panied by extensive ligand rearrangements. This resulted in the formation of pyrazaboles of the type $R_2B(\mu\text{-pz})_2BR_2$ as the only isolated boron-containing species.

Triply bridged diboron units are also contained in dibora cations of the type $[RB(\mu\text{-pz})_3BR]^+$. Only two examples of such species have so far been described in the literature. The first one, $[C_2H_5B(\mu\text{-pz})_3BC_2H_5]^+$, was obtained as a minor product on interaction of ethylboryl ditosylate, $C_2H_5B(OTs)_2$ (OTs = $O_3SC_6H_4\text{-4-}CH_3$), with pz^- and was isolated as the hexafluorophosphate salt; no experimental details were given.[5] The structure of the species was, however, confirmed by ^1H NMR[5] and X-ray diffraction[13] data. The second example, $[HB(\mu\text{-pzMe}_2)_3BH]^+$ ($HpzMe_2$ = 3,5-dimethylpyrazole), was accidentally obtained in low yield when $K[HB(pzMe_2)_3]$ was reacted with MCl_5 (M = Nb, Ta). Although the process of formation of the cation is not well understood, its structure was again confirmed by NMR and X-ray crystallographic data.[6]

When potassium pyrazolide, Kpz, was reacted with $C_2H_5BX_2$ (X = OTs, O_3SCF_3(=OTf)) in 3:2 molar ratio, the desired cation $[C_2H_5B(\mu\text{-pz})_3BC_2H_5]^+$ was obtained in about 20% (X = OTs) or 40% (X = OTf) yield, respectively. The tosylate salt of the cited cation is extremely hygroscopic, and it is best to convert it immediately to the hexafluorophosphate salt. The triflate salt is only slightly soluble in water but readily dissolves in methanol or acetone. Remarkably, no defined boron-containing product could be obtained from $KpzMe_2$ and $C_2H_5BX_2$ under analogous reaction conditions.

In another set of experiments, $[RB(pz)_3]^-$ ions (R = H, pz) were reacted with $C_2H_5BX_2$. Both $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ gave only the cation $[C_2H_5B(\mu\text{-pz})_3BC_2H_5]^+$, and no species with unsymmetrical substitution at the boron atoms could be obtained. In the reaction of $[HB(pz)_3]^-$, the yield of the cation was comparable to the one obtained in the preparation originating from the pz^- ion; for $[B(pz)_4]^-$, the yield was only about 5%. No other defined boron-containing products could be identified as products in these reactions. On the other hand, when stereochemically pure $[HB(pzMe)_3]^-$ (HpzMe = 3-methylpyrazole) was reacted with $C_2H_5BX_2$, the desired unsymmetrical cation $[HB(\mu\text{-pzMe})_3BC_2H_5]^+$ was obtained. NMR spectral data of the species clearly confirm its structure and also the formation of only one isomer. This latter observation tends to suggest that the ion $[HB(pzMe)_3]^-$ reacts as such and no intermediate cleavage of a boron–pyrazolyl bond is involved. Surprisingly, $[HB(pzMe_2)_3]^-$ reacted with $C_2H_5BX_2$ to form the species $[HB(\mu\text{-pzMe}_2)_3BH]^+$.

The foregoing observations suggest a directive influence of the pyrazole methyl groups with respect to the resulting product but do not explain the differing rearrangements of the boron substituents. Presumably, in the above case of reacting the $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ ions, an unsymmetrically B-substituted ion, $[RB(\mu\text{-pz})_3BC_2H_5]^+$ (R = pz, H), is formed initially, but this is followed rapidly by displacement of the boron-bonded R by an ethyl group. On the other hand, the results of the reaction of $K[HB(pzMe_2)_3]$ with $C_2H_5BX_2$ illustrate that a reverse ligand exchange, i.e., displacement of ethyl by H, is also possible.

