Synthesis and Chloride Affinity of Sterically Demanding Ditopic Lithium Bis(pyrazol-1-yl)borates

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Abstract. The synthesis and full characterization of the sterically demanding ditopic lithium bis(pyrazol-1-yl)borates $Li_2[p-C_6H_4(B(Ph)pz^R_2)_2]$ is reported ($pz^R = 3$ -phenylpyrazol-1-yl (3^{Ph}), 3-*t*-butylpyrazol-1-yl (3^{Ph})). Compound 3^{Ph} crystallizes from THF as THF-adduct 3^{Ph} (THF)₄ which features a straight conformation with a long Li…Li distance of 12.68(1) Å. Compound 3^{Ph}

1 Introduction

Poly(pyrazol-1-yl)borates ("scorpionates") are among the most widely used ligand systems in coordination chemistry [1, 2]. Our group is particularly interested in *ditopic* scorpionate ligands that have potential for applications in homogeneous catalysis (bimetallic catalysts) or materials science (coordination polymers). So far, our main focus was on poly(pyrazol-1-yl)borate derivatives with 1,1'-ferroceny-lene [3–8] or m- / p-phenylene [9–12] bridges. These ligands have been used for the preparation of (hetero)bi- and (hetero)trimetallic complexes, metallomacrocycles, ferrocene-based multiple-decker sandwich complexes and coordination polymers.

With respect to polymer generation, the simultaneous binding of two scorpionate fragments to the same metal centre is desired behaviour and leads to the assembly of a stable polymer backbone. When it comes to the synthesis of discrete dinuclear complexes from ditopic scorpionates, however, ligand coordination has to be restricted to only one poly(pyrazol-1-yl)borate fragment per metal centre, and this can most easily be achieved by steric protection. It is well-known in scorpionate chemistry that introduction of appropriate substituents R into the 3-positions of the pyrazolvl rings allows extensive control over the ligand's steric demand and thus over its ability to kinetically stabilize reactive complex fragments [13]. Given this background, the purpose of this paper is to describe the synthesis and full characterization of the phenyl- and *t*-butyl-substituted bis-(pyrazol-1-yl)borates 3^{Ph} and 3^{tBu} (Scheme 1) and to report

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Institut für Anorganische Chemie der J. W. Goethe-Universität Max-von-Laue-Straße 7 D-60438 Frankfurt (Main) Fax: +49(0)69-79829260 E-mail: Matthias.Wagner@chemie.uni-frankfurt.de was found to function as efficient and selective scavenger of chloride ions. In the presence of LiCl it forms anionic complexes $[3'^{Bu}Cl]^-$ with a central Li-Cl-Li core (Li…Li = 3.75(1) Å).

Keywords: Lithium; Anion recognition; Poly(pyrazol-1-yl)borate; Scorpionate ligand; Crystal structures

unexpected differences in the affinity of their lithium salts towards chloride ions.



Scheme 1 Synthesis of the sterically demanding ditopic scorpionate ligands 3^{Ph} and 3^{rBu} . (i) toluene/*n*Bu₂O, -78 °C to r.t.; (ii) toluene, reflux.

2 Results and Discussion

2.1 Synthesis and Spectroscopy

Phenylborane 2 (Scheme 1) was synthesized from the readily available *p*-diborylated benzene derivative 1 [14] and 2 equivalents of PhLi in a toluene/*n*Bu₂O mixture. Subsequent treatment of 2 with 2 equivalents of Lipz^R and 2 equivalents of Hpz^R in refluxing toluene provided the corresponding lithium scorpionates 3^{Ph} (R = Ph) and $3'^{Bu}$ (R = *t*Bu) in good yields. Recrystallization of 3^{Ph} from THF/ Et₂O gave the THF-adduct 3^{Ph} (THF)₄ in analytically pure form. The microanalytical results for $3'^{Bu}$, however, were not in accord with the theoretical values. An investigation



