Half-sandwich Pyrazolylborate Complexes of the Lanthanides: the Molecular Structures of [Yb{HB(3-Bu^t-5-Me-pyrazolyl)$_3$}I(thf)] and [Yb{HB(3Bu^t-5-Me-pyrazolyl)$_3$}I-(3,5-lutidine)$_2$]†

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Reaction of $\mathrm{YbI_2}$ with 1 equiv. of K[HB(3-Bu^t-5-Me-pyrazolyl)$_3$] gives the ether-soluble complex [Yb{HB(3-Bu^t-5-Me-pyrazolyl)$_3$}I(thf)], **1**, in good yields; complex **1** reacts with good donor ligands to give simple adducts [Yb{HB(3-Bu^t-5-Me-pyrazolyl)$_3$}I(3,5-lutidine)$_2$] **2** and [Yb{HB(3-Bu^t-5-Me-pyrazolyl)$_3$}I(*tert*-butylisonitrile)] **3**; complexes **1** and **2** have been structurally characterized.

The chemistry of the lanthanides in low oxidation states is being widely studied because of their potential in organic synthesis and because of their unusual structural and electronic features.[1] Much of the focus for these studies has centred around the metallocene derivatives which have proved particularly amenable to structural characterization and which have displayed an impressive variety of reactivity.[2] More recently there has been increasing interest in broadening the range of ancillary ligands and divalent lanthanide complexes with amides,[3] phospholes,[4] thiolates,[5] alkyls,[6] and alkoxides[7] have been reported. The polypyrazolylborates[8] have proven to be versatile ligands capable of binding to a wide range of metal centres ranging in size from $\mathrm{Be^{2+}}$ to $\mathrm{Ba^{2+}}$.[9] Several complexes with the lanthanides in the 3+ state are known[8] and it has recently been shown that the *tris*-dimethylpyrazolylborate ligand (Tp*) complexes effectively to lanthanide 2+ centres yielding six-coordinate 'sandwich' compounds of the type Ln(Tp*)$_2$ (Ln = Sm, Eu, Yb).[10,11] By increasing the size of the substituents in the 3-position of the pyrazole we hoped to isolate the corresponding 'half-sandwich' complexes which might be expected to have a reduced coordination number and hence enhanced reactivity. Furthermore such a complex would offer binding sites for both neutral and anionic ligands. Here we describe the synthesis of the first 'half-sandwich' *tris*-pyrazolylborate complexes of a divalent lanthanide metal.‡

Stirring a mixture of $\mathrm{YbI_2}$ with KHB(3-Bu^t-5-Me-pyrazolyl)$_3$ (KTp$^{\mathrm{Bu^t,Me}}$) in thf rapidly leads to the formation of a bright yellow air- and moisture-sensitive solution together with a fine off-white precipitate, [eqn. (1)].

$$\mathrm{YbI_2 + KTp^{Bu^t,Me} \rightarrow [YbTp^{Bu^t,Me}I(thf)] + KI\downarrow} \qquad (1)$$

After removal of solvent the product is readily extracted into diethyl ether from which a canary yellow solid may be recovered. The compound is very soluble in ethereal solvents and moderately so in hexanes. Crystallization from diethyl ether yielded analytically pure crystals of **1** which were characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy.§

In order to confirm the identity of **1** and establish the coordination geometry at the metal a single-crystal X-ray study was undertaken.¶ The molecular structure is shown in Fig. 1. The ytterbium centre is five-coordinate with the I–Yb–B vector being approximately linear [I–Yb–B = 169.5(2)°]. The ytterbium–iodine distance in **1** is 3.065(1) Å, slightly shorter than those observed in [YbI$_2$(3,5-lutidine)$_4$] of 3.130(1) Å,[13] consistent with the reduced coordination number. The thf molecule lies in the cleft between two *tert*-butyl substituents of the pyrazolyl groups [I–Yb–O angle of 92.8(2)°]. The average Yb–N distance of 2.458(8) Å is similar to that in the closely related but six-coordinate complex Yb(Tp*)$_2$[11] [2.480(4) Å]. The reduced coordination number is however reflected in the Yb–B distance which decreases from 3.468(8) Å in Yb(Tp*)$_2$ to 3.400(8) Å in **1**. The apparent inconsistency between the two measurements is the result of a slight twisting of the pyrazolyl groups around the B–N bond. Variable-temperature ^{1}H NMR studies show only a single pyrazolyl environment even at −100 °C. However, the fact that the thf molecule in **1** is not displaced by diethyl ether during recrystallization, suggests that it is fairly strongly bound and hence that rearrangement of the coordination sphere of the metal is probably facile. In contrast, addition of the better donor ligand 3,5-lutidine to a pentane solution of **1** gives good yields of the complex [YbTp$^{\mathrm{Bu^t,Me}}$I(3,5-lut)$_2$] **2**, as dark red crystals. The complex is diamagnetic and was characterized by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy.|| The presence of the additional ligand is consistent with the more basic nature of the lutidine ligand. A single-crystal X-ray diffraction study¶ of **2** shows a six- rather than five-coordinate structure broadly similar to **1**. The molecular structure of **2** is shown in Fig. 2. The lutidine ligands lie in two of the clefts between the *tert*-butyl groups. Both the Yb–I distance [3.123(1) Å] and the average Yb–N [2.532(6) Å] in **2** are slightly longer than in **1**. More severe distortion of the pyrazolylborate ligand than in **1**, however, leads to a significantly shorter Yb–B distance, 3.389(9) Å.

