Journal of Organometallic Chemistry, 356 (1988) C57–C60
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Unexpected regiochemistry in the reaction of benzotriazole with KBH_4: synthesis of a new class of poly(azolyl)borate ligands

F.J. Lalor *, S. Miller and (in part) N. Garvey

Department of Chemistry, University College, Cork (Irish Republic)

(Received August 30th, 1988)

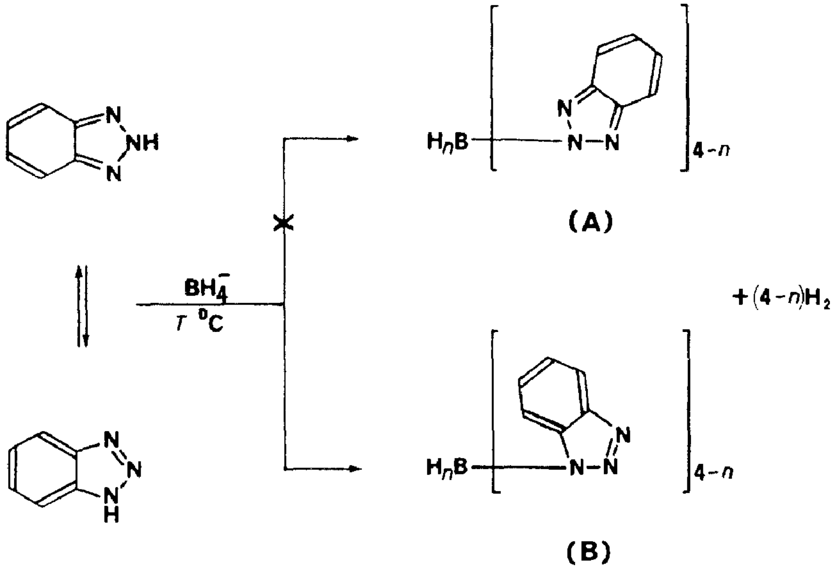
Abstract

The reaction of KBH_4 with molten benzotriazole leads to the formation of a series of poly(benzotriazoly)borate anions $[H_nB(C_6H_4N_3)_{4-n}]^-$ where $n = 2$, 1 and 0 depending on the temperature. The regiospecificity of the process differs from that of pyrazole/BH_4^- reactions in that B–N bond-formation takes place in a manner that maximises steric crowding at boron (i.e. at the triazole N(1) atoms). The complex-forming abilities of the new ligands have been investigated, and show some interesting differences from those of the poly(1-pyrazolyl)borate analogues.

Despite the recent resurgence of interest in the chemistry of poly(1-pyrazolyl)borate ligands [1] there have been remarkably few systematic attempts to develop analogous ligand systems based on heterocycles other than pyrazole. (An exception is the work of Zaidi, Siddiqi, and their co-workers which has mainly been concerned with derivatives of indazole [2]). Our discovery that the chemistry of some poly(1-pyrazolyl)borate complexes of molybdenum is critically dependent on the pattern of ring-substitution [3] has prompted us to search for related ligands with altered steric and electronic properties. We now report that the reaction of KBH_4 with molten benzotriazole leads to smooth evolution of hydrogen and successive formation of the poly(benzotriazolyl)borate anions $[H_nB(C_6H_4N_3)_{4-n}]^-$ (I, $n = 2$; II, $n = 1$, III, $n = 0$. Scheme 1), the value of n in the final product being determined by the reaction temperature. The potassium salt of III was readily obtained in analytically pure form, but I and II were more conveniently characterised as their thallous salts *. Avoidance of steric crowding at boron dominates the reaction of 3(5)-monosubstituted pyrazoles with KBH_4 and produces exclusively 3-substituted poly(1-pyrazolyl)borate anions [4]. Similar regiospecificity in the pre-

---

* Except where the contrary is stated correct microanalytical data were obtained for all new compounds.