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of the sample using total reflection X-ray fluorescence (TXRF) spectroscopy revealed contamination with substantial amounts of bromide (from the previous salt metathesis reactions) and chloride salts. Again with the help of TXRF spectroscopy, we identified the commercial PhLi as the source of chloride ions (ca. 5-10 mol%). In an attempt to separate LiCl and LiBr from intermediate 2, we extracted the compound into hexane prior to further use. However, from a subsequent TXRF analysis it became evident that the contaminants were still present in the extract. Our current working hypothesis is that the aminoborane 2 itself acts as solubilizer for lithium halides by providing a Lewis acidic boron site for halide binding and a Lewis basic nitrogen atom for simultaneous Li⁺ complexation. The reason why these salt impurities are tolerable in the synthesis of $3^{\rm Ph}$, but cause problems in the case of $3^{t\rm Bu}$ becomes obvious when we look at the crystal structure analysis of the latter compound: 3^{tBu} acts as an "inverse chelator" of chloride ions and therefore crystallizes together with one equivalent of LiCl (see below).

Consistent with an amino(diorganyl)borane derivative [15], the ¹¹B NMR spectrum of **2** contains a signal at 36.2 ppm. Compounds **3**^{Ph} and **3**^{*t*Bu} show resonances at δ (¹¹B) = 2.6 and 2.5, respectively, testifying to the presence of tetra-coordinate boron nuclei [15].

The Me₂N-groups of **2** give rise to two signals both in the ¹H- and in the ¹³C NMR spectrum, which indicates hindered rotation about the B-N bonds as a result of pronounced N-B π -bonding. Integral ratios of 12:10:4 for the proton resonances of the Me₂N-, the C₆H₅-, and the C₆H₄ fragments, respectively, clearly prove the successful introduction of one phenyl ring at each boron atom.

Compounds $\mathbf{3}^{\text{Ph}}$ and $\mathbf{3}^{\text{rBu}}$ show characteristic resonances at $\delta(^{1}\text{H}) = 6.37$, 7.57 ($\mathbf{3}^{\text{Ph}}$) and 5.94, 7.39 ($\mathbf{3}^{\text{rBu}}$) / $\delta(^{13}\text{C}) =$ 101.6, 139.7 ($\mathbf{3}^{\text{Ph}}$) and 99.4, 137.8 ($\mathbf{3}^{\text{rBu}}$), assignable to the proton / carbon atoms in the positions 4 and 5 of the pyrazol-1-yl rings. In both cases, the integral ratio of these proton signals on one hand and the singlet of the C₆H₄ bridge on the other fully agrees with the proposed ditopic bis(pyrazol-1-yl)borate structure (Scheme 1).

2.2 X-ray Crystallography

Compound 2 crystallizes from toluene with two crystallographically independent molecules $(2, 2_A)$ in the asymmetric unit. Since all key structural parameters of 2 and 2_A are the same within experimental error margins, only the structure of 2 is discussed here (Figure 1). The lithium scorpionate 3^{Ph} crystallizes from THF as THF-adduct $3^{Ph}(THF)_4$ (Figure 2). Single crystals of 3^{rBu} , grown from THF/Et₂O in the presence of [12]crown-4, contain one equivalent of LiCl; the corresponding Li⁺ cation is coordinated by one molecule of crown ether and one molecule of Et₂O (Li(12c4)(Et₂O)[3^{rBu} Cl]; Figure 3). Crystallographic data of the compounds 2, $3^{Ph}(THF)_4$, and Li(12c4)(Et₂O)[3^{rBu} Cl] are compiled in Table 1.

The monoaminoborane **2** adopts a centrosymmetric structure in the solid state (Figure 1). As to be expected, both boryl- and both amino groups have a planar configuration and are inclined at a small dihedral angle

Table 1 Crystallographic data of the compounds 2, 3^{Ph}(THF)₄, and Li(12c4)(Et₂O)[3^{tBu}Cl]^a)

