Inorg. Chem. **1982**, *21*, 445–447

insoluble in diethyl ether and monoglyme but dissolves in CH_2Cl_2 and water.

The formation of the observed products according to eq 1 can be explained by a two-step process in which the second step is a known fast reaction. The first step is probably a slow reaction of (μ-$Me_2N)B_2H_5$ with TMPD to give an intermediate $(TMPD)BH_2^+$ salt of the *mono*borane adduct of the dimethylamide anion[12] (eq 2). The second step would then be

$$TMPD + (\mu\text{-}Me_2N)B_2H_5 \rightarrow [(TMPD)BH_2][Me_2N{\cdot}BH_3] \quad (2)$$

a fast hydride ion transfer from this anion to (μ-$Me_2N)B_2H_5$ to give the observed products (eq 3). The reaction shown by

$$Me_2N{\cdot}BH_3^- + (\mu\text{-}Me_2N)B_2H_5 \rightarrow Me_2N{\cdot}2BH_3^- + {}^1/_2[Me_2NBH_2]_2 \quad (3)$$

eq 3 has been reported previously and is sufficiently rapid to fit into this scheme.[13]

Experimental Section

Standard high-vacuum techniques and equipment were used in this work.[14] *N,N,N′,N′*-Tetramethyl-*o*-phenylenediamine (Eastman) was purified by vacuum distillation from solid sodium hydroxide pellets. (μ-$Me_2N)B_2H_5$ was prepared by a published literature method.[15] Potassium hexafluorophosphate was purchased from Alfa and was used without further purification. Diethyl ether and 1,2-dimethoxyethane (monoglyme) were stored over $LiAlH_4$ and were vacuum transferred into reaction vessels immediately before use. Boron-11 NMR spectra were obtained at 32.1 or 80.2 MHz with a Varian HA-100 or a Brucker WM-250 spectrometer, respectively, equipped with standard accessories. Chemical shifts are relative to $(C_2H_5)_2O{\cdot}BF_3$, and downfield shifts are positive. Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer.

Reaction of TMPD with (μ-$Me_2N)B_2H_5$. Typically, a weighed 1–2-mmol sample of TMPD was allowed to react at room temperature in a sealed evacuated vessel with ca. 2.5–5 mmol of (μ-$Me_2N)B_2H_5$ in 5–10 mL of monoglyme or diethyl ether until it was certain that no more solid colorless crystalline product was depositing (10–20 days). The vessel was then opened on the vacuum line (noncondensable gas was not present), and the volatile products were removed. Fractionation through a trap −63 °C separated $(Me_2NBH_2)_2$ as a volatile crystalline solid; its identity was confirmed by gas-phase infrared spectroscopy. Boron-11 NMR monitoring was accomplished by using closed reaction vessels of ca. 10-mL internal volume suitably designed to fit in the probe of the HA-100 spectrometer. The NMR reactions were on an approximately 1-mmol scale. For long reaction times, the yield of III was 80–90%.

The colorless crystalline involatile solid reaction product was stable in air and dissolved without reaction in neutral or alkaline water or in CH_2Cl_2. A solution of the solid in water was treated with aqueous KPF_6, and the resulting colorless precipitate was recrystallized from hot water and dried in air. The infrared spectrum of this solid was identical with that reported for $[(TMPD)BH_2]PF_6$.[11]

Infrared spectrum (KBr pellet) of $[(TMPD)BH_2][Me_2N{\cdot}2BH_3]$ (relative intensity): 3090 (w), 3030 (m), 3010 (s), 2980 (m), 2950 (s), 2910 (m), 2860 (w), 2810 (vw), 2495 (s), 2460 (s), 2325 (vs), 2265 (vs) 2225 (s), 2200 (s), 2150 (m, sh), 2050 (w), 1480 (s), 1465 (s), 1450 (s), 1420 (m), 1380 (vw), 1255 (m), 1195 (s), 1180 (vs), 1165 (vs), 1 150 (vs), 1135 (s), 1030 (m), 1015 (s), 965 (m, sh), 955 (m), 925 (s), 865 (w), 815 (m), 800 (m), 770 (s), 755 (w, sh), 725 (w), 545 (w, sh), 530 (m) cm^{-1}.

