Borazines and Their Transition Metal Complexes

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Borazines and alkyl substituted borazines are six membered planar heterocyclic rings of three nitrogen and three boron atoms in alternation; they are iso electronic and isostructural analogs of benzene and alkyl benzenes.

The synthesis of borazine, $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$, from $\text{B}_2\text{H}_6\cdot2\text{NH}_2$ was first reported by Alfred Stock in 1926 [1]. A more convenient synthetic approach from boron trichloride and ammonium or alkylammonium halides results in formation of B-trichloroborazine or B-trichloro-N-trialkylborazine, respectively [2]. The synthesis of borazines from sodium borohydride and ammonium halides has also been demonstrated [3]. Symmetric B-trialkylborazines may be prepared by reaction of B-trichloroborazine with an appropriate alkali-metal-alkyl or Grignard reagent [4]; asymmetric B-alkylborazines may be prepared similarly [5]. Asymmetric N-alkylborazines are prepared by reaction of mixtures of ammonium and alkylammonium halides with boron trichloride or alkali-metal borohydrides [6]. Another route to asymmetric N-alkylborazines is by reaction of methyl lithium with B-trialkylborazine followed by addition of alkyl halide to yield N-monoalkyl-, N-dialkyl-, and N-trialkyl-B-trialkylborazines [7].

A battery of physical measurements have been performed on several borazines to determine if any similarities to arenes exist. Electron diffraction analyses of borazines have shown that the B-N bond is shorter than a B-N single bond [8]. Calorimetric studies indicate that the boron nitrogen bond energy is a function of substituents on both boron and nitrogen [9]. The boron-11 NMR shift is related to the donor ability of substituents on the boron atoms [10,11]. The nitrogen lone pairs on the borazine appear to be delocalized to boron; the extent of delocalization is dependent on the nature and location of the ring substituents.

In an attempt to find organic chemistry analogous to that of arene metal tricarbonyl complexes, borazine metal tricarbonyl complexes of chromium, molybdenum, and tungsten have been prepared and investigated. The borazine complexes are made from fac-$\text{(H}_3\text{CCN})_3\text{M(CO)}_3$ or photolytically from $\text{M(CO)}_6$ [12,13].

The X-ray structure of hexaethylborazine chromium tricarbonyl is a piano stool molecule with a puckered ring [14]. The carbonyl infrared stretching frequencies of several borazine metal complexes suggest that borazines and arenes cause comparable electronic perturbations of the chromium tricarbonyl moiety [15]. The metal to ligand charge transfer band of borazine chromium tricarbonyl complexes occurs at lower energy than for the analogous arene molecule suggesting that borazines are better acceptor ligands than arenes [16].

The wealth of organic chemistry demonstrated to occur on the ring of arene chromium tricarbonyl complexes is not observed for analogous borazine complexes. Borazines are easily displaced from metal tricarbonyl complexes by basic metal anions, e.g., $\text{SnCl}_3$, and by neutral sigma donors, e.g., phosphites to yield free borazine and $\text{L}_3\text{M(CO)}_3$ [16,17,18].
References


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