After completion of the tri-deposition, the matrix was allowed to warm slowly to −95 °C whereapon it melted and formed a toluene-solvated metal atom solution. This solution was stirred and slowly warmed further in the presence of a powdered SiO_2 catalyst support (20 g, preheat treated at 500 °C for 3 h in dry air, cooled, and handled under pure nitrogen prior to and during transfer to the reaction chamber where it was placed under vacuum prior to the metal vapor reaction). During the warming period of about 2 h, the solution turned from dark red-brown to a clear solution. Major color change occurred in the −50 to −20 °C range, and we presume this is the range where metal nucleation/deposition along with toluene reaction occurred. After reaching room temperature the mixture was vacuum siphoned and placed under nitrogen in airless glassware. Toluene was removed under vacuum and the resultant dark powder placed in a reactor in the inert atmosphere box. The catalyst was then outgassed at room temperature to less than 1×10^{-5} torr and subsequently used without further treatment.

Initial rates for three catalysis reactions are summarized in Table I and Figure 1. The remarkable finding is that addition of Mn, itself an almost inactive catalyst, substantially increased the catalytic activity of the Co/SiO_2 system. Indeed, only 2.5 atom % Mn increased the activity for hydrogenation by 10^2. Even higher activities were obtained by adding more Mn, up to 51 atom %, where the rate for 1-butene hydrogenation at −60 °C was controlled by diffusion.[10] These data show that the activity of Mn/SiO_2 is 10^2 lower than that of Co/SiO_2[11] and at least 10^4 lower than $Co\text{-}Mn/SiO_2$.

Catalyst life was studied by repeating 1-butene hydrogenation experiments. After hydrogenation cycles such that each site was used over 470 times, no sign of deactivation was noted.

In summary, for 1-butene hydrogenation and isomerization as well as 1,3-butadiene hydrogenation, we have found small amounts of Mn greatly increase the activity of a Co/SiO_2 SMAD catalyst. Large amounts of Mn are detrimental, however, as is any amount of Cr. Addition of Fe caused a slight increase in activity.

To the best of our knowledge this type of *activation* of one metal on another has not been observed before for heterogeneous bimetallic systems, although Sinfelt and others have reported extensively on *selectivity* differences due to a second metal (eg., Cu-Ni).[12] Naturally we are actively trying to ascertain if this is an electronic effect, an ensemble effect, or simply a dispersion effect.

The discovery that Mn activates SMAD Co/SiO_2 catalysts is timely. There is a great deal of interest currently in both homogeneous cluster chemistry and heterogeneous catalysis in making "early-late" transition-metal clusters and catalysts, and this impetus is mainly based on the supposition that the combination of two such metals may lead to unusual CO activation mechanisms and hence affect selectivity in Fischer-Tropsch reduction products.

Although SMAD catalysts are new materials, and extrapolation of these data to other catalyst systems perhaps is not justified, we do believe our results at least show such activation procedures are possible. Currently we are investigating other catalytic reactions with these bimetallic SMAD materials and will report these data and physical characterization data at a later time.

Acknowledgment. Support of the National Science Foundation and Phillips Petroleum Co. is acknowledged with gratitude.

Registry No. Co, 7440-48-4; Fe, 7439-89-6; Mn, 7439-96-5; Cr, 7440-47-3; 1-butene, 106-98-9; 1,3-butadiene, 106-99-0; butene, 25167-67-3; butane, 106-97-8.

---

[10] The reactions were carried out in a 496 cm³ recirculation system. Usually 0.2 g of catalyst was employed. The ratio of 1-butene to Co metal was 76 in the case of 3.4 wt % Co-3.3 wt % Mn/SiO_2. Below −60 °C (213 K) experimental problems with butene liquefaction were encountered.

[11] Co/SiO_2 (SMAD) is a very effective hydrogenation catalyst itself compared with conventional Co or Ni systems. Such findings are not unusual for SMAD catalysts.[6]

[12] Sinfelt, J. H.; Carter, J. L.; Yates, P. J. C. *J. Catal.* **1972**, *24*, 283-296. Sinfelt, J. H. *Acc. Chem. Res.* **1977**, *10*, 15. Sinfelt, J. H. *Science (Washington, D.C)* **1977**, *195*, 641.

