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Unsymmetrical polypyrazolylborate via boron cations

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Abstract

Convenient new procedures were developed for preparing unsymmetric pyrazolylborate, $[H_2B(pz)(pz')]^-$. Reaction of 3,5-dimethylpyrazole with $BH_3 \cdot THF$ complex gives 3,5-dimethylpyrazole borane. Treatment of this compound with I_2 at room temperature gives the cation $[H_2B(3,5\text{-}Me_2pzH)_2]^+$. When the reaction temperature was lowered to −30 °C we obtained the compound $[H_2B(3,5\text{-}Me_2pzH)(I)]$, whose reactions with different pyrazoles in THF give the unsymmetric $[H_2B(3,5\text{-}Me_2pzH)(pzH')]^+I^-$. Reaction of the boronium iodides with NaH produces $[H_2B(3,5\text{-}Me_2pz)(pz')]^-Na^+$.

Introduction

The use of polypyrazolylborates as ligands is a subject which has been steadily increasing since they were first reported by Trofimenko [1]. This fact is well reflected by the different reviews concerning the topic which have been published in recent times. [2–4]

The most remarkable property of this kind of ligand is that their presence sometimes allows the synthesis of certain compounds which otherwise would have been very difficult to obtain. The preparation of an air-stable molybdenum(III) complex by Lincoln and co-workers [5] is an illustrative example in this direction.

Despite the existence of a rather large variety of pyrazoles [6] and therefore of polypyrazolylborate possibilities, most of the work done so far deals with either the pyrazole or the 3,5-dimethylpyrazole derivatives. Therefore, the consideration of possible changes in the electronic or steric effects due to modifications on the pyrazole moiety has generally been disregarded. Nevertheless, the electronic properties for this kind of ligand can be quite substantially modified. So, if we consider the pK_a of the 2-pyrazole nitrogen as an indicator of its donor strength, some very different changes at the 4-position of the pyrazole can lead to huge differences in its basicity. This is shown in Table 1 for several pyrazoles with similar steric requirements.

A similar consideration can be made for the steric effect. Thus, the cone angles [7] found for $RB(pz)_3Mo$ and $RB(3,5\text{-}Mepz)_3Fe$ are 180 and 225°, respectively [8, 9]. These results clearly indicate that the steric requirements strongly depend on the substituent at the 3-pyrazole position. Therefore, a marked steric effect should be expected along a series of 3-substituted polypyrazolylborate metal complexes [10].

TABLE 1. pK_a values of several pyrazoles [11]

		pK_a
3,5-H	4-CH_3	3.09
3,5-H	4-H	2.52
3,5-H	4-Br	0.69
3,5-H	4-NO_2	−1.96
3,5-CH_3	4-CH_3	4.63
3,5-CH_3	4-H	4.12
3,5-CH_3	4-Br	2.30

The synthesis of polypyrazolylborates is usually made following Trofimenko's classical methods, by letting molten pyrazole react with an alkali metal borohydride. The first example of an asymmetrically substituted species, $[H_2B(3,5\text{-}Me_2pz)(pz')]^-$, was reported by us some years ago, via 3,5-dimethylpyrazole borane [12]. However the yields of this synthetic method are quite low and its selectivity is not too high. Therefore, several experimental modifications to the original method have been proposed in order to solve some of the most common problems. This report presents the results obtained in our effort to achieve chiral polypyrazolylborates.

Experimental

All the compounds were manipulated under an atmosphere of dry oxygen-free argon and in dry degassed solvents. IR spectra (KBr pellets) were recorded on a

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Beckman Acculab 3 spectrometer, ^1H NMR spectra were obtained with a Bruker WH 90 or a Varian M 60 (ppm values).

