coordination with nickel (in **2**), the phenolate becomes robust toward oxidation, as shown by a shift of the phenolate oxidation potential from $\sim$+0.5 V for uncoordinated **1** at 25 °C and pH 10 to $\sim$+0.9 V vs. SCE for **2**.

Registry No. 2, 99797-10-1; 4, 99797-11-2.

Supplementary Material Available: Tables of fractional coordinates and isotropic temperature factors, anisotropic temperature factors, bond lengths, and bond angles (4 pages). Ordering information is given on any current masthead page.

---

(14) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Faculty of Pharmaceutical Sciences
University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan
Yoichi Iitaka

Department of Medicinal Chemistry
Hiroshima University School of Medicine
Kasumi, Hiroshima 734, Japan
Tohru Koike
Eiichi Kimura*

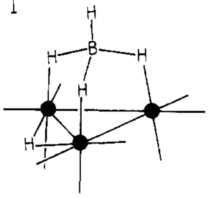
Received September 11, 1985

Ferraborane Cluster Chemistry: Reactions of $[(\mu\text{-H})Fe_3(CO)_9BH_3]^-$ with Lewis Bases Leading to Substitution via H_2 Elimination or to Cluster Degradation

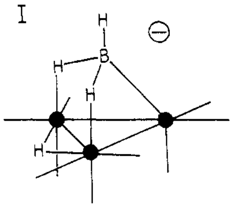
Sir:

We have recently characterized the ferraborane cluster $(\mu\text{-H})Fe_3(CO)_9BH_4$ (I′)[1] and its conjugate base $[(\mu\text{-H})Fe_3(CO)_9BH_3]^-$ (I).[2] I is a novel example of monoborane supported

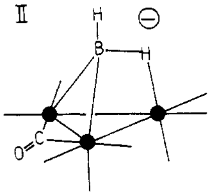
I′



I

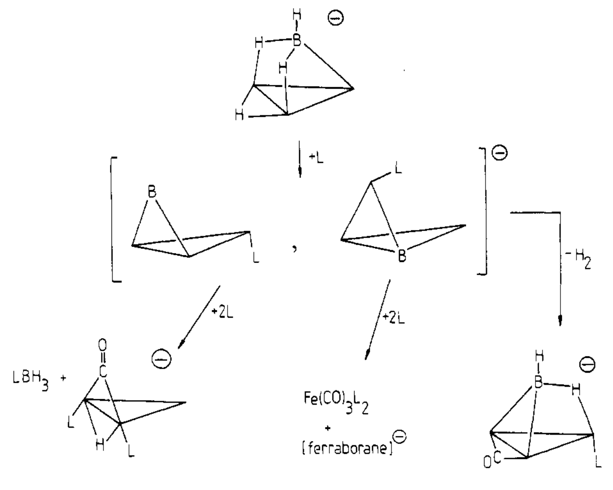


II



on a multinuclear metal framework and, as such, provokes a study of the competitive interplay between metal and boron cluster sites for association with Lewis bases. The stabilization of BH_3 by Lewis bases is well documented and coordination complexes such as BH_3·THF are commercially available. We wondered if, in I, the BH_3 unit would behave toward Lewis bases, L, in a manner typical of simple BH_3 complexes, thereby being displaced as L·BH_3 from the cluster, or whether substitution reactions typical of metal carbonyls would predominate. Qualitative investigations of metal carbonyl–ligand substitution reactions far outnumber detailed kinetic studies.[3] The limited data available point toward substitution of the first CO taking place by an associative mechanism for good nucleophilic ligands[3,4] and via a dissociative mechanism for poor nucleophiles.[3-5] The reaction of one metal–boron cluster system with base has been mechanistically examined.[6,7] The study outlined below is an investigation of the reactions of I with Lewis bases of varying nucleophilicity. We show that cluster substitution is via H_2 rather than CO elimination, and only occurs specifically at low ligand concentration. As the concentration of ligand increases, cluster degradation predominates. Kinetic studies evidence an associative mechanism, and we postulate an adduct intermediate that is consistent with the observed reaction products.