Registry No. III, 79466-65-2; (μ-$Me_2N)B_2H_5$, 23273-02-1; TMPD, 704-01-8.

---

[12] Aftandilian, V. D.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1961**, *83*, 2471.

[13] Keller, P. C. *Inorg. Chem.* **1971**, *10*, 1528.

[14] Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969.

[15] Keller, P. C. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 307.

Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

Unsymmetrical Cleavage Reactions of B_4H_{10} and $THF{\cdot}B_3H_7$ with the Chelating Base *N,N,N′,N′*-Tetramethyl-*o*-phenylenediamine (TMPD)

Philip C. Keller

Received June 24, 1981

Triborane(7) complexes ($L{\cdot}B_3H_7$) react with monodentate Lewis bases in a variety of ways. The reactions are intricate and depend on the relative properties of the coordinating base (L) and the attacking base (L′). Depending on these factors, reaction patterns can be recognized which result in ligand displacement (eq 1), partial cleavage forming $B_2H_4{\cdot}2L'$ and

$$L' + L{\cdot}B_3H_7 \rightarrow L'{\cdot}B_3H_7 + L \quad (1)$$

$L'{\cdot}BH_3$ (eq 2), complete cleavage forming $L'{\cdot}BH_3$ and $(L'{\cdot}$

$$3L' + L{\cdot}B_3H_7 \rightarrow B_2H_4{\cdot}2L' + L'{\cdot}BH_3 + L \quad (2)$$

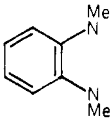
$BH)_x$ polymer (eq 3), and, finally, no reaction at all (eq 4).

$$3L' + L{\cdot}B_3H_7 \rightarrow 2L'{\cdot}BH_3 + (1/x)(L'{\cdot}BH)_x + L \quad (3)$$

$$L' + L{\cdot}B_3H_7 \rightarrow \text{no reaction} \quad (4)$$

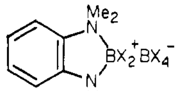
These reactions and their proposed mechanisms have been discussed by Ritter and co-workers[1] and by Paine and Parry.[2,3]

Recently we have been investigating the reactions of the chelating bidentate ligand *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine (TMPD) with substrates including boron

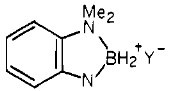


TMPD

halides,[4] diborane(6),[5] and μ-(dimethylamino)diborane(6).[6] In all cases the products have been ionic (I and II), thus falling into the category of unsymmetrical cleavage reactions.



I, X = F, Cl



II, $Y^- = BH_4^-, B_2H_7^-, Me_2N{\cdot}2BH_3^-$

As an extension of this work we have examined the reactions of TMPD with trimethylamine–triborane(7), tetrahydrofuran–triborane(7), and tetraborane(10). The results are reported in this paper.

Results and Discussion

B_4H_{10} and TMPD. In toluene solution at 0 °C, B_4H_{10} and TMPD react slowly to produce the ionic product III, expected from the boron chemistry of TMPD and the well-established acid–base reactions of B_4H_{10} (eq 5).[8] The product separates

$$TMPD + B_4H_{10} \xrightarrow[\text{toluene}]{} \underset{\text{III}}{[(TMPD)BH_2]B_3H_8} \quad (5)$$

---

[1] W. R. Deever, E. R. Lory, and D. M. Ritter, *Inorg. Chem.*, **8**, 1263 (1969).

[2] R. T. Paine and R. W. Parry, *Inorg. Chem.* **11**, 268 (1972).

[3] R. T. Paine and R. W. Parry, *Inorg. Chem.*, **14**, 689 (1975).

