hexane. Filtration and evaporation of solvent yielded a yellow-orange solid identified as B_9Cl_8H (15 mg, 0.04 mmol, 34%).

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Registry No. $(n\text{-}Bu_4N)_2B_9Cl_9$, 68694-93-9; $(n\text{-}Bu_4N)_2B_9Br_9$, 72402-96-1; $(n\text{-}Bu_4N)_2B_9I_9$, 72402-94-9; B_9Cl_9, 31304-34-4; $(n\text{-}Bu_4N)B_9Cl_9$, 72402-98-3; $(n\text{-}Bu_4N)B_9Br_9$, 72402-95-0; B_9Br_9, 12589-31-0; $(n\text{-}Bu_4N)B_9I_9$, 72403-00-0; B_9Cl_8H, 72275-11-7; $(n\text{-}Bu_4N)_2B_9Cl_8H$, 72402-97-2; $(n\text{-}Bu_4N)B_9Cl_8H$, 72402-99-4; $(n\text{-}Bu_4N)_2B_9H_9$, 68380-71-2.

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Molecular Addition Compounds. 7. Synthesis of Addition Compounds of Boron Trifluoride, Borane, and Alane with *N,N,N′,N′*-Tetramethylethylenediamine and Triethylenediamine by Precipitation from Ether Solvents[1]

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Triethylenediamine (TED) precipitates BF_3 from diethyl ether (Et_2O) as TED·2BF_3 and as TED·BF_3 from tetrahydrofuran (THF). *N,N,N′,N′*-Tetramethylethylenediamine (TMED) and TED precipitate BH_3 from both Et_2O and THF as TMED·2BH_3 and TED·2BH_3, respectively. From Et_2O, TMED precipitates AlH_3 as TMED·2AlH_3. In THF, TMED reacts with AlH_3 to afford TMED·AlH_3. Thus the patterns of behavior exhibited by BF_3, BH_3, and AlH_3 with TED and TMED in Et_2O and in THF are all different. Since TMED·AlH_3 is modestly soluble in THF, TMED cannot precipitate alane quantitatively from this solvent. However, TED reacts instantly and quantitatively with alane in Et_2O and THF to give the highly insoluble mono adduct TED·AlH_3. Consequently, the quantitative precipitation of alane from ether solvents is feasible with TED.

Introduction

Over the years, various workers have carried out experiments involving addition compounds of *N,N,N′,N′*-tetramethylethylenediamine (TMED) and triethylenediamine (TED) with boron trifluoride, borane, and alane.[3-8] These adducts are highly insoluble in the usual organic solvents (THF, Et_2O, $CHCl_3$, pentane, and benzene). During the course of our work, it became desirable to achieve the convenient precipitation of borane and alane from ether solvents. Surprisingly, no work has been reported in the literature on the precipitation of borane and alane from their solution in ether solvents using TMED or TED.

Recently we reported the successful precipitation of BF_3 from such ether solvents by TMED and ethylenediamine (EDA).[1,3] Irrespective of the mode of addition or the amount of the reactants, TMED always precipitates BF_3 as TMED·2BF_3.[3] The reaction between EDA and BF_3 affords either the mono or the bis adduct, depending upon the solvents utilized.[1] In continuation of the above study, we now wish to report our exploration of the precipitation under standardized conditions of boron trifluoride, borane, and alane from ether solvents (Et_2O, THF) with TMED and TED.

Experimental Section

The reaction flasks and other glass equipment used for experiments were oven-dried and assembled in a stream of dry nitrogen gas. The special techniques for the manipulation of air-sensitive materials are described elsewhere.[9] $Et_2O\cdot BF_3$ and TMED were distilled from calcium hydride. TED was purified by sublimation under reduced pressure. Aluminum hydride was prepared according to the published procedure.[10] The ^1H NMR, ^{11}B NMR, and ^{27}Al NMR spectra were recorded on Varian T-60 and FT-80A instruments. The ^1H, ^{11}B, and ^{27}Al chemical shifts are in δ relative to Me_4Si, $Et_2O\cdot BF_3$, and $Al(NO_3)_3$ standards, respectively. Infrared spectra were recorded with the Perkin-Elmer 700 spectrometer.

