Some Novel 3,5-Dimethylpyrazolylborato Compounds: Crystal and Molecular Structures of $[B\{Me_2C_3N_2H\}_3\{Me_2C_3N_2H_2\}]$ and $[HB\{Me_2C_3N_2H\}_3BH]^+ (TaCl_6)^-$

Donald C. Bradley,* Michael B. Hursthouse,* Joy Newton, and Nigel P. C. Walker
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, U.K.

From reactions involving $K[HB(Me_2pz)_3]$ separately with $(C_5H_5)_2TiCl_2$, $NbCl_5$, and $TaCl_5$, the novel compounds $[B(Me_2pz)_3(Me_2pzH)]$ (**1**), $NbCl_4[HB(Me_2pz)_3]$ (**3**), $[HB(Me_2pz)_3BH]^+ (MCl_6)^-$ (**4**; M = Nb, Ta), and $MCl[HB(Me_2pz)_3](Me_2pz)_3$ (**5**; M = Nb) (Me_2pzH = 3,5-dimethylpyrazole) have been isolated and *X*-ray single crystal structure determinations carried out on (**1**) and (**4**; M = Ta).

The reaction of KBH_4 with 3,5-dimethylpyrazole (Me_2pzH) appears to be limited to trisubstitution with the formation of potassium hydro-tris-(3,5-dimethylpyrazolyl)borate, $K[HB(Me_2pz)_3]$, in contrast to the formation of the tetrakisborato derivative $K[B(pz)_4]$ using pyrazole (pzH).[1]

In the course of investigating reactions of $K[HB(Me_2pz)_3]$ with Group 4 and 5 metal chlorides we have isolated the tetrasubstituted species $B(Me_2pz)_3(Me_2pzH)$ (**1**). From the reaction of $(C_5H_5)_2TiCl_2$ and $K[HB(Me_2pz)_3]$ in a 1 : 2 molar ratio (**1**) was isolated in 20% yield together with a titanium(III) product $(C_5H_5)_2Ti[HB(Me_2pz)_3]$ (**2**) (62% yield). The blue

$B(Me_2pz)_3(Me_2pzH)$
(**1**)

$(C_5H_5)_2Ti[HB(Me_2pz)_3]$
(**2**)

$NbCl_4[HB(Me_2pz)_3]$
(**3**)

$[HB(Me_2pz)_3BH]^+(MCl_6)^-$
(**4**) M = Nb, Ta

$MCl[HB(Me_2pz)_3](Me_2pz)_3$
(**5**) M = Nb

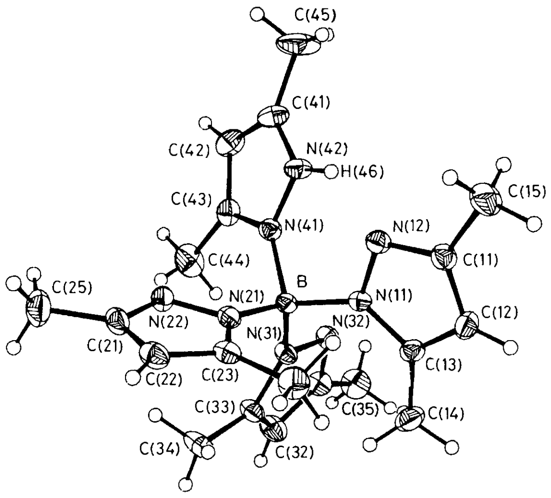

Figure 1. The structure of $B(Me_2pz)_3(Me_2pzH)$, (**1**).