	2	$3^{\mathrm{Ph}}(\mathrm{THF})_4$	$Li(12c4)(Et_2O)[3^{tBu}Cl]$
formula	$C_{22}H_{26}B_2N_2$	$C_{70}H_{74}B_2Li_2N_8O_4 \times 2 C_4H_8O_6$	$C_{58}H_{84}B_2ClLi_3N_8O_5 \times C_4H_8O_5$
fw	340.07	1271.08	1123.33
colour, shape	colourless, plate	colourless, block	colourless, rod
temp /K	173(2)	173(2)	173(2)
radiation	MoK _α , 0.71073 Å	MoK _α , 0.71073 Å	MoK _α , 0.71073 Å
crystal system	triclinic	monoclinic	triclinic
space group	$P\overline{1}$	$P2_1/c$	$P\overline{1}$
a /Å	6.0587(10)	13.2478(8)	12.6187(13)
b /Å	12.380(2)	12.6110(6)	16.6078(15)
c /Å	13.860(2)	22.2436(12)	17.7305(17)
α /°	75.443(13)		94.139(7)
β /°	80.541(14)	102.101(5)	104.713(8)
γ /°	84.431(14)		107.826(7)
V/\dot{A}^3	990.8(3)	3633.6(3)	3375.7(6)
Z	2	2	2
$D_{\rm calcd.}$ /g cm ⁻³	1.140	1.162	1.105
F(000)	364	1356	1208
μ / mm^{-1}	0.065	0.073	0.108
crystal size /mm	$0.22 \times 0.19 \times 0.09$	0.45 imes 0.39 imes 0.35	0.19 imes 0.10 imes 0.09
no. of rflns collected	8575	52842	28928
no. of indep rflns (R_{int})	3693 (0.0816)	8013 (0.0763)	11754 (0.1403)
data/restraints/parameter	3693 / 0 / 240	8013 / 0 / 434	11754 / 0 / 739
$GOOF$ on F^2	0.962	1.024	1.036
$R1, wR2 (I > 2\sigma(I))$	0.0601, 0.1201	0.0588, 0.1466	0.1055, 0.1930
R1, $wR2$ (all data)	0.1122, 0.1386	0.0799, 0.1593	0.2027, 0.2322
largest diff peak and hole $/eA^{-3}$	0.204, -0.162	0.268, -0.252	0.648, -0.312

^{a)} Crystallographic data of the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 678023 (2), 678022 ($3^{\text{Ph}}(\text{THF})_4$), 678021 (Li(12c4)(Et₂O)[$3'^{\text{Bu}}$ Cl]). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

relative to each other $(C(11)B(1)C(21)//C(2)N(1)C(3) = 6.8^{\circ})$. The B(1)-N(1) bond (1.412(3) Å) is somewhat longer than the corresponding bond in $(C_6F_5)_2BN(CH_2)_4$ (1.366(3) Å) [16], but compares well with the value in $p-C_6H_4(B(C_6F_5)NMe_2)_2$ (1.395(11) Å) [14].



Figure 1 Structure of **2** in the crystal. Displacement ellipsoids are drawn at the 50 % probability level.

In the centrosymmetric molecules of $3^{\text{Ph}}(\text{THF})_4$, each Li⁺ ion is chelated by one bis(pyrazol-1-yl)borate moiety (N(12)-Li(1) = 2.053(3) Å, N(22)-Li(1) = 2.048(3) Å, $N(12)-Li(1)-N(22) = 96.3(1)^{\circ}$ and further bonded to two THF molecules (Figure 2). The phenylene bridge lies in the plane bisecting the N(11)-B(1)-N(21) angle, whereas the phenyl substituents are oriented almost orthogonal to it (dihedral angle $C_6H_4//C_6H_5 = 79.9^\circ$). The overall conformation of the molecule is such that the Li⁺ ions are pointing away from each other which results in a very long Li…Li distance of 12.68(1) Å. It is important to note that the THF-adduct $3^{Ph}(THF)_4$ also forms when the crystals are grown in the presence of excess [12]crown-4. This is most likely due to the shielding effect of the phenyl substituents on the pyrazolyl rings, because the lithium of the related unsubstituted derivative salt [*n*- $C_6H_4(B(C_6F_5)pz_2)_2]^{2-}$ crystallizes with two crown ether ligands instead of the four THF donors under the same conditions [14].