Scheme I



I reacts with CO (1 atm, <1 molar equiv, 45 °C) to form II[2] quantitatively (by NMR) and H_2 is eliminated. Thus, ligand association is with the trimetal frame of I and causes elimination of two skeletal hydrogens thus destroying the integrity of the BH_3 unit but not the integrity of the cluster itself. With excess water (i.e. a Lewis base of low nucleophilicity with respect to a metal but with a strong affinity for boranes), degradation of cluster I occurs, yielding $B(OH)_3$ and $[(\mu\text{-H})Fe_3(CO)_{10}(\mu\text{-CO})]^-$. However, the reaction is markedly slower than the action of H_2O on free BH_3 or on complexed L·BH_3. With $\geq$5-fold excess of NEt_3 (a base that coordinates readily to BH_3 but only weakly to metals), I undergoes adduct formation with $\approx$20% reaction leading to cluster fragmentation, seen by the formation of $Et_3N\cdot BH_3$ and $[(\mu\text{-H})Fe_3(CO)_{10}(\mu\text{-CO})]^-$. The evidence for an adduct is spectroscopic,[8] but reversible loss of the amine to regenerate I was observed in our attempts to isolate the species. With a large excess of NEt_3, I is completely fragmented. I reacts with $PhMe_2P$ (a ligand possessing a strong affinity for both metal and boron centers) by three competitive pathways, one substitution and two fragmentation. We have studied this competition in detail and note that the reactions of the aforementioned Lewis bases with I are consistent with the conclusions drawn below.

When I reacts with $PhMe_2P$, the formation of fragmentation vs. substitution products is highly dependent on phosphine concentration. When $PhMe_2P$ is added to a solution of I at levels of <1 molar equiv, the reaction favors substitution with concomitant cluster retention. The product, $[Fe_3(CO)_8(\mu\text{-CO})(PhMe_2P)BH_2]^-$,[9] is a derivative of II, and therefore H_2 elimination

---

(1) Vites, J.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4633.

(2) Vites, J. C.; Housecroft, C. E.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1984**, *3*, 1591.

(3) Atwood, J. D. "Inorganic and Organometallic Reaction Mechanisms", Brooks/Cole: Monterey, CA, 1985.

(4) Darensbourg, D. J.; Zalewski, D. J. *Organometallics* **1985**, *4*, 92.

(5) Keister, J. B.; Dalton, D. M.; Smesko, S. A.; Modi, S. P.; Malik, P.; Barnett, D. J.; Duggan, T. P. "Abstracts of Papers", 188th National Meeting of the American Chemical Society, Philadelphia, PA, 1984; American Chemical Society: Washington DC, 1984; INOR 205. Dalton, D. M.; Barnett, D. J.; Duggan, T. P.; Keister, J. B.; Malik, P. T.; Modi, S. P.; Shaffer, M. R.; Smesko, S. A.; *Organometallics* **1985**, *4*, 1854.

(6) Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.

(7) Jan, D.-Y.; Hsu, L.-Y.; Shore, S. G. "Abstracts of Papers", 188th National Meeting of the American Chemical Society, Philadelphia, PA, 1984; American Chemical Society: Washington, DC, 1984; INOR 180.

(8) In addition to ^{11}B and ^1H NMR spectroscopic changes during the reaction, we observe no H_2 or CO gas evolution by GLC analysis.

from I has taken place in preference to CO loss.[10] Note that II itself reacts with 1 equiv of $PhMe_2P$ in a straightforward CO substitution reaction that yields $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]^-$ as the only product. Thus the presence of the *endo*-hydrogens appears to provide I with a special mode of reactivity.

In the presence of ≥10-fold excess of $PhMe_2P$, I undergoes complete fragmentation. A first-order rate dependence on each of [I] and $[PhMe_2P]$ was determined.[11] Thus, we suggest that the initial reaction of the ligand with the cluster substrate is an associative process leading to an adduct intermediate. Although we have no direct spectroscopic evidence for the latter, the formation of the final products can be rationalized in terms of the open-cluster intermediates shown in Scheme I. The addition of a pair of electrons supplied by the phosphorus donor should cause I to open from a tetrahedral to a "butterfly" geometry.[7,12] Further attack by $PhMe_2P$ causes fragmentation by cleavage of a butterfly "wing-tip". Thus, one pathway is defined by the formation of $PhMe_2P{\cdot}BH_3$ and $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]^-$[13] and provides a route to a specifically disubstituted derivative of $[(\mu\text{-}H)Fe_3(CO)_{10}(\mu\text{-}CO)]^-$. This in itself is unusual since direct reaction of the latter with phosphine ligand is reported to lead to cluster fragmentation rather than to a substituted product,[14] although our own studies indicate that fragmentation is accompanied by a reaction yielding a mixture of substituted multimetal derivatives.[15] The second pathway generates $Fe(CO)_3(PhMe_2P)_2$ and an unstable phosphine-substituted ferraborane anion that we have not been able to isolate. Attempts to force the reaction specifically along a single fragmentation path have not been successful.