Ti^{III} complex had previously been obtained by the reaction of $(C_5H_5)_2TiCl$ with $K[HB(Me_2pz)_3]$.[2]

The structure of (**1**) has been determined by single crystal *X*-ray analysis† and is shown in Figure 1. The N–H proton, H(46), is clearly located on N(42) and has caused a lengthening of the B–N(41) bond (1.595 Å) compared to the other B–N bonds (1.546, 1.532, 1.521 Å). Another feature is the distortion of the BN_4 group from regular tetrahedral symmetry with NBN values 105.7—114.0°. The room temperature n.m.r. spectrum [(CD_2Cl_2) δ 1.53 (Me), 2.20 (Me), 5.78 (4-H), 13.88 (N–H) in 12:12:4:1 ratio] shows that the N–H proton is scrambling among four equivalent 3,5-dimethylpyrazolyl groups. At low temperature (−53 °C, CD_2Cl_2) the molecule is frozen into a conformation in which all four rings are distinguishable *i.e.* 8 methyl signals (δ 1.15, 1.23, 1.34, 1.62, 2.00, 2.09, 2.22, and 2.24) and 5 proton signals (δ 5.63, 5.68, 5.76, 5.79, and 5.97) due to four ring protons and one N–H were observed. The mechanism for the formation of (**1**) is obscure but it might result from disproportionation of $HB(Me_2pz)_3$ radicals produced by dissociation of an unstable $(C_5H_5)_2Ti[HB(Me_2pz)_3]_2$ species. In any event the existence of (**1**) proves that the boron atom can accommodate four 3,5-dimethylpyrazolate groups.

Reactions of $K[HB(Me_2pz)_3]$ with MCl_5 (M = Nb, Ta) have also yielded some interesting new compounds. Thus equimolar proportions (M = Nb) in CH_2Cl_2 gave, on addition of hexane, $NbCl_4[HB(Me_2pz)_3]$ (**3**)‡ as a brown solid (41% yield) and, after concentration of the filtrate to a red oil followed by addition of chloroform, a primrose yellow salt $[HB(Me_2pz)_3BH]^+(NbCl_6)^-$ (**4**; M = Nb)‡ (30% yield) was obtained. The n.m.r. spectrum of (**4**; M = Nb) confirmed the presence of the dibora-cation [(CD_2Cl_2) ^1H, δ 2.40 (Me), 5.98 (4-H), ratio 6:1; ^{13}C, δ 12.05 (Me), 108.25 (3,5-ring carbons), 148.76 p.p.m. (4-ring carbon), ratio 2:2:1]. With the $TaCl_5$ reaction there were problems in separating the tantalum analogue $[HB(Me_2pz)_3BH]^+(TaCl_6)^-$ (**4**; M = Ta) from other species, but a single crystal of (**4**; M = Ta) was obtained and subjected to *X*-ray diffraction analysis† thereby establishing beyond doubt the structure of this novel dibora-cation (Figure 2).

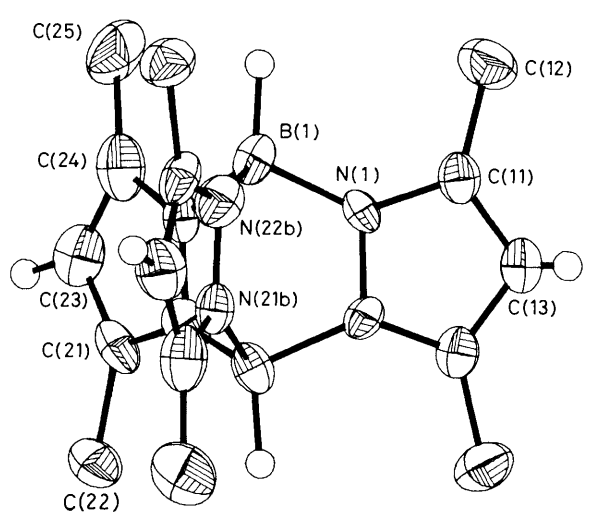

Figure 2. The structure of the cation $HB(Me_2pz)_3BH^+$ in (**4**; M = Ta).

The *B,B*-diethyl derivative of the unsubstituted μ-trispyrazolyl species $[EtB(H_3C_3N_2)_3BEt]^+$ was previously synthesized by Trofimenko[3] using a different route. The above reactions show some dependence on the solvent and are still being investigated but one other type of complex which has also been isolated and characterized by n.m.r. [(CD_2Cl_2) δ 1.75 (Me), 2.10 (2 × Me), 2.20 (Me), 5.70 (4-H), 5.98 (4-H)] is $MCl[HB(Me_2pz)_3](Me_2pz)_3$ (**5**; M = Nb).‡ The mechanisms of these reactions are as yet unclear but it is presumed that acid-catalysed cleavage of B–N(pyrazolyl) bonds takes place to generate the required fragments, *e.g.* 3,5-dimethylpyrazolate ligands in (**5**).