3,5-Dimethylpyrazole borane (1), (3,5-Me$_2$pzH)BH$_3$

A solution of BH_3 in THF (120 ml, *c*. 120 mmol) was added to a solution of 10 g of 3,5-dimethylpyrazole in 50 ml of THF. After 1 h the solvent from the reaction was removed under reduced pressure. The reaction products were washed with petroleum ether (5×10 ml) and the white solid obtained was recrystallized using a THF/petroleum ether solvent mixture. Yield 10.3 g (90%). IR (cm^{-1}); ν BH, 2260–2240; ν NH, 3280. ^1H NMR ($CDCl_3$/TMS): 2.24 (s, 6H), 5.92 (s, 1H), 8.55 (s, 1H). *Anal.* Calc.: C, 54.61; H, 10.08; N, 25.47. Found: C, 54.73; H, 9.91; N, 25.26%.

3,5-Dimethylpyrazole monoiodoborane (3), [H$_2$B(3,5-Me$_2$pzH)(I)]

A solution of iodine (11.4 g, 45 mmol) in THF (100 ml) was added dropwise to a stirred solution of **1** (9.9 g, 91 mmol) in THF (10 ml), and the reaction mixture was kept at −30 °C. As the addition proceeds hydrogen evolution from the reaction mixture can be observed as well as the disappearance of the colour due to the presence of I_2. An excess of I_2 at the end of the reaction should be avoided.

The reaction mixture was used immediately without attempting to isolate **3**.

Dihydro-bis(3,5-dimethylpyrazole)boronium iodide (4a)

A solution of iodine (3.2 g, 12.7 mmol) in THF (50 ml) was added dropwise, and at room temperature, to a stirred solution of **3** (25.5 mmol) in THF. After 2 h of reaction 100 ml of pentane were added to the reaction mixture, and the white crystals which precipitated were collected and recrystallized from CH_2Cl_2/pentane. Yield 2.7 g (70%).

MW (osmometric in acetone) 335. Molar conductivity (acetone): 135 cm^2 ohm^{-1} mol^{-1}. m.p. 134 °C. IR (cm^{-1}): ν BH, 2275, 2235; ν NH, 3270. ^1H NMR (CD_2Cl_2/TMS): 2.32 (s, 6H), 2.46 (s, 6H), 6.10 (s, 2H), 8.36 (s, 2H). *Anal.* Calc.: C, 36.18; H, 5.46; N, 16.87. Found: C, 35.92; H, 5.53; N, 16.75%.

Dihydro(3,5-dimethyl-1-pyrazole)(X-pyrazole)boronium iodide, (4b–d)

Solutions of the appropriate pyrazole in THF (40 mmol) were added at −30 °C to a freshly prepared solution of **3** in THF (40 mmol). In each case the solutions formed were colorless. The boronium iodide started to precipitate after 5–10 min. After 3 h the reaction mixture was filtered keeping the temperature at −30 °C. Addition of petroleum ether to the filtrate produced a further crop of products.

4b, from CH_2Cl_2/ether. Yield 85%. m.p. 123 °C. IR (cm^{-1}): ν BH, 2270, 2218; ν NH, 3265. ^1H NMR (CD_2Cl_2/TMS): 2.30 (s, 3H), 2.48 (s, 3H), 6.05 (s, 1H), 6.25 (t, 1H), 7.55 (d, 1H), 7.68 (d, 1H). *Anal.* Calc.: C, 31.17; H, 4.34. Found: C, 31.12; H, 4.18%.

4c, from CH_2Cl_2. Yield 80%. m.p. 149 °C. IR (cm^{-1}): ν BH, 2280, 2225; ν NH, 3280. ^1H NMR (CD_2Cl_2/TMS): 2.35 (s, 3H), 2.51 (s, 3H), 6.10 (s, 1H), 6.25 (s, 1H), 6.50–7.50 (m, 10H). *Anal.* Calc.: C, 55.66; H, 4.86. Found: C, 55.30; H, 4.79%.

4d, from CH_2Cl_2. Yield 70%. m.p. 127 °C. IR (cm^{-1}): ν BH, 2284, 2234; ν NH, 3268. ^1H NMR (CD_2Cl_2/TMS): 2.27 (s, 3H), 2.40 (s, 3H), 2.51 (s, 3H), 5.98 (s, 1H), 6.30 (s, 1H), 7.51 (s, 1H). *Anal.* Calc.: C, 34.10; H, 4.76. Found: C, 34.01; H, 4.63%.

