to be close to the one of the reactants for this exothermic reaction.[43]

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Registry No. 1, 71213-98-4; 2, 71213-97-3; 3, 71171-41-0; RhCl(PH$_3$)$_3$, 71171-40-9; RhCl(PPh$_3$)$_3$, 14694-95-2.

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Reaction of 1,8-Bis(dimethylamino)naphthalene, a Highly Basic and Weakly Nucleophilic Amine, with Several Polyboranes and with Boron Trifluoride

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Whereas strong bases such as OH$^-$, H$^-$, CH$_3^-$, and (C$_6$H$_5$)$_3$P=CH$_2$ readily deprotonate B$_{10}$H$_{14}$, weaker bases, L, such as acetonitrile and dialkyl sulfides react with this polyborane to form the bis adduct L$_2$B$_{10}$H$_{12}$ accompanied by the liberation of H$_2$.[1] There is some suggestion that the intermediate base strength tertiary amines deprotonate B$_{10}$H$_{14}$[2] although further reaction can also take place[3] to give [R$_3$NH]$^+$[R$_3$N–B$_{10}$H$_{13}$]$^-$ and eventually (R$_3$N)$_2$B$_{10}$H$_{12}$ with the liberation of hydrogen.[4,5] The outcome of B$_2$H$_6$ reactions with amines is considerably dependent on the nature of the base. Ammonia promotes the formation of the salt[6] [(H$_3$N)$_2$BH$_2^+$][BH$_4^-$] whereas simple trialkylamines combine with B$_2$H$_6$ to give only the borane adduct R$_3$N·BH$_3$.[7] Certain chelating species in which donor sites are favorably disposed such as in the N-methylated *o*-phenylenediamine produce salts from diborane[8] similar in structure to the salt obtained from ammonia and diborane.

1,8-Bis(dimethylamino)naphthalene is a remarkably strong base, pK_a = 12.3, for an aromatic amine, with steric factors dictating weak nucleophilic behavior. Relief of molecular strain in the neutral molecule upon protonation, as well as intramolecular hydrogen bonding, is thought to contribute to the high pK_a.[9-11] The present study examines the reactions of 1,8-bis(dimethylamino)naphthalene with a cross section of polyboranes, B$_2$H$_6$, B$_5$H$_9$, and B$_{10}$H$_{14}$, as well as with BF$_3$ in order to establish competitive preferences of this amine toward adduct formation, proton abstraction, or amine-complexed boronium ion/borohydride ion salt formation.

Experimental Section

Materials. 1,8-Bis(dimethylamino)naphthalene (sold as proton sponge) was obtained from Aldrich Chemical Co., B$_{10}$H$_{14}$ from K and K Laboratories, B$_5$H$_9$ from Callery Chemical Co., and B$_2$H$_6$ from Olin Mathieson Chemical Corp.

Nuclear Magnetic Resonance Data. Both the ^{1}H and ^{11}B NMR spectra were obtained on a HA-100 spectrometer operating at 100 and 32.1 MHz, respectively; boron-11-decoupled ^{1}H spectra at 100 MHz were observed while irradiation was done at 32.1 MHz by using

a Fluka 6160B frequency synthesizer, which is noise modulated by a homemade pseudo-random-noise generator. The noise bandwidth is controlled by a Hewlett-Packard 200CD wide-range audio oscillator. The signal is amplified by an Electronic Navigation Industries 320L rf power amplifier and applied to the double-tuned transmitter coil of the HA-100. Similarly the proton-decoupled ^{11}B spectra at 32.1 MHz were observed while irradiation was done at 100 MHz.

The proton chemical shifts were measured relative to tetramethylsilane (τ = 10.00) as an internal standard. The ^{11}B chemical shifts were measured by using boron trichloride (δ = −46.8 relative to boron trifluoride ethyl ether complex) as an external secondary standard. Positive values of the ^{1}H and ^{11}B chemical shifts are at higher field than those with negative values.

