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N-Triazolylboranes[1]

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1,3-Dimethyl-2-(*N*-triazolyl)-1,3,2-diazaboracycloalkanes, (tz)$\overline{BNCH_3(CH_2)_nNCH_3}$ (where Htz = 1,2,3-triazole (**1**), 1,2,4-triazole (**2**), benzotriazole (**4**); n = 2, 3), have been synthesized by condensation procedures. The resultant species are monomeric and contain three-coordinate boron; they do not dimerize at temperatures as low as −50 °C. Compounds of type **1**, however, exist as a mixture of the 1- and 2-isomers, whereas **2** and **4** are the 1-isomers exclusively. Only species of type **2** are fluxional at elevated temperatures; those of type **1** and **4** are static up to 80 °C. However, the monomeric *N*-triazolylboranes have remaining Lewis acidity and can complex with additional Htz. On the basis of this feature, representative bis(1-triazolyl)diorganylborates, $Na[(tz)_2BR_2]$ (Htz = 1,2,4-triazole; R = C_2H_5 or $^1/_2$ C_8H_{14} where $(C_8H_{14})BH$ = 9-borabicyclo[3.3.1]nonane), were readily obtained by the reaction of (dimethylamino)diorganylboranes with 1 molar equiv of Htz and subsequent treatment with 1 molar equiv of M(tz) (M = alkali metal). The salts were converted to some representative complexes, e.g., $R_2B(\mu\text{-tz})_2Pd(\pi\text{-}CH_2CHCH_2)$.

Introduction

The few neutral N-bonded boron derivatives of triazoles that have been described in the literature generally exist as intermolecular complexes containing four-coordinate boron. These may be dimers with the central B_2N_4 ring of pyrazaboles, cyclic tetramers with a central B_4N_{12} ring, or oligomers/polymers of undetermined structures.[2] Only one monomeric species containing trigonal boron has been mentioned in the literature,[3] but the compound was obtained in low yield and, on the basis of NMR data, was not completely pure. Furthermore, the poly(1-triazolyl)borate $K[HB(tz)_3]$ (where Htz = 1,2,4-triazole) was obtained in low yield from the reaction of Htz with KBH_4 and was identified as the complex $Co[(tz)_3BH]$,[4] and some poly(1-triazolyl)borates derived from benzotriazole[5,6] and a few transition-metal complexes thereof[6] have been described most recently. The preparation of *N*-triazolylboranes containing trigonal boron and a study of the general chemistry of N-bonded boron derivatives of triazoles was the primary objective of the current investigation.

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDDl_3$ (unless otherwise noted) on a Varian VXR-400 (^{11}B, variable-temperature, and high-resolution spectra) or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. Unless otherwise noted, ^{13}C NMR spectra were recorded in the proton-decoupled mode. Electron impact (EI) mass spectral data were obtained on a VG ZAB-2F spectrometer under standard operating conditions. Data are listed to m/z 30 for 5% or greater relative abundances (in parentheses) only.

All nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received. Preparations and handling of materials were done in anhydrous atmosphere under argon cover.

1,3-Dimethyl-2-(1,2,3-triazol-*N*-yl)-1,3,2-diazaboracyclohexane (1a). A solution of 7.9 g (54 mmol) of 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclohexane[7] in 50 mL of hexane was added with stirring to a solution of 9.5 g (67 mmol) of *N*-(trimethylsilyl)-1,2,3-triazole in 50 mL of hexane. The mixture was stirred overnight at ambient temperature, and a small amount of colorless precipitate was filtered off. Volatiles were distilled off the clear filtrate under atmospheric pressure, and the residue was distilled under vacuum to give 9.5 g (98%) of the desired product, bp 128 °C (2 Torr). Anal. Calcd for $C_7H_{14}BN_5$ (M_r = 179.03): C, 46.96; H, 7.88; B, 6.04; N, 39.12. Found: C, 47.57; H, 8.14; B, 5.80; N, 39.91.

