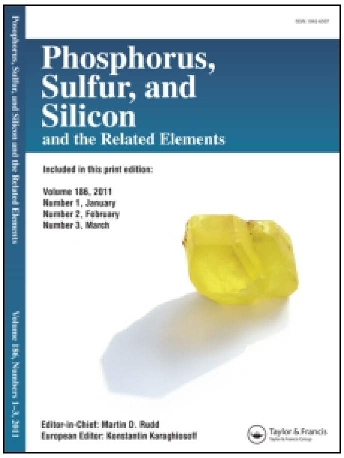


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CATALYTIC DEHYDROCOUPLING OF AMINE-BORANE ADDUCTS TO FORM AMINOBORANES AND BORAZINES

Cory A. Jaska[a]; Karen Temple[a]; Alan J. Lough[a]; Ian Manners[a]
[a] University of Toronto, Toronto, Canada

To cite this Article Jaska, Cory A. , Temple, Karen , Lough, Alan J. and Manners, Ian(2004) 'CATALYTIC DEHYDROCOUPLING OF AMINE-BORANE ADDUCTS TO FORM AMINOBORANES AND BORAZINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 733 — 736

To link to this Article: DOI: 10.1080/10426500490426683

URL: http://dx.doi.org/10.1080/10426500490426683

Phosphorus, Sulfur, and Silicon, 179:733–736, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490426683

CATALYTIC DEHYDROCOUPLING OF AMINE-BORANE ADDUCTS TO FORM AMINOBORANES AND BORAZINES

Cory A. Jaska, Karen Temple, Alan J. Lough, and Ian Manners
University of Toronto, Toronto, Canada

(Received August 17, 2003; accepted October 3, 2003)

A mild, catalytic dehydrocoupling route to aminoboranes and borazine derivatives from either primary or secondary amine-borane adducts has been developed using late transition metal complexes as precatalysts. The dehydrocoupling of $Me_2NH{\cdot}BH_3$ *was found to be catalyzed by 0.5 mol%* $[Rh(1,5\text{-}cod)(\mu\text{-}Cl)]_2$ *in solution at 25°C to give* $[Me_2N{-}BH_2]_2$ *(**1**) quantitatively after ca. 8 h. This new catalytic method was extended to other secondary adducts* $RR'NH{\cdot}BH_3$ *which afforded the dimeric* $[(1,4\text{-}C_4H_8)N{-}BH_2]_2$ *(**2**) and* $[PhCH_2(Me)N{-}BH_2]_2$ *(**3**) or the monomeric aminoborane* ${}^iPr_2N{=}BH_2$ *(**4**) under mild conditions. The catalytic dehydrocoupling of* $NH_3{\cdot}BH_3$*,* $MeNH_2{\cdot}BH_3$*, and* $PhNH_2{\cdot}BH_3$ *at 45°C affords the borazine derivatives* $[RN{-}BH]_3$ *(**5**:* $R = H$*; **6**:* $R = Me$*; **7**:*$R = Ph$*). TEM analysis of the contents of the reaction solution for the* $[Rh(1,5\text{-}cod)(\mu\text{-}Cl)]_2$ *catalyzed dehydrocoupling of* $Me_2NH{\cdot}BH_3$ *together with Hg poisoning experiments suggested a soluble heterogeneous catalyst involving Rh(0) nanoclusters.*

Currently, there is much interest in the development of catalytic methods towards the formation of new bonds involving the *p*-block elements.[1] For example, the catalytic dehydrocoupling of silanes, germanes and stannanes are now well established routes toward high molecular weight polysilanes,[2] polygermanes,[3] and polystannanes.[4] There are now numerous examples of both catalytic homo- and hetero-dehydrocoupling bond forming reactions. Recently, we reported the first examples of the transition metal-catalyzed formation of P—B bonds.[5] The dehydrocoupling of phosphine-borane adducts at 60–130°C in the presence of a range of precatalysts (e.g., Rh^I complexes) was found to provide a new route to phosphinoborane rings, chains, and

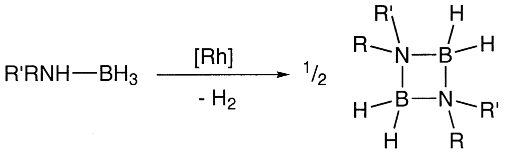
Address correspondence to Ian Manners, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, M5S 3H6 Ontario, Canada. E-mail: imanners@chem.utoronto.ca

macromolecules.[6] We have now extended this dehydrocoupling chemistry to amine-borane adducts, which form monomeric or dimeric aminoboranes and borazine derivitives under mild conditions.[7]

RESULTS AND DISCUSSION

Treatment of $Me_2NH{\cdot}BH_3$ in toluene with a catalytic amount (0.5 mol%) of $[Rh(1,5\text{-cod})(\mu\text{-}Cl)]_2$ was found to result in the quantitative formation of $[Me_2N–BH_2]_2$ (**1**) after 8 h at 25°C (Eq. 1). Raising the temperature to 45°C allowed the dehydrocoupling reaction to be performed as a neat mixture of the catalyst and the molten adduct. This reduced the reaction time to 2 h and allowed **1** to sublime directly out of the neat mixture in high yields.

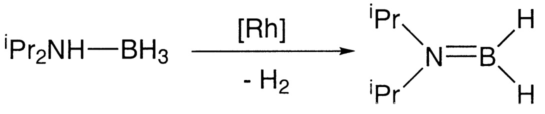
This catalytic dehydrocoupling strategy also can be generalized to other secondary amine-borane adducts. For example, the cyclic pyrrolidine-borane $(1,4\text{-}C_4H_8)NH{\cdot}BH_3$ and the unsymmetrically substituted $PhCH_2(Me)NH{\cdot}BH_3$ were found to undergo catalytic dehydrocoupling to afford the cyclic dimers $(1,4\text{-}C_4H_8)N–BH_2]_2$ (**2**) and $[PhCH_2(Me)N–BH_2]_2$ (**3**) respectively.



