Preliminary Communication

Synthesis and structural characterization of volatile poly(3,5-dimethyl-1-pyrazolyl)-borate-complexes of Ca, Sr, and Ba

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Abstract

The complexes [MTp^*_2] ($Tp^* = HB(3,5\text{-}Me_2pz)_3$; M = Ca, **1**; Sr, **2**; Ba, **3**) are produced when the iodides MI_2 react with KTp^* in tetrahydrofuran (THF). If BaI_2 is treated with only 1 mol equiv. of KTp^* in THF, the compound [$Tp^*BaI(THF)_n$] **4** is produced. Some reactions of complex **4** have been studied, particularly adduct formation with hexamethylphosphoramide, HMPA, to furnish [$Tp^*BaI(HMPA)_2$] **5** and the reactions with KBp^* ($Bp^* = H_2B(3,5\text{-}Me_2pz)_2$) and KTp^*, that yield [$Tp^*Ba(Bp^*)(THF)$] **6** and complex **3**, respectively.

Key words: Calcium; Barium; Strontium; Poly(pyrazolyl)borates; X-ray structure

Interest in the coordination and organometallic chemistry of the heavier alkaline-earth elements, Ca, Sr and Ba, has increased considerably over the past five years [1], in part because of the search for soluble or volatile materials usable in the preparation, by sol–gel or chemical vapour deposition methods, of oxide materials of practical utility (such as $BaTiO_3$ [2], high-temperature superconducting ceramics [3] and materials with valuable electronic properties [4]). Although it is not easy to satisfy the high coordination needs of these large M^{2+} cations, particularly those of Ba^{2+} ($r_{Ba^{2+}} = 1.35$ Å [5] for $CN = 6$), coordinatively saturated structures of relatively low coordination numbers (6 or lower) can be achieved by means of sterically demanding ligands, such as the poly(pyrazolyl)borate [6], bulky amide, aryloxide and related groups [1(c),7].

The recent publication of several contributions dealing with the chemistry of the alkaline-earth elements, including complexes of the tris(pyrazolyl)borates [1,7,8] (Tp), has prompted us to present our own findings in this area. Here we report preliminary results on the synthesis and structural characterization of some complexes of Ca^{2+}, Sr^{2+} and Ba^{2+} with $HB(3,5\text{-}Me_2pz)_3$-(Tp^*) (see Scheme 1). While this manuscript was being prepared, a preliminary report on the synthesis and structural characterization by X-ray methods of $BaTp^*_2$ was published in *J. Organomet. Chem.* by Chisholm, Caulton and co-workers [9].

Treatment of the iodides MI_2 with 2 mol equiv. of KTp^* in THF, yields white precipitates of the expected complexes MTp^*_2 (M = Ca, **1**; Sr, **2**; Ba, **3**). The three compounds are insoluble in water and also show low solubility in common organic solvents. Crystalline samples of analytical purity [10*] can be obtained by successively washing the crude solids with H_2O, EtOH, and Et_2O and subliming the resulting residues at *ca.* 200°C at 10^{-3} torr. The barium derivative is soluble in THF and also in hot toluene. Crystals suitable for X-ray studies [11*] have been obtained from the latter solvent. Data collection at −100°C provides results essentially identical to those found at −165°C [9] and therefore they will not be discussed further.

When a THF solution of BaI_2 reacts with 1 equiv. of KTp^* (Scheme 1) a white, crystalline solid, also exhibiting good solubility properties in THF, is produced. This contains only one Tp^* per barium and can be formulated as [$Tp^*BaI(THF)_n$] **4**. However, when dried under vacuum it quickly loses crystallinity and it crumbles to a white powder that contains only one molecule of THF per barium according to NMR data. Addition of hexamethylphosphoramide to solutions of **4** yields the adduct [$Tp^*BaI(HMPA)_2$] **5**, which has been structurally characterized by X-ray studies [12*]. Owing to non-resolvable disorder associated with the thermal motion of the hexamethylphosphoramide (HMPA) units, the N and C atoms of these molecules have been refined only isotropically. This leads to *R* values somewhat higher than usual [12*], but nevertheless the

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* Reference number with asterisk indicates a note in the list of references.