Reaction of 1,8-Bis(dimethylamino)naphthalene with Diborane. Into a dry 5-mm NMR tube was added 1,8-bis(dimethylamino)naphthalene (107 mg, 0.50 mmol). After evacuation of the tube and its contents, HCCl$_2$F (1.50 mmol) and B$_2$H$_6$ (0.50 mmol) were condensed, sequentially, into the tube at −190 °C. The tube was sealed and warmed slowly from −190 °C to room temperature. The ^{11}B NMR spectrum of the sample exhibited only two sets of peaks in a 1:1 area ratio: a sharp 1:4:6:4:1 quintet at δ = +36.5, J(BH) = 80 Hz, assigned to BH$_4^-$ and a very broad poorly defined 1:2:1 triplet at δ = +23.9, J(BH) $\simeq$ 110 Hz, for the BH$_2$ group.[6,8] Both sets of peaks, when subjected to ^{1}H irradiation at 100 MHz, collapsed to singlets. The ^{1}H NMR spectrum shows a sharp 1:1:1:1 quartet [J(^{11}B–H) = 81 Hz], which upon ^{11}B decoupling collapses to a singlet at τ = 11.0; this resonance is assigned to the BH$_4^-$ anion. A broad peak at τ = 8.8, which sharpens considerably upon irradiation at 32.1 MHz and is approximately half the area of the resonance at τ = 11.0, is assigned to the BH$_2$ group. The methyl hydrogens of the complexed 1,8-bis(dimethylamino)-naphthalene are located at τ = 7.83, and the aromatic hydrogens appear as a multiplet between τ = 3.0 and τ = 3.6. After the solution stood overnight, a few crystals separated; these crystals, when dissolved in HCCl$_2$F, exhibited the same NMR spectra as given above.

Reaction of 1,8-Bis(dimethylamino)naphthalene with Boron Trifluoride. The same procedure as in the diborane reaction was employed but using a 2:1 ratio of boron trifluoride/1,8-bis(dimethylamino)-naphthalene. When the NMR tube was warmed from −190 °C to room temperature, a solid was present which would not dissolve to any usable extent in HCCl$_2$F. The liquid portion, which did not exhibit a ^{11}B spectrum, was separated by syringe from the solid. The solid completely dissolved in acetonitrile and exhibited in the ^{11}B NMR spectrum a 1:1 ratio of a singlet (δ = +0.6 (BF$_4^-$)) and a 1:2:1 triplet (δ = −2.3, J(BF) = 27 Hz (BF$_2$ group)).[8,12]

Reaction of Pentaborane(9) with 1,8-Bis(dimethylamino)-naphthalene. Into a 5-mm NMR tube was added a solution of 1,8-bis(dimethylamino)naphthalene (0.40 mmol) in dry benzene (0.80 mmol). After degassing of the solution in a high-vacuum system, it was cooled to −190 °C, and B$_5$H$_9$ (0.40 mmol) was condensed on top of the contents of the tube. The NMR tube was then sealed and warmed to room temperature over a 15-min period. After the tube and its contents were shaken, only a single liquid phase was present which was clear and colorless and exhibited only the ^{11}B NMR pattern of B$_5$H$_9$. However, a very slow evolution of H$_2$ was evident, and after an overnight period (12 h) two liquid layers were present. The upper layer (clear, colorless) exhibited no observable ^{11}B NMR signal; the lower layer (light yellow) showed a strong spectrum which proved to be a composite of unreacted B$_5$H$_9$ and B$_9$H$_{14}^-$ ion. Six days later H$_2$ evolution ceased, and the clear upper layer was partially reduced in volume. The ^{11}B NMR spectrum of the lower layer showed that B$_9$H$_{14}^-$ ion[13–17] was present [δ = +7.9 (doublet, J(BH) = 138 Hz), +19.7 (doublet, J(BH) = 104 Hz), +22.1 (doublet, J(BH) = 130 Hz), in an area ratio of 1:1:1 for the three types of resonances, respectively] with a very small amount of B$_3$H$_8^-$ ion[1] (δ = +28.7) also present. Some minor peaks appeared at δ +34, +39, and +44 and could not be assigned. The ^{11}B-decoupled ^{1}H NMR spectrum exhibited broad peaks at τ = 10.8 (bridge hydrogen), 8.7, and 7.9 and one peak assumed to overlap with the strong methyl resonance of 1,8-bis-(dimethylamino)naphthalene at τ = 7.4. When the reaction was carried out in DCCl$_3$, essentially the same results were obtained. These observed ^{1}H NMR shifts for B$_9$H$_{14}^-$ ion in these organic solvents are in reasonable agreement with those observed in aqueous solution.[14]