The thf molecule of **1** may also be displaced by isonitriles. Thus, addition of *tert*-butylisonitrile to a solution of **1** in pentane gives an immediate colour change from yellow to orange and upon standing red–orange crystals of [YbTp$^{\mathrm{Bu^t,Me}}$I((C≡NBu^t)] **3**, were obtained. The complex is diamagnetic and was characterized by elemental analysis, infrared, ^{1}H and ^{13}C NMR spectroscopy.** Although coordination of isonitriles to trivalent lanthanides is well precedented,[13] we are unaware of any examples of such ligands bound to divalent centres, in spite of considerable interest in the use of $\mathrm{SmI_2}$ to couple isontriles to alkyl halides.[14] The C≡N stretch was observed in the IR spectrum at 2172 cm^{-1}, higher than in the free ligand (2134 cm^{-1}), as consistent with the absence of

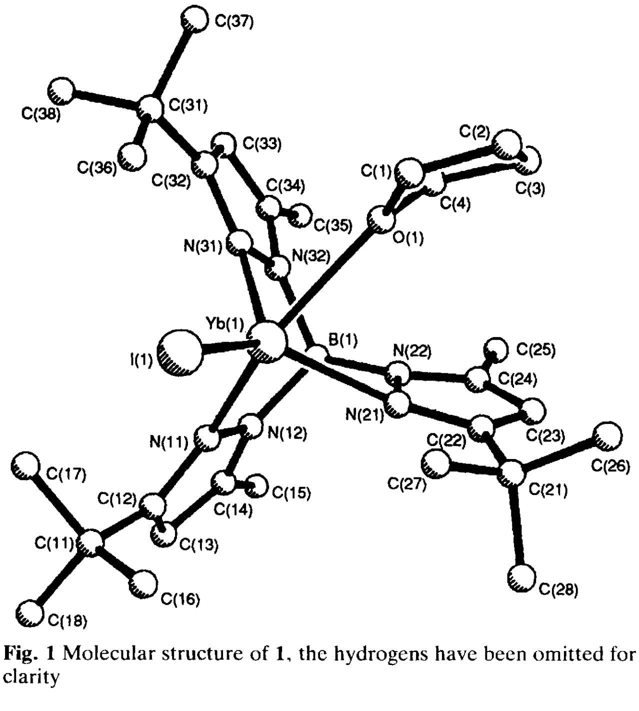

Fig. 1 Molecular structure of **1**, the hydrogens have been omitted for clarity

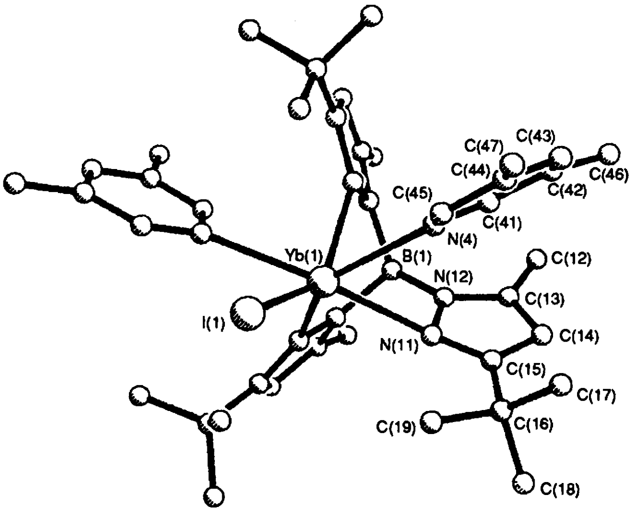

Fig. 2 Molecular structure of **2**, the hydrogens have been omitted for clarity

back-bonding to the ligand but significantly lower than in Ln(η-C_5H_5)$_3$ complexes in which it tends to fall in the range 2203 to 2208 cm^{-1} and for which the electrophilicity of the metal centre would be expected to be considerably greater than in **3**. We note that in the trivalent complex [{Sm(η-C_5Me_5)$_2$(C≡NBu^t)}$_2$(μ-O)] the observed C≡N stretching frequency of 2170 cm^{-1} was ascribed to the extreme steric congestion at the metal.[13] No reaction of **1** with CO under 1 atmosphere pressure was observed.

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Footnotes

† *Note added in proof*: Since submission of this manuscript we have become aware of the following publication in this area: L. Hasinoff, J. Takats and X. W. Zhang, *J. Am. Chem. Soc.*, 1994, **116**, 8833. We are grateful to Professor Josef Takats for prior disclosure of results and enlightening discussions.

