in during 30 min to the solution of Me_3C–$COOBEt_2$ (5.68 g, 33.5 mmol) in chloroform (10 ml) at 0°C. The solvent was removed in vacuo, to give **1** (7.90 g, yield 100%) as a colourless liquid.

Table 2
Selected bond angles (°)

O(11)–B(1)–C(11)	115.0(2)	O(21)–B(2)–C(61)	115.4(2)
O(11)–B(1)–C(15)	107.3(2)	O(21)–B(2)–C(65)	107.1(2)
C(11)–B(1)–C(15)	107.4(2)	C(61)–B(2)–C(65)	106.9(2)
O(11)–B(1)–N(11)	104.2(2)	O(21)–B(2)–N(21)	105.4(2)
C(11)–B(1)–N(11)	111.9(2)	C(61)–B(2)–N(21)	111.6(2)
C(15)–B(1)–N(11)	110.8(2)	C(65)–B(2)–N(21)	110.2(2)
B(1)–O(11)–C(31)	124.3(2)	B(2)–O(21)–C(81)	126.0(2)
N(12)–N(11)–B(1)	124.1(2)	N(22)–N(21)–B(2)	123.8(2)
C(23)–N(12)–H(1)	126.5(1)	C(73)–N(22)–H(2)	129.0(2)
N(11)–N(12)–H(1)	122.9(1)	N(21)–N(22)–H(2)	120.0(2)
O(12)–C(31)–O(11)	123.4(2)	O(22)–C(81)–O(21)	123.3(2)

Table 3
Selected torsion angles (°)

N(12)–N(11)–B(1)–O(11)	98.0(2)	N(22)–N(21)–B(2)–O(21)	91.7(2)
C(31)–O(11)–B(1)–N(11)	−62.6(2)	C(81)–O(21)–B(2)–N(21)	−69.4(2)
B(1)–O(11)–C(31)–O(12)	0.7(3)	B(2)–O(21)–C(81)–O(22)	7.1(3)
C(21)–N(11)–B(1)–O(11)	−74.6(3)	C(71)–N(21)–B(2)–O(21)	−91.1(3)
C(21)–N(11)–B(1)–C(11)	160.5(2)	C(71)–N(21)–B(2)–C(61)	142.9(3)
N(12)–N(11)–B(1)–C(11)	−26.9(3)	N(22)–N(21)–B(2)–C(61)	−34.3(4)
C(21)–N(11)–B(1)–C(15)	40.6(3)	C(71)–N(21)–B(2)–C(65)	24.3(4)
B(1)–N(11)–N(12)–C(23)	−174.5(2)	B(2)–N(21)–N(22)–C(73)	177.9(2)
C(31)–O(11)–B(1)–C(11)	60.3(3)	C(81)–O(21)–B(2)–C(61)	54.2(3)
C(31)–O(11)–B(1)–C(15	179.8(2)	C(81)–O(21)–B(2)–C(65)	173.1(2)
N(12)–N(11)–B(1)–C(15)	−146.8(2)	N(22)–N(21)–B(2)–C(65)	−153.0(2)
N(11)–B(1)–C(11)–C(12)	−63.0(2)	N(21)–B(2)–C(61)–C(62)	−61.4(3)
B(1)–N(11)–C(21)–C(22)	173.7(2)	B(2)–N(21)–C(71)–C(72)	−177.5(2)
B(1)–O(11)–C(31)–C(32)	−177.8(2)	B(2)–O(21)–C(81)–C(82)	−172.4(2)