Sodium dihydro(3,5-dimethyl-1-pyrazolyl)(1-pyrazolyl)-borate (5c)

To sodium hydride (0.96 g, 40 mmol) suspended in 20 ml THF was added dihydro(3,5-dimethyl-1-pyrazole)(1-pyrazole) boronium iodide (5.45 g, 18 mmol) dissolved in 50 ml of THF. After 2 h at room temperature, the mixture was filtered and the solvent of the filtrate evaporated to give **5c**, in almost quantitative yield. m.p. 240 °C (decomp.). IR (cm^{-1}): ν BH, 2260, 2360. ^1H NMR (D_2O/TSP as internal standard): 2.12 (s, 3H), 2.25 (s, 3H), 5.87 (s, 1H), 6.28 (t, 1H), 7.48 (d, 1H), 7.58 (d, 1H).

Synthesis of 5a, 5b and 5d

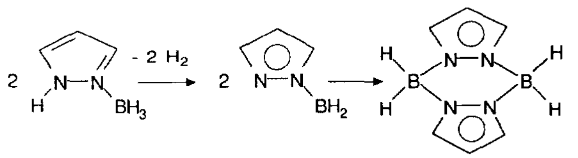
All these compounds were prepared in the same manner as described for **5c**. The spectroscopic data, IR and ^1H NMR, are in complete concordance with the structure (see Scheme 2).

Results and discussion

In our previous work we reported an alternative way to the 'classical one' to synthesize **1**, in which $LiBH_4$ was reacted with 3,5-dimethylpyrazole hydrochloride. The best yield obtained for the desired product using this method was 38%. In our search to a simpler and more efficient synthetic route, we attempted Ryschewitsch's method [13] to prepare Me_2HNBH_2I. We also studied the reaction of $NaBH_4$ with 3,5-dimethylpyrazole and iodine. In neither case could we improve our initial results. However, if $BH_3 \cdot THF$ is reacted with the 3,5-dimethylpyrazole **1** can be obtained with a yield over 90% (eqn. (1)).

$$\text{C}_4\text{H}_4\text{OBH}_3 + \text{3,5-Me}_2\text{pzH} \longrightarrow \underset{\textstyle 1}{(\text{3,5-Me}_2\text{pzH})\text{BH}_3} + \text{C}_4\text{H}_4\text{O} \qquad (1)$$

If this same reaction is attempted with pyrazole, 4-nitropyrazole or diphenylpyrazole, the reaction does not proceed as expected. In these cases, the main product is a pyrazole-borane dimer instead of the pyrazole borane. An explanation of this behaviour can be given in terms of the acidity of these pyrazole compounds, which favor their dimerization via H_2 elimination under the ordinary experimental conditions used (eqn. (2)). These results also agree with our earlier observation that, among the different systems tried to obtain **1**, the only one which seems to work properly was that for the reaction between 3,5-dimethylpyrazole hydrochloride and $LiBH_4$.

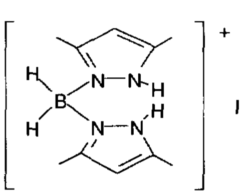

(2)

Pyrazole monoiodoboranes and bispyrazole-boronium iodides

The synthesis of dihydro-bis(1-pyrazol)borates is possible by making use of anionic intermediates [12]. In this case, reaction of the neutral pyrazole adduct **1** with NaH led to the obtention of sodium trihydro-(pyrazolyl)borate (**2**), $Na(H_3B(3,5\text{-dimethylpyrazolyl}))$. Replacement of one of the hydrides of **2** by a 1-pyrazolyl moiety, although possible, requires quite severe reactions conditions and the yields are quite poor. Thus a strategy was developed to facilitate the entrance of the second pyrazolyl group by using a better leaving group than -H. The chosen chemical was iodine, and the sample reaction is given in eqn. (3).