Precipitation of Boron Trifluoride with Triethylenediamine. (a) Determination of Stoichiometry by ^1H NMR. Two different reactions were carried out in individual centrifuge vials maintained at 25 °C. The vials were charged with TED (5 mmol), benzene (3.0 mmol, internal standard), and CCl_4 (5 mL). An aliquot (0.6 mL) was taken from the first vial, and the amount of TED was estimated via ^1H NMR. To the second vial was added 5.0 mmol of $Et_2O\cdot BF_3$ with stirring. The ^1H NMR spectrum of the supernatant liquid, following centrifugation, indicated that all TED had been precipitated from solution, and no signal attributable to TED was detectable.

(b) Determination of Stoichiometry by GLC. In a 50-mL centrifuge vial were dissolved 5.0 mmol of TED and 3.0 mmol of *n*-dodecane (internal standard) in 10 mL of THF. The amount of TED present in the solution was determined by GLC analysis with a 6 ft × 0.25 in. column packed with 10% SE-30 on Chromosorb W. The solution was then treated with 5.0 mmol of $Et_2O\cdot BF_3$ with constant stirring; a white solid precipitated. GLC analysis of the supernatant liquid indicated that it was free of TED. The adduct was collected by centrifugation, washed several times with *n*-pentane, and dried. There was obtained 0.88 g (98% yield) of TED·BF_3: mp 199–201 °C;[11] IR and ^1H NMR spectra superimposable with those reported in literature;[11] ^{11}B NMR (CH_3CN) δ −0.32 (q, $J = 13$ Hz).

When the same reaction was carried out in diethyl ether, a different result was realized. Thus, treatment of 5.0 mmol of TED in Et_2O with 5.0 mmol of $Et_2O\cdot BF_3$ yielded a precipitate. GLC analysis of the supernatant liquid revealed the presence of 2.5 mmol of residual TED. The reaction mixture was treated further with 5.0 mmol of $Et_2O\cdot BF_3$. The GLC analysis now indicated no TED in the solution. The adduct was collected by centrifugation, washed several times with Et_2O, and dried. There was obtained 1.23 g (99% yield) of TED·2BF_3: mp >300 °C; IR spectrum identical with that reported in the literature;[4] ^1H NMR (acetone-d_6) δ 3.47 (s, 12 H); ^{11}B NMR (CH_3CN) δ −0.24 (q, $J = 12$ Hz).

Precipitation of Borane with *N,N,N′,N′*-Tetramethylethylenediamine and Triethylenediamine. Determination of Stoichiometry. Identical reactions were carried out in THF and in Et_2O at 25 °C. The following

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[1] Part 6: Brown, H. C.; Singaram, B. *Inorg. Chem.* **1979**, *18*, 53.

[2] Postdoctoral research associate on Grant No. GM 10937 from the National Institutes of Health.

[3] Brown, H. C.; Singaram, B.; Schwier, J. R. *Inorg. Chem.* **1979**, *18*, 51.

[4] McDivitt, J. R.; Humphrey, G. L. *Spectrochim. Acta, Part A* **1974**, *30a*, 1021.

[5] Miller, N. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 1033.

[6] Gatti, A. R.; Wartik, T. *Inorg. Chem.* **1966**, *5*, 2075.

[7] Davidson, J. M.; Wartik, T. *J. Am. Chem. Soc.* **1960**, *82*, 5506.

[8] Dilts, J. A.; Ashby, E. C. *Inorg. Chem.* **1970**, *4*, 855.

[9] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975; Chapter 9.

[10] Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464.

[11] Van Paasschen, J. M.; Geanangel, R. A. *Can. J. Chem.* **1975**, *53*, 723.