NMR data: $\delta(^1H)$ 7.81 (s) + 7.66 (s) (1 H total, ratio = ca. 5.5:1), 3.04 (2 H, t, J = 6), 2.41 (s) + 2.39 (s) (3 H total, ratio = ca. 5.5:1), 2.03 (1 H, p, J = 6) (note: the signals at 3.04 and 2.03 are slightly unsymmetrical); $\delta(^{11}B)$ 23.8 (s, $h_{1/2}$ = 130 Hz); $\delta(^{13}C)$ 135.4, 133.4 (small), 126.7 (small), 48.5 (two overlapping signals), 37.1, 26.0. The mass spectrum exhibited a strong parent ion cluster with a base peak at m/z 179.

1,3-Dimethyl-2-(1,2,4-triazol-1-yl)-1,3,2-diazaboracyclohexane (2a) was prepared in a fashion analogous to that for the preceding compound using 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclohexane[7] and 1-(trimethylsilyl)-1,2,4-triazole as reagents. The compound, bp 144 °C (2 Torr) and mp 47–49 °C, was obtained in 79% yield. Anal. Calcd for $C_7H_{14}BN_5$ (M_r = 179.03): C, 46.96; H, 7.88; B, 6.04; N, 39.12. Found: C, 47.03; H, 8.21; B, 6.53; N, 38.01.

NMR data: $\delta(^1H)$ 8.20 (1 H, s), 8.14 (1 H, s), 3.03 (4 H, t, J = 6), 2.44 (6 H, s), 2.00 (2 H, p, J = 6); $\delta(^{13}C)$ 153.6, 147.7, 48.5, 37.2, 26.0. The mass spectrum exhibited a strong parent ion cluster with a base peak at m/z 179.

The compound has previously been obtained by the alternate procedure given below.[3] However, the previous product was not obtained quite pure.

Alternate Procedure. A mixture of 16.8 g (171 mmol) of 1,3-dimethyl-1,3,2-diazaboracyclohexane[8] and 10.0 g (145 mmol) of 1,2,4-triazole was heated to reflux for 18 h. After that period, hydrogen evolution had ceased and excess of 1,3-dimethyl-1,3,2-diazaboracyclohexane was distilled off. The residue was distilled twice (10-cm silvermantle column) under vacuum to give 18.6 g (72%) of the desired compound **2a**, identical (NMR data) with the preceding material.

1,3-Dimethyl-2-(1,2,3-triazol-*N*-yl)-1,3,2-diazaboracyclopentane (1b) was prepared in a fashion analogous to that for **1a** employing 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane[7] and *N*-(trimethylsilyl)-1,2,3-triazole as reagents. The compound, bp 102 °C (2 Torr), was obtained in 90% yield. Anal. Calcd for $C_6H_{12}BN_5$ (M_r = 165.01): C, 43.67; H, 7.33; B, 6.55; N, 42.44. Found: C, 41.62; H, 7.60; B, 6.11; N, 39.97.

NMR data $\delta(^1H)$ 7.82 (s) + 7.79 (s) (1 H total, ratio = ca. 10:1), 3.37 (s) + 3.35 (s) (2 H total, ratio = ca. 1:5.5), 2.95 (s) + 2.75 (s) (3 H total, ratio = ca. 5.5:1); $\delta(^{11}B)$ 24.1 (s, $h_{1/2}$ = 100 Hz); $\delta(^{13}C)$ 136.2, 133.4 (small), 127.0 (small), 51.3, 51.1 (small), 34.0, 33.6 (small). The mass spectrum exhibited a strong parent ion cluster with a base peak at m/z 165.

1,3-Dimethyl-2-(1,2,4-triazol-1-yl)-1,3,2-diazaboracyclopentane (2b) was prepared in a fashion analogous to that for **1a** employing 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane[7] and 1-(trimethylsilyl)-1,2,4-triazole as reagents. The compound, bp 100 °C (2 Torr) and mp 37–39 °C, was obtained in 87% yield. Anal. Calcd for $C_6H_{12}BN_5$ (M_r = 165.01): C, 43.67, H, 7.33; B, 6.55; N, 42.44. Found: C, 44.34; H, 7.37; B, 6.21; N, 40.99.

NMR data: $\delta(^1H)$ 8.38 (1 H, s), 8.15 (1 H, s), 3.36 (4 H, two closely overlapping s), 2.77 (6 H, two closely overlapping s); $\delta(^{11}B)$ 24.8 (s, $h_{1/2}$ = 90 Hz); $\delta(^{13}C)$ 154.0, 148.3, 51.0, 33.6. The mass spectrum exhibited a strong parent ion cluster with a base peak at m/z 165.