The anionic moiety of Li(12c4)(Et₂O)[**3**^{*i*^{Bu}Cl]} contains two Li⁺ ions bridged by a chloro ligand (Figure 3; Cl(1)-Li(1) = 2.304(10) Å, Cl(1)-Li(2) = 2.321(8) Å, $Li(1)-Cl(1)-Li(2) = 108.4(3)^{\circ}$). A chelating bis(pyrazol-1yl)borate unit completes the trigonal-planar coordination sphere of each Li⁺ ion (we note additional short contacts $Li(1)\cdots C(51) = 2.620(10)$ Å and $Li(2)\cdots C(54) =$ 2.668(10) Å).



Figure 2 Structure of $3^{\text{Ph}}(\text{THF})_4$ in the crystal. H atoms and solvent THF are omitted for clarity, displacement ellipsoids are drawn at the 30 % probability level.

Selected bond lengths/Å, bond angles/°, torsion angles/°, and dihedral angles/°: B(1)-N(11) = 1.588(2), B(1)-N(21) = 1.583(2), B(1)-C(1) = 1.624(2), B(1)-C(31) = 1.633(2), N(12)-Li(1) = 2.048(3), O(61)-Li(1) = 1.976(3), O(71)-Li(1) = 1.974(3); N(11)-B(1)-N(21) = 109.0(1), N(12)-Li(1)-N(22) = 96.3(1), O(61)-Li(1)-O(71) = 103.2(1); C(1)-B(1)-C(31)-C(32) = -7.0(2); $C_6H_4//C_6H_5 = 79.9^\circ$.



Figure 3 Structure of Li(12c4)(Et₂O)[$3'^{Bu}$ Cl] in the crystal. H atoms, solvent THF and the [Li([12]crown-4)(Et₂O)] cation are omitted for clarity, displacement ellipsoids are drawn at the 30 % probability level.

The molecular structure of $[3'^{Bu}Cl]^-$ clearly proves that the ligand framework is well-designed to bring two small metal ions into sufficiently close proximity so that they can bind to a common substrate (Li…Li = 3.75(1) Å). In the past, we have already shown that ligands of the type present in $3'^{Bu}$ are able to support diamond-shaped Mn₂Cl₂ and linear Ti-O-Ti cores [11]. Moreover, the fact that the bidentate Lewis acid 3^{tBu} acts as an efficient chloride scavenger is not only interesting in its own right, but explains the lithium chloride contamination of the sample (in this context it is also important to mention that we detected substantial amounts of chloride impurity in commercial [12]crown-4 used for the crystallization of 3^{tBu} (TXRF spectroscopy)). As already stated above, the starting material 2 contained not only chloride but also bromide ions. As a result, Li([12]crown-4)Br [17] co-crystallized with the target compound Li(12c4)(Et₂O)[3^{tBu}Cl]. To get an estimate of the selectivity of 3^{tBu} for chloride over bromide, we have reinvestigated the diffraction data of Li(12c4)(Et₂O)[3^{*t*Bu}Cl] using the new structure model Li(12c4)(Et₂O)[$3^{tBu}X$] (X = Cl. Br). We assumed that Cl⁻ and Br⁻ were sharing the same position and the same displacement parameters and refined the ratio of the site occupancy factors. The result for the specimen investigated was a site occupation by Clof 99.7(5)%.

3 Conclusion

We have synthesized sterically demanding ditopic lithium bis(pyrazol-1-yl)borates with phenyl- (3^{Ph}) and t-butyl substituents (3^{tBu}) in the 3-positions of the pyrazolyl rings. Single crystals of both compounds were grown from THF/ Et₂O in the presence of Li(Cl,Br). X-ray crystallography revealed profound differences in the chloride affinities of 3^{Ph} and 3^{tBu} : The former compound crystallizes as THF-adduct $3^{Ph}(THF)_4$ and can thereby be separated from the lithium halide contaminants in analytically pure form. In contrast, 3^{tBu} functions as inverse chelator of Cl⁻ and forms anions [3^{tBu}Cl]⁻ featuring a bent Li-Cl-Li core (the compound cocrystallizes with Li([12]crown-4)Br). In the investigated single crystal, the selectivity of $3^{\prime Bu}$ for Cl⁻ over Br⁻ was close to 100 %. We have determined the cell constants of 10 other crystals which were either identical with the ones determined for Li(12c4)(Et₂O)[3^{tBu}Cl] (6 species) or for Li([12]crown-4)Br (4 species). However, it cannot be fully excluded that the differences in the parameters of the compound $Li(12c4)(Et_2O)[3^{tBu}Br]$ hypothetical and Li(12c4)(Et₂O)[3^{tBu}Cl] are too small to allow for an unambiguous differentiation.