0020-1669/80/1319-0455$01.00/0

procedure in THF is typical. A standard solution of borane–methyl sulfide (BMS) in THF was prepared and estimated[9] via hydrolysis to be 1.0 M in BH_3. To 10 mL of this solution, in a 50-mL centrifuge vial, was added 5 mL of TED in THF (1.0 M). A thick precipitate formed immediately. This was centrifuged. Hydrolysis of an aliquot of the supernatant solution evolved no hydrogen, revealing the complete precipitation of borane from the solution. Thus, 5.0 mmol of TED precipitated completely 10 mmol of borane. The adduct, $TED{\cdot}2BH_3$, was collected as usual, washed several times with Et_2O, and dried: 0.67 g (96% yield); mp >300 °C; IR spectrum superimposable with that reported in the literature;[4] ^1H NMR (Me_2SO-d_6) δ 3.02 (s, 12 H); ^{11}B NMR (CH_3CN) δ −10.47 (q, J = 99 Hz).

The same adduct precipitated on addition of BMS to excess TED.

Similar results were realized with TMED. The bis adduct, $TMED{\cdot}2BH_3$ (mp 182.5–184 °C), precipitated from both Et_2O and THF solutions. The IR and ^1H NMR spectra of $TMED{\cdot}2BH_3$ were similar to those reported earlier;[6] ^{11}B NMR (CH_3CN) δ −10.3 (q, J = 98 Hz).

The above reaction was also followed by GLC with a 6 ft × 0.25 in. column packed with 10% Se-30 on Chromosorb W, in a manner similar to that described for the precipitation of BF_3. The results indicated that both TMED and TED precipitate BH_3 from Et_2O and THF solutions as the corresponding bis adducts.

Preparation of $TED{\cdot}BH_3$. The bis adduct, $TED{\cdot}2BH_3$ (0.7 g, 5 mmol), and TED (0.56 g, 5 mmol) were mixed thoroughly in a flask and melted together at ~160 °C to form a clear liquid. On cooling, the clear liquid crystallized out to form $TED{\cdot}BH_3$: 1.23 g (98% yield); mp 168–170 °C; the IR spectrum was identical with that reported in the literature;[6] ^1H NMR (Me_2SO-d_6) δ 2.80 (s, 12 H); ^{11}B NMR (CH_3CN) δ −11.18 (q, J = 98 Hz).

Precipitation of Alane with Triethylenediamine. Stoichiometric Study. Comparable reactions were carried out in THF and Et_2O at 25 °C. The following procedure in THF is representative. A 0.5 M solution of AlH_3 in THF was prepared following the published procedure.[10] To 10 mL of this solution, in a centrifuge vial, was added 2.5 mL of a 1 M solution of TED in THF. The precipitated adduct was centrifuged. Upon hydrolysis, 1 mL of the supernatant solution evolved 0.6 mmol of hydrogen, revealing the presence of 2.5 mmol of residual AlH_3 in solution. The reaction mixture was further treated with 2.5 mmol of TED. Hydride estimation, as well as ^{27}Al NMR, now revealed that AlH_3 was no longer present in the solution. The precipitate was collected by centrifugation, washed with THF, and dried. There was obtained 0.68 g (96% yield) of $TED{\cdot}AlH_3$: mp 280 °C dec; IR (Nujol) 1770 (w), 1720 (m), 870 (m), 740 (s), and 700 (m) cm^{-1}; ^1H NMR (C_6H_6) δ 2.80 (br s, 12 H).

Similar results were obtained when the reaction was monitored for residual TED by GLC. The same alane adduct precipitated from Et_2O as the reaction solvent. The results were identical, utilizing reverse addition.

Precipitation of Alane Using *N,N,N′,N′*-Tetramethylethylenediamine. Determination of Stoichiometry. A 50-mL centrifuge vial was charged with 10 mL of 0.5 M AlH_3 in THF. To this solution at 25 °C was added, with stirring, 0.38 mL of TMED (2.5 mmol). The precipitate was centrifuged, and the residual AlH_3 in the supernatant solution was estimated by hydrolysis. A 1-mL aliquot gave 12.4 mmol of hydrogen. This corresponded to the presence of 4.1 mmol of AlH_3 in solution. The solution was then treated with 2.5 mmol of TMED (0.38 mL) with stirring. After centrifugation, a 1-mL aliquot of the clear supernatant solution gave 4.6 mmol of hydrogen. This indicated that 1.53 mmol of AlH_3 is still present in the solution, attributed to the solubility of $TMED{\cdot}AlH_3$ in THF. At 25 °C the solubility of $TMED{\cdot}AlH_3$ is 0.157 M in THF, 0.044 M in Et_2O, and 0.010 M in pentane. The adduct was collected by centrifugation, washed with Et_2O, and dried. There was obtained 0.49 g (67% yield) of $TMED{\cdot}AlH_3$: mp 140–143 °C; IR (Nujol) 1760 (m), 1720 (s), 1710 (m), 1700 (m) cm^{-1};[7] ^1H NMR (C_6H_6) δ 3.83 (br s, 4 H), 2.5 (br s, 12 H); ^{27}Al NMR (THF) δ +128.5 (br s).