The reaction of B$_5$H$_9$ with 1,8-bis(dimethylamino)naphthalene in a 1:1 mole ratio was repeated by using methylene chloride as the solvent instead of benzene. No appreciable reaction was evident in the ^{11}B NMR within the first hour at ambient temperature, but at the end

of 3 days more than 80% of the B$_5$H$_9$ had disappeared and the remaining portion of the ^{11}B NMR spectrum resembled, for the most part, that of the B$_9$H$_{14}^-$ ion.[13–17] After 23 days nearly all of the B$_5$H$_9$ had disappeared, and the solution exhibited the ^{11}B NMR pattern of B$_9$H$_{14}^-$ ion with ^{11}B–H doublets centered at δ = +8.6, +19.7, and +22.3.

Reaction of 1,8-Bis(dimethylamino)naphthalene with Decaborane(14). Upon mixture of a solution of 1,8-bis(dimethylamino)naphthalene (4.1 mmol) in 5 mL of dry benzene with a solution of B$_{10}$H$_{14}$ (4.1 mmol) in 8.8 mL of dry benzene two layers were immediately formed. When the walls of the glass vessel holding the mixed solutions were scratched, light yellow crystals precipitated from the lower layer. The crystals, recrystallized from methylene chloride at 0 °C, do not melt at 360 °C and exhibit the ^{11}B NMR spectrum found for the B$_{10}$H$_{13}^-$ ion:[18] δ = −7 (broad with high-field shoulder), J(BH) $\simeq$ 150 Hz; δ = +3.6, J(BH) = 135 Hz; δ = +34, J = 150 Hz; these three doublets are found in an area ratio of 3:5:2.

Discussion

Quantitative proton abstraction from B$_{10}$H$_{14}$ is observed with use of 1,8-bis(dimethylamino)naphthalene (I), producing the B$_{10}$H$_{13}^-$ ion with no trace of adduct formation.

I reacts with B$_2$H$_6$, however, to give the salt II with a

II
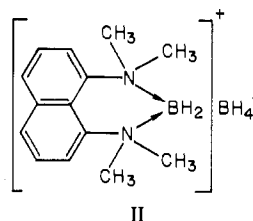
chelated cation. Obviously, the [BH$_2$]$^+$ entity is sufficiently small to fit into the chelating "cavity" of the two somewhat rigidly held dimethylamino groups with the minimum of steric interaction, and "bonding" interactions of the boron with both nitrogens in the cation avoid the steric problems associated with a mono- or bis(borane) adduct. No spectroscopic evidence was found either for borane adduct formation or for proton abstraction giving a B$_2$H$_5^-$ species. Allowing the salt II to react with excess B$_2$H$_6$ did produce the B$_3$H$_8^-$ ion, and though it is tempting to speculate that this might have come about by the reaction of small equilibrium quantities of B$_2$H$_5^-$ with a borane unit of the diborane, it is known that B$_3$H$_8^-$ can be obtained from the reaction of the BH$_4^-$ anion with B$_2$H$_6$.[19,20]

Boron trifluoride behaves in a manner similar to that for diborane, reacting with I to form the salt [(1,8-bis(dimethylamine)naphthalene)BF$_2^+$][BF$_4^-$]. Again no evidence of neutral adduct formation is observed.

The reaction of B$_5$H$_9$ with I is more complicated, giving as the primary boron product the B$_9$H$_{14}^-$ ion and no spectroscopic evidence of adduct formation.[17,21,22] A complete characterization of the cation and other minor boron-containing products has proved elusive, but it is to be noted that the B$_9$H$_{14}^-$ ion has been observed as a major product[16,17] of the "decomposition" of the unstable B$_5$H$_8^-$ ion. Attempts to carry out the B$_5$H$_9$ reaction with I at sufficiently low temperatures in the hope of direct observation of a possible B$_5$H$_8^-$ ion intermediate were thwarted by the reluctance of the I to react at all with B$_5$H$_9$ until ambient conditions were imposed. It is to be noted, however, that very slow proton transfers to 1,8-bis(dimethylamino)naphthalene have been previously observed in several other instances[10,11] and may account for the difficulty in obtaining direct evidence of the B$_5$H$_8^-$ ion. The higher reactivity of B$_{10}$H$_{14}$, as compared to that of B$_5$H$_9$, toward 1,8-bis(dimethylamino)naphthalene may well be attributed to the known acidity differences[23] in favor of the larger polyborane.

