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Synthesis and structural characterisation of the phenyl/scorpionate hybrid ligand $[Ph(pz)BC_5H_{10}]^-$

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Dedicated to the memory of Swiatoslaw Trofimenko, the pioneer of scorpionate chemistry.

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ABSTRACT

The new phenyl/scorpionate hybrid ligand $[Ph(pz)BC_5H_{10}]^-$ has been synthesised and structurally characterised as K^+ and Tl^+ salt. The ligand is specifically designed to create half-sandwich complexes in which the metal ion is chelated by the π-electron system of the phenyl ring and by the electron lone pair of the pyrazolyl nitrogen atom. This structural motif is established both by $K[Ph(pz)BC_5H_{10}]$ and by $Tl[Ph(pz)BC_5H_{10}]$.

1. Introduction

Since the pioneering work of Ewen, Brintzinger, Kaminsky et al. on the stereoselective polymerisation of α-olefins with *ansa*-metallocene catalysts [1,2], there is an increasing interest in the development of novel custom-tailored *ansa*-complexes. Nowadays, these compounds are still used mainly for catalytic purposes [3], but have also found medical applications [4,5].

Initially, the term "*ansa*-complex" was coined for metallocenes containing an interannular bridge between both cyclopentadienyl rings (η^5:η^5-coordination mode) [6]. Later on, this definition was expanded to include compounds in which a π-bonded moiety is linked to any one of the other ligands on the same metal centre (in many cases this results in an η^5:η^1-coordination mode). The function of the bridging handle is to restrict the free rotation of the π-bonded ligand and/or to reduce the angle between the centroid of the π-system, the metal ion, and the second donor group to a value smaller than in comparable unbridged molecules ("constrained geometry complexes") [7,8].

A wealth of information has been gathered on numerous ligand classes that are able to create *ansa*-complexes. These ligands must be thoroughly compared in order to establish their relationship to one another. The goal is to create versatile toolboxes of donor environments with smoothly varying properties, so that the most suitable derivative can easily be selected for the rational de novo design of efficient catalysts. In another context we have already investigated the two ligand series $R_3P/[R_2(BH_3)P]^-/[R_3Si]^-$ and $R_3PE/[R_2(BH_3)PE]^-/[R_3SiE]^-$ (E = O, S, Se, Te) with the aim to evaluate the impact of subtle differences in the charge distribution of these isoelectronic species on their coordination behaviour [9–12]. We are now extending our research to the π-donor-containing *ansa*-ligands $[Ph\text{-}BR_2pz]^-$ and $[Cp\text{-}CR_2pz]^-$. The rationale behind the design of these molecules is the following: (i) A cyclopentadienyl and a phenyl ring are both potential six-electron donors but differ in their charge state. (ii) By the same token, poly(pyrazol-1-yl)borates ("scorpionates" [13,14]) are the negatively charged analogues of poly(pyrazol-1-yl)methanes [15]. Thus, similar to the examples mentioned above, the linked systems $[Ph\text{-}BR_2pz]^-$ and $[Cp\text{-}CR_2pz]^-$ are ideally suited to study the effect of slight alterations in the electronic structure of otherwise closely related ligands on their binding properties.

The purpose of this paper is to report on the phenyl/mono(pyrazol-1-yl)borate hybrid ligand [**2**]$^-$ und to describe its K^+ and Tl^+ complexes K[**2**] and Tl[**2**] (Scheme 1).

2. Results and discussion

Transition metal complexes bearing an *ansa*-$[Cp\text{-}BMe_2pz]^{2-}$ ligand are already known in the literature and have been shown to possess a largely unstrained molecular framework [16,17]. We therefore directed our initial synthesis efforts to the corresponding

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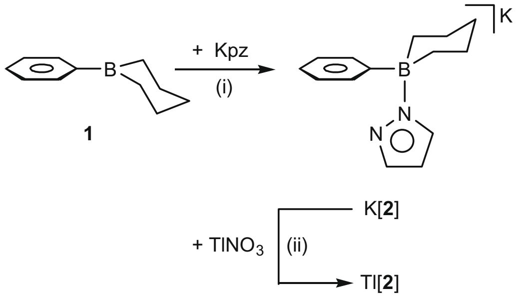

Scheme 1. Synthesis of K[**2**] and Tl[**2**]. (i) toluene, r.t., 2 d. (ii) H_2O/THF, r.t., 15 min.