Different results were obtained for the same experiment in diethyl ether. Thus, when 2.5 mmol of TMED was added to 5.0 mmol of AlH_3 in Et_2O, hydride estimation of the supernatant liquid revealed the complete precipitation of AlH_3. The polymeric precipitate was collected by centrifugation, washed with Et_2O, and dried. The product was $TMED{\cdot}2AlH_3$, 0.44 g (100% yield): mp 95–99 °C; IR (Nujol) 1780 (w), 1760 (m), 1720 (w), 1700 (w) cm^{-1}; ^{27}Al NMR (THF) δ +129.8.

Anal. Calcd for $C_6H_{22}Al_2N_2$: N, 15.9. Found: N, 15.6.

Table I. Formation of 1:1[a] and 1:2[b] Adducts by Precipitation of Boron Trifluoride, Borane, and Alane from Diethyl Ether and Tetrahydrofuran with Triethylenediamine and *N,N,N′,N′*-Tetramethylethylenediamine

	THF		EE	
Lewis acid	TED	TMED	TED	TMED
BF_3	1:1[c]	1:2[c]	1:2[c]	1:2[c]
BH_3[e]	1:2[c]	1:2[c]	1:2[c]	1:2[c]
AlH_3	1:1[c]	1:1[d]	1:1[c]	1:2[c]

[a] 1:1 = $TED{\cdot}MX_3$ or $TMED{\cdot}MX_3$. [b] 1:2 = $TED{\cdot}2MX_3$ or $TMED{\cdot}2MX_3$. [c] Complete precipitation at 25 °C. [d] Incomplete precipitation at 25 °C. [e] $TED{\cdot}BH_3$ prepared by melting together TED and $TED{\cdot}2BH_3$. $TMED{\cdot}BH_3$, mp −3 to −1 °C, has been prepared previously by a corresponding procedure.[13]

Table II. Summary of Data on Addition Compounds of Boron Trifluoride, Borane, and Alane with *N,N,N′,N′*-Tetramethylethylenediamine and Triethylenediamine

addn compd	mp, °C	pptn from solvent	spectroscopic data, δ (multiplicity) ^{11}B	^{27}Al
$TMED{\cdot}2BF_3$	210–212	THF, EE	−0.74 (q)	
$TMED{\cdot}BF_3$		*b*		
$TED{\cdot}2BF_3$	>300	EE	−0.24 (q)	
$TED{\cdot}BF_3$	199–201	THF	−0.32 (q)	
$TMED{\cdot}2BH_3$	185.2–184	THF, EE	−10.30 (q)	
$TMED{\cdot}BH_3$	−3 to −1	*a*	−8.2 (q)[c]	
$TED{\cdot}2BH_3$	>300	THF, EE	−10.47 (q)	
$TED{\cdot}BH_3$	168–170	*a*	−11.18 (q)	
$TMED{\cdot}2AlH_3$	95–99	EE		+129.8 (br s)
$TMED{\cdot}AlH_3$	140–143	THF		+128.5 (br s)
$TED{\cdot}2AlH_3$		*b*		
$TED{\cdot}AlH_3$	280	THF, EE		

[a] Does not precipitate in this form. Prepared by redistribution of 1:2 addition compound with a second equivalent of amine. [b] Attempted redistribution failed. [c] Recalculated from the reported shift based on methyl borate as standard.[13]

Similar results were obtained when the above reaction was followed by GLC analysis for residual TMED.

