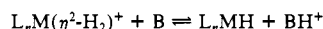


tween **4a** and the neutral hydride **3**, but no exchange could be detected between **3** and **4b**, establishing that **4a** is more acidic than **4b**. These observations may explain the fact that dihydrogen complexes apparently catalyze the equilibration of H₂/D₂ mixtures to give HD.^{3b,7} The exchange of complexed H₂ for complexed D₂ is often facile,^{3b} and activation of the coordinated hydrogen (deuterium) toward deprotonation would allow a catalytic amount of a proton acceptor (such as water) to facilitate H⁺/D⁺ exchange. Alternative mechanisms which invoke tetrahydride intermediates formed by ligand dissociation are less satisfactory.⁷ The H/D exchange reactions observed by Kubas in the solid state remain inexplicable.^{3b}

We are continuing to investigate systematically the effects of changing ligand environments on the coordination of dihydrogen to related ruthenium complexes.

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(21) For the equilibrium



then

$$K_{eq} = [L_nMH][BH^+] / [L_nM(\eta^2-H_2)^+][B]$$

in dilute solution. It follows that

$$pK_{eq} = pK_a - pK_{BH^+}$$

or

$$pK_a = pK_{eq} + pK_{BH^+}$$

where pK_{BH^+} for HNEt₃⁺ in CH₃CN is known.²² Since $[L_nMH] = [BH^+]$, then pK_{eq} can be calculated if $[L_nMH]$, $[L_nM(\eta^2-H_2)^+]$, and $[B]$ are known. The relative concentration, $[L_nMH]/[L_nM(\eta^2-H_2)^+]$, can be found by ¹H NMR integration, and $1/[B]$ can be calculated from the known starting quantity of B and $[L_nMH]/[L_nM(\eta^2-H_2)^+]$ at equilibrium.

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Transition-Metal-Promoted Reactions of Boron Hydrides. 10.¹ Rhodium-Catalyzed Syntheses of B-Alkenylborazines

Anne T. Lynch and Larry G. Sneddon*

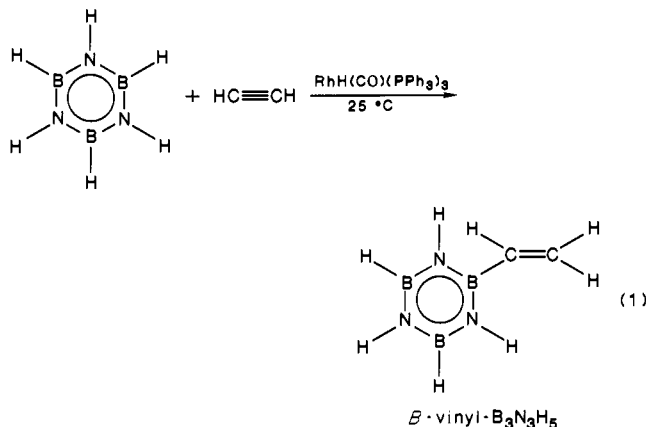
Department of Chemistry and
Laboratory for Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

Received June 8, 1987

We have previously shown¹⁻⁹ that transition-metal reagents can be used to activate the B-H bonds in a variety of polyhedral boranes and carboranes and that this activation can induce numerous important synthetic transitions. We have now initiated studies of the application of transition-metal catalysts to promote the reactions of boron nitrogen ring compounds and report here

the development of a metal-catalyzed, high yield route to B-alkenylborazines.

We have previously shown that various metal catalysts will promote the reactions of pentaborane(9) with alkynes¹⁻⁴ to give alkenyl-substituted pentaboranes. We have now found that borazine will undergo analogous reactions in the presence of rhodium catalysts.¹⁰



In a typical reaction, 2.218 g (27.5 mmol) of borazine (Callery) and 30 mmol of acetylene were reacted in the presence of 0.0090 g (9.8 × 10⁻³ mmol) of RhH(CO)(PPh₃)₃¹¹ for 4 h at room temperature. Fractionation of the resulting reaction mixture gave 0.306 g (2.87 mmol) of *B*-vinyl-B₃N₃H₅¹² stopping in a -70 °C trap and 1.890 g (23.5 mmol) of unreacted borazine. This corresponds to a 71.8% yield based on consumed borazine and 293 catalyst turnovers during the 4-h period.