1: R = R' = Me
2: R = R' = (1,4-C_4H_8)
3: R = $PhCH_2$, R' = Me

(1)

When $^{i}Pr_2NH{\cdot}BH_3$ was treated with a Rh catalytst, dehydrocoupling to form the monomeric species $^{i}Pr_2N{=}BH_2$ (**4**) was observed (Eq. 2). The formation of the monomeric **4** is likely due to the steric bulk of the nitrogen substituents, which prevents dimerization.

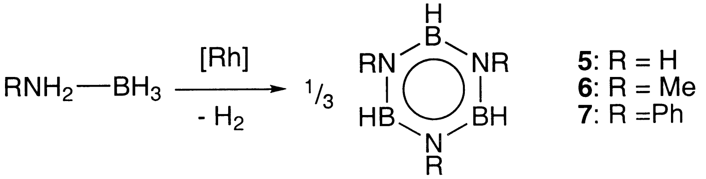


4

(2)

Primary amine-boranes or $NH_3{\cdot}BH_3$ also undergo catalytic dehydrocoupling to afford borazine derivitives. For example, when ammonia-borane was treated with a catalytic amount of $[Rh(1,5\text{-cod})(\mu\text{-}Cl)]_2$ in tetraglyme at 45°C, the formation of borazine **5** was observed after ca. 48–84 h (Eq. 3). However, attempts to isolate pure samples of **5** by vacuum fractionation resulted in only 10% yield. It is suggested that **5** undergoes further intermolecular dehydrocoupling to give oligomeric and/or polymeric B—N species. This may be a facile process, as the thermal (70°C) dehydrocoupling of borazine has been reported to yield poly(borazylene) along with small amounts of diborazine (1,2′-$(B_3N_3H_5)_2$) and borazanaphthalene ($B_5N_5H_8$).[8]

When $MeNH_2{\cdot}BH_3$ was treated with a catalytic amount of [Rh(1,5-cod)(μ-Cl)]$_2$ in monoglyme at 45°C, the formation of the cyclic trimer $[MeNH{-}BH_2]_3$ initially was detected by ^{11}B NMR. This was followed by further loss of hydrogen to give *N*-trimethylborazine $[MeN{-}BH]_3$ (**6**). Isolation by vacuum fractionation yielded pure samples of **6** in moderate yields (40%). Again, yields may be limited by undesirable intermolecular dehydrocoupling. In the case of $PhNH_2{\cdot}BH_3$, catalytic dehydrocoupling to give *N*-triphenylborazine $[PhN{-}BH]_3$ (**7**) was observed to occur rapidly in monoglyme in the presence of catalytic amounts of [Rh(1,5-cod)(μ-Cl)]$_2$ at 25°C.



(3)

The observation that all catalytic trials involving Rh precatalysts resulted in the formation of a black, opaque solution raised the problem of whether the catalysis is homogeneous or heterogeneous. Heterogeneous catalysis involving Rh colloids was immediately considered. In an attempt to more directly detect the colloidal species, a catalytic dehydrocoupling experiment involving $Me_2NH{\cdot}BH_3$ was initiated and an aliquot was removed from the reaction mixture after 6 h and evaporated to dryness. Analysis by transmission electron microscope (TEM) of this sample showed the presence of small (~2 nm) Rh nanoclusters.

Monitoring the extent of reaction by ^{11}B NMR initially indicated the presence of an induction period in which no dehydrocoupling occurs. During this induction period, the formation of colloidal metal was not observed by visual inspection. Following this induction period, colloidal metal was observed to form and the dehydrocoupling reaction proceeded rapidly. After partial conversion of $Me_2NH{\cdot}BH_3$ to **1**, mercury was added to the reaction mixture. Subsequently, a dramatic drop in the dehydrocoupling rate was observed, with little further conversion

(<5%) to **1** as the added Hg had poisoned the active catalytic species. A dehydrocoupling trial initiated in the presence of Hg also showed no conversion to **1** by ^{11}B NMR. This verifies that the addition of mercury inhibits the catalytic dehydrocoupling and suggests the operation of a heterogeneous process involving soluble Rh(0) colloids as the true active catalyst.

REFERENCES

[1] F. Gauvin, J. F. Harrod, and H. G. Woo, *Adv. Organomet. Chem.*, **42,** 363 (1998).
[2] C. Aitken, J. F. Harrod, and E. Samuel, *J. Am. Chem. Soc.*, **108,** 4059 (1986).
[3] C. Aitken, J. F. Harrod, A. Malek, and E. Samuel, *J. Organomet. Chem.*, **349,** 285 (1988).
[4] T. Imori, V. Lu, H. Cai, and T. D. Tilley, *J. Am. Chem. Soc.*, **117,** 9931 (1995).
[5] H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough, and I. Manners, *Angew. Chem. Int. Ed.*, **38,** 3321 (1999).
[6] H. Dorn, R. A. Singh, J. A. Massey, et al., *J. Am. Chem. Soc.*, **122,** 6669 (2000).
[7] a) C. A. Jaska, K. Temple, A. J. Lough, and I. Manners, *Chem. Commun.*, 962 (2001); b) C. A. Jaska, K. Temple, A. J. Lough, and I. Manners, *J. Am. Chem. Soc.*, **125,** 9424 (2003).
[8] P. J. Fazen, E. E. Remsen, J. S. Beck, et al., *Chem. Mater.*, **7,** 1942 (1995).