In contrast to the work reported here using $(C_5H_5)_2TiCl_2$ it has previously been found (and we have confirmed) that MCl_4 (M = Ti, Zr) compounds undergo monosubstitution with $K[HB(pz)_3]$ and $K[HB(Me_2pz)_3]$.[4] Moreover, recent work using $NbCl_5$ in reactions with $K[HB(pz)_3]$ and $K[H_2B(pz)_2]$ have shown ready reduction to Nb^{IV} products although the Nb^V containing salts $K[NbCl_5\{HB(pz)_3\}]$ and $K[NbCl_5\{H_2B(pz)_2\}]$ were isolated from low-temperature reactions.[5] Previous work has focussed on the value of $[HB(pz)_3]^-$ and $[HB(Me_2pz)_3]^-$ as tridentate σ-bonding counterparts of the π-bonding $C_5H_5^-$ and $C_5Me_5^-$ with the isolation of stable Cu-carbonyl[6] and Mo-nitrosyl[7,8] complexes. McCleverty and coworkers[7] have reported the susceptibility of the metal-co-ordinated $[HB(Me_2pz)_3]^-$ ligand to halogen substitution at the 4-position in the 3,5-dimethylpyrazolylato ring and it appears from our work that this ligand is capable of other modes of reactivity.

---

† *Crystal data* for (**1**): $C_{20}H_{29}BN_8$, *M* = 392.3, monoclinic, *a* = 13.681(3), *b* = 11.061(2), *c* = 14.747(1) Å, β = 102.59(1)°, *U* = 2177.8 Å^3, space group $P2_1/c$, *Z* = 4, D_c = 1.193 g cm^{-3}, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 0.71 cm^{-1}. The structure was solved by direct methods and refined by least squares using intensity data {4741 recorded, 2140 observed [$I \geqslant 1.5\sigma(I)$]} measured on a CAD4 diffractometer giving *R* = 0.045.

Crystal data for (**4**; M = Ta): $C_{15}H_{23}B_2Cl_6N_6Ta$, *M* = 702.3, orthorhombic, *a* = 11.684(9), *b* = 7.651(1), *c* = 14.463(2) Å, *U* = 1293.0 Å^3, space group $P2_122_1$ (standard setting $P2_12_12$): *Z* = 4; D_c = 1.798 g cm^{-3}; λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 46.52 cm^{-1}. The structure was solved by heavy atom techniques and refined by least squares using intensity data {1391 recorded, 1186 unique observed [$I \geqslant 1.5\sigma(I)$]} measured on a CAD4 diffractometer giving *R* = 0.031. The data were corrected for absorption errors using the DIFABS method, ref. 9.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Satisfactory C, H, N, and Cl analyses and mass spectra were obtained for (**3**), (**4**; M = Nb), and (**5**).

We thank S.E.R.C. for support and I.C.I. for co-operation in a CASE award (J. N.).

Received, 19th October 1983; Com. 1378

References

1 S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.
2 L. E. Manzer, *J. Organomet. Chem.*, 1975, **102**, 167.
3 S. Trofimenko, *J. Am. Chem. Soc.*, 1969, **91**, 5410.
4 J. K. Koube and S. S. Wreford, *Inorg. Chem.*, 1976, **15**, 231; D. L. Reger and M. E. Tarquini, *ibid.*, 1982, **21**, 840.
5 L. G. Herbert-Pfalzgraf and M. Tsunoda, *Polyhedron*, 1983, **2**, 203.
6 C. S. Arcus, J. L. Wilkinson, C. Mealli, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, 1974, **96**, 7564.
7 J. A. McCleverty, D. Seddon, N. S. Bailey, and N. W. Walker, *J. Chem. Soc., Dalton Trans.*, 1976, 898.
8 J. A. McCleverty A. E. Rae, I. Wolochowicz, N. A. Bailey, and J. M. A. Smith, *J. Organomet. Chem.*, 1979, **168**, C1.
9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.