Metal-Induced Oxidative Fusion of Boranes. Synthesis of $B_{12}H_{16}$, the First Neutral Dodecaborane

Cynthia T. Brewer and Russell N. Grimes*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Received February 21, 1984

Transition-metal-promoted oxidative fusion of small *nido*-carborane anions to generate large, carbon-rich carborane cages was discovered several years ago[1] and has been elaborated in a series of synthetic, structural, and mechanistic investigations.[2,3] While the most success experienced thus far has involved the high-yield conversion of $R_2C_2B_4H_5^-$ ions to $R_4C_4B_8H_8$ via complexation with transition metals,[2a] fusion via metal complexation has been extended to other carborane and metallacarborane systems.[3] It has not, however, been employed in reactions of boron hydrides (although $PdCl_2$-induced coupling of B_5H_9 to give the linked-cage borane $1,2'\text{-}(B_5H_8)_2$, has been reported[4]). Metal-promoted fusion of boranes under mild conditions could furnish one-step, nonpyrolytic synthetic routes to known species such as $B_{10}H_{14}$[5] and also allow facile, "rational" syntheses of new boron hydrides that might not be otherwise accessible. In this communication we report the preparation of $B_{10}H_{14}$ from $B_5H_8^-$ and of $B_{12}H_{16}$, a new borane, from $B_6H_9^-$ via metal-induced fusion.

The reaction of $Na^+B_5H_8^-$ (obtained by treatment of B_5H_9 with NaH) with an approximately equimolar quantity of $RuCl_3$ in tetrahydrofuran solution at −78 °C for 3 h and then for 30 min at room temperature followed by extraction with CH_2Cl_2 and elution on a silica column gave $B_{10}H_{14}$ in 27% isolated yield (40 mg), identified from NMR and mass spectra. Fusion of $B_5H_8^-$ is not observed with $FeCl_2$ alone, but when both $FeCl_2$ and $FeCl_3$ are present, $B_{10}H_{14}$ and the linked-cage borane $2,2'\text{-}(B_5H_8)_2$[8] are obtained in about equal amounts (ca. 20% total isolated yield). When $FeCl_3$ alone is allowed to react with $B_5H_8^-$ in THF, $2,2'\text{-}(B_5H_8)_2$ but not $B_{10}H_{14}$ is obtained.

Treatment of $K^+B_6H_9^-$ (prepared from 9.2 mmol each of B_6H_{10} and KH) with 6.0 mmol $FeCl_2$ and 10.6 mmol $FeCl_3$ in dimethyl ether at −78 °C for 2 h followed by extraction with *n*-hexane, separation in a −78 °C trap, vacuum sublimation at 50-60 °C, and a final sublimation at room temperature gave colorless crystals characterized as $B_{12}H_{16}$ (140 mg, 43% yield based on B_6H_{10} consumed). No other borane products were detected. Dodecaborane(16), an air-stable solid (mp 64-66 °C dec), exhibits an electron-impact mass spectrum containing a cutoff at m/e 148 corresponding to the $^{11}B_{12}{}^1H_{16}^+$ parent ion and a parent envelope consistent with the presence of 12 boron atoms; extensive loss of hydrogen is evident (base peak at m/e 138). No significant intensities appear above m/e 148. The 115.8-MHz ^{11}B FT NMR spectrum in hexane consists of seven resonances in a 1:2:1:4:2:1:1 integrated area ratio, at δ 15.4, 13.4, 11.4, 4.6, −18.3, −40.7, and −43.0 relative to $BF_3{\cdot}OEt_2$, respectively. This is consistent with a framework of C_s symmetry containing four borons on the mirror plane. From the $^{11}B-^{11}B$ two-dimensional (2D) NMR spectrum, the observed pattern of cross (off-diagonal) peaks reveals couplings (hence bonds) between specific boron atoms;[9a] the cage connec-

---

[1] (a) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1974**, *96*, 7116; (b) *Inorg. Chem.* **1976**, *15*, 1343.

[2] (a) Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982**, *104*, 5983 and references therein. (b) Venable, T. L.; Maynard, R. B.; Grimes, R. N., manuscript in preparation; (c) *Abstr. Pap.—Am. Chem. Soc.* **1982**, *183rd*, INOR-140.

[3] Recent reviews of this work: (a) Grimes, R. N. *Acc. Chem. Res.* **1983**, *16*, 22; (b) *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55.

[4] Corcoran, E. W., Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182.

[5] Improved multistep syntheses of $B_{10}H_{14}$, (a) via conversion of $B_5H_8^-$ to $B_9H_{14}^-$ and subsequent reaction with boron trihalides[6] and (b) from $B_{11}H_{14}^-$, which is in turn prepared from $NaBH_4$,[7] have been reported recently.