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Metal–Metal Bonding in Transition-Metal Compounds

Sir:

The characterization of binuclear transition-metal complexes containing "short" metal–metal bonds has provoked much activity recently in both experimental and theoretical chemistry.[1] Binuclear complexes are known for most transition elements, but those containing the Cr$_2$ unit have been of particular interest since they show a wide variation in metal–metal bond lengths (several species have $R_e < 1.9$ Å) and their electronic structure is amenable to theoretical investigation via MSW–SCF–Xα and conventional CI procedures.[2] Molecules and solids containing dimers or larger aggregates of transition-metal atoms are however difficult to treat accurately by quantum chemistry techniques because of the important electronic effects associated with the incomplete atomic d-electron shells. In this situation one may fall back on a more qualitative discussion of bonding in such systems. One way of thinking about compounds containing metal–metal bonds is to take as reference systems one or more homonuclear transition-metal systems in which the bonding factors are well understood and try to assess the effects of ligands as changes in the electronic environment of the metal–metal bonds.

Reasonably accurate molecular orbital theories exist for only two homonuclear transition-metal systems, namely, the perfectly periodic bulk metals M$_\infty$[3,4] and the diatomic molecules M$_2$ of the 3d transition elements.[5] In this paper, I suggest that, for complexes in which the metal formal oxidation state is low ($\leq +2$) and ligand–ligand repulsions do not have a dominating effect on structure, the systems M$_2$ and M$_\infty$ can serve as useful reference points in a discussion of metal–metal bonding in transition-metal compounds. An important qualitative bonding principle, which offers the basis for a working hypothesis for all systems containing aggregates of transition-metal atoms,[6] has emerged from these recent detailed MO studies: simply put, it suggests that structural properties of metal–metal bonds are the result of the competition of *attractive* forces between adjacent transition-metal atoms due to the metal d electrons and repulsive forces due to the overlap of metal s (p) electrons with the adjacent metal atom cores, provided that one is dealing with low-spin systems. In high-spin systems of large multiplicity and in bulk ferro-

magnets, the spin correlation energy, which acts as an effective repulsive force, must also be considered.

The cores of transition-metal atoms occupy a significant fraction, η, of the equilibrium atomic volume ($0.2 \leq \eta \leq 0.35$) compared with s,p-bonded metals ($\eta < 0.1$). As a result the bottom of the conduction band in transition metals, which corresponds to the lowest s,p-bonding (valence) MO in a molecule, may be close to or even above the s-orbital energy of the free metal atom when the solid is near its equilibrium volume: hence as one puts electrons into the s,p band, the system is destabilized relative to the free metal atoms.[3] On the other hand for partially filled "d bands", the d-electron interactions are strongly attractive and become more so rapidly as the internuclear distance R decreases (the cohesive energy due to the d electrons varies roughly as $1/R^5$).[3,6] The equilibrium structure occurs when these two opposing forces cancel one another. The bonding between transition-metal atoms is thus rather different from that encountered with main-group elements. Usually we argue that large orbital overlap is directly related to significant net bonding for incomplete shells, but this qualitative argument is spoiled in transition metals because it fails to take into account the large destabilizing energy shifts due to the core repulsion experienced by the s,p electrons in structures near equilibrium atomic volume.

Local density functional calculations on the 3d diatomic molecules have suggested a similar picture of metal–metal bonds in M$_2$ systems.[5] At large separations, bonding 4s-like orbitals provide an attractive force which, neglecting the effects of spin correlation and d electrons, would give a bonding contribution varying from ~ 0.5 eV (K$_2$) to ~ 2 eV (Cu$_2$), the increase resulting from the contraction of the outer parts of the 4s orbitals. As d-orbital overlap becomes substantial, an additional force draws the nuclei together and increases the binding energy, provided that the molecular orbitals of d-orbital parentage are incompletely filled—thus this remark does not apply to the dimers of the group 1B metals (d^{10} systems). The equilibrium separation is determined by the point where this force, together with the s (p) force, which becomes repulsive at small R due to core penetration, balances the electrostatic repulsion due to incomplete screening of the