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1,3-Dimethyl-2-(1-benzotriazolyl)-1,3,2-diazaboracyclohexane (4a) was prepared from 1,3-dimethyl-1,3,2-diazaboracyclohexane[8] and benzotriazole by the alternate procedure described above. The compound, bp 170 °C (1 Torr), was obtained in 89% yield. Anal. Calcd for $C_{11}H_{16}BN_5$ (M_r = 229.10): C, 57.67; H, 7.04; B, 4.72; N, 30.57. Found: C, 581.2; H, 6.98; B, 4.49; N, 31.20.

NMR data: $\delta(^1H)$ 8.10 (1 H, d, J = 8), 7.27 (1 H, d, J = 8), 7.15 (1 H, t, J = 8), 7.05 (1 H, t, J = 8), 3.11 (4 H, two overlapping t), 2.38 (6 H, s), 2.08 (2 H, p, J = 6); $\delta(^{11}B)$ 23.8 (s, $h_{1/2}$ = 150 Hz); $\delta(^{13}C)$ 146.1, 136.8, 127.6, 123.9, 119.8, 111.9, 48.7, 37.4, 26.2. Mass spectrum (14 eV): m/z 230 (7), 229 (100), 228 (15), 200 (62), 199 (17), 186 (22), 111 (12), 83 (23).

1,3-Dimethyl-2-(1-benzotriazolyl)-1,3,2-diazaboracyclopentane (4b) was prepared in a manner analogous to that of **1a** originating from 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane[7] and *N*-(trimethylsilyl)benzotriazole.[2] The compound was obtained in 85% yield as a colorless material, mp 58–60 °C and bp 160 °C (1 Torr). Anal. Calcd for $C_{10}H_{14}BN_5$ (M_r = 215.07): C, 55.85; H, 6.56; B, 5.03; N, 32.56. Found: C, 55.81; H, 6.58; B, 5.11; N, 32.31.

NMR data: $\delta(^1H)$ 8.13 (1 H, d, J = 8), 7.62 (1 H, 3, J = 8), 7.50 (1 H, t, J = 8), 7.37 (1 H, t, J = 8), 3.46 (4 H, s), 2.68 (6 H, s); $\delta(^{11}B)$ 26.0 (s, $h_{1/2}$ = 160 Hz); $\delta(_{13}C)$ 146.4, 136.6, 127.9, 124.2, 120.0, 112.2, 51.1, 33.9. Mass spectrum (14 eV): m/z 216 (22), 215 (100), 214 (26), 187 (8), 186 (52), 185 (14), 172 (8), 159 (5), 119 (34), 91 (23), 64 (5).

Na[(st)$_2$B(C$_2$H$_5$)$_2$] (Hst = 1,2,4-Triazole). Solid 1,2,4-triazole (1.89 g, 27.4 mmol) was added to a stirred solution of 3.10 g (27.4 mmol) of (dimethylamino)diethylborane, $(CH_3)_2NB(C_2H_5)_2$,[9] in 20 mL of benzene. An exothermic reaction occurred, and the mixture was stirred for 2 h at ambient temperature. One molar equivalent (2.50 g, 27.4 mmol) of Na(st) was added, and the mixture was refluxed for 5 h. The insoluble material was collected and recrystallized from acetonitrile to afford 5.26 g (84%) of colorless crystalline product, mp 156–158 °C. Anal. Calcd for $C_8H_{14}BN_6Na$ (M_r = 228.0): C, 42.13; H, 6.19; B, 4.74; N, 36.85; Na, 10.08. Found: C, 42.45; H, 5.97; B, 4.47; N, 37.18; Na, 10.46.

NMR data (solution in $(CD_3)_2SO$): $\delta(^1H)$ 7.90 (1 H, s), 7.62 (1 H, s), 0.79 (2 H, q, J = 8), 0.55 (3 H, t, J = 8); $\delta(^{11}B)$ −0.2 (s, $h_{1/2}$ = 270 Hz); $\delta(^{13}C)$ 149.6, 144.3, 11.1*, 8.4.

