Inorganica Chimica Acta, 139 (1987) 71–73

Polypyrazolylborate Complexes of Yttrium and Lanthanum*

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We have recently been exploring the chemistry of metal halide complexes of early transition metals containing polypyrazolylborate ligands [1, 2]. These molecules are useful starting materials for the synthesis of new organometallic complexes [1c, d]. Thus, for example, we have prepared $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ [1a], $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Me_2$ [1c], $[HBpz_3]CpZrCl_2$ and $[H(\mu\text{-}H)Bpz_2]CpZrCl_2$ [1d] (pz = pyrazolyl ring). In this work, complexes such as $[HBpz_3]_2ZrCl_2$ containing two pyrazolylborate ligands could not be prepared. A possible reason for this failure is that two of these bulky ligands will not fit around a $ZrCl_2$ fragment. Other workers have noted that $[HBpz_3]_2TiCl_2$ could not be formed [3]. It was decided to attempt the preparation of $[HBpz_3]_2MX$ (M = Y, La) complexes because these metals are much larger than zirconium. In addition, the eight-coordinate complexes $[\eta^3\text{-}HBpz_3]_2[\eta^2\text{-}HBpz_3]M$ (M = Y, La, Ce, Pr, Sm, Gd, Er, Yb, Lu) and $[HBpz_3]_2ErCl{\cdot}THF$ [4] were known. Reported here are the syntheses and properties of $[HBpz_3]_2MCl(H_2O)$ (M = Y, La), including structural characterization of the yttrium complex by X-ray crystallography. We also report preliminary results on the synthesis of $[HBpz_3]_2YCl$ and $[H_2Bpz_2]_3Y$.

Experimental

Aquobis[hydrotris(pyrazolyl)borato]chloroyttrium(III) {$[HBpz_3]_2YCl(H_2O)$} (1)

Yttrium chloride dihydrate (0.50 g, 2.2 mmol) and $NaHBpz_3$ (0.52 g, 2.2 mmol) were placed in a 100 ml round bottomed flask. The flask was cooled to –78 °C and 50 ml of precooled tetrahydrofuran (THF) was added. The reaction mixture was stirred at –78 °C for 4 h, was filtered, and the solvent was removed under vacuum. This residue was extracted with 50 ml of benzene, filtered, and the solvent was evaporated under vacuum to yield a white solid (0.40 g, 0.70 mmol, 64%). Recrystallization from benzene gave clear crystals suitable for X-ray analysis. The data from this analysis are given in Table I. ^1H NMR spectrum ($CDCl_3$): δ 7.68, 7.26 (6, 6; d, d; $J = 2.8$ Hz; 3-H, 5-H(pz)); 6.03 (6, t, $J = 2.8$ Hz, 4-H(pz)); 4.53 (2, broad s, H_2O). ^{13}C NMR spectrum ($CDCl_3$): δ 142.2, 135.1 (6, 6; s, s; 3-C, 5-C(pz)), 104.1 (6, s, 4-C(pz)). ^{11}B NMR spectrum ($CDCl_3$ at 330 K): δ – 3.16 (d, $J_{BH} = 105$ Hz). IR spectrum (Nujol mull) cm^{-1}: 3600, 3300 (OH), 2460 (BH). The mass spectrum shows clusters with highest peaks at *m/e* 549 ($M^+ - 18$ (H_2O)) and 515 ($M^+ - 53$ ($H_2O + Cl$)). *Anal.* Calc. for $C_{18}H_{22}B_2N_6OClY$: C, 38.03; H, 3.90. Found: C, 37.70; H, 4.47%.