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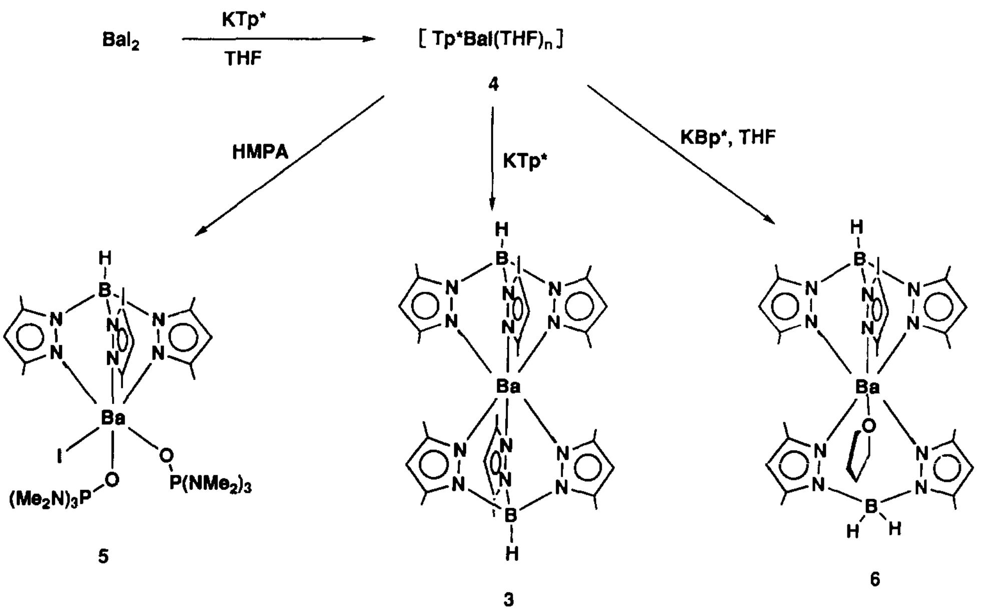

Scheme 1.

characterization of **5** is unambiguous. As shown in Fig. 1, the barium atom is six-coordinate with distorted octahedral geometry, formed by the N atoms of the Tp*, the two HMPA oxygens and the iodide. The average Ba–N separation, 2.84(4) Å, compares well with the corresponding distance in **3** (2.754(3) Å from our data, 2.760(1) Å in ref. 9) and similarly, the Ba–O distance to the HMPA, mean 2.60(3) Å, is identical within experimental error to the corresponding distance of 2.579(8) Å in the aryloxide complex $[Ba(OC_6H_2\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}Me)_2(HMPA)_2] \cdot C_7H_8$ [13]. The intra-ligand N–Ba–N angle of 68(1)° is somewhat smaller than the analogous angle in other structurally characterized $[MTp^*_2]$; *e.g.* 71.3(1)° in **3**, 75.5(1)° in $[SmTp^*_2]$ [14], 79.3(1)° in $[YbTp^*_2]$ [15].

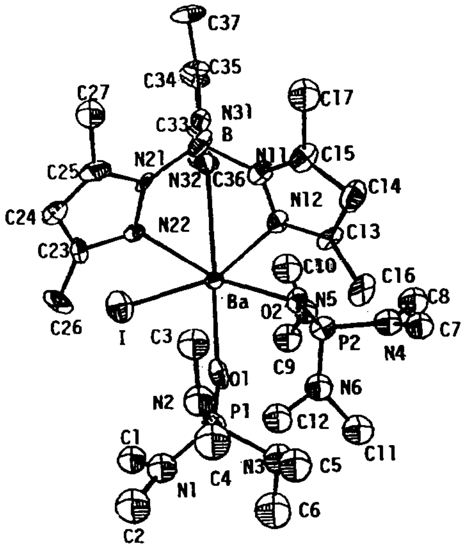

Fig. 1. ORTEP drawing of compound **5** and atom labelling scheme, showing the thermal ellipsoids at 20% probability.

The reaction of CaI_2 or SrI_2 with 1 mol equiv. of KTp* gives only the corresponding $[MTp^*_2]$ and unreacted MI_2. It is likely that some kind of equilibrium between the mono- and the bis-Tp* compounds is established in solution, but the very low solubility of the Ca and Sr $[MTp^*_2]$ products strongly favours the formation of the latter compounds.

Not unexpectedly, the reaction of **4** with 1 mol equiv. of KTp* (Scheme 1) yields $[BaTp^*_2]$. The preparation of a mixed Tp*–Bp* compound (Bp* = $H_2B(3,5\text{-}Me_2pz)_2$) was accomplished successfully by treatment of **4** with KBp* in THF. Complex **6** is a white crystalline solid and although we have not attempted its characterization by X-ray crystallography, NMR data furnish unambiguous evidence in support of the proposed formulation. For example, four singlets with relative intensity 2:2:1:1 and two singlets, 2:2, are expected in the ^1H NMR spectrum for the methyl groups of the Tp* and Bp* ligands, respectively, and are found at δ 1.77, 2.27, 1.86, 2.27 (Tp*) and 2.03, 2.33 ppm (Bp*). A similar situation is found in the $^{13}C\{^1H\}$ NMR spectrum (δ 12.3, 13.0, 12.5, 12.9, 12.6, 13.0 ppm), whereas the $^{11}B\{^1H\}$ NMR spectrum exhibits two broad singlets for the two BH_n entities.