4 Experimental Section

General Considerations. All reactions and manipulations of air-sensitive compounds were carried out in dry, oxygen-free argon using standard Schlenk ware. CDCl₃ was passed through a 4 Å molecular sieves column prior to use. All other solvents were freshly distilled under argon from Na/benzophenone. Compound 1 [14], (H,Li)pz^{Ph}, and (H,Li)pz'^{Bu} were prepared following literature procedures [13, 18, 19]. NMR: Bruker AMX 250, AMX 300, AMX 400, Bruker DPX 250 spectrometers. ¹H- and ¹³C NMR spectra are calibrated against residual solvent signals. ¹¹B NMR spectra were run at room temperature. Abbreviations: s = singlet, d = doublet, m = multiplet, n.o. = signal not observed, pz = pyrazol-1-yl, Ph =

phenyl ring at boron, $Ph^* = phenyl ring at a pyrazol-1-yl substituent. Elemental analyses were performed by the microanalytical laboratory of the University of Frankfurt.$

Synthesis of 2. PhLi (2.0 M, 2.80 mL, 5.60 mmol) in nBu_2O was added dropwise at -78 °C to a stirred solution of 1 (0.957 g, 2.80 mmol) in toluene (40 mL). The reaction mixture was allowed to warm to room temperature and stirred for 10 h, whereupon a colourless precipitate formed. After filtration, the filtrate was evaporated to dryness *in vacuo*, leaving behind a colourless solid. Yield: 0.828 g (87 %). Crystals suitable for X-ray diffraction were grown by recrystallization of the crude product from toluene.

¹¹**B** NMR (96.3 MHz, CDCl₃): 36.2 ($h_{1/2} = 270$ Hz), ¹**H** NMR (250.1 MHz, CDCl₃): 2.98, 3.02 (2 × s, 2 × 6H, NCH₃), 7.33 (s, 4H, C₆H₄), 7.32–7.43 (m, 10H, Ph). ¹³**C** NMR (62.9 MHz, CDCl₃): 41.6, 41.6 (2 × NCH₃), 127.2 (Ph-*m*), 127.3 (Ph-*p*), 132.0 (C₆H₄), 132.9 (Ph-*o*), n.o. (CB).

Synthesis of 3^{Ph} . A solution of 2 (0.252 g, 0.74 mmol) in toluene (30 mL) was added to a suspension of Lipz^{Ph} (0.222 g, 1.48 mmol) and Hpz^{Ph} (0.213 g, 1.48 mmol) in toluene (20 mL). The mixture was heated to reflux for 10 h and cooled to room temperature again. All volatiles were removed *in vacuo* and the resulting colour-less residue was washed with hexane (30 mL) and dried *in vacuo*. Yield: 0.520 g (84 %). Anal. Calcd. for C₅₄H₄₂B₂Li₂N₈ [838.42] × 4 THF [72.11]: C, 74.61; H, 6.62; N, 9.94. Found: C, 74.48; H, 6.62; N, 9.92 %. Crystals of 3^{Ph} (THF)₄ suitable for X-ray analysis were grown by diffusion of Et₂O into a saturated solution of 3^{Ph} in THF at room temperature.