TABLE I. Crystal Data for $[HBpz_3]_2YCl(H_2O){\cdot}C_6H_6$

a, b, c (Å)	11.546(3), 14.06(4), 9.981(3)
α, β, γ (°)	92.08(2), 111.07(2), 77.90(2)
Space group	$P\bar{1}$
Radiation	Mo Kα, graphite monochromator λ = 0.71073 Å
Crystal dimensions (mm)	0.2 × 0.2 × 0.1
Linear absorption coefficient μ (cm^{-1})	21.1
Diffractometer	CAD-4
Decay corrections max, average	1.133, 1.063
Scan, max θ	ω/2θ, 21°
No. of reflections	2384
Structure solution	Patterson method
Hydrogen atoms	in calculated positions
Refinement	full-matrix least-squares
Weights	$w = [\sigma^2(F) + 0.0004F^2]^{-1}$ for reflections with $I > 3\sigma(I)$, otherwise 0.0
Final R, R_w	0.041, 0.054

Aquobis[hydrotris(pyrazolyl)borato]chlorolanthanum(III) {$[HBpz_3]_2LaCl(H_2O)$} (2)

Lanthanum chloride dihydrate (1.0 g, 3.8 mmol) and $NaHBpz_3$ (1.2 g, 5.1 mmol) were placed in a 250 ml round bottomed flask, and 150 ml of THF was added by syringe. The reaction mixture was stirred at room temperature for 2 h, was filtered, and the solvent was removed under vacuum. This residue was extracted with 100 ml of benzene, filtered, and the benzene was removed under vacuum to yield a white solid (0.91 g, 1.5 mmol, 65% yield). ^1H NMR spectrum ($CDCl_3$): δ 7.63, 7.08 (6, 6; d, d; $J = 3.0$, 2.7 Hz; 3-H, 5-H(pz)); 5.94 (6, t, $J = 2.9$ Hz, 4-H(pz)). ^{13}C NMR spectrum ($CDCl_3$): δ 141.7, 135.5 (6, 6; s, s; 3-C, 5-C(pz)), 103.9 (6, s, 4-C(pz)). IR spectrum (Nujol mull) (cm^{-1}): 3280 (OH), 2460 (BH). The mass spectrum shows clusters with the highest peak at *m/e* 565 ($M^+ - 53$ ($H_2O + Cl$)). *Anal.* Calc. for

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*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

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0020-1693/87/$3.50

$C_{18}H_{22}B_2N_6OClLa$: C, 34.96; H, 3.58. Found: C, 35.07; H, 3.65%.

Results and Discussion

The reaction of $MCl_3(H_2O)_2$ (M = Y, La) with Na[HBpz$_3$] yields $[HBpz_3]_2MCl(H_2O)$ (M = Y (**1**), La (**2**)) in good yield. The reaction was carried out with less than two equivalents of ligand to avoid formation of $[HBpz_3]_3M$ and pyrazole impurities. These complexes are thermally very stable and only slowly decompose in air. The solid state structure of $[HBpz_3]_2YCl(H_2O)\cdot C_6H_6$ has been determined by X-ray crystallography; an ORTEP is pictured in Fig. 1. The benzene of crystallization is not shown and does not interact with the yttrium molecule. The coordination geometry of the yttrium complex is best viewed by analogy to Cp_2MX_n complexes and our earlier structure of $[H(\mu\text{-}H)Bpz_2]CpZrCl_2$ as a bent sandwich geometry. In this description, the plane of the donor atoms of each [HBpz$_3$] ligand is analogous to the Cp plane in Cp_2MX_n complexes. The dihedral angle of these planes is 128.6° and is very similar to that observed for $[H(\mu\text{-}H)Bpz_2]CpZrCl_2$ of 127.8°. For comparison to cyclopentadienyl complexes, the analogous (ring centroid)–Y–(ring centroid) angle in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ is 128.1° [5] and $(C_5Me_5)_2YCl(THF)$ is 136.4° [6].