$$2\ \underset{\mathbf{1}}{(3,5\text{-Me}_2\text{pzH})\text{BH}_3} + \text{I}_2 \longrightarrow 2\ \underset{\mathbf{3}}{(3,5\text{-Me}_2\text{pzH})\text{BH}_2\text{I}} + \text{H}_2 \qquad (3)$$

When solutions of **1** are treated, at room temperature, with stoichiometric amounts of I_2 (or equivalent amount of I_2 solutions), the I_2 was quickly consumed and a gas evolved from the reaction medium. The resulting reaction solution behaved quite differently from Me_3BH_2I [13], since it react neither with water nor with nitrogenated bases such as pyrazole or pyridine. The IR spectrum for the white solid that precipitated by pentane addition to the reaction mixture showed two sharp bands corresponding to B–H stretching. Its ^1H NMR, molecular weight determination, elemental analysis and molar conductivity, in acetone, can be explained by the formation of the salt, **4**.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(4)

This last result seems to indicate that when **1** is treated with I_2, some 3,5-dimethyl(pyrazolyl)-monoiodoborane is formed which decomposes fast to form **4**.

In order to avoid this undesirable decomposition, the reaction temperature was lowered and THF solutions of **1** were reacted with I_2 at −30 °C. At these experimental conditions the desired products were obtained after 1 h of reaction time. The unsymmetrical dihydrobispyrazoleboronium iodides **4b**, **4c** and **4d** were synthesized using this method (Scheme 1).

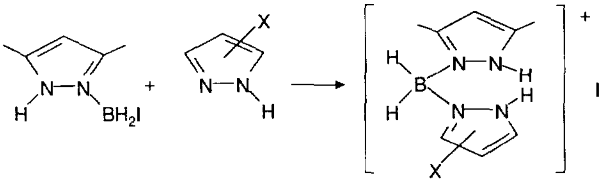
*Dihydro(3,5-dimethyl-1-pyrazole)(X-1-pyrazole)boronium iodide (X=H (**4b**); 3,5-diphenyl (**4c**); 4-methyl (**4d**))*

Solutions of the appropriate pyrazole derivative in THF (40 mmol) were added dropwise to a stirred solution of **3** freshly prepared. The temperature of the reaction was kept at −30 °C. After 3 h the solid which precipitated was filtered at −30 °C. Addition of petroleum ether to the filtrate resulted in the precipitation of more of the desired product. The solids so obtained were recrystallized from CH_2Cl_2/ether for X=H and CH_2Cl_2 for the two other cases. The yields obtained for **4b**, **4c** and **4d** were 85, 80 and 70%, respectively.

Unsymmetrical sodium dihydro(1-pyrazolyl)borates

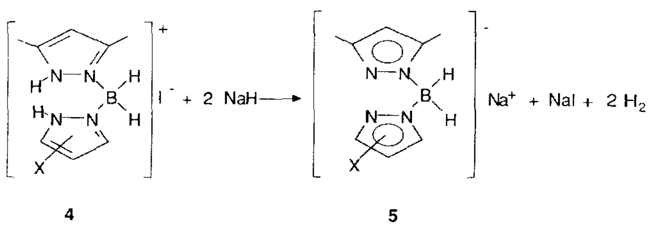
The corresponding unsymmetrical dihydro(1-pyrazolyl)borate alkali metal salts **5**, were readily available from the reaction of **4** with NaH or Na (powder) in THF (Scheme 2).

The unsymmetrical ligands herein prepared were tested with different metal salts in order to obtain their


4

X	3,5-Me	H	3,5-Ph	4-Me
4	a	b	c	d

Scheme 1.



X	3,5-Me	H	3,5-Ph	4-Me
5	a	b	c	d

Scheme 2.

corresponding complexes, i.e. $\{H_2B[(3,5\text{-diphenyl-pz})(3,5\text{-dimethyl-pz})]\}_2Zn$ [14].

Further research on the synthesis of chiral polypyrazolylborates $[HB(pz)(pz')(pz'')]^-$ and their reactivity towards metal complexes is in progress.

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