‡ A trivalent half-sandwich complex of yttrium(III) has recently been reported.[15]

§ *Characterizing data for* **1**: elemental analysis for $C_{28}H_{48}BIN_6OYb$: C 40.70 (42.30), H 6.20 (6.10) N 10.50 (10.55%). IR (KBr pellet) ν_{B-H} 2566 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6), δ 1.06 (m, 4H, thf), 1.47 (s, 27H, CMe$_3$), 2.16 (s, 9H, Me), 3.21 (m, 4H, thf), 5.65 (s, 3H, CH). ^{13}C NMR (100.6 MHz, C_6D_6), δ 13.5 (q, CH$_3$), 25.4 (t, CH$_2$ thf), 32.1 (q, C*Me*$_3$), 32.6 (s, *C*Me$_3$), 69.6 (t, CH$_2$ thf), 102.9 (d, CH), 145.3 (s), 163.7 (s).

¶ *Crystal data* for **1** [YbTp$^{Bu^t,Me}$I(thf)]: $M = 871.73$, crystal size 0.40 × 0.15 × 0.75 mm, monoclinic, space group $P2_1/n$, $a = 11.407(2)$, $b = 16.216(5)$, $c = 18.789(7)$ Å, $\beta = 99.44(2)°$, $U = 3248(2)$ Å^3, $Z = 4$, $F(000) = 1752$, $D_c = 1.69$, μ(Mo-Kα) = 3.65 mm^{-1}; 6872 reflections collected with $5 \leqslant 2\theta \leqslant 50°$ at 291 K; of these 5986 were unique and the 3961 in which $F \geqslant 6\sigma(F)$ were used in structural analysis; refinements converged to $R = 0.051$, $R_w = 0.0511$ [$w^{-1} = \sigma F^2 + 0.000314(F)^2$] for 321 variables. For **2** [YbTp$^{Bu^t,Me}$I(3,5-lut)$_2$]: $M = 937.8$, crystal size 0.14 × 0.85 × 0.65 mm, monoclinic, space group $C2/c$, $a = 40.690(8)$, $b = 11.354(1)$, $c = 20.769(5)$ Å, $\beta = 115.14(2)°$, $U = 8686(3)$ Å^3, $Z = 8$, $F(000) = 3760$, $D_c = 1.43$, μ(Mo-Kα) = 2.88 mm^{-1}; 9351 reflections collected with $5 \leqslant 2\theta \leqslant 50°$ at 291 K; of these 8953 were unique and the 5385 in which $F \geqslant 6\sigma(F)$ were used in structural analysis; refinements converged to $R = 0.0393$, $R_w = 0.0442$ [$w^{-1} = \sigma F^2 + 0.002024(F)^2$] for 442 variables.

The structure was solved by heavy-atom methods and refined using routine procedures.

All measurements were made on a Nicolet R3mV four-circle diffractometer using Mo-Kα ($\lambda = 0.71073$ Å) radiation. Corrections for Lorentz, polarization, and an empirical correction for absorption were applied. Crystallographic calculations were carried out with the SHELXTL PLUS suite of programs on a Microvax II computer. The structure of **1** was solved by direct methods and developed by alternating cycles of Fourier syntheses and full-matrix least-squares procedures. Disorder in one of the *tert*-butyl groups was successfully modelled over two sites. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‖ *Characterizing data for* **2**: elemental analysis for $C_{38}H_{58}BIN_8Yb$: C 48.55 (48.70), H 6.15 (6.20), N 11.95 (11.95%). IR (KBr pellet) ν_{B-H} 2526 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6), δ 1.74 (s, 12H, Me lut), 1.34 (s, 27H, C*Me*$_3$), 2.29 (s, 9H, Me), 6.61 (s, 4H, *o*-H lut), 5.64 (s, 3H, CH), 8.18 (s, 2H, *p*-H lut). ^{13}C NMR (100.6 MHz, C_6D_6), δ 13.5 (q, Me), 17.9 (q, Me lut), 31.8 (q, C*Me*$_3$), 32.5 (s, *C*Me$_3$), 103.0 (d, CH pz), 132.7 (s, 3-C lut), 137.4 (d, 4-CH lut), 145.1 (s, C), 147.9 (s, C), 163.8 (d, 2-CH lut).

** *Characterizing data for* **3**: elemental analysis for $C_{29}H_{49}BIN_7Yb$: C 42.05 (43.20), H 6.15 (6.10), N 12.05 (12.15%). IR ν_{B-H} 2556 cm^{-1}, $\nu_{N\equiv C}$ 2172 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6), δ 0.73 (s, 9H, NC*Me*$_3$), 1.55 (s, 27H, C*Me*$_3$ pz), 2.16 (s, 9H, Me pz), 5.68 (s, 3H, CH pz). ^{13}C NMR (100.6 MHz, C_6D_6), δ 13.4 (q, Me), 29.2 (q, *Me*$_3$CNC), 30.7 (q, Me$_3$*C*NC), 32.2 (q, C*Me*$_3$ pz), 32.7 (s, *C*Me$_3$ pz), 102.8 (d, CH), 145.3 (s, *C*Me or *C*Me$_3$), 163.7 (s, *C*Me$_3$ or *C*Me).

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