phenyl/mono(pyrazol-1-yl)borate hybrid ligand $[\mathrm{Ph\text{-}BMe_2pz}]^-$ bearing two methyl groups at the boron atom. However, the preparation of the required starting material $\mathrm{PhBMe_2}$ turned out to be a challenge, as has already been noted by Nöth et al., who obtained mixtures of $\mathrm{BMe_3}$, $\mathrm{PhBMe_2}$, $\mathrm{Ph_2BMe}$, and $\mathrm{Ph_3B}$ when they tried to replace the two chloro substituents of $\mathrm{PhBCl_2}$ by methyl groups using $\mathrm{SnMe_4}$ [18]. In our hands, the reactions between $\mathrm{PhBBr_2}$ and MeMgCl in toluene/THF, $\mathrm{PhB(OMe)_2}$ or $\mathrm{PhB(O_2C_6H_4)}$ and $\mathrm{(AlMe_3)_2}$ in hexane/heptane, as well as $\mathrm{BrBMe_2}$ and PhLi in toluene/n-$\mathrm{Bu_2O}$ gave equally poor results. In view of this background, we decided to switch from $\mathrm{PhBMe_2}$ to $\mathrm{Ph\text{-}BC_5H_{10}}$ [19,20] (**1**; Scheme 1), because a boracyclohexane fragment is less likely to take part in substituent scrambling than a $\mathrm{BMe_2}$ moiety. The cations $\mathrm{K^+}$ and $\mathrm{Tl^+}$ were chosen as counterions, because potassium and thallium salts of poly(pyrazol-1-yl)borates are valuable reagents for further syntheses of transition metal scorpionate complexes.

2.1. Synthesis, NMR spectroscopic and mass spectrometric characterisation

The potassium salt K[**2**] was synthesised in good yields from **1** and 1 equiv. of Kpz in toluene (Scheme 1). Transmetallation to the thallium complex Tl[**2**] was achieved by treatment of K[**2**] with 1 equiv. of $\mathrm{TlNO_3}$ in a mixture of carefully degassed H_2O and THF (Scheme 1).

Both compounds were characterised by ^{11}B, ^{1}H and ^{13}C NMR spectroscopy in d_8-THF solutions. The ^{11}B NMR spectra of K[**2**] and Tl[**2**] are characterised by signals at −4.4 ppm and −4.0 ppm, respectively, thereby testifying to the presence of four-coordinate boron nuclei [21]. The ^{1}H NMR spectrum of K[**2**] reveals three multiplets for the phenyl protons ($\delta(^1\mathrm{H}) = 6.82, 6.96, 7.06$). Resonances at 5.99 ppm (pzH-4), 7.24 ppm and 7.66 ppm (pzH-3,5), each integrating to 1H, can be assigned to the protons of the pyrazolyl group. The borinane ring gives rise to two multiplets at $\delta(^1\mathrm{H}) = 0.65$–$0.85$ and 1.29–1.60. A similar picture is shown by the ^{1}H NMR spectrum of Tl[**2**]. The ^{13}C NMR spectra of K[**2**] and Tl[**2**] do not show any peculiarities and therefore do not merit further discussion.

The ESI mass spectrum of K[**2**] in THF shows three peaks at $m/z = 225$, 331 and 489 (negative measurement mode). While the first peak is clearly due to the free ligand $[\mathbf{2}]^-$, the peak at $m/z = 489$ can be assigned to a potassium ion wrapped by *two* ligand molecules. These findings indicate that monomers K[**2**] coexist with dimeric aggregates $(\mathrm{K}[\mathbf{2}])_2$ in THF solution. The peak at $m/z = 331$, which fits to ions of the composition $[\mathrm{K}[\mathbf{2}]\mathrm{+pz}]^-$, gives interesting insight into the reactivity of our scorpionate ligand, because it points towards a rather weak B–N adduct bond.

2.2. X-ray crystal structure determination

The potassium salt K[**2**] crystallises from toluene as centrosymmetric dimer $(\mathrm{K}[\mathbf{2}])_2$ with two crystallographically independent molecules, $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{A}}$ and $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{B}}$, in the asymmetric unit. Single crystals of Tl[**2**] were also grown from toluene. Crystal data and structure refinement details of $(\mathrm{K}[\mathbf{2}])_2$ and Tl[**2**] are compiled in Table 1.

Table 1
Selected crystallographic data for $(\mathrm{K}[\mathbf{2}])_2$ and Tl[**2**].

