

Oxidation of Elemental Transition Metals by Decaborane to form Metalloboranes

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Oxidation of active metal slurries in ethers using decaborane(14) produces metalloborane complexes of the type $M(B_{10}H_{12})_2^{2-}$ ($M = Zn, Ni, Co$).

While boron hydrides are considered standard reducing agents, we have recently discovered a set of reactions in which a borane acts as an oxidizing agent.¹ Decaborane(14), $B_{10}H_{14}$, reacts with slurries of elemental nickel, zinc, and cobalt to give the corresponding $M(B_{10}H_{12})_2^{2-}$ complexes in which the metal is in a 2+ oxidation state.² This reaction of a borane with an elemental transition metal to yield a metalloborane is unprecedented.

Highly reactive elemental metal slurries were prepared by the Rieke method.³ Typically, this involved the reduction of anhydrous metal halide with an alkali metal in ethereal

solvents containing an electron transfer agent such as naphthalene. The reductions were carried out either in an inert atmosphere or *in vacuo*. The resulting black slurries contained very finely divided particles and were not pyrophoric. These zero-valent metal slurries remained very reactive for several days if stirred continuously. A slight excess of decaborane was added directly to the reduction mixtures.

In a typical reaction, 0.64 g of anhydrous $ZnCl_2$ was dissolved in 15 ml of freshly distilled $(MeO)[CH_2]_2(OMe)$ in an argon atmosphere. To this was added 0.35 g of K and the reaction was then stirred vigorously at 50 °C overnight. The

slurry was cooled to room temperature and 1.5 g of $B_{10}H_{14}$ were added and the reaction stirred for one hour. Following aqueous work-up the product was precipitated as $[Me_4N]_2[Zn(B_{10}H_{12})_2]$. Recrystallization from methanol-acetone solution yielded 0.48 g (24%) of the yellow crystalline product. This yield is significantly better than that reported in the literature for other methods of preparation.^{2a} Analogous reactions formed $[Me_4N]_2[Ni(B_{10}H_{12})_2]$ in 13% yield and $[Me_4N]_2[Co(B_{10}H_{12})_2]$ in somewhat lower yields.

¹¹B N.m.r. spectra of the diamagnetic nickel and zinc compounds were obtained and are identical to those of authentic samples prepared by other means.²

Preliminary work with other transition metals and boranes

suggests that boranes other than $B_{10}H_{14}$ also act as oxidizing agents under appropriate conditions.

Received, 6th October 1981; Com. 1172

References

- 1 One report of a borane as an oxidizing agent has appeared previously, N. N. Greenwood and H. Schick, *Chem. Commun.*, 1969, 935.
 - 2 For the first reports of the compounds see F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1968, 7, 2072; N. N. Greenwood and N. F. Travers, *J. Chem. Soc. A*, 1968, 15.
 - 3 R. D. Rieke, *Acc. Chem. Res.*, 1977, 10, 301.
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