[4] D. D. Axtell, A. C. Cambell, P. C. Keller, and J. V. Rund, *J. Coord. Chem.*, **5**, 129 (1976).

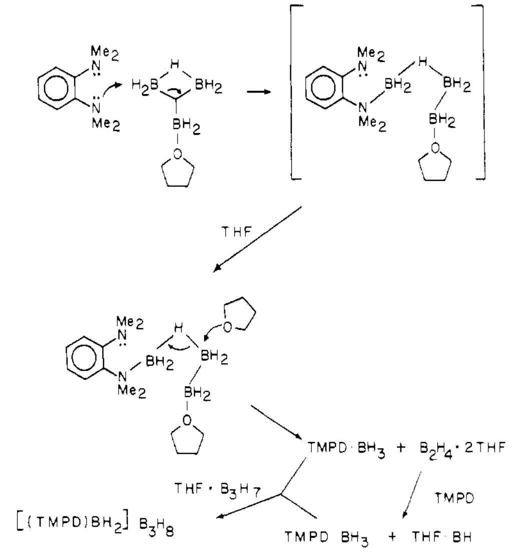
[5] P. C. Keller and J. V. Rund, *Inorg. Chem.*, **18**, 3197 (1979).

[6] P. C. Keller, *Inorg. Chem.*, preceding paper in this issue.

[7] R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1969).

0020-1669/82/1321-0445$01.25/0

Scheme I



from solution as a colorless crystalline air-stable solid. It dissolves in CH_2Cl_2, THF, and hot water and is slightly soluble in C_2H_5OH and cold water. The spectroscopic properties of III (IR and NMR) are those anticipated for a salt of the previously characterized cation[5] and anion.[9]

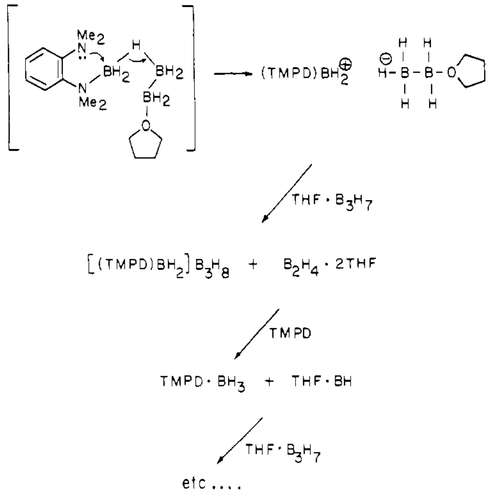
L·B_3H_7 and TMPD. As shown by boron-11 NMR spectroscopy, $Me_3N{\cdot}B_3H_7$ and TMPD fail to react in $CHCl_3$ over a period of 14 days at room temperature. In contrast, $THF{\cdot}B_3H_7$ and TMPD react completely in THF within 10 min at room temperature to form $[(TMPD)BH_2]B_3H_8$ (III) as the only isolable and characterizable product. The mass balance of the reaction approximates eq 6. A boron-11 NMR spectrum of the reacting solution taken 10 min after mixing shows only signals characteristic of the salt III and a weak broad featureless signal at −15.2 ppm which may be associated with the uncharacterized $(THF{\cdot}BH)_x$ polymer.

$$3(THF{\cdot}B_3H_7) + 2TMPD \rightarrow 2[(TMPD)BH_2]B_3H_8 + 2THF + (THF{\cdot}BH) \quad (6)$$

The failure of TMPD to react with $Me_3N{\cdot}B_3H_7$ may be rationalized in terms of the model proposed by Paine and Parry.[2,3] The amine stabilizes the B_3H_7 fragment by strong inductive electron donation, thereby reducing its Lewis acid strength and rendering it susceptible to attack only by bases such as triphenylphosphine, which are much stronger than TMPD.