(C$_2$H$_5$)$_2$B(μ-st)$_2$Pd(π-CH$_2$CHCH$_2$). To a stirred mixture of 2.1 g (9.3 mmol) of Na[(st)$_2$B(C$_2$H$_5$)$_2$] (see above) and 30 mL of methylene chloride was added 1.7 g (2.3 mmol) of $[(\pi\text{-}CH_2CHCH_2)PdCl]_2$, and the mixture was stirred overnight at ambient temperature. The colorless insoluble material was filtered off, and the clear solution was evaporated to leave a colorless solid. The latter was redissolved in methylene chloride, and hexane was added slowly to precipitate 3.04 g (93%) of the desired compound, mp 108–110 °C. Anal. Calcd for $C_{11}H_{19}BN_6Pd$ (M_r = 352.5): C, 37.48; H, 5.43; B, 3.07; N, 23.84; Pd, 30.18. Found: C, 37.77; H, 5.36; B, 2.80; N, 23.81; Pd, 30.17.

NMR data: $\delta(^1H)$ 8.20 (2 H, s), 7.95 (2 H, s), 5.76 (1 H, ill-resolved h), 4.18 (2 H, d, J = 7), 3.24 (2 H, d, J = 12), 1.2–0.6 (10 H, m); $\delta(^{11}B)$ 0.7 (s, $h_{1/2}$ = 210 Hz); $\delta(^{13}C)$ 154.6, 147.1, 116.5, 59.0, 13.4*, 9.0. Mass spectrum (15 eV): m/z 327 (6), 326 (73), 325 (12), 324 (46), 323 (100), 322 (75), 109 (34), 108 (67), 107 (28), 70 (28), 69 (14), 42 (19), 41 (39).

(C$_2$H$_5$)$_2$B(μ-st)$_2$Pd(π-CH$_2$CCH$_3$CH$_2$) was prepared in a fashion analogous to that for the preceding compound employing $[(\pi\text{-}CH_2CCH_3CH_2)PdCl]_2$ as reagent. The compound, mp 55–58 °C, was purified by dissolving the crude material in THF and precipitation with diethyl ether. It was obtained in essentially quantitative yield.

NMR data: $\delta(^1H)$ 8.20 (2 H, s), 7.98 (2 H, s), 3.94 (2 H, s), 3.08 (2 H, s), 2.23 (3 H, s), 1.1–0.6 (10 H, m); $\delta(^{11}B)$ 0.7 (s, $h_{1/2}$ = 280 Hz); $\delta(^{13}C)$ 154.1, 146.6, 132.3, 57.8, 23.3, 13.5*, 11.5*, 8.6.

Na[(st)$_2$B(C$_8$H$_{14}$)]. Solid 1,2,4-triazole (6.35 g, 91.8 mmol) was added to a stirred solution of 15.2 g (91.8 mmol) of 9-(dimethylamino)-9-borabicyclo[3.3.1]nonane, $(CH_3)_2NB(C_8H_{14})$,[10] in 200 mL of benzene. The mixture was stirred overnight, and 8.37 g (91.8 mmol) of Na(st) was added. The stirred mixture was refluxed for 40 h, and the insoluble material was collected and recrystallized from acetonitrile to yield 19.9 g (77%) of the desired colorless product, mp 374–376 °C dec. Anal. Calcd for $C_{12}H_{18}BN_6Na$ (M_r = 280.12): C, 51.45; H, 4.68; B, 3.86; N, 30.00; Na, 8.21. Found: C, 51.18; H, 4.54; B, 3.70; N, 30.11; Na, 8.19.

NMR data (solution in $(CD_3)_2SO$): $\delta(^1H)$ 8.01 (1 H, s), 7.59 (1 H, s), 1.5–1.8 (6 H, m), 1.2* (1 H); $\delta(^{11}B)$ 1.1 (s, $h_{1/2}$ = 340 Hz); $\delta(^{13}C)$ 150.5, 145.5, 30.9, 24.3, 21.0*.