[6] Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1952.

[7] Dunks, G. B.; Barker, K.; Hedaya, E.; Hefner, C.; Palmer-Ordonez, K.; Remec, P. *Inorg. Chem.* **1981**, *20*, 1692.

[8] Gaines, D. F.; Jorgenson, M. W.; Kulzick, M. A. *J. Chem. Soc., Chem. Commun.* **1979**, 380.

0002-7863/84/1506-2722$01.50/0

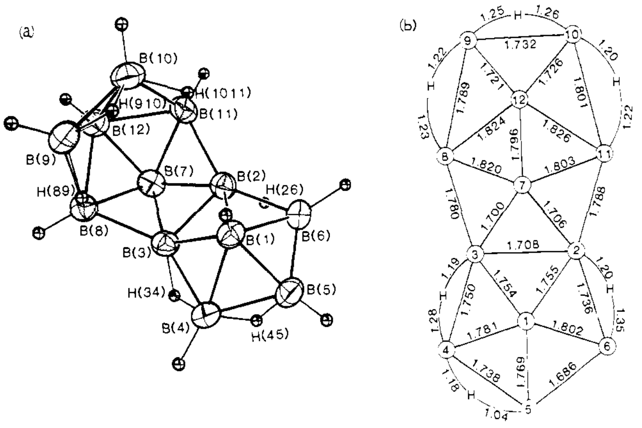

Figure 1. (a) ORTEP drawing of molecular structure. (b) Connectivity diagram showing bond distances. Estimated standard deviations are ≤0.01 and ≤0.06 Å for B-B and B-H distances, respectively.

tivities thus deduced indicate open B_8 and B_6 units joined at a common B-B edge, with B-H-B bridges located on the perimeter.[9b] The proton NMR spectrum exhibits three broad B-H-B resonances that convey little structural information.

An X-ray structural analysis[10] has confirmed the boron connectivity pattern implied by the 2D NMR evidence and reveals that the two borane units are oriented with their open faces directed away from each other, as depicted in Figure 1. The molecule contains six B-H-B bridges, two of which [H(26) and H(34)] can be regarded as quasi-terminal H atoms since B(2) and B(3) have no other attached hydrogens. While the molecule has no solid-state symmetry, tautomerism of H(45) in solution between equivalent B-B edges would produce mirror symmetry on the NMR time scale, in agreement with the ^{11}B NMR data. The compound is structurally related to several other boranes having 13-18 boron atoms, in which two borane cages share a common edge; perhaps most similar to $B_{12}H_{16}$ are $B_{16}H_{20}$,[11] $B_{18}H_{22}$,[12] and i-$B_{18}H_{22}$,[13] in which the open sides of the respective cage fragments face in opposite directions. The $B_{12}H_{16}$ geometry clearly reflects its synthesis from $B_6H_9^-$, as shown by the presence of two pyramidal B_6 fragments whose apex borons are B(1) and B(12). The merger of these hexaborane units is related, in a formal sense, to the metal-induced fusion of $R_2C_2B_4H_4^{2-}$ (a cage-isoelectronic counterpart of $B_6H_9^-$) to form $R_4C_4B_8H_8$;[2a] however, the structure of the latter carborane indicates that fusion of the two C_2B_4 units occurs face to face. As a possible rationale for the different conformation observed in $B_{12}H_{16}$, we note that steric crowding of the B-H-B bridges is minimized during the fusion process if the two pyramidal B_6 units bond in "trans" fashion. It is, however, conceivable that other isomers of $B_{12}H_{16}$ (as yet unobserved) can form during metal-promoted fusion or perhaps via rearrangement of the compound described here.

From the observation that $FeCl_2$ is required in the fusion of both $B_5H_8^-$ and $B_6H_9^-$, taken together with the earlier work on carborane fusion (in which metallacarborane intermediates have been isolated and characterized[2a,3]), we infer that the reactions described here involve intermediate metal-borane complexes such as $Fe(B_5H_x)_2$, $Ru(B_5H_x)_2$, and $Fe(B_6H_x)_2$; however, no such complexes have been isolated. The $FeCl_3$ functions as an oxidizer and is convenient although other oxidants (e.g., I_2) can be employed. In the $RuCl_3$-$B_5H_8^-$ reaction, Ru^{3+} evidently serves as both complexing agent and oxidant.