Although at first glance the TMPD–$THF{\cdot}B_3H_7$ reaction does not fit any of the patterns of eq 1–4, the overall process can be explained within this framework by a several step sequence of events. In Scheme I we propose that initial reaction occurs in a manner paralleling eq 2. A THF molecule attacks the complex to displace $B_2H_4{\cdot}2THF$ and the monoborane adduct of TMPD. The latter would be an excellent hydride ion donor and should react readily with $THF{\cdot}B_3H_7$ to produce $B_3H_8^-$.[10] Although $TMPD{\cdot}BH_3$ has not been observed, it is almost certainly the key active intermediate in the reaction of $THF{\cdot}BH_3$ with TMPD to form products of type II above.[11]

Scheme II



Several paths can be suggested to account for the fate of $B_2H_4{\cdot}2THF$. Direct reaction with TMPD could occur to displace BH_3 as shown, and the $TMPD{\cdot}BH_3$ would combine with $THF{\cdot}B_3H_7$ as discussed above. Alternatively, the $B_2H_4{\cdot}2THF$ may spontaneously decompose to $THF{\cdot}BH_3$ and $(THF{\cdot}BH)_x$ polymer with the former product then reacting with TMPD to form $TMPD{\cdot}BH_3$.

An alternative sequence involving unsymmetrical cleavage of the initial complex also deserves passing consideration. Rather than displacement of the bridge hydrogen by THF as illustrated in Scheme I, the free dimethylamino nitrogen on TMPD could displace the bridge hydrogen in the opposite direction to form ionic products as shown in Scheme II. The reaction could then proceed as shown by hydride ion transfer to $THF{\cdot}B_3H_7$ and other reactions previously discussed. This alternative pathway requires proposing a second unobserved intermediate for which there is little precedent. On these grounds it should be regarded as the less likely of the two.

Experimental Section

Equipment. Standard high-vacuum and inert-atmosphere techniques were used in this work.[12] Boron-11 NMR spectra were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz. Chemical shifts are relative to $(C_2H_5)_2O{\cdot}BF_3$, and downfield shifts are positive. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer.

Materials. Standard published procedures were used for the preparation of B_4H_{10},[13] $Me_3N{\cdot}B_3H_7$,[14] and $THF{\cdot}B_3H_7$.[15,16] TMPD was obtained from Eastman and was vacuum distilled from KOH pellets before use. Toluene, chloroform, methylene chloride, and tetrahydrofuran (THF) were dried by standard methods, stored in evacuated bulbs, and vacuum transferred directly into reaction vessels as needed.

Reaction of B_4H_{10} with TMPD. A 0.172-g (1.05-mmol) sample of TMPD and 1.01 mmol of B_4H_{10} were allowed to react in 5 mL of toluene for 2 h at 0 °C. During this period, a voluminous colorless solid separated from solution. The reaction was allowed to stand at room temperature for another 20 h before it was opened to the vacuum line. Only a trace of noncondensable gas was present. Volatile materials were removed and tested for the presence of boranes by treatment with acidified methanol. No hydrogen was formed. The collected solid product weighed 0.210 g (weight calculated, based on eq 5, 0.219 g). Boron-11 NMR (CH_2Cl_2): broad triplet (intensity

---

(8) S. G. Shore in "Boron Hydrides" E. L. Muetterties, Ed., Academic Press, New York, 1975, p 114.

(9) D. F. Gaines, R. Schaeffer, and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963), and earlier references cited therein.

(10) The reaction of ether·B_3H_7 complexes with hydride ion donors such as tetrahydroborate to form $B_3H_8^-$ is established in the literature: R. W. Parry, R. W. Rudolph, and D. F. Shriver, *Inorg. Chem.*, **3**, 1479 (1964).

(11) Although ref 5 does not include reactions of B_2H_6 with TMPD in THF, it has been found subsequently that reactions in this medium proceed as in monoglyme.

(12) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, 1969.

(13) D. F. Gaines and R. Schaeffer, *Inorg. Chem.*, **3**, 438 (1964).

(14) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2669 (1961).

