into the P-N bond and coordination to the metal substrate. The latter would be responsible to the carbonyl formation (both coordination to the metal and interaction with the nitrogen are possible for the nonfixed CO_2).

It is known that CO_2 can insert into the P-N bond of free PN_3 to afford $P(O_2CNMe_2)_x(NMe_2)_{3-x}$ (x = 1, 2).[18] From the reaction of $P(O_2CNMe_2)(NMe_2)_2$ with I we have isolated the complex $RhCl[P(O_2CNMe_2)(NMe_2)_2]_2$ (V) that shows in its IR spectrum in Nujol mull bands at 1710 (s) and 1632 (vs) cm^{-1} due to inserted CO_2. This complex does not afford Rh-carbonyl species on heating up to 150 °C, nor does it liberate carbon dioxide.

That the carbamato species are present in IV and are not formed upon heating is confirmed by the analysis of the ^1H NMR spectrum of IV. The insertion of CO_2 into the P-N bond of PN_3 causes loss of P-H coupling. In fact the compounds $P(O_2CNMe_2)_x(NMe_2)_{3-x}$ present two different proton resonances: a singlet (at 2.96 ppm for both compounds with $x = 1$ and $x = 2$) attributed to the $P(O_2CNMe_2)$ methyls, and a doublet (at 2.75 ppm, $J_{P-H} = 9.8$, for $x = 1$; 2.66 ppm, $J_{P-H} = 10.2$, for $x = 2$) due to the $P(NMe_2)$ methyl groups.

The ^1H NMR sectrum of IV presents a singlet at 2.98 ppm and a triplet centered at 2.80 ppm, $J = 10.2$, with an intensity ratio 1:2.[19] Aging the solution causes change of the spectrum to a complex multiplet, and the complexes isolated at this stage present a N:P ratio lower than 3.

Attempts to obtain IV from V and CO_2 afforded impure material as a carbonyl complex was formed.[20]

Such an insertion of CO_2 into the P-N bond of the coordinated phosphine takes place also when the complex $Pd_2Cl_4[P(NMe_2)_3]_2$ is exposed to carbon dioxide in a THF solution. The white compound formed shows IR bands at 1710 (s) and 1620 (vs) cm^{-1} (Nujol mull).[21]

Further study is in progress in order to elucidate the mode of bonding of the coordinated CO_2 in these and related complexes.

Acknowledgment. Financial support from CNR, Rome, is gratefully acknowledged.

Registry No. I, 12081-16-2; II, 79255-72-4; III, 110-18-9; IV, 79255-73-5; V, 79255-74-6; $RhCl[P(NMe_2)_3][Me_2N)_2P-P(NMe_2)_2]$, 79255-75-7.

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(18) G. Oertel, H. Malz, and H. Holtschmidt, *Chem. Ber.*, **97**, 891 (1964).

(19) The triplet structure suggests a P-P coupling through the metal. A similar pattern is presented by the compound $RhCl[P(O_2CNMe_2)(NMe_2)_2]_2$: singlet at 3.1 ppm and triplet at 3.0 ppm, $J_{P-H} = 10.7$.

(20) The rate of reaction of IV with CO_2 is quite slow, and the reduction to CO takes place also at -20 °C.

(21) Once isolated from the solution, the white complex decomposes easily at -10 °C, and this prevented its full characterization.

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Unsymmetrical Cleavage Reaction of μ-(Dimethylamino)diborane(6)

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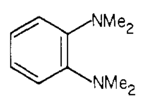
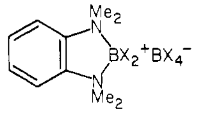
The literature contains a number of reports on reactions of μ-aminodiboranes with ammonia,[1,2] primary,[3] secondary,[3] and teritary amines,[1,2,4] phosphines,[5] methyl isocyanate,[6] sodium hydride,[7] etc. In all cases, the products are simple 1:1 adducts of the form (donor)-BH_2-NR_2-BH_3 (although in the case of methyl isocyanate a subsequent hydroboration occurs[6]). There are no known examples of the formation of ionic "unsymmetrical cleavage"[8] products with μ-aminodiboranes, although reactions of this type are not uncommon in the acid-base chemistry of diborane(6).[9]

In recent papers we reported that the bidentate base *N*,*N*,*N′*,*N′*-tetramethyl-*o*-phenylenediamine (TMPD) reacts with

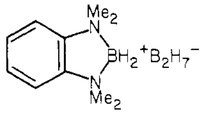


TMPD

boron trichloride and trifluoride[10] and with diborane(6)[11] to give ionic products I or II.