(C$_8$H$_{14}$)B(μ-st)$_2$Pd(π-CH$_2$CHCH$_2$). To a stirred mixture of 1.0 g (3.8 mmol) of Na[(st)$_2$B(C$_8$H$_{14}$)] (see above) and 30 mL of methylene chloride was added 0.65 g (1.8 mmol) of $[(\pi\text{-}CH_2CHCH_2)PdCl]_2$, and the mixture was stirred overnight at ambient temperature. The colorless precipitate was filtered off, and the clear solution was evaporated under reduced pressure to leave 1.5 g of colorless solid. The latter was redissolved in methylene chloride, and hexane was added slowly to precipitate the desired compound in essentially quantitative yield. The compound decomposes near 190 °C. Anal. Calcd for $C_{15}H_{23}BN_6Pd$ (M_r = 404.6): C, 44.53; H, 5.73; B, 2.67; N, 20.77; Pd, 26.30. Found: C, 44.37; H, 5.69; B, 2.59; N, 20.83; Pd, 26.29.

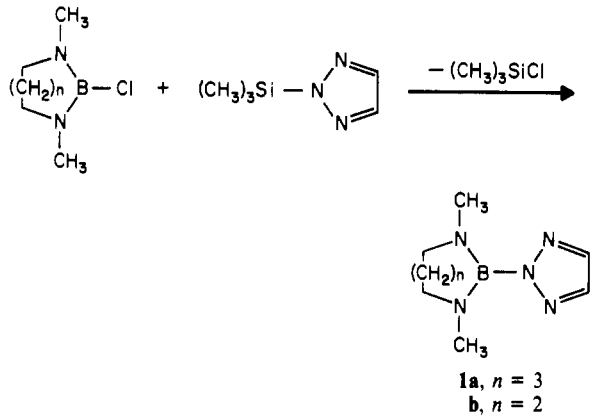
NMR data: $\delta(^1H)$ 8.30* (2 H, s), 8.2–7.8* (2 H, broad unresolved), 5.74 (1 H, ill-resolved h), 4.21 (1 H, d, J = 7), 4.0* (1 H, broad unresolved), 3.20 (1 H, d, J = 12), 3.2–3.0* (1 H, broad unresolved), 2.6* and 2.2–1.0* (14 H, unresolved m); $\delta(^{11}B)$ 0.2 (s, $h_{1/2}$ = 330 Hz).

(C$_8$H$_{14}$)B(μ-st)$_2$Pd(π-CH$_2$CCH$_3$CH$_2$) was prepared in a fashion analogous to that for the preceding compound employing $[(\pi\text{-}CH_2CCH_3CH_3)PdCl]_2$ as reagent. The crude product was obtained in essentially quantitative yield. It was recrystallized from acetonitrile to give pale yellow crystals decomposing near 190 °C.

NMR data: $\delta(^1H)$ 8.28 (2 H, s), 8.0* (2 H, broad unresolved), 3.96 (1 H, s), 3.75* (1 H, s?), 3.05 (1 H, s), 2.95* (1 H, s), 2.19* (3 H, s), 2.0–0.9 (14 H, unresolved); $\delta(^{11}B)$ 0.1 (s, $h_{1/2}$ = 450 Hz). The 10-eV mass spectrum exhibited a parent ion cluster at m/z 419.

Results and Discussion

N-bonded boron derivatives of triazoles containing trigonal boron have been obtained via a Si–N cleavage in the reaction of 2-chloro-1,3,2-diazaboracycloalkanes with 2-(trimethylsilyl)-1,2,3-triazole, as illustrated in eq 1.



(1)

1a, n = 3
b, n = 2

The resultant *N*-triazolylboranes (**1**) were obtained as the monomeric species, as is clearly evident from the ^{11}B NMR spectra: only signals in the 24 ppm region, which are indicative of three-coordinate boron,[11] were observed at room temperature. This situation is analogous to that of the corresponding 1-pyrazolylboranes, where incorporation of the boron into a 1,3,2-diazaboracycloalkane ring system also prevented dimerization to form a pyrazabole system containing a central B_2N_4 ring.[3,12–14] This latter observation has been studied by CNDO calculations.[15]

However, the compounds of type **1** were obtained as a mixture of 1- and the (depicted in eq 1) 2-triazolylborane isomers. The presence of the isomers can be seen in the NMR spectra of the products. For example, the ^1H NMR spectrum of **1b** (solution in CD_2Cl_2) at 20 °C exhibits only two signals for the triazolyl moiety at δ (approximate relative intensities in parentheses) 7.79 (11)/7.75 (1). At −50 °C the resolution increased to show three signals at δ 7.88 (1)/7.86 (10)/7.83 (1), suggesting an isomer ratio of about 5:1 for the N(2) versus the N(1) derivative, since only the latter will exhibit two ^1H resonance signals (and of equal intensity) for the triazolyl group. The isomeric *N*-triazolylboranes could not be recognized in the ^1H NMR spectrum of the compound in toluene solution over a temperature range from 20 to 90 °C, apparently due to the close spacings of the signals ($\delta(^1H)$ (relative intensities in parentheses): at 20 °C, 7.43 (1), 3.00 (3),