Anal. Found: C, 59.84; H, 9.93; N, 11.92. Anal. Calc. for $C_{12}H_{23}BN_2O_2$: C, 60.52; H, 9.74; N, 11.76. ^{1}H-NMR (500 MHz, 273 K) δ: 15.3 (br, 1H, NH), 7.65 (d, 1H, CH), 7.60 (d, 1H, CH), 6.38 (t, 1H, CH), 1.21 (s, 9H, $(CH_3)_3C$), 0.8–0.5 (m, 10H, $B(C_2H_5)_2$); ^{13}C-NMR, δ (50.28 MHz): 185.7 (C=O), 134.7 (CH), 130.3 (CH), 105.4 (CH), 39.7 ($(CH_3)_3\mathit{C}$), 27.3 ($(\mathit{C}H_3)_3C$, 11.8 (br, BCH_2), 8.7 ($BCH_2\mathit{C}H_3$); ^{11}B-NMR, δ (96.24 MHz): 7.0; IR (CCl_4): 3300–2300 cm^{-1} (N–H···O), 1700 cm^{-1} (C=O···H).

3.3. Reaction of $(9\text{-}H\text{-}9\text{-}BBN)_2$ with pyrazole and 2,2-dimethylpropanoic acid

A solution of pivalic acid (0.204 g, 2.0 mmol) and pzH (0.130 g, 2.0 mmol) in toluene (7 ml) to a cooled (0°C) solution of $(9\text{-H-BBN})_2$ (0.243 g, 1.0 mmol) in toluene (5 ml) was added. The cooling bath was removed and the reaction was allowed to warm up to room temperature. Hydrogen (42 Nml, 95%) evolved. Evaporation of the solvent afforded a crystalline solid **2** (0.55 g, yield 96%). Anal. Found: C, 67.58; H, 9.80; N, 9.85. Anal. Calc. for $C_{16}H_{27}BN_2O_2$: C, 66.25; H, 9.32; N, 9.66. ^{1}H-NMR (300 MHz): (1.13, s, 9H, t-Bu); (1.1–1.9, m, 14H, 9-BBN); (6.40, t, 1H, pz); (7.60, d, 1H pz), (7.76, d, 1H, pz); ^{11}B-NMR (96.24 MHz) δ: 6.3; IR (CCl_4): 3125 cm^{-1} (N–H···O), 1690 and 1630 cm^{-1} (C=O···H).

3.4. Preparation of $Me_3CCOO(BEt_2)_2pz$ **3** in the reaction of the Me_3CCOOH*pzH complex with Et_3B

Et_3B (6.0 g, 61.2 mmol) was added at −20°C to the solution of Me_3CCOOH*pzH (4.18 g, 24.6 mmol) in heptane (15 ml). During 1 h the temperature was raised gradually to 20–30°C. To complete the reaction the solution was stirred for 10 min at 55°C. The total volume of ethane evolved was 1.05 Nl (95%). After evaporation of the solvent a colourless, oily liquid **3** was obtained (7.50 g, yield 100%).

Table 4
Crystal data and refinement data for 2

Empirical formula	$C_{16}H_{27}BN_2O_2$
Formula weight	290.21
Crystal class	Triclinic
Space group	$P\bar{1}$
Unit cell parameters	
a (Å)	10.419(1)
b (Å)	12.642(2)
c (Å)	14.611(2)
α(°)	70.065(9)
β (°)	74.857(9)
γ(°)	81.99(1)
V (Å^3)	1743.7(3)
Z	4
$D_{\text{calc.}}$ (Mg m^{-3})	1.105
F(000)	632
Crystal size (mm)	$0.20 \times 0.32 \times 0.38$
Absorption coefficient (mm^{-1})	0.071
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å), graphite-monochromated
Temperature (K)	293(2)
Scan type	$\theta - 2\theta$
2θ range for data collection	4.06–50.10
Standard reflections	Two measured every 70 reflections
Crystal decay (%)	2.19
Index ranges	$0 \leq h \leq 12$, $-14 \leq k \leq 15$, $-16 \leq l \leq 17$
Reflections collected	6227
Independent reflections	5867 ($R_{\text{int}} = 1.71\%$)
Reflections observed [$I > 2\sigma(I)$]	3339
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0668 \cdot P)^2$, where $P = (F_o^2 + F_c^2)/3$
Data/restraints/parameters	5866/0/536
Final R indices (observed data)	$R_1 = 0.0480$, $wR_2 = 0.1118$
R indices (all data)	$R_1 = 0.0975$, $wR_2 = 0.1334$
Goodness-of-fit on F^2	0.985 (all) 1.143 (observed)
Extinction coefficient	0.006(1)
Largest difference peak and hole (e Å^{-3})	+0.179 and −0.127