I, X = H, Cl, F

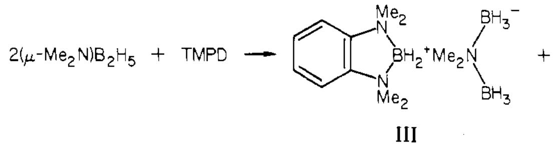


II

The ortho substitution of the amino groups in TMPD and the bulk of the *N*-methyl substituents appear to strongly favor a chelating coordination of BX_2^+ (X = H, Cl, F). In this paper we describe the action of TMPD on (μ-Me_2N)B_2H_5 to give the first example of the formation of unsymmetrical cleavage products with a μ-aminodiborane(6).

Results and Discussion

Over a period of 10-20 days, TMPD reacts with excess (μ-$(CH_3)_2N$)B_2H_5 in diethyl ether or monoglyme according to eq 1. The ionic product III is insoluble in either solvent and crystallizes as the reaction proceeds. In one experiment in which the reaction was monitored at 1-5-day intervals by boron-11 NMR spectroscopy, the spectra showed only a steadily diminishing (μ-Me_2N)B_2H_5 signal and a steadily increasing sharp triplet due to $(Me_2NBH_2)_2$. No intermediate species or other byproducts could be detected.



III

$\frac{1}{2}(Me_2NBH_2)_2$ (1)

The product III exhibits the spectral properties expected of a salt of the known (TMPD)BH_2^+ and $Me_2N{\cdot}2BH_3^-$ ions.[7,11] The boron-11 NMR spectrum in CH_2Cl_2 consists of a broad triplet of unit intensity (δ 6.1, J = 118 Hz, cation) and a quartet of intensity 2 (δ -11.2, J = 91 Hz, anion) in good agreement with published data for these species.[7,11] The infrared spectrum is essentially a superposition of the absorptions of the component ions with a few minor shifts. The salt is

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(6) Molinelli, R.; Smith, S. R.; Tanaka, J. *J. Chem. Soc., Dalton Trans.* **1972**, 1363.

(7) Keller, P. C. *Inorg. Chem.* **1971**, *10*, 2256.

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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 $(\mu\text{-}Me_2N)B_2H_5$ 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

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

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

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

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. $(\mu\text{-}Me_2N)B_2H_5$ 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 $(\mu\text{-}Me_2N)B_2H_5$. 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 $(\mu\text{-}Me_2N)B_2H_5$ 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; $(\mu\text{-}Me_2N)B_2H_5$, 23273-02-1; TMPD, 704-01-8.

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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 $L'{\cdot}BH_3$ (eq 2), complete cleavage forming $L'{\cdot}BH_3$ and $(L'{\cdot}BH)_x$ polymer (eq 3), and, finally, no reaction at all (eq 4).

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

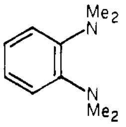
$$3L' + L{\cdot}B_3H_7 \rightarrow B_2H_4{\cdot}2L' + L'{\cdot}BH_3 + L \qquad (2)$$

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

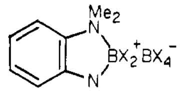
$$L' + L{\cdot}B_3H_7 \rightarrow \text{no reaction} \qquad (4)$$

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

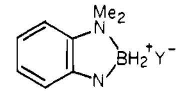
Recently we have been investigating the reactions of the chelating bidentate ligand *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine (TMPD) with substrates including boron halides,[4] diborane(6),[5] and μ-(dimethylamino)diborane(6).[6] In all cases the products have been ionic (I and II), thus falling into the category of unsymmetrical cleavage reactions.



TMPD



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

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

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

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