(15) G. Kodama, R. W. Parry, and J. C. Carter, *J. Am. Chem. Soc.*, **81**, 3534 (1959).

(16) R. Schaeffer and F. N. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).

1) 8.2 ppm, $J = 120$ Hz, symmetrical multiplet (intensity 3), −29.0 ppm, $J = 31$ Hz. Acid hydrolysis of the solid product followed by precipitation with aqueous KPF_6 gave $[(TMPD)BH_2]PF_6$, which was identified by its infrared spectrum.[5]

Infrared spectrum (KBr) of $[(TMPD)BH_2]B_3H_8$ in cm^{-1} (relative intensity): 3050 (vw), 3030 (vw), 3010 (w), 2990 (vw), (2940) (vw), 2480 (m), 2450 (s), 2390 (s), 2295 (w), 2275 (w,sh), 2120 (w), 2075 (w,sh), 1480 (m), 1465 (m,sh), 1455 (m), 1410 (w), 1255 (m), 1195 (m,sh), 1190 (s), 1180 (s), 1165 (s), 1148 (s), 1130 (s), 1110 (m), 1028 (w), (w), 1010 (s), 960 (m), 945 (w), 925 (s), 870 (w), 825 (s), 815 (m), 805 (m), 765 (s), 755 (m), 710 (w), 545 (w), 530 (m).

Reaction of $Me_3N{\cdot}B_3H_7$ with TMPD. A solution of 0.114 g (1.15 mmol) of $Me_3N{\cdot}B_3H_7$ and 0.224 g (1.36 mmol) of TMPD in ca. 1 mL of $CHCl_3$ at room temperature was periodically monitored by boron-11 NMR spectroscopy over 14 days. Neither the appearance of the solution nor the NMR spectrum (starting material) showed any change during this period.

Reaction of $THF{\cdot}B_3H_7$ with TMPD. A 0.178-g (1.59 mmol) sample of $THF{\cdot}B_3H_7$ reacted with 0.331 g (2.02 mmol) of TMPD in 5 mL of THF in a 100-mL vessel to produce a slightly turbid solution that did not change in appearance over a 1-h period. An experiment in an NMR reaction vessel using proportionally smaller quantities showed a boron-11 NMR spectrum characteristic of $[(TMPD)BH_2]B_3H_8$ (see above) and a weak broad structureless signal centered at −15.2 ppm. The 100-mL vessel was opened (a trace of noncondensable gas was present), and all volatile materials were removed by continuous pumping over a 2-day period, leaving 0.281 g of a colorless solid residue (weight calculated from eq 6, 0.275 g). The infrared spectrum of the residue contained all the bands of $[(TMPD)BH_2]B_3H_8$ plus those of an impurity, presumably $(THF{\cdot}BH)_x$. Recrystallization from water gave pure $[(TMPD)BH_2]B_3H_8$. Vacuum-line separation of volatile materials gave a small quantity of TMPD (IR spectrum) and THF free of borane contamination (acid hydrolysis).

Registry No. III, 79550-23-5; B_4H_{10}, 18283-93-7; TMPD, 704-01-8; $THF{\cdot}B_3H_7$, 12544-89-7; $Me_3N{\cdot}B_3H_7$, 12076-72-1.

Contribution from the Laboratory of Analytical Chemistry,
Faculty of Science, Nagoya University,
Chikusa, Nagoya 464, Japan

Activation Volumes for Substitution of Diaqua[*meso*-tetrakis(*N*-methyl-4-pyridyl)porphinato]cobalt(III) with Thiocyanate. Evidence for a Dissociative Mechanism

Shigenobu Funahashi, Masahiko Inamo, Koji Ishihara,
and Motoharu Tanaka*

Received April 17, 1981

Reactions of metalloporphyrins with monodentate ligands have been extensively investigated in order to determine the mechanisms of axial ligand substitution in metalloporphyrins.[1] The overall reaction that takes place can be represented by eq 1, where MP, S, and X refer to metalloporphyrin, solvent molecule, and monodentate ligand, respectively.

$$MPS_2 + 2X \rightleftharpoons MPX_2 + 2S \qquad (1)$$

The reactions are first order in the metalloporphyrin for all the cases studied. The plots of the first-order rate constants against ligand concentration are linear in most cases, while in some systems they show curvature and eventual saturation.