Attempted Synthesis of $TED{\cdot}2AlH_3$. To 10 mmol of AlH_3 in THF (20 mL) was added 5 mmol of TED in THF (5 mL) at 25 °C with stirring. Following the addition, THF was pumped off at 12 mmHg. The white solid residue obtained was powdered and mixed thoroughly to give 0.85 g of the adduct: mp 158–160 °C dec.

On hydrolysis of 0.34 g of the adduct (2.0 mmol) with methanol (40 mmol), 12.0 mmol of hydrogen was evolved. Analysis of the clear hydrolysate using GLC (101 SE-30) revealed the presence of THF (2.0 mmol) and TED (2.0 mmol). Hence, the solid obtained is not pure $TED{\cdot}2AlH_3$ but a mixture of $TED{\cdot}AlH_3$ and $THF{\cdot}AlH_3$.[12]

Results and Discussion

For convenience in following the discussion, the experimental results are summarized in Tables I and II.

Our main objective was to establish conditions for the precipitation of BF_3, BH_3, and AlH_3 from Et_2O and THF. Consequently, we were interested both in the stoichiometry of the reaction between the above Lewis acids with the difunctional Lewis bases TMED and TED and in the solubilities of the products. Generally speaking, a monofunctional Lewis acid can react with a difunctional Lewis base to afford either the mono adduct or the bis adduct, depending upon the nature of the acid and base involved and the particular solvent used for the reaction.[1,3] For example, TMED reacts with $Et_2O{\cdot}BF_3$ in either Et_2O or THF to give the bis adduct $TMED{\cdot}2BF_3$, even in the presence of excess TMED. We had reported that this adduct exhibited a singlet at δ −0.74 in the ^{11}B NMR spectrum. It is difficult to exclude an ionic structure when

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(12) Wiberg, E.; Gösel, W. *Z. Naturforsch.* **1956**, *116*, 485.

(13) Gatti, A. R.; Wartik, T. *Inorg. Chem.* **1966**, *5*, 329.

only a single resonance line is observed, since $(TMED)_2{\cdot}BF_2^+$ and BF_4^- may have very similar ^{11}B chemical shifts.[14] The single resonance had been realized by recording the spectrum on a Varian FT-80A instrument using 2K data points. However, when the spectrum was recorded by utilizing 8K data points, the singlet was resolved into a nice quartet with J_{BF} value of 14.7 Hz. This unambiguously supports the structure $TMED{\cdot}2BF_3$ for the bis adduct.

Triethylenediamine reacts with $Et_2O{\cdot}BF_3$ in Et_2O and THF according to eq 1 and 2, respectively. Both the mono and the

$$\mathrm{TED} + 2\mathrm{Et_2O{\cdot}BF_3} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \mathrm{TED{\cdot}2BF_3} \qquad (1)$$

$$\mathrm{TED} + \mathrm{Et_2O{\cdot}BF_3} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{TED{\cdot}BF_3} \qquad (2)$$

bis adducts were known in literature, prepared by different routes.[4,11]

Irrespective of the mode of addition and the quantity of the reactants, both TMED and TED react instantaneously with BMS in Et_2O, as well as in THF, to afford the bis adduct (eq 3 and 4).

$$\mathrm{TMED} + 2\mathrm{BH_3{\cdot}SMe_2} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{Et_2O/THF}} \mathrm{TMED{\cdot}2BH_3} \qquad (3)$$

$$\mathrm{TED} + 2\mathrm{BH_3{\cdot}SMe_2} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{Et_2O/THF}} \mathrm{TED{\cdot}2BH_3} \qquad (4)$$

On heating of a 1:1 mixture of $TED{\cdot}2BH_3$ and TED to 160 °C, a clear melt is obtained, which on cooling crystallizes to give $TED{\cdot}BH_3$ (eq 5).

$$\mathrm{TED} + \mathrm{TED{\cdot}BH_3} \xrightarrow[\text{(ii) cool to 25 °C}]{\text{(i) 160 °C}} 2\mathrm{TED{\cdot}BH_3} \qquad (5)$$