It seems clear that metal-promoted fusion of boranes offers a useful approach to the controlled synthesis of designed cage species, in which the metal ion mediates low-energy conjoining of separate polyhedral fragments. Our efforts are now directed to determining the scope of this reaction as applied to boranes and to the optimization of certain syntheses, including that of $B_{10}H_{14}$ where the attainment of high yields from $B_5H_8^-$ salts appears a reasonable goal.

Acknowledgment. This work was supported by the U.S. Army Research Office. The Nicolet NMC-360 FT NMR spectrometer was obtained in part through a grant to the Department of Chemistry from the National Science Foundation.

Supplementary Material Available: Tables of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

---

[9] (a) Venable, T. L.; Hutton, W. C.; Grimes, R. N. J. Am. Chem. Soc. **1984**, 106, 29. (b) A complete description and analysis of the 2D spectrum of $B_{12}H_{16}$ will be presented in the full report.

[10] Brewer, C. T.; Sinn, E.; Swisher, R. G.; Grimes, R. N., to be reported in full at a later date. Crystal data: space group $Pna2_1$, a = 10.686 (3) Å, b = 8.686 (4) Å, c = 11.351 (4) Å, V = 1054 Å^3, R = 0.045 for 1021 reflections having $F_o > 3\sigma(F_o^2)$.

[11] Friedman, L. B.; Cook, R. E.; Glick, M. D. Inorg. Chem. **1970**, 9, 1452.

[12] Simpson, P. G.; Lipscomb, W. N. J. Chem. Phys. **1963**, 39, 26.

[13] Simpson, P. G.; Folting, K.; Dobrott, R. D.; Lipscomb, W. N. J. Chem. Phys. 39, **1963**, 2339.

Catalysis of the Exchange of Hydrogen and Carbon Isotopes in the Water/Hydrogen and Bicarbonate/Formate Redox Couples: A Comparison of the Exchange Current Densities on Palladium

Shuchi Chao, Charles J. Stalder, David P. Summers, and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received December 9, 1983

We wish to report that the exchange of hydrogen and carbon isotopes in the CO_3H^-/HCO_2^- aqueous redox couple occurs at a rate that is of the same order of magnitude as the hydrogen isotope exchange in the H_2O/H_2 aqueous redox system at 298 K using a Pd-based heterogeneous catalyst when the various species are at about unit activity and near the thermodynamic composition. Recent research results from this laboratory[1] have established that various forms of supported Pd are capable of effecting the equilibration of the $H_2O/H_2/CO_3H^-/HCO_2^-$ redox system at 298 K and 1 atm H_2, eq 1. Results from the equilibration using the Pd-based catalysts accord well with earlier findings[2] using an enzyme for the reduction of CO_3H^- to HCO_2^- that establish the equilibrium ratio CO_3H^-/HCO_2^- to be approximately one at 298 K and 1 atm H_2 in H_2O solvent. Since CO_3H^- is an aqueous equivalent of CO_2, the findings with the Pd-based catalysts establish that molecules having a C-H bond can be made under mild conditions from H_2 and CO_2. Like several other noble metals, Pd is known to be an excellent electrode surface from which to evolve H_2 from aqueous electrolyte solution.[3] However, there are no known electrode surfaces that are similarly highly regarded with respect to the reduction of CO_2 in aqueous electrolyte solution. Since we have found that supported Pd will effect the reduction of CO_3H^- under mild conditions, we have undertaken a study of the exchange of hydrogen (^{1}H = H, ^{2}H = D) and carbon (^{12}C, ^{13}C) isotopes in the system represented by eq 1 in order to establish the efficacy of Pd electrode surfaces for the reduction of aqueous CO_2 near the thermodynamic potential.

$$H_2 + CO_3H^- \xrightleftharpoons{\text{supported Pd}} HCO_2^- + H_2O \qquad (1)$$

Various compositions (concentration, ratio, and isotopic distribution) of CO_3H^-/HCO_2^- have been dissolved in H_2O solvent

---

[1] Stalder, C. J.; Chao, S.; Summers, D. P.; Wrighton, M. S. J. Am. Chem. Soc. **1983**, 105, 6318.

[2] (a) Klibanov, A. M.; Albert, B. N.; Zale, S. E. Biotechnol. Bioeng. **1982**, 24, 25. (b) Ruschig, U.; Muller, U.; Willnow, P.; Hopner, T. Eur. J. Biochem. **1976**, 70, 325.

[3] Bockris, J. O'M.; Reddy, A. K. N. "Modern Electrochemistry"; Plenum Press: New York, 1970; Vol. 2, p 1238.

0002-7863/84/1506-2723$01.50/0