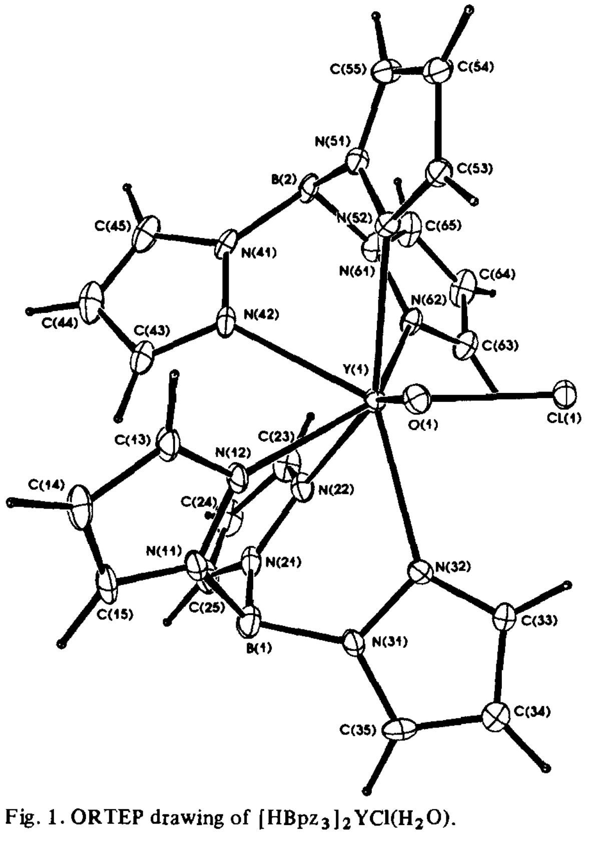

Fig. 1. ORTEP drawing of $[HBpz_3]_2YCl(H_2O)$.

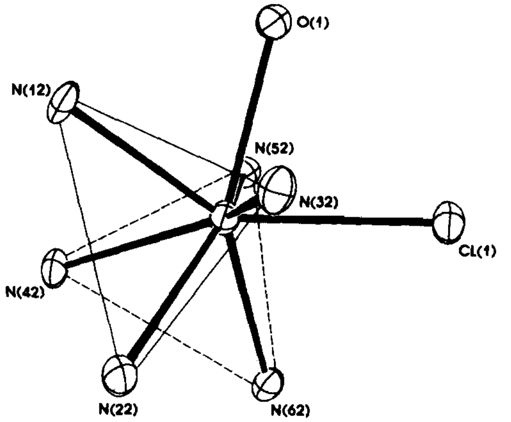

Fig. 2. ORTEP drawing of $[HBpz_3]_2YCl(H_2O)$ oriented perpendicular to the Cl–Y–O plane. Only the metal and donor atoms are shown for clarity. The nitrogen donor atoms for each ligand have been connected for emphasis.

Figure 2 shows a view of the molecule oriented perpendicular to the Cl–Y–O plane. The four nitrogen atoms that are brought into closer contact by the canting of the planes are staggered such that the closest interligand contact is between N(22) and N(42) at 2.914 Å. The remaining two nitrogen donor atoms are over 3.3 Å apart and nearly eclipsed in this view, leaving room for the Cl and O donor atoms. The Y–N distances are in the range 2.460–2.516 Å with Y–Cl and Y–O distances of 2.657 and 2.403 Å, respectively. Finally, the two molecules in the unit cell are related by a center of inversion and are oriented so that the intermolecular O–Cl distances are short at 3.190 Å. This distance, coupled with the fact that the IR data show terminal and hydrogen bonded O–H stretching bands, indicates possible intermolecular hydrogen bonding between the H_2O and Cl ligands.

The six pyrazolyl rings are non-equivalent in this structure. In the ambient temperature solution NMR spectra (both ^1H and ^{13}C) for both **1** and **2**, only one resonance is observed for each ring hydrogen or carbon atom type. Thus, a dynamic process is equilibrating the rings. As shown in Fig. 3 for the yttrium complex **1**, this dynamic process can be slowed on the NMR time scale. The limiting spectrum was nearly reached at –88 °C. The center resonance, presumably the 3-position hydrogen atom, is split to the greatest degree. Data for the lanthanum complex **2** are similar with a lower activation energy for the dynamic process. The most reasonable mechanism to explain these data is a trigonal-twist rotation of the polypyrazolylborate ligands about the Y–B axes, as proposed earlier for our zirconium complexes [1, 2]. In contrast, the spectrum of $[\eta^3\text{-}HBpz_3]_2$-