In an analogous reaction, borazine (2.472 g, 30.7 mmol) and 30 mmol of propyne were reacted in the presence of 0.0066 g (7.2 × 10⁻³ mmol) of RhH(CO)(PPh₃)₃ for 10 h at 55 °C. Fractionation of the resulting reaction mixture gave 0.364 g (3.02 mmol) of *B*-propenyl-B₃N₃H₅ stopping in a -65 °C trap and 2.187 g (27.16 mmol) of unreacted borazine. This corresponds to a 85.2% yield based on consumed borazine and 419 catalyst turnovers during the 10-h period. GLC analysis¹³ of the product indicated that it was composed of a 80:20 mixture of *B*-*trans*-1-propenyl-B₃N₃H₅¹⁴ and *B*-2-propenyl-B₃N₃H₅.¹⁵ Pure samples

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(12) ¹¹B NMR (160.5 MHz, ppm, C₆D₆) 31.5 (d, B_{4,6}, J_{BH} = 129 Hz), 31.2 (s, B₂); ¹H NMR (200.13 MHz, ppm, C₆D₆) ~4.5 (q, J_{BH} = 128 Hz), 5.03 (t, J_{NH} = 49 Hz), 5.72 (m, ABC pattern, J's calcd from PANIC simulation: J_{HA-HB} = 2.76 Hz, J_{HA-HC} = 19.73 Hz, J_{HB-HC} = 13.62 Hz); exact mass calcd for ¹¹B₃¹²C₃¹⁴N₃¹H₅ 107.0997, found 107.1000; IR spectrum (gas phase, NaCl windows, 10 cm cell) 3480 s, 3080 sh, m, 3070 m, 2980 m, 2970 m, 2600 m, 2520 vs, 2440 m, 1910 w, br, 1620 s, 1540 m, 1475 vs, br, 1425 s, sh, 1380 vs, 1350 s, sh, 1290 w, br, 1140 w, sh, 1125 m, 1120 m, 1015 m, 955 s, 930 vs, 920 vs, 735 s, 720 vs, 690 m, 680 m.

(13) Tricresyl phosphate (TCP) 6% on 60-80 mesh Chromsorb P, 120 °C; R_v(B₃N₃H₅) = 1.0; R_v(*B*-2-propenyl-B₃N₃H₅) = 4.88; R_v(*trans*-1-propenyl-B₃N₃H₅) = 6.38.

(14) ¹¹B NMR (160.5 MHz, ppm, C₆D₆) 31.6 (d, B_{4,6}, J_{BH} = 136 Hz), 31.3 (s, B₂); ¹H NMR (250.15 MHz, ppm, C₆D₆) 1.65 (d of d, CH₃, J_{CH₃-NH} = 6.4 Hz, J_{CH₃-HB} = 1.5 Hz), 4.52 (q, BH, J_{BH} = 119 Hz), 5.04 (t, NH, J_{NH} = 44.9 Hz), 5.44 (d of d, CH, J_{HB-HA} = 17.7, J_{HB-CH₃} = 1.2), 5.95 (d of q, CH, J_{HA-HB} = 18.0 Hz, J_{HA-CH₃} = 6.1); exact mass calcd for ¹¹B₃¹²C₃¹⁴N₃¹H₁₀ 121.115, found 121.113; IR spectrum (film, NaCl windows) 3440 vs, 3000 m, 2960 m, 2930 m, 2910 m, 2880 m, sh, 2850 m, 2600 sh, w, 2580 m, 2500 vs, 2440 m, sh, 2420 m, 1640 vs, 1460 vs, br, 1390 s, 1370 vs, 1340 s, 1310 m, 1280 w, 1270 w, 1145 w, 1125 m, 1075 w, 1055 w, 1035 w, 980 s, 920 s, 900 vs, 785 m, 715 s, 620 m.

(15) ¹¹B NMR (160.5 MHz, ppm, C₆D₆) 31.6 (d, B_{4,6}, J_{BH} = 132 Hz), 32.0 (s, B₂); ¹H NMR (250.15 MHz, ppm, C₆D₆) 1.63 (s, CH₃), 4.76 (q, BH, J_{BH} = 127 Hz), 5.19 (t, NH, J_{NH} = 50.0 Hz), 5.27 (s, CH, br), 5.43 (s, CH, br); exact mass calcd for ¹¹B₃¹²C₃¹⁴N₃¹H₁₀ 121.115, found 121.116; IR spectrum (film, NaCl windows) 3440 s, 3050 m, 2950 m, 2930 m, 2910 m, sh, 2850 w, 2580 w, sh, 2500 s, 2420 w, 1625 m, 1615 m, 1505 s, sh, 1460 vs, br, 1410 s, 1395 s, 1380 s, 1345 m, sh, 1330 m, 1260 w, 1080 w, 1040 w, 980 w, 920 s, 900 vs, 740 m, 715 s, 625 m.

