

H₂ Activation and Base Promoted Hydride Transfer Reactions Using Transition Metal Diphosphine Complexes: The Development of a Multi-Step Process to Regenerate Ammonia Borane.

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Introduction

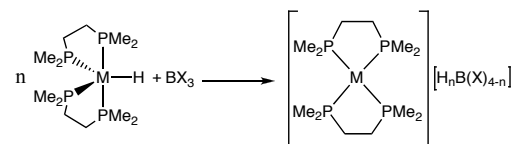
Ammonia borane, AB, NH₃BH₃, is being examined as a chemical hydrogen storage material for fuel-cell powered vehicles. This unique material stores hydrogen via a combination of hydridic B–H bonds and protonic N–H bonds. AB exhibits several attractive physical properties for the storage and transportation of hydrogen such as a low molecular weight and high gravimetric weight capacity of hydrogen (19.6%). [1] The major hurdle is the lack of an efficient process to regenerate AB from spent material. Spent material consists mainly of polymeric or cyclic oligomers rich in B–N bonds. [2] A critical step in the regeneration process is a method to form the hydridic B–H bonds. Our efforts in this regard are focused on the formation of B–H bonds using phosphine ligated transition metal hydrides generated from H₂ and a base. The thermodynamic hydride donor ability can vary depending on the nature of the phosphine ligand and the metal. For example, the rhodium hydride complex HRh(dmpe)₂ (dmpe = 1,2-Bis(dimethylphosphino)ethane) has been found to be equal in hydride donor strength to triethyl borohydride. [3] In our proposed regeneration scheme we digest spent AB fuel with alcohols [4], phenols, or thiols to BX₃ compounds (BX₃ = aryl, alkyl or thio borate esters). Computational studies are used to select BX₃ candidates with favorable hydride affinities for reaction with the metal hydride complexes. As envisioned, both metal and X are recycled in the process and only H₂ is consumed stoichiometrically. Herein we report on the formation of B–H bonds via hydride transfer reactions from HRh(dmpe)₂ and the less costly HCo(dmpe)₂.

Materials and Methods

General Procedures. NMR spectra were recorded on a Varian Inova 500 MHz spectrometer. ³¹P chemical shifts are proton decoupled and referenced to H₃PO₄ as an external reference. ¹¹B chemical shifts are reported relative to BF₃·OEt₂ as an external reference. All syntheses were performed under N₂ using standard Schlenk or glovebox techniques. In a typical reaction between HM(dmpe)₂ and BX₃, 1/3 equiv. of solid BX₃ was added to 15 mg HM(dmpe)₂ in ≈1.5 ml of C₆H₅CF₃ or THF and the reaction was monitored by ³¹P and ¹¹B NMR spectroscopy. Occasionally reactions are heated to 55°C until homogeneous. Electronic structure calculations were performed using B3LYP/6-311+G** level of density functional theory on the following isodesmic reaction for BX₃ compounds of widely varying structures for X: HBEt₃[−] + BX₃ $\xrightarrow{\Delta H^\circ}$ BEt₃ + HBX₃[−]

Results and Discussion

Our results indicate the Co and Rh hydrides are capable of transferring hydride ligands to several BX₃ compounds according to the reaction in **Scheme 1**. Results listing the hydride transfer products and calculated hydride affinities of selected BX₃ compounds are summarized in **Table 1**. HRh(dmpe)₂ has been found to transfer a hydride ligand to nearly all BX₃ compounds except trialkoxyboranes. HCo(dmpe)₂ is a weaker hydride donor, transferring a hydride ligand only to BX₃ complexes with greater hydride affinities. In reactions with B(OPh)₃, hydride transfer occurred with Rh to yield HB(OPh)₃[−] and the stable B(OPh)₄[−] anion. B(SPh)₃ more readily undergoes ligand redistribution, yielding the reduced products [H₂B(SPh)₂][−] and [H₃B(SPh)][−]. Furthermore, in the presence of neutral donor ligands such as NEt₃, [H₃B(SPh)][−] is converted to Et₃N·BH₃ and Rh(dmpe)₂[[SPh]]. Initial results between HCo(dmpe)₂ and B(SPh)₃ indicate reduction to BH₃ coordinated to the dmpe ligand.



Scheme 1. The hydride transfer reaction from HM(dmpe)₂ to BX₃.

| BX ₃ | Hydride Affinity | Co | Rh |
|---|------------------|--|--|
| B(O ⁱ Bu) ₃ | 36 | ✗ | ✗ |
| B(OPh) ₃ | 72 | ✗ | HB(OPh) ₃ [−] , B(OPh) ₄ [−] |
| B(SPh) ₃ | 84 | H ₂ B(SPh)-dmpe, H ₃ B-dmpe | [H ₃ B(SPh)] [−] , [H ₂ B(SPh) ₂] [−] |
| B(OC ₆ F ₅) ₃ | 92 | HB(OC ₆ F ₅) ₃ [−] , B(OC ₆ F ₅) ₄ [−] | HB(OC ₆ F ₅) ₃ [−] , B(OC ₆ F ₅) ₄ [−] |

Table 1. Selected BX₃ compounds tested to accept H[−] from HM(dmpe)₂, (M = Co, Rh).

Significance

We have demonstrated an important step in a process to regenerate AB from spent material by forming B–H bonds directly from H₂ and a base. Theory has guided this promising approach by identifying BX₃ compounds capable of accepting a hydride ligand. Future work will focus on optimizing these chemical steps to promote this overall energetically uphill process.

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References

- Marder, T. B., *Angew. Chem., Int. Ed.* 46, 8116 (2007).
- Stephens, F. H., Pons, V., Baker, T. R. *J. Chem. Soc., Dalton. Trans.* 25, 2613 (2007).
- Dubois, D. L., Blake, D. M., Miedaner, A., Curtis, C. J., Dubois, M. R., Franz, J. A., Linehan, J. C. *Organometallics* 25, 4414 (2006).
- Camaioni, D. M., Heldebrandt, D. J., Linehan, J. C., Shaw, W. J., Li, J., DuBois, D. L., Autrey, T. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 52, 509 (2007).