In conclusion, the reactions of I with Lewis bases not only emphasize the delicate balance between cluster substitution and degradation, but also show that, under mild conditions, I is subject to substitution via H_2 rather than CO elimination. In the latter pathway, ligand association is presumed to occur at the metal. Before cleavage of additional base can take place, the Fe_3B cluster extrudes two skeletal hydrogens and closes to the original tetrahedral form. In addition, we note that even under conditions of high ligand concentration where cluster degradation leads to the formation of $L{\cdot}BH_3$, the reaction is slower than when base L reacts with free BH_3 or even when L displaces a weaker base L′ from $L'{\cdot}BH_3$.[16] This, too, evidences the special nature of the cluster-bound BH_3 in I.

Acknowledgment. The support of the National Science Foundation (Grant CHE-84-08251) is gratefully acknowledged.

Registry No. I, 92055-45-3; PMe_2Ph, 672-66-2; NEt_3, 121-44-8; CO, 630-08-0; H_2O, 7732-18-5.

---

(9) $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]^-$: IR ν_{CO} (toluene, cm^{-1}) 2052 w, 1990 vs, 1963 s, 1934 m, 1872 m; ^{31}P NMR ($CD_3C(O)CD_3$, 20 °C) δ 30.2 (m, 1 P); ^{11}B NMR ($CD_3C(O)CD_3$, −20 °C) δ 56.8 (br, dd, $\{^1H\}J_{BH} \approx 140$ Hz (terminal), $J_{BH} \approx 40$ Hz (bridge)); ^1H NMR ($CD_3C(O)CD_3$, −20 °C) δ 7.49–7.37 (m, 5 H, *Ph*Me_2P), 1.25 (m, 6 H, Ph*Me*$_2$P), 6.0 (br, 1 H, terminal BH), −11.6 (br, 1 H, Fe–H–B).

(10) We have noted that H_2 elimination is a prominent feature of another reaction of I: Housecroft, C. E.; Fehlner, T. P. *Organometallics* **1986**, *5*, 379.

(11) [I]PPN (0.192 mmol) in acetone (6.0 mL) was divided into four equal aliquots and each was reacted with $PhMe_2P$: 0.48, 0.96, 1.44 and 1.44 mmol respectively. Each reaction was followed by ^{11}B NMR for a period of 2–3 half-lives; ^{11}B NMR integrals were used as measures of [I]. The overall second-order rate constant was determined as 0.074 $M^{-1}\,min^{-1}$ at 30 °C.

(12) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(13) $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]^-$ exhibits a characteristic resonance at δ −14.3 in the ^1H NMR spectrum close to that of the unsubstituted $[(\mu\text{-}H)Fe_3(CO)_{10}(\mu\text{-}CO)]^-$ (δ −14.75).

(14) Lourdichi, M.; Pince, R.; Dahan, F.; Mathieu, R. *Organometallics* **1983**, *2*, 1417.

(15) Housecroft, C. E., unpublished observations.

(16) Fehlner, T. P. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed., Academic Press: New York, 1975; p 175.

Department of Chemistry
University of Notre Dame
Notre Dame, Indiana 46556

Catherine E. Housecroft
Thomas P. Fehlner*

Received September 12, 1985

Structural Characterization of Two Isomeric Hydrazido(2–) Intermediates in the Conversion of Molybdenum-Bound Dinitrogen to Ammonia and Hydrazine[1]

Sir:

The hydrazido(2–) (NNH_2) ligand is the only nitrogen–hydride intermediate to be detected or isolated from the reactions of bis(dinitrogen) complexes of molybdenum that form ammonia and hydrazine.[2,3] The reactions of *trans*-$[Mo(N_2)_2(triphos)(PPh_3)]$ (**1**), where triphos = $Ph_2P(CH_2CH_2PPh_2)$, with anhydrous HCl and HBr in a variety of organic solvents lead to ammonia and hydrazine in varying yields.[4–6] In all of these latter reactions two isomeric hydrazido(2–) complexes ($[MoX(NNH_2)(triphos)(PPh_3)]X$ where X = Br or Cl) are formed during the reaction. Examples of these isomers have been separated and shown to behave differently in reactions with acid. On the basis of these differences in chemistry, we originally assigned one isomer (**A** isomer) as having coordinated X trans to $[NNH_2]$ and the other isomer (**B** isomer) as having PPh_3 trans to $[NNH_2]$.[5] A recent crystal structure of an **A** isomer and a **B** isomer revealed a much more subtle difference that results from the configuration at the center phosphorus atom of the triphos ligand and not an interchange of ligands.