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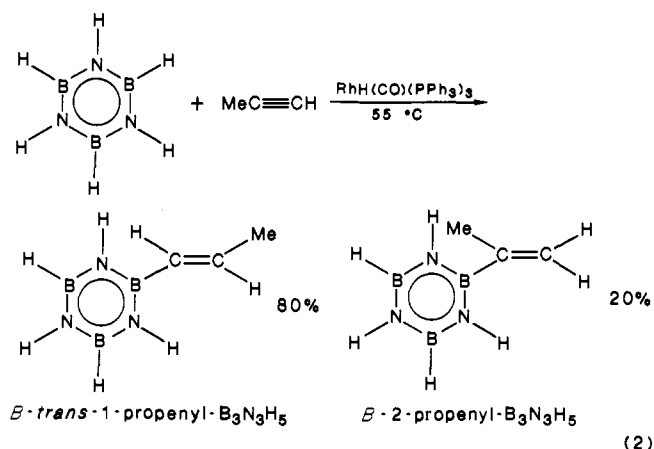
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of each isomer were obtained by preparative GLC.



Alkenylborazines are of particular importance since it may be possible to convert these compounds to polymeric boron-nitrogen materials analogous to, for example, polystyrene. Such polymers may then be useful for the formation of boron nitride ceramics,¹⁶⁻²¹ in the same way that organosilicon polymers have been found to be precursors to silicon carbide.^{19,22,23} Several alkenyl-substituted derivatives of borazine have previously been reported;²⁴⁻²⁶ however, it has been necessary in most cases to block the remaining ring nitrogen and boron positions with alkyl groups. This results in steric repulsion to polymerization¹⁷ and lowers the BN/C ratios in these polymers. The synthetic method reported herein yields the parent compounds in high yields in a one-step reaction. Furthermore, we have observed that when reactions are carried out under more forcing conditions di-*B*-alkenyl products can be obtained.

Reactions 1 and 2 are the first reported transition-metal-catalyzed reactions of borazine; however, based on our previous work with boranes, it is now expected that transition-metal catalysts will be able to induce a wide variety of borazine reactions. In fact, all available experimental evidence indicates that the B-H bonds in borazine are considerably weaker than those in, for example, pentaborane(9): the B-H bond lengths are longer, 1.258 (14) Å²⁷ versus 1.181 (3) and 1.186 (2) Å in pentaborane(9);²⁸ the IR B-H stretching frequencies are lower, 2527, 2520, and 2514 cm⁻¹ versus 2610 and 2598 cm⁻¹;^{29,30} and the B-H NMR coupling constants are smaller, 133 Hz versus 175 and 165 Hz.³¹ These data all suggest that borazine should oxidatively add (a key step

in most catalytic reactions) to transition metals much more readily than pentaborane(9).

Thus, while the mechanisms of reactions 1 and 2 are still unproven, the results of our studies are consistent with a reaction sequence similar to that which we have proposed for reactions with polyhedral boranes.¹⁻⁴ This could involve oxidative addition of the borazine at the metal center, displacement of a coordinated ligand by acetylene, and alkyne-insertion and reductive-elimination steps. Such a sequence is also in agreement with the mechanisms which have been proposed for the RhH(CO)(PPh₃)₃-catalyzed hydrosilylation of alkynes.³²

We are now investigating the use of transition-metal catalysts to promote a number of transformations involving borazines, and, indeed, we have recently demonstrated³³ the high yield metal-catalyzed dehydrocoupling of borazine to yield the B-N coupled dimer [B₃N₃H₅]₂. This result and related reactions will be reported in future publications.

Preliminary results³⁴ have now also demonstrated that these *B*-alkenylborazines will readily undergo thermally induced polymerizations under mild conditions (<125 °C) and that upon heating to higher temperatures (~600 °C) these polymers are converted to ceramic materials. These studies will be reported in future publications.

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Facile Insertion of Nitriles into Paramagnetic Chromium(III) Alkyls. Crystal Structure of a μ_2 -Ketimino Complex

Darrin S. Richeson, John F. Mitchell, and Klaus H. Theopold*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853

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The importance of paramagnetic compounds in catalytic and stoichiometric organometallic reactions is rapidly gaining acceptance.¹ We are exploring the reactivity of a novel class of electron deficient alkyl complexes of chromium(III). An earlier publication dealt with compounds containing the cyclopentadienyl ligand.² Here we report on the insertion of nitriles³ into the chromium-carbon bond of the analogous pentamethylcyclopentadienyl complexes.

Treatment of chromium(III) alkyls of the type RCrCl₂(THF)₃ (R = Me, Et, Ph)⁴ with Cp*Li (Cp* = η⁵-Me₅C₅) afforded a series of purple crystalline complexes (1-3) in good yield.⁵ On the basis

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