Compound	$(\mathrm{K}[\mathbf{2}])_2$	Tl[**2**]
Formula	$\mathrm{C_{28}H_{36}B_2K_2N_4}$	$\mathrm{C_{14}H_{18}BN_2Tl}$
Formula weight	528.43	429.48
Colour, shape	colourless, block	colourless, block
T (K)	173(2)	173(2)
Radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.8824(9)	8.8624(5)
b (Å)	11.5100(10)	10.0019(8)
c (Å)	13.0560(12)	16.0146(9)
α (°)	79.856(7)	90
β (°)	77.938(7)	104.154(4)
γ (°)	79.111(7)	90
V (Å^3)	1411.6(2)	1376.45(16)
Z	2	4
$D_{\mathrm{calcd.}}$ (g cm^{-3})	1.243	2.073
$F(000)$	560	808
μ (mm^{-1})	0.359	11.717
Crystal size (mm^3)	0.19 × 0.16 × 0.15	0.18 × 0.12 × 0.10
No. of reflections collected	15456	18358
No. of independent reflections [$R_{(\mathrm{int})}$]	5266 (0.0541)	2581 (0.0877)
Data/restraints/parameters	5266/0/325	2581/0/164
Goodness-of-fit (GOF) on F^2	1.034	1.115
R_1, wR_2 ($I > 2\sigma(I)$)	0.0499, 0.1231	0.0314, 0.0757
R_1, wR_2 (all data)	0.0703, 0.1317	0.0346, 0.0773
Largest difference peak and hole (e Å^{-3})	0.796, −0.307	1.557, −1.933

The key structural parameters of the borate anions in $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{A}}$ and $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{B}}$ are rather similar, however, subtle but noteworthy differences are observed regarding the coordination of the $\mathrm{K^+}$ ion to the anionic moiety.

Each ligand molecule in $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{A}}$ and $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{B}}$ chelates a $\mathrm{K^+}$ ion by the phenyl ring and the pyrazolyl group and thus adopts an *ansa*-mode (the molecular structure of $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{A}}$ is shown in Fig. 1).

$\mathrm{K^+}$-phenyl coordination occurs via the π-electron system of the organic moiety. In $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{A}}$, the $\mathrm{K^+}$ ions are displaced from positions above the centroids (COG(Ph)) of the phenyl rings (K(1)–COG(Ph) = 3.281 Å) towards the *ipso*-carbon atoms. As a consequence, the corresponding K(1)–C distances are spread over the wide range from 3.096(3) Å to 3.995(4) Å; the shortest contact, K(1)–C(21) = 3.096(3) Å, is equal to the sum of the ionic radius of $\mathrm{K^+}$ and the half-thickness of benzene (3.03 Å [22]). Contrary to $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{A}}$, the $\mathrm{K^+}$ ions in $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{B}}$ adopt an η^6-coordination mode (K–COG(Ph) = 3.010 Å) as evidenced by the narrow spread of K–C distances (3.253(3)–3.399(3) Å).

In $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{A}}$, the torsion angle B(1)–N(11)–N(12)–K(1) possesses a value of 41.3(3)° which indicates that the pyrazolyl donor binds to the metal centre partly via the electron lone pair and partly via the p-orbital of N(12); the corresponding K(1)–N(12) bond length amounts to 2.857(2) Å. K(1) is not only attached to N(12), but also to N(12B), thereby creating a dimeric structure containing a central $\mathrm{K_2N_2}$ four-membered ring (K(1)–N(12B) = 2.909(2) Å; B(1B)–N(11B)–N(12B)–K(1) = −70.2(2)°). The general structural motif of $\mathrm{K^+}$-pyrazolyl binding is the same in $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{A}}$ and $(\mathrm{K}[\mathbf{2}])_2^{\mathrm{B}}$. However, in the latter dimer, the pyrazolyl bridge is less symmetrically coordinating, because it acts as true σ-donor towards one potassium ion (B–N–N–K = −2.3(3)°; K–N = 2.751(2) Å) and as true π-donor towards the other (B–N–N–K = 97.9(2)°; K–N = 3.118(2) Å). For more information on the structural diversity of related potassium (pyrazol-1-yl)borates, the reader is referred to Refs. [16,22–24].

In Tl[**2**], the phenyl(pyrazol-1-yl)borate again acts as *ansa*-ligand towards the metal centre (Fig. 2). We observe Tl(1)–C bond