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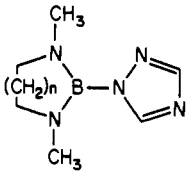
2.96 (2); at 70 °C, 7.47 (1), 3.02 (3), 2.98 (2); at 90 °C, 7.48 (1), 3.04 (3), 2.98 (2)). However, a small shoulder emerged at δ 26.6 off the main signal at δ 25.6 in the ^{11}B NMR spectrum with the line sharpening that accompanied the temperature increase. The ^{11}B NMR spectrum recorded in $CDCl_3$ at 20 °C exhibited a small shoulder at δ 25.1 off the main peak at δ 24.1, thus also indicating the presence of isomers; only one signal at δ 23.9 ($h_{1/2}$ = 300 Hz) was observed at −50 °C (in CD_2Cl_2). This latter observation is clear evidence that even at low temperatures only species containing three-coordinate boron are present. This is in contrast to the corresponding pyrazole derivatives, which have been found to dimerize at lower temperatures (although not to a pyrazabole structure!).[13]

The preceding results establish the existence of two isomers for **1**, but both of which contain three-coordinate boron only. Furthermore, the compounds do not dimerize at temperatures as low as −50 °C, and they are not fluxional up to +80 °C; i.e., the boryl group does not shift from one nitrogen atom to another.

The existence of nonfluxional isomers of **1** can best be explained by the presence of static isomers in the starting material *N*-(trimethylsily)-1,2,3-triazole. Indeed, although the 2-isomer predominates, the presence of the 1-isomer in the cited (commercial) reagent has been noted previously (whereas *N*-(trimethylsilyl)benzotriazole was found to be the pure 1-isomer).[2] This suggests that electronic factors render N-substituted 1,2,3-triazoles to be static. The lack of fluxionality in the boron derivatives of 1,2,3-triazole is in contrast to corresponding pyrazole and imidazole derivatives.[13] In this context it is of interest to note that N-bonded silicon[16,17] and germanium[17] derivatives of pyrazole are also fluxional. Surprisingly, N-bonded germanium derivatives of imidazole were found to be static,[17] whereas those of trigonal boron are fluxional.[13]

As noted above, the triazolylboranes of type **1** do not dimerize at temperatures as low as −50 °C. Since the corresponding pyrazole derivatives form dimers (although not of a pyrazabole structure) at −40 °C,[13] steric factors do not seem to play a role. Rather, these differences must also be explained by electronic effects. On the other hand, the ^{11}B chemical shifts of the monomeric 1-pyrazolylboranes are virtually identical with those of the monomeric *N*-triazolylboranes, suggesting very similar Lewis acidity for the boron sites. Therefore, it is most likely that the two-coordinate nitrogen atoms of the 1,2,3-triazole ring of the *N*-triazolylboranes have less Lewis basicity as compared to that of the pyrazole and imidazole rings in the corresponding boron derivatives.

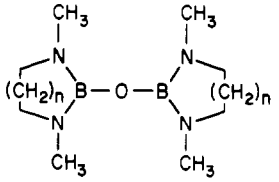
The same process as illustrated in eq 1 was also used for the preparation of 1-triazolylboranes of type **2** derived from 1,2,4-



2a, n = 3
b, n = 2

triazole. Compound **2a** has previously been obtained (as an impure material) from a condensation of 1,3-dimethyl-1,3,2-diazaboracyclohexane with 1,2,4-triazole.[3] Indeed, the latter process has been repeated, and pure **2a** was obtained; but only after repeated distillations. The reflux temperature of a neat reagent mixture was insufficient to provide for the formation of **2b** in an analogous procedure, but the latter compound was prepared by the reaction as illustrated in eq 1.