¹¹**B** NMR (96.3 MHz, THF-d₈): 2.6 ($h_{1/2} = 580$ Hz). ¹**H** NMR (300.0 MHz, THF-d₈): 6.37 (d, 4H, ${}^{3}J_{HH} = 2.2$ Hz, pzH-4), 6.79–6.82 (m, 4H, Ph-o), 6.97 (s, 4H, C₆H₄), 7.02–7.10 (m, 6H, Ph-m/p), 7.16–7.21 (m, 4H, Ph*p), 7.26-7.32 (m, 8H, Ph*-o), 7.57 (d, 4H, ${}^{3}J_{HH} = 2.2$ Hz, pzH-5), 7.60–7.64 (m, 8H, Ph*-m). ¹³C NMR (75.5 MHz, THF-d₈): 101.6 (pzC-4), 125.7 (Ph-p), 127.2 (Ph-m), 127.4 (Ph*-p), 127.7 (Ph*-o), 128.8 (Ph*-m), 134.6, 134.7 (Ph-o, C₆H₄), 137.0 (Ph*-i), 139.7 (pzC-5), 154.3 (pzC-3), n.o. (CB).

Synthesis of 3'^{Bu}. A mixture of neat Lipz'^{Bu} (0.229 g, 1.76 mmol) and neat Hpz'^{Bu} (0.219 g, 1.76 mmol) was added to a stirred solution of 2 (0.300 g, 0.88 mmol) in toluene (20 mL) at room temperature. The resulting slurry was heated to reflux for 15 h and cooled to room temperature again. All volatiles were removed *in vacuo* and the resulting colourless residue was washed with hexane (30 mL) and dried *in vacuo*. Crystals of Li(12c4)(Et₂O)[3'^{Bu}Cl] were grown by slow diffusion of Et₂O into a saturated solution of 1 equivalent of 3'^{Bu} and 2 equivalents of [12]crown-4 in THF at room temperature. Anal. Calcd. for C₅₈H₈₄B₂ClLi₃N₈O₅ [1051.22] × THF [72.11] × Li([12]crown-4)Br [263.06]: C, 60.64; H, 7.85; N, 8.08. Found: C, 60.82; H, 7.65; N, 7.91 %.

¹¹**B** NMR (80.3 MHz, THF-d₈): 2.5 ($h_{1/2} = 510$ Hz), ¹**H** NMR (300.0 MHz, THF-d₈): 1.30 (s, 36H, C(CH₃)₃), 5.94 (d, 4H, ³ $J_{HH} = 2.1$ Hz, pzH-4), 6.76–6.79 (m, 4H, Ph-o), 6.87 (s, 4H, C₆H₄), 7.07–7.12 (m, 6H, Ph-m/p), 7.39 (d, 4H, ³ $J_{HH} = 2.1$ Hz, pzH-5). ¹³C NMR (75.5 MHz, THF-d₈): 31.5 (C(CH₃)₃), 32.7 (C(CH₃)₃), 99.4 (pzC-4), 126.5 (Ph-p), 127.5 (Ph-m), 134.8, 135.3 (Ph-o, C₆H₄), 137.8 (pzC-5), 162.9 (pzC-3), n.0. (CB).

X-ray Crystal Structure Determinations of 2, 3^{Ph}(THF)₄, and Li(12c4)(Et₂O)[3^{rBu}Cl]

Data collections were performed on a Stoe-IPDS-II two-circle-diffractometer with graphite-monochromated MoK_{α} radiation. An empirical absorption correction with the MULABS option in the program PLATON [20] was performed for Li(12c4)(Et₂O)[3^{*t*Bu}Cl]. The structures were solved by direct methods [21] and refined with full-matrix least-squares on F^2 using the program SHELXL97 [22]. Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. Compound **2** crystallises with two crystallographically independent molecules (**2**, **2**_A) in the asymmetric unit. Compound **3**^{Ph}(THF)₄ crystallises together with two equivalents of THF in the crystal lattice; compound Li(12c4)(Et₂O)[**3**'^{Bu}Cl] contains one equivalent of THF in the crystal lattice. CCDC reference numbers: 678023 (**2**), 678022 (**3**^{Ph}(THF)₄), 678021 (Li(12c4)(Et₂O)[**3**'^{Bu}Cl]).

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