Unusual ligand redistribution reactions have also been observed in other instances. For example, the reaction of $K[(C_6H_5)_2B(pz)_2]$ with $(C_2H_5)_2BOTf$ readily gave the desired pyrazabole $(C_6H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$. This reaction was found to proceed much more smoothly than the reaction of $[B(pz)_4]^-$ with $(C_2H_5)_2BOTs$ to yield the pyrazabole $(pz)_2B(\mu\text{-pz})_2B(C_2H_5)_2$.[4] As a matter of fact, this latter reaction is not easily duplicated but most often yields the symmetrical pyrazabole $R_2B(\mu\text{-pz})_2BR_2$ with R = C_2H_5 under apparently identical conditions. Thus, the present study illustrates that the ligand-exchange reactions are not yet well understood and often are unpredictable.

Finally, it is worth mentioning that a fairly strong solvent effect has been noticed not only for terminal but also for bridging pz groups of pyrazaboles when the ^1H NMR spectra are recorded. For example, the terminal-pz ^1H signals of $(pz)_2B(\mu\text{-pz})_2B(C_2H_5)_2$ were observed at δ 7.73/6.94/6.26 in $CDCl_3$[10] and at δ 7.61/6.97/6.26 in CD_3CN, and the bridging-pz ^1H signals were found at δ 7.76/7.46/6.52 in $CDCl_3$[10] but at δ 7.91/7.44/6.61 in CD_3CN. The corresponding values for $(pz)_2B(\mu\text{-pz})_2B(pz)_2$ are δ (in $CDCl_3$) 7.70/6.81/6.16 (terminal pz) and 7.67/6.70 (bridging pz)[10] but δ (in CD_3CN) 7.57/6.75/6.07 and 7.51/6.65, respectively. This may impair the assignments of ^1H NMR signals of pyrazaboles by correlation if different solvents are employed.

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Polynuclear Pyrazolyl-Bridged Spiro Species Containing Boron and Metal Centers[1]

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A series of chain-type polynuclear pyrazolyl-bridged spiro species containing boron and metal centers have been prepared. Reaction of the tetrakis(1-pyrazolyl)borate ion, $[B(pz)_4]^-$ (Hpz = pyrazole), with 1 molar equiv of a metal halide species LMX (L = nonreactive ligand(s); M = metal, e.g., Pd; X = halogen) yielded covalent compounds of the type $(pz)_2B(\mu\text{-pz})_2ML$; with 2 molar equiv of LMX, trinuclear cationic species of the type $[LM(\mu\text{-pz})_2B(\mu\text{-pz})_2ML]^+$ were obtained. Corresponding reactions using *B,B*-bis(1-pyrazolyl)pyrazaboles gave the trinuclear $[R_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2ML]^+$ (R = noncoordinating substituent) and tetranuclear $[LM(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2ML]^{2+}$ ions, respectively. Reactions of metal dihalides, MX_2 (e.g., M = Zn, Pd, Pt), with *B*-(1-pyrazolyl)pyrazaboles yielded species of the types $R_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BMX_2$ and $X_2M(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2MX_2$. In addition, the pentanuclear compound $Cl_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2Zn(\mu\text{-pz})_2B(\mu\text{-pz})_2ZnCl_2$ was obtained from $Zn[B(pz)_4]$ and $ZnCl_2$.

Introduction

The complexes $[(\eta^3\text{-}CH_2CRCH_2)Pd(\mu\text{-pz})_2B(\mu\text{-pz})_2Pd(\eta^3\text{-}CH_2CRCH_2)]^+$ and $[(\eta^3\text{-}CH_2CRCH_2)Pd(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2Pd(\eta^3\text{-}CH_2CRCH_2)]^{2+}$ (Hpz = pyrazole) were first mentioned in 1972, but only limited experimental data were presented.[2] Four additional species in which a tetrakis(1-pyrazolyl)borate unit bridges between two metal centers, i.e., $LM(\mu\text{-pz})_2B(\mu\text{-pz})_2ML'$ (L and L′ = various ligands; M = Ti,[3] Th,[4] Ru,[5] Pd[6]), have since

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