The reaction of anhydrous HCl with solid **1** gave $[MoCl(NNH_2)(triphos)(PPh_3)]Cl$, as a mixture of **2A** and **2B**, as reported previously.[5] $PPhMe_2$ (4-fold excess) was added dropwise with swirling to a brown-green toluene solution of the mixture of **2A** and **2B**. This solution was allowed to stand under N_2 for 15 h, at which time solvent was decanted from the amber, coffin-shaped crystals.[7] The crystals were washed in the flask with toluene (3 × 15 mL) and pentane (15 mL) and suction-filtered with use of a water aspirator. The yield of crystals of $[MoCl(NNH_2)(triphos)(PPh_3)]Cl$ (**2A**)[8] suitable for X-ray diffraction studies was 9.6%. (Usual yields of **2A** as a powder were 20%.)

In a similar experiment, PPh_2Me was added to a solution of **2A** and **2B** in toluene. After isolation of **2A** as a powder, the filtrate volume was reduced by 50%. After the mixture was allowed to sit under N_2 for 18 h, the solvent was decanted from the olive green, layered-looking rectangular prisms of $[MoCl(NNH_2)(triphos)(PPh_2Me)]Cl$ (**2B′**),[9] which were washed with toluene (3 × 15 mL) and pentane (15 mL) and suction-dried; yield 14%. This same complex together with the **A** isomer analogue was observed in the $^{31}P\{^1H\}$NMR spectrum of a solution of $Mo(N_2)_2(triphos)(PPh_2Me)$ in THF solution after treatment with

---

(1) (a) Reactions of Coordinated Dinitrogen. 17. (b) Part 15: George, T. A.; Howell, D. B. *Inorg. Chem.* **1984**, *23*, 1502–1503.

(2) (a) Anderson, S. N.; Fakley, M. E.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1973–1980. (b) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197–292.

(3) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461–7467.

(4) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6153–6154.

(5) (a) Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K. *Inorg. Chem.* **1983**, *22*, 1968–1970. (b) Baumann, J. A.; Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K.; Noddings, C. M. *Inorg. Chem.* **1985**, *24*, 3568–3578.

(6) (a) Bossard, G. E.; George, T. A.; Lester, R. K. *Inorg. Chim. Acta* **1982**, *64*, L227–L228. (b) Bossard, G. E.; George, T. A.; Howell, D. B.; Lester, R. K. In "Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1982; pp 71–73.

(7) In the absence of $PPhMe_2$ and acid, **2A** precipitates and **2B** slowly decomposes in solution. $PPhMe_2$ reacts with **2B** to form $[MoCl(NNH_2)(triphos)(PPhMe_2)]Cl$, which remains in solution and does not react further to give ammonia under these conditions. There is no evidence that **2A** and **2B** are interconvertible.

(8) For elemental analysis and $^{31}P\{^1H\}$ and ^1H NMR data, see ref 5.

(9) Anal. Calcd for $C_{47}H_{48}Cl_2MoN_2P_4{\cdot}0.5C_7H_8$: C, 62.04; H, 5.36; N, 2.87. Found: C, 62.23; H, 5.54; N, 2.11. $^{31}P\{^1H\}$NMR [80.984 MHz, CD_2Cl_2, 23 °C, $PhP_a(CH_2CH_2P_bPh_2)_2$, Ph_3P_x, $^2J_{P_aP_b} = 0.0$ Hz]: 68.97 (d, $^2J_{P_aP_x} = 169.1$ Hz, P_a), 35.52 (d, $^2J_{P_bP_x} = 18.4$ Hz, P_b), 7.32 ppm (dt, P_x). Chemical shifts (ppm) are referenced to 85% H_3PO_4, and positive values are downfield.

0020-1669/86/1325-0405$01.50/0