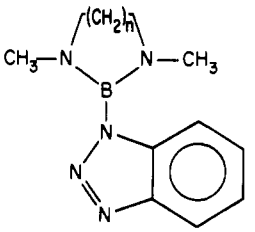
Compounds of both type **1** and type **2** are extremely sensitive to moisture and require handling under strictly anhydrous conditions. The initial hydrolysis products are diboryl oxides of type **3**, which have previously been prepared and characterized.[18]



3

At room temperature, the compounds of type **2** also exist as monomers only, as is evident from the ^{11}B NMR data. The room-temperature ^1H and ^{13}C NMR data, i.e., observation of two signals each for the CH groups, indicate that the boron is localized at N(1) of the triazole ring, and there is no evidence for isomerism involving bonding of boron to N(4). However, when **2b** was heated in toluene solution, the (C)H NMR signals of the triazolyl moiety began to merge and collapsed to a singlet at 70 °C, although the two signals of the diazaboracycloalkane ring were not affected. This observation can be interpreted either by (most likely) a 1,2-shift of the boryl moiety, analogous to what has been observed for the corresponding pyrazole derivatives, or by a 1,3-shift, analogous to that of the corresponding imidazolylboranes.[13] On cooling of a solution of **2b** in CD_2Cl_2 to −50 °C, only minor positional changes were observed in the ^1H NMR spectrum. The ^{11}B NMR signal broadened ($h_{1/2}$ = 300 Hz at −50 °C) but was not otherwise affected by the temperature change, exhibiting only one signal for three-coordinate boron at δ 24.7. This is clear evidence that no dimerization occurs at the cited temperature, thus contrasting the behavior of the corresponding pyrazole derivative.

The condensation of 1,3-dimethyl-1,3,2-diazaboracycloalkanes with a triazole was also used for the preparation of the benzotriazole derivative **4a**, and **4b** was obtained by the reaction of *N*-(trimethylsilyl)benzotriazole with 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane, according to eq 1.



4a, n = 3
b, n = 2

For compounds of type **4** both ^1H and ^{13}C NMR spectral data indicated the presence of only the N(1)-bonded isomer, which is in contrast to the situation encountered with **1**. The regiospecificity of **4** involving only B–N(1) bonding, despite the fact that this may involve more steric crowding, is again likely due to electronic factors: B–N(2) bonding would force the benzene ring into a quinonoid form, thus resulting in a loss of aromatic delocalization energy. This same feature would also explain why the N-trimethylsilylated benzotriazole exists only as the 1-isomer.

It was also of interest to see if other dissimilarities exist between pyrazole and triazole derivatives of boron. In analogy to the monomeric 1-pyrazolylboranes, the boron atom of the corresponding *N*-triazolylboranes has remaining Lewis acidity and can complex with free triazole. The resultant products contained the expected four-coordinate boron but were not uniform (as based on NMR data) and no pure compound could be isolated. Therefore, in analogy to recent work,[10] (dimethylamino)boranes, $(CH_3)_2NBR_2$, were reacted with 1 molar equiv of 1,2,4-triazole (=Htz) to give an intermediate 1:1 molar complex (δ(^{11}B) = ca. 2.2). The latter was not isolated but was reacted in situ with Na(tz) to form salts of the type $Na[(tz)_2BR_2]$ (R = C_2H_5, $^1/_2$

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C_8H_{14} where $(C_8H_{14})BH$ = 9-borabicyclo[3.3.1]nonane) in good yield.

These salts behave analogous to the corresponding bis(1-pyrazolyl)borates[4,19] and were converted to representative complexes, e.g., $R_2B(\mu\text{-tz})_2Pd(\pi\text{-}CH_2CHCH_2)$, pyrazole analogues of which have been described earlier.[10,20] Thus, replacement of the pyrazole by triazole moieties in poly(1-pyrazolyl)borates does not seem to affect the coordination behavior of the poly(triazolyl)borate anions.