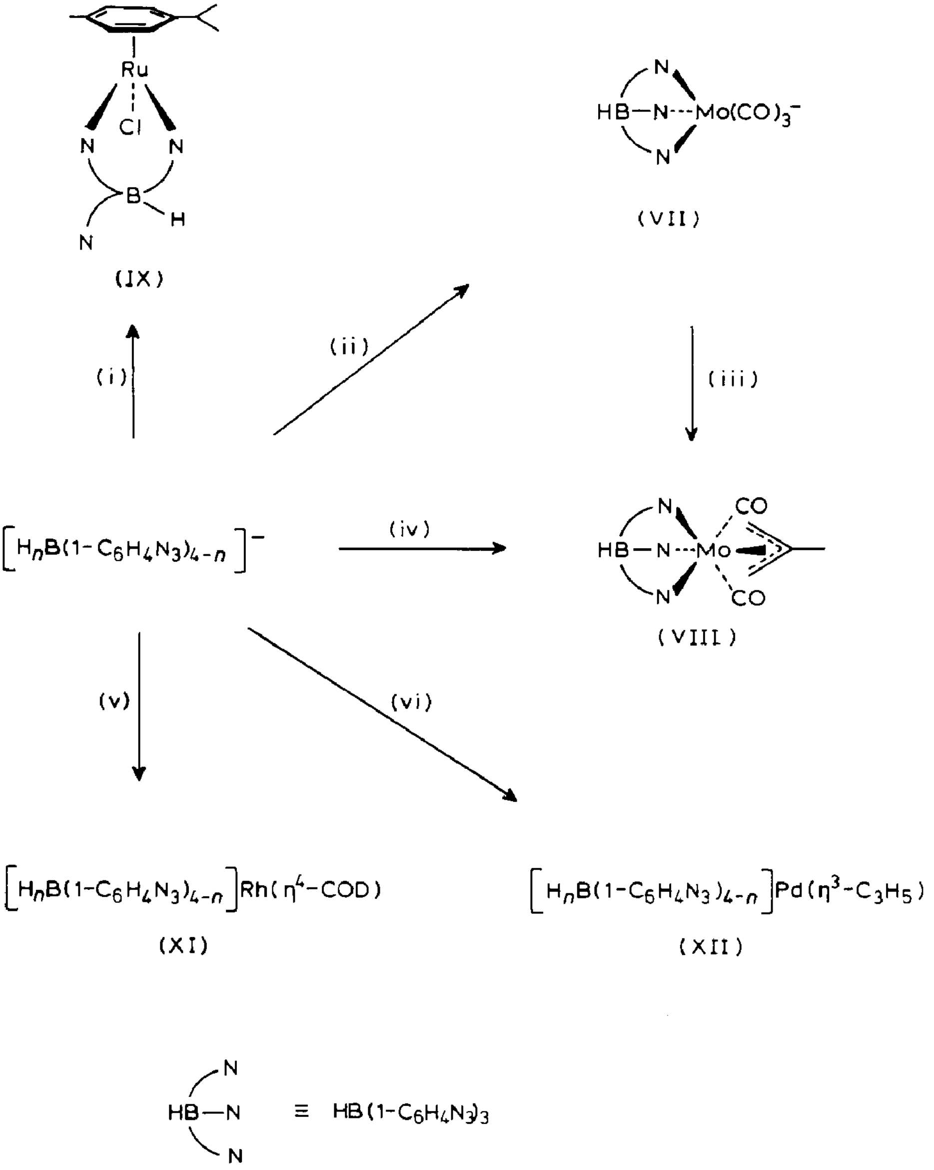


Scheme 1. I: T 100–130 °C, $n = 2$; II: T 170–200 °C, $n = 1$; III: T 240–260 °C, $n = 0$.

sent system would imply B–N bond-formation at the triazole N(2) atom only, i.e. structure (*A*) of Scheme 1. However, the ^{13}C NMR spectra of all three anions exhibit resonances for six inequivalent carbon nuclei, showing that the structure actually adopted is that of the more crowded regioisomer (*B*). While it is still possible that structure (*A*) is the kinetically-controlled product of the synthesis, we deduce that minimalisation of steric crowding does not energetically compensate for the loss of aromatic delocalisation in the quinonoid ring-systems of (*A*) and hence that (*B*) is the thermodynamically-favoured regioisomer. These results imply that the analogous structures proposed for a series of poly(indazolyl)borates [2] are probably correct despite the reservations on this point which have been expressed elsewhere [1].

The anions I and II behave like the poly(1-pyrazolyl)borates in that they yield stable 2/1 complexes $[H_nB(1\text{-}C_6H_4N_3)_{4-n}]_2M$ (IV, $n = 2$, M = Fe, Co, Ni, Cu; V, $n = 1$, M = Mn, Fe, Co, Ni, Cu) when aqueous solutions of their potassium salts are mixed with those of salts of the appropriate divalent transition metal cations. In contrast $K[B(1\text{-}C_6H_4N_3)_4]$, which is insoluble in water, reacts with $FeCl_2$ in ethanol to yield a stable 1/1 complex $[B(1\text{-}C_6H_4N_3)_4]FeCl$ (VI), although complexes of this type are very unstable in the poly(1-pyrazolyl)borate series [1]. Unlike their poly(1-pyrazolyl)borate analogues, most of the complexes of type IV–VI are very sparingly soluble in organic solvents. Hence entirely satisfactory microanalytical data could not be obtained in every case, although all results were in reasonable agreement with the proposed structures. The insolubility of the complexes suggest that the solids may have polymeric structures and there are also other indications of significant structural differences from their poly(1-pyrazolyl)borate analogues. Thus the colours of the dihydrobis(1-benzotriazolyl)borato complexes (IV) differ markedly from the corresponding dihydrobis(1-pyrazolyl)borato derivatives. Furthermore the reflectance spectrum of the green copper(II) complex shows a single broad band at 13 888 cm^{-1} assignable to the $^2T_{2g} \leftarrow {}^2E_g$ transition of an approximately octahedral Cu^{2+}

ion in contrast to the square-planar geometry of the lilac-coloured dihydrobis(1-pyrazolyl)borate analogue [5]. Intra- or inter-molecular B–H...Cu interaction is contra-indicated by the presence of a normal ν(B–H) band at ca. 2430 cm^{-1} (broad) in the IR spectrum of IV (M = Cu) [6]. It seems more likely that the metal centre attains 6-coordination via intermolecular N → Cu bonding utilising the "extra" lone pairs on the triazole N(3) atoms. Unfortunately, we could not obtain suitable crystals in order to test this suggestion by an X-ray crystallographic study.