Full lists of crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

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References and notes

1 See for example: (a) T.P. Hanusa, *Chem. Rev., 93* (1993) 1023; (b) K.G. Caulton, M.H. Chisholm, S.R. Drake, K. Folting and J.C. Huffman, *Inorg. Chem., 32* (1993) 816; (c) P.B. Hitchcock, M.F. Lappert, G.A. Lawless and B. Royo, *J. Chem. Soc., Chem. Commun.,* (1990) 1141; (d) K.F. Tesh, T.P. Hanusa, J.C. Huffman and C.J. Huffman, *Inorg. Chem., 31* (1992) 5572; (e) S.R. Drake, M.B. Hurthouse, K.M. Malik and S.A.S. Miller, *J. Chem. Soc., Chem. Commun.,* (1993) 478.

2 K.S. Mazdeyasni, R.T. Dolloff and J.S. Smith II, *J. Amer. Ceramic Soc., 52* (1969) 523; S.-G. Yoon, J.-D. Park, J.-H. Choi and H.-G. Kim, *J. Vac. Sci. Technol., A9* (1991) 281; D.C. Bradley, *Chem. Rev., 89* (1989) 1317.

3 A.D. Berry, R.T. Gaskill, E.J. Holm, R. Cukanskas, R. Kaplan and R.L. Henry, *Appl. Phys. Lett., 52* (1988) 1743; H. Yamane, H. Kurosawa, T. Hirai, K. Watanabe, H. Iwasaki, N. Kobayashi and Y. Muto, *Supercond. Sci. Technol., 2* (1989) 115.

4 L.G. Hubert-Pfalzgraf, *Nouv. J. Chem., 11* (1987) 663.

5 R.D. Shannon, *Acta Crystallogr., A32* (1976) 751.

6 S. Trofimenko, *Chem. Rev., 93* (1993) 943; S. Trofimenko, *J. Am. Chem. Soc., 89* (1967) 3170.

7 See for example: J.M. Boncella, C.J. Coston and J.K. Cammack, *Polyhedron, 10* (1991) 769; K.G. Caulton, M.H. Chisholm, S.R. Drake and W.E. Streib, *Angew. Chem., Int. Ed. Engl., 90* (1986) 5502; D.C. Bradley, M.B. Hursthouse, A.A. Ibrahim, K.M.A. Malik, M. Motevalli, R. Möseler, H. Powell, J.D. Runnacles and A.C. Sullivan, *Polyhedron, 9* (1990) 2959; P. Miele, J.-D. Foulon, N. Hovnanian and L. Cot, *Polyhedron, 12* (1993) 267; K.G. Caulton, M.H. Chisholm, S.R. Drake and K. Folting, *Inorg. Chem., 30* (1991) 1500; F.T. Edelman, *Comments Inorg. Chem., 12* (1992) 259.

8 Y. Sohrin, H. Kokusen, S. Kihara, M. Matsui, Y. Kushi and M. Shiro, *J. Am. Chem. Soc., 115* (1993) 4128.

9 S.G. Dutremez, D.B. Leslie, W.E. Streib, M.H. Chisholm and K.G. Caulton, *J. Organomet. Chem., 462* (1993) C1.

10 Analytical data for selected complexes. (**1**) Found: C, 56.42; H, 6.99; N, 25.91, $C_{30}H_{44}B_2CaN_{12}$. Calc.: C, 56.79; H, 6.99; N, 26.49%. (**2**) Found: C, 52.53; H, 6.39; N, 24.72. $C_{30}H_{44}B_2N_{12}Sr$. Calc.: C, 52.83; H, 6.51; N, 24.64%. (**3**) Found: C, 49.17; H, 6.13; N, 23.23. $C_{30}H_{44}B_2BaN_{12}$. Calc.: C, 49.24; H, 6.07; N, 22.97%. (**5**) Found: C, 54.99; H, 6.35; N, 18.09. $C_{27}H_{58}BBaIN_{12}O_2P_2$. Calc.: C, 55.67; H, 6.38; N, 18.49%.

11 Crystallographic data for **3**: $a = 11.137(3)$, $c = 25.427(5)$ Å with $Z = 3$. Space group $R3$. $R(F) = 0.029$ and $R_w(F) = 0.032$ with 962 reflections $[I < 2\sigma(I)]$. Final refinement with unit weights and anisotropic thermal motion for non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions.

12 Crystallographic data for **5**: $a = 44.01(1)$, $b = 11.479(9)$, $c = 17.691(6)$; $\beta = 100.63(3)°$ with $Z = 8$. Crystals of **5** are monoclinic, space group $C2/c$. 1868 observed reflections $[I < 2\sigma(I)]$ led to $R(F) = 0.088$ and $R_w(F) = 0.089$. Because of the non-resolvable disorder due to the thermal motion of HMPA ligands, the N and C atoms of these molecules have been refined only isotropically. A final mixed refinement was undertaken with isotropic and anisotropic thermal parameters and the H atoms were included with fixed isotropic contributions at their calculated positions.

13 T.R. Belderraín, J.P. Espinós, A. Fernández, D. Leinen, M. Paneque, A.R. González-Elipe and E. Carmona, to be submitted.

14 J. Takats, X.W. Zhang, V.W. Day and T.A. Eberspacher, *Organometallics, 12* (1993) 4286.

15 A. Sella, personal communication.