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Stability Rules for d^5/d^6 Mixed-Valent Dimers. Effects from the Donor/Acceptor Capability of the Metal (Ru vs Os) and from the Occupancy of the Mediating Ligand Orbital (LUMO vs HOMO)

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Electrochemical stability constants were determined for the mixed-valent intermediates in the redox series $[(bpy)_2M(bptz)M(bpy)_2]^{4+/5+/6+}$ and $[(bpy)_2M(adc\text{-}Me^{2-})M(bpy)_2]^{2+/3+/4+}$; M = Ru, Os; bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, adc-Me^{2-} = 1,2-diacetylhydrazido(2-). The trends observed allow us to rationalize in a consistent fashion the stability of the mixed-valence forms toward disproportionation: The equilibrium constant K_c depends on the π-donor/π-acceptor character of the metals and on the occupancy and electron population at the coordinating centers of the interacting ligand π orbital. Recent literature examples support this more practically oriented concept, which thus can be used in the design of new stable mixed-valent complexes.

Polynuclear complexes with mixed-valent metal configurations are of interest for the study of electron-transfer processes,[1] in the design of components for molecular electronics,[2] and because of their relevance to biochemically important systems.[3] An essential requirement for the investigation of mixed-valent complexes is their stability toward redox disproportionation as measured by the equilibrium constant K_c (eq 1).

$$2[M\text{-}L\text{-}M]^{n+} \rightleftharpoons [M\text{-}L\text{-}M]^{(n-1)+} + [M\text{-}L\text{-}M]^{(n+1)+}$$

$$K_c = \frac{\{[M\text{-}L\text{-}M]^{n+}\}^2}{\{[M\text{-}L\text{-}M]^{(n-1)+}\}\{[M\text{-}L\text{-}M]^{(n+1)+}\}} \qquad (1)$$

$$\log K_c = (E_1 - E_2)/0.059\ \text{V} = \Delta E/0.059\ \text{V}$$

We have recently demonstrated[4] for one particular, widely used type of complexes, viz. for dimers $[L_nRu^{II}\text{-}(\mu\text{-A})\text{-}Ru^{III}L_n]^{5+}$,[1,5] that K_c is primarily related to the orbital overlap between the metal atoms and the π-accepting conjugated ligand bridge A; distance and orientation between the metals or the number and alternancy[5b] of metal-connecting π centers seemed to be of minor importance. A convenient, relative estimate of this overlap[4] in the case of a given ligand series can be obtained in the form of squared Hückel MO[6] coefficients c_E^2(LUMO) for the lowest unoccupied MO (LUMO) at the coordinating heteroatom (E) donor centers.

We have now extended these investigations (which are of very practical importance for the design of new mixed-valence systems)[4-7] to two further areas: We apply our previous explanation[4] to an exchange of the metal (Ru → Os) using a given π-acceptor ligand system, and we make an attempt to interpret the effects of metal and ligand exchange in mixed-valent ruthenium and osmium complexes $[L_nM^{II}\text{-}(\mu\text{-D})\text{-}M^{III}L_n]^{3+}$ which contain a formally dianionic bridging *donor* ligand D^{2-}.[8]

As metal fragments, we employed $[M(bpy)_2]^{2+/3+}$ (M = Ru, Os; bpy = 2,2'-bipyridine), which differ from pentamminemetal fragments[1,9] $[M(NH_3)_5]^{2+/3+}$ in three ways: (i) they require *two* ligand donor centers in order to achieve coordination number 6; (ii) they contain relatively stabilized t_{2g} orbitals, resulting in rather positive redox potentials;[10] and (iii) complexes of these fragments are often soluble in aprotic media, making it possible to neglect the effects caused by hydrogen bonding.

As the acceptor ligand, we used the centrosymmetric bischelating system 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), which is distinguished by a LUMO localized at the four tetrazine nitrogen atoms;[11] the π-donor ligand employed was the 1,2-diacetylhydrazido(2-) (adc-Me^{2-}) ligand, which can be derived from the neutral oxidized azodiacetyl (adc-Me) form. Azodicarbonyl bridging ligands[7] adc-R are unique in several ways: They contain a small, redox-active conjugated π system with four of the six centers coordinating to the two metals; the HOMO of the 1,2-diacetylhydrazido(2-) form (LUMO of the non-reduced adc-R state) has about 90% of its electron population on the coordinating heteroatom centers ($\sum c_{N,O}^2 = 0.91$);[7] substituents R at the carbon π centers can be varied from donor (NR_2, OR, alkyl) to acceptor groups (e.g. CF_3, Ph, 4-ROOC-C_6H_4),[7,12] and finally, the edge-sharing of two five-membered chelate rings in such complexes of "S-frame" ligands[11c,13e] leads to rather small metal-metal distances

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