Scheme 2. Reagents: (i) [(η^6-$C_{10}H_{14}$)$RuCl_2$]$_2$, thf, room temperature; (ii) $(CH_3CN)_3Mo(CO)_3$, thf, reflux; (iii) 2-methyl-3-chloro-1-propene, dmf, 70 °C; (iv) $MoCl(CO)_2(CH_3CN)_2$(η^3-$2MeC_3H_4$), thf, room temperature; (v) [(η^4-COD)RhCl]$_2$, dmf, room temperature; (vi) [(η^3-C_3H_5)PdCl]$_2$, CH_2Cl_2, room temperature.

A representative selection of the organometallic derivatives of the new ligands are shown in Scheme 2. The red anionic hydrotris(1-benzotriazolyl)borato(tricarbonyl)-molybdenum(0) complex (VII) is much less stable than its yellow poly(1-pyrazolyl)borate analogues [7], but was readily characterised by conversion into the air-stable η^3-2-methylpropenyl complex (VIII), which was also prepared directly from the anionic ligand II. Reaction of the latter with $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ ($C_{10}H_{14}$ = 4-isopropyltoluene) unexpectedly yielded a covalent complex (IX), which is isomeric with the anticipated [8] ionic product $[(\eta^6\text{-}C_{10}H_{14})Ru\{\eta^3\text{-}HB(1\text{-}C_6H_4\text{-}N_3)_3\}]Cl$ (X) and which we formulate as containing a *dihapto* $[HB(1\text{-}C_6H_4N_3)_3]^-$ ligand (Scheme 2). Attempts to convert IX into X have so far been unsuccessful. Finally, the ligands I–III react with the rhodium complex $[\eta^4\text{-}(COD)RhCl]$ (COD = 1,5-cyclooctadiene) and II, III with the π-allylpalladium complex $[(\eta^3\text{-}C_3H_5)PdCl]$ to yield stable derivatives of general formula $LRh(\eta^4\text{-}COD)$ (XI) and $LPd(\eta^3\text{-}C_3H_5)$ (XII), respectively (Scheme 2). The hydrotris(1-benzotriazolyl)borato complexes (XI, XII; ($L = HB(1\text{-}C_6H_4N_3)_3$)) are stereochemically non-rigid in solution at room temperature, as evidenced by the equivalence of all three benzotriazolyl groups in their ^1H and ^{13}C NMR spectra. Unfortunately the spectra of the tetrakis(1-benzotriazolyl)borato complexes (XI, XII; $L = B(1\text{-}C_6H_4N_3)_4$), which would have given insight into the nature of the dynamic process involved [9], could not be obtained owing to the very low solubility of these complexes. An X-ray crystallographic study of the rhodium complex (XI, $L = HB(1\text{-}C_6H_4N_3)_3$) has been completed and will be described in detail elsewhere [10]. It confirms the B–N(1) bonding in the ligand proposed above, but also reveals that, unlike its square-planar poly(1-pyrazolyl)-borato analogues [11], the complex is five-coordinate in the solid state.

Studies of the new ligands and of their complexes are continuing.

References

1 S. Trofimenko, Progr. Inorg. Chem., 34 (1986) 115; K. Niedenzu and S. Trofimenko, Topics Curr. Chem., 131 (1986) 1 and ref. therein.

2 Z.A. Siddiqi, S. Khan, K.S. Siddiqi and S.A.A. Zaidi, Synth. React. Inorg. Met.-Org. Chem., 14 (1984) 303 and ref. therein.

3 T. Desmond, F.J. Lalor, G. Ferguson, B. Ruhl and M. Parvez, J. Chem. Soc., Chem. Commun., (1983) 55.

4 T. Desmond, F.J. Lalor, G. Ferguson and M. Parvez, J. Organomet. Chem., 277 (1984) 91 and ref. therein.

5 J.P. Jesson, S. Trofimenko and D.R. Eaton, J. Am. Chem. Soc., 89 (1967) 3148.

6 C.A. Kosky, P. Ganis and G. Avitabile, Acta, Cryst. B, 27 (1971) 1859, 2493; R.B. King and A. Bond, J. Am. Chem. Soc., 96 (1974) 1338 and ref. therein.

7 S. Trofimenko, J. Am. Chem. Soc., 91 (1969) 588.

8 R.J. Restivo, G. Ferguson, D.J. O'Sullivan and F.J. Lalor, Inorg. Chem., 14 (1975) 3046.

9 M. Cocivera, G. Ferguson, F.J. Lalor and P. Szczecinski, Organometallics, 1 (1982) 1139.

10 G. Ferguson, F.J. Lalor, S. Miller and B. Ruhl, in preparation.

11 M. Cocivera, G. Ferguson, B. Kaitner, F.J. Lalor, D.J. O'Sullivan, M. Parvez and B. Ruhl, Organometallics, 1 (1982) 1132.