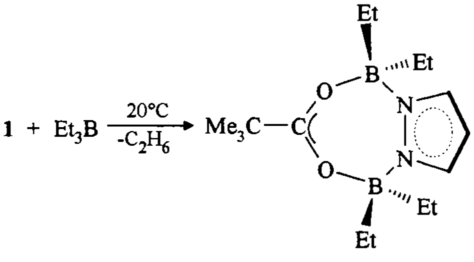
Anal. Found: C, 62.66; H, 10.71; N, 9.40. Calc. for $C_{16}H_{32}B_2N_2O_2$: C, 62.79; H, 10.54; N, 9.15. ^{1}H-NMR (300 MHz) δ: 7.55 (d, 2H, CH), 6.28 (t, 1H, CH), 1.26 (s, 9H, $(CH_3)_3C$), 0.70–0.55 (m, 20H, $B(C_2H_5)_2$); ^{13}C-NMR (50.28 MHz) δ: 189.9 (COO), 136.6 (CH), 104.6 (CH), 41.0 ($(CH_3)_3\mathit{C}$), 27.1 ($(\mathit{C}H_3)_3C$), 14.7 (br, BCH_2), 8.9 ($BCH_2\mathit{C}H_3$).^{11}B-NMR (96.24 MHz) δ: 10.3; IR (CCl_4): 1590 cm^{-1} (C=O···B).

*3.5. Preparation of PhCOOBEt$_2^*$pz*H **4** in the reaction of PhCOOH with pzH and Et$_3$B (pz* = 3,5-dimethylpyrazolyl)*

Et_3B (3.90 g, 39.8 mmol) was added at 0°C to the solution of PhCOOH (2.02 g, 16.6 mmol) and pz*H (1.60 g, 16.6 mmol) in heptane (15 ml). The mixture was stirred for 2 h at ambient temperature, then was heated for 30 min at 70°C. Cooling to room temperature afforded colourless crystals of **4** (3.85 g, yield 81%). Anal. Found: C, 66.95; H, 8.10; N, 10.00. Anal. Calc. for $C_{16}H_{23}BN_2O_2$: C, 67.15; H, 8.10; N, 9.79. ^{1}H-NMR (200 MHz) δ: 14.2 (br, 1H, NH), 8.15 (m, 2H, Ph), 7.53–7.38 (m, 3H, Ph), 5.88 (s, 1H, pz*), 2.35 (s, 6H, Me), 0.79 (s, 10H, BEt_2); ^{11}B-NMR (64.16 MHz) δ: 8.8.

*3.6. Crystal Structure of **2***

A sample of **2** (0.3 g) was dissolved in toluene (15 ml) at 25°C. Slow cooling in a 0°C freezer gave crystals suitable for X-ray analysis. Crystal data, data collection and refinement parameters for **2** are summarized in Table 4. A single crystal was measured on a Siemens P3 diffractometer at room temperature. The unit cell was determined by the automating indexing of 24 well centered reflections. Two standard reflections were monitored every 70 measurements; no significant crystal decay was detected during data collection. After correction for the Lorentz-polarization effect and crystal decomposition, the equivalent reflections were averaged. The structure was solved by direct methods using the SHELXS-86 [16] program which revealed the position of the oxygen, nitrogen, boron atoms and the majority of the carbon atoms. The distribution of the peaks showed that the compound crystallizes with two independent molecules in the asymmetric unit. Full-matrix least-squares refinement method against F^2 values was carried out by using the SHELXL-93 [17] program. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of tert-butyl groups were refined with fixed geometry, riding on their carrier atoms, with fixed isotropic displacement parameter equal to 1.5 times the value of the equivalent isotropic displacement parameter of the parent carbon. For the other hydrogen atoms positional and isotropic thermal parameters were refined. The magnitude of the thermal parameters observed for one of the ^{t}Bu-groups