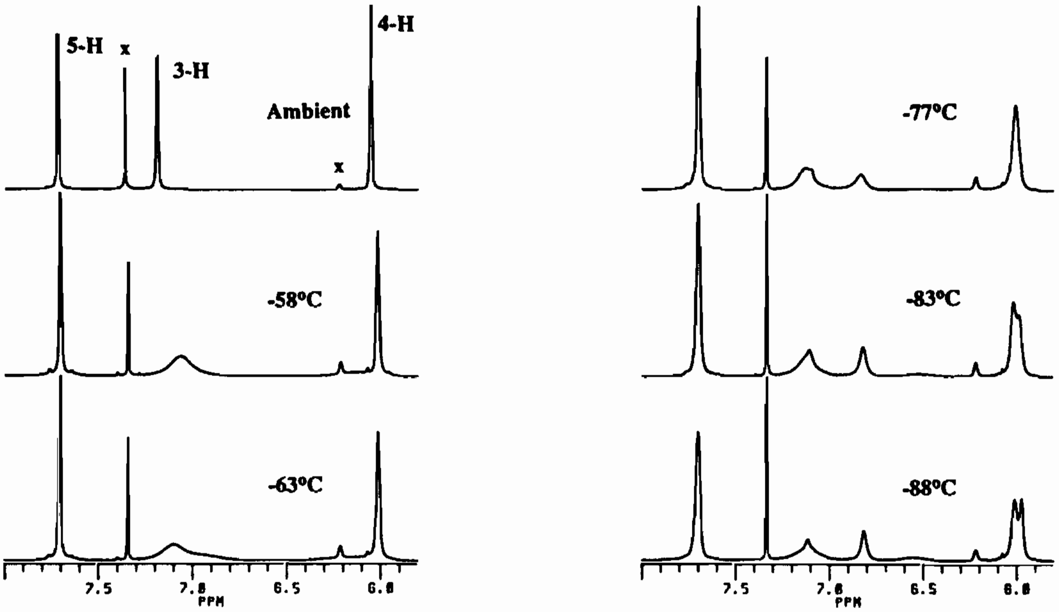

Fig. 3. Variable temperature ^1H NMR data on $[HBpz_3]_2YCl(H_2O)$ of the aromatic region in CD_2Cl_2. The sharp resonance at 7.35 is benzene and the small resonance at 6.22 is an impurity.

$[\eta^2\text{-}HBpz_3]Y$ is complex [4a]. A detailed analysis [4c] of the ^1H NMR spectrum of the paramagnetic-shifted resonance of $[\eta^3\text{-}HBpz_3]_2[\eta^2\text{-}HBpz_3]Yb$ showed that this molecule is stereochemically rigid at ambient temperature on the NMR time scale. The reasons for these surprising differences in rather similar molecules are unclear.

The anhydrous complex $[HBpz_3]_2YCl$ has also been prepared. The complex shows equivalent pyrazolyl rings by ^1H NMR at room temperature and is thus fluxional. At −90 °C, this dynamic process can be slowed to yield resonances in a ratio of *ca.* 2:1 for each hydrogen atom type.

Reaction of $K[H_2Bpz_2]$ with YCl_3 yields $[H_2Bpz_2]_3Y$. IR spectra indicate that there are weakly bridging B–H–Y interactions. Further characterization of this molecule and anhydrous trispyrazolylborate complexes is in progress.

Supplementary Material

Tables of bond distances, bond angles, positional parameters, torsion angles and thermal parameters are available from the Editor in Chief or the authors. The table of calculated and observed structure factors is also available from the authors.

Acknowledgements

The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this project and the NSF (CHE 84-11172) and NIH (RR-02425) for funds supporting NMR instrumentation.

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