There are several reasonable mechanisms[2] for the axial ligand substitution in metalloporphyrins (see Mechanisms I–III).

Mechanism I

$$MPS_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MPS + S \qquad (2)$$

$$MPS + X \xrightarrow{k_2} MPSX \qquad (3)$$

$$MPSX + X \xrightarrow{\text{fast}} MPX_2 + S \qquad (4)$$

Mechanism II

$$MPS_2 + X \overset{K}{\rightleftharpoons} MPS_2\cdots X \xrightarrow{k} MPSX + S \qquad (5)$$

$$MPSX + X \xrightarrow{\text{fast}} MPX_2 + S \qquad (6)$$

Mechanism III

$$MPS_2 + X \rightarrow [MPS_2X]^{\ddagger} \xrightarrow{\text{fast}} MPSX + S \qquad (7)$$

$$MPSX + X \xrightarrow{\text{fast}} MPX_2 + S \qquad (8)$$

The dissociative mechanism involves the dissociation of the solvent molecule coordinated to the central metal ion in metalloporphyrin to produce a pentacoordinated intermediate (step 2). This intermediate species then reacts with the entering ligand (step 3).

In Mechanism II the reaction proceeds via an interchange between a ligand and a solvent molecule in a rapidly formed outer-sphere complex ($MPS_2\cdots X$).

The third mechanism is an associative type. The first ligand incorporated in the metalloporphyrin labilizes the axial solvent molecules.[3-8] The intermediate MPSX reacts much faster with X than does the disolvato porphyrin complex, and thus the concentration of the intermediate is very low.

In Mechanism III the rate should be first order in X for all concentrations of X. In the reaction systems where first-order rate constants, k_0, increase with increasing concentration of X up to a limiting value, Mechanism III cannot be operating. Mechanisms I and II both predict a falling-off of the k_0 with increasing concentration of the incoming ligand. Mechanism I gives the following dependence of k_0 with respect to [X]:

$$k_0 = \frac{k_1[X]}{k_{-1}/k_2 + [X]} \qquad (9)$$

For Mechanism II, we have

$$k_0 = \frac{k[X]}{K^{-1} + [X]} \qquad (10)$$

Thus eq 10 is identical in form with eq 9 with

$$k_0 = \frac{p[X]}{q + [X]} \qquad (11)$$

Under conditions ($q >> [X]$) where the increase of k_0 with [X] does not fall off, we obtain only $k_2k_1k_{-1}^{-1}$ or kK.

The reaction of [*meso*-tetrakis(*N*-methyl-4-pyridyl)porphine]cobalt(III) (represented by CoTMpyP) with thiocyanate ion has been studied by several groups[5,6] with similar results. Although the mechanisms have been discussed, no clear con-

---

(1) Hambright, P. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: New York, 1975; Chapter 6, pp 233–278.

(2) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1965.

(3) Thusius, D. *J. Am. Chem. Soc.* **1971**, *93*, 2629.

(4) Fleischer, E. B.; Krishnamurthy, M. *J. Am. Chem. Soc.* **1971**, *93*, 3784.

(5) Pasternack, R. F.; Cobb, M. A. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4327.

(6) Ashley, K. R.; Berggren, M.; Cheng, M. *J. Am. Chem. Soc.* **1975**, *97*, 1422.

(7) Ashley, K. R.; Au-Young, S. *Inorg. Chem.* **1976**, *15*, 1937.

(8) Pasternack, R. F.; Parr, G. R. *Inorg. Chem.* **1976**, *15*, 3087.

0020-1669/82/1321-0447$01.25/0