(3)

Scheme 3.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
O(11)	4148(2)	7316(1)	798(1)	48(1)
O(12)	5482(2)	8648(1)	584(1)	65(1)
N(11)	2521(2)	8829(1)	1133(1)	45(1)
N(12)	2901(2)	9866(2)	943(2)	53(1)
B(1)	3037(3)	8098(2)	391(2)	43(1)
C(11)	3461(3)	8875(2)	−749(2)	49(1)
C(12)	2247(3)	9594(2)	−1076(2)	70(1)
C(13)	1016(4)	8970(3)	−893(3)	91(1)
C(14)	696(3)	8061(3)	128(3)	84(1)
C(15)	1902(3)	7326(2)	463(2)	58(1)
C(16)	2525(3)	6548(2)	−163(3)	76(1)
C(17)	3224(4)	7140(3)	−1242(3)	86(1)
C(18)	4085(3)	8091(3)	−1375(2)	70(1)
C(21)	1781(3)	8543(3)	2061(2)	69(1)
C(22)	1690(3)	9394(3)	2457(2)	85(1)
C(23)	2405(3)	10220(3)	1729(2)	70(1)
C(31)	5241(2)	7656(2)	851(2)	46(1)
C(32)	6232(2)	6720(2)	1250(2)	54(1)
C(41)	7058(3)	7139(2)	1759(3)	97(1)
C(42)	7124(4)	6435(3)	357(3)	119(1)
C(43)	5527(3)	5694(2)	1994(3)	113(1)
O(21)	8628(2)	2692(1)	4590(1)	54(1)
O(22)	8640(2)	829(1)	5012(1)	62(1)
N(21)	10749(2)	2248(1)	5160(1)	48(1)
N(22)	11196(2)	1163(2)	5438(2)	53(1)
B(2)	10122(3)	2833(2)	4203(2)	47(1)
C(61)	10818(2)	2338(2)	3312(2)	52(1)
C(62)	12305(3)	2567(2)	2975(2)	66(1)
C(63)	12649(4)	3780(3)	2713(3)	94(1)
C(64)	11821(3)	4398(2)	3420(3)	78(1)
C(65)	10336(3)	4159(2)	3784(2)	60(1)
C(66)	9566(4)	4681(3)	2958(3)	83(1)
C(67)	9923(5)	4152(3)	2121(3)	91(1)
C(68)	10059(4)	2859(3)	2479(2)	70(1)
C(71)	10994(3)	2673(2)	5812(2)	66(1)
C(72)	11589(3)	1870(3)	6489(2)	80(1)
C(73)	11700(3)	918(2)	6233(2)	69(1)
C(81)	8038(2)	1746(2)	4904(2)	50(1)
C(82)	6528(3)	1897(2)	5114(2)	72(1)
C(91)	5923(3)	777(4)	5754(3)	146(2)
C(92)	6132(4)	2301(4)	4128(3)	159(2)
C(93)	6044(4)	2724(4)	5679(4)	162(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

(atoms C(91), C(92), C(93) suggests a possibility of some rotational disorder about the C(81)–C(82) bound which was not modelled. Final results gave $R_1 = 0.048$ and $wR_2 = 0.1118$. Atomic coordinates for the non-hydrogen atoms and equivalent isotropic displacement coefficients are presented in Table 5.

4. Supplementary material

Listings of bond length and angles anisotropic thermal parameters and hydrogen atom parameters, tables of calculated and observed structure factors have been deposited at the Cambridge Crystallographic Data Center.

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