The addition compounds of TMED and TED with AlH_3 have been reported earlier.[7,8] Conventionally, they are synthesized by reacting the hydrochloride or hydrobromide of the Lewis base with lithium aluminum hydride (eq 6 and 7).

$$\mathrm{TMED{\cdot}2HCl} + 2\mathrm{LiAlH_4} \xrightarrow{\mathrm{TMED}} 2\mathrm{TMED{\cdot}AlH_3} + 2\mathrm{LiCl} + 2\mathrm{H_2} \qquad (6)$$

$$\mathrm{TED{\cdot}HBr} + \mathrm{LiAlH_4} \xrightarrow{\mathrm{Et_2O}} \mathrm{TED{\cdot}AlH_3} + \mathrm{LiBr} + \mathrm{H_2} \qquad (7)$$

When diethyl ether is used as the solvent, the hydrochloride of the amine cannot be used. The byproduct, which is insoluble in diethyl ether, will precipitate along with the desired product.

The reaction between TMED and AlH_3 afforded either the mono or the bis adduct, depending upon the solvent used. In diethyl ether, TMED precipitated $TMED{\cdot}2AlH_3$ (eq 8).

$$\mathrm{TMED} + \mathrm{AlH_3} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \mathrm{TMED{\cdot}2AlH_3} \qquad (8)$$

On the other hand, in THF, $TMED{\cdot}AlH_3$ precipitated (eq 9).[7]

$$\mathrm{TMED} + \mathrm{AlH_3} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{TMED{\cdot}AlH_3} \qquad (9)$$

TED precipitated AlH_3 as the 1:1 complex, irrespective of the solvent used (eq 10). $TED{\cdot}2AlH_3$ was not formed in THF

$$\mathrm{TED} + \mathrm{AlH_3} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{Et_2O\ or\ THF}} \mathrm{TED{\cdot}AlH_3} \qquad (10)$$

even in the presence of 2 molar equiv of AlH_3.

Previous workers[15,16] have correlated the Al–H frequency in the IR spectrum with the coordination number of the aluminum in the aluminum hydride adducts. At present, we do not have sufficient evidence to decide whether both four- and five-coordinate aluminum is present in the above adducts.

Conclusion

In the present study, the stoichiometry and the completeness of the precipitation of BF_3, BH_3, and AlH_3 from Et_2O and THF utilizing TMED and TED as the precipitating agents have been established. Thus, TED precipitates BF_3 from THF completely in a 1:1 molar ratio, whereas, in Et_2O, it separates completely in a 1:2 molar ratio. Both TMED and TED precipitate BH_3 completely from Et_2O as well as from THF, in 1:2 molar ratio. TMED precipitates AlH_3 from Et_2O completely in 1:2 molar ratio. It reacts with AlH_3 in THF in 1:1 molar ratio, but the precipitation is not complete.

The reaction of TED with AlH_3 in both Et_2O and THF proceeds to form the 1:1 addition compound. In both cases, the precipitation of the adduct proceeds quantitatively.

Thus it is now possible to utilize either TMED or TED to precipitate quantitatively BF_3, BH_3, or AlH_3 from ether solvents such as Et_2O or THF.

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Registry No. $TMED{\cdot}2BF_3$, 67813-45-0; $TED{\cdot}2BF_3$, 53289-14-8; $TED{\cdot}BF_3$, 15730-60-6; $TMED{\cdot}2BH_3$, 5843-33-4; $TMED{\cdot}BH_3$, 5843-32-3; $TED{\cdot}2BH_3$, 15531-41-6; $TED{\cdot}BH_3$, 15531-40-5; $TMED{\cdot}2AlH_3$, 72049-53-7; $TMED{\cdot}AlH_3$, 32995-50-9; $TED{\cdot}AlH_3$, 3521-04-8; TED, 280-57-9; TMED, 110-18-9; $Et_2O{\cdot}BF_3$, 109-63-7; BH_3, 13283-31-3; AlH_3, 7784-21-6.

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(14) Hartman, J. S.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 874.

(15) Young, A. R.; Ehrlich, R. *Inorg. Chem.* **1965**, *4*, 1358.

(16) Greenwood, N. N.; Thomas, B. S. *J. Chem. Soc. A* **1971**, 814.