the triplet observed for $O(CH_2)_4NH \cdot BH_2CN$, shows multiple resonance which is not readily resolved. Future proposals of models for the mechanism of cyanoborane–amine formation by the reaction of cyanotrihydroborate with amine salts must accomodate this hydrogen exchange.

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Use of a Substituent Effect in Borazine Chemistry for the Synthesis of 2,4-Dichloroborazine

O. T. BEACHLEY, Jr.,* and T. R. DURKIN

A two-step reaction sequence has been developed for the specific synthesis of 2,4-dichloroborazine, $HCl_2B_3N_3H_3$, using readily available starting materials. The procedure involves the initial preparation of a new unsymmetrically substituted borazine, $Cl_2[N(CH_3)_2]B_3N_3H_3$, from $Cl_3B_3N_3H_3$ and $N(CH_3)_2H$. This reaction to form $Cl_2[N(CH_3)_2]B_3N_3H_3$ is essentially quantitative and demonstrates the existence of a strong substituent effect in borazine chemistry. The compound $Cl_2[N(CH_3)_2]B_3N_3H_3$ is then allowed to react with B_2H_6 in diethyl ether to form $HCl_2B_3N_3H_3$. The factors influencing the B_2H_6 reaction have been studied in order to optimize the yield of $HCl_2B_3N_3H_3$. The compound $Cl[N(CH_3)_2]_2B_3N_3H_3$ has also been prepared but its instability at room temperature limits its usefulness as a synthetic intermediate. The ^1H nmr data and the thermal stability of the compounds in the series $Cl_{3-x}[N(CH_3)_2]_xB_3N_3H_3$ are compared.

Introduction

The syntheses of unsymmetrically substituted borazines present unusual problems in inorganic chemistry. A series of B-disubstituted borazines[1] $(H)(X)(Y)B_3N_3H_3$ in which X and Y are CN, OCN, or Cl has recently been reported. These compounds, which have unique combinations of electron-withdrawing and electron-donating substituents, are readily prepared from an appropriate B-chloroborazine and silver(I) salt. However, the initial starting material for their synthesis, 2,4-dichloroborazine, $HCl_2B_3N_3H_3$, is not readily available. There is no known procedure for the specific preparation of $HCl_2B_3N_3H_3$. The compound has only been obtained previously in small yields from reactions designed to prepare $H_2ClB_3N_3H_3$.[2,3]

In this paper, we report the results of a research project designed to develop a series of reactions for the specific synthesis of $HCl_2B_3N_3H_3$ in high yield from readily available starting materials. Our approach to the problem was to make use of a reaction,[4] the exchange of a dimethylamino group for hydrogen on a boron of a borazine ring using B_2H_6, which we discovered while studying the Lewis basicity of $H_2[N(CH_3)_2]B_3N_3H_3$. Therefore, we synthesized the previously unkown compound $Cl_2[N(CH_3)_2]B_3N_3H_3$ and studied its reactions with diborane. During the course of this research, we also prepared $Cl[N(CH_3)_2]_2B_3N_3H_3$ in order to evaluate it as a potential precursor to B-monosubstituted borazines. The series of compounds $Cl_x[N(CH_3)_2]_{3-x}B_3N_3H_3$ has been investigated with respect to their spectral and physical properties in order to study systematically the substituent effects of the Cl and $N(CH_3)_2$ groups.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum line or a purified nitrogen atmosphere. All solvents were dried by conventional procedures. The compound[5] $Cl_3B_3N_3H_3$ was prepared by allowing BCl_3 to react with NH_4Cl in a tube at 200° and purified by recrystallization from *n*-pentane. Diborane[6] was prepared from $NaBH_4$ and H_3PO_4. The compound[7] $[N(CH_3)_2]_3B_3N_3H_3$ was synthesized from $Cl_3B_3N_3H_3$ and excess $N(CH_3)_2H$ in *n*-pentane.

Preparation of $Cl_2[N(CH_3)_2]B_3N_3H_3$. The new compound $Cl_2[N(CH_3)_2]B_3N_3H_3$ was prepared by allowing $Cl_3B_3N_3H_3$ (1 mol) to react with a stoichiometric quantity (2 mol) of $N(CH_3)_2H$. In a typical experiment, 1.689 g (9.18 mmol) of freshly recrystallized $Cl_3B_3N_3H_3$ was dissolved in 25 ml of dry diethyl ether. To this solution, 18.26 mmol of $N(CH_3)_2H$ was added by condensation at −196°. Upon allowing the mixture to warm slowly to room temperature with stirring, a white precipitate ($N(CH_3)_2H_2Cl$) formed. After 30 min, the reaction mixture was filtered to remove $N(CH_3)_2H_2Cl$ and then the ether was removed from the filtrate by vacuum distillation. The compound $Cl_2[N(CH_3)_2]B_3N_3H_3$ (1.635 g, 92.3% yield based on $Cl_3B_3N_3H_3$) remained in the flask as a white crystalline solid. It had a melting point of 92–92.5° and was identified by its analytical data and spectral properties. The compound can be recovered unchanged after standing at room temperature for several days. It can be purified by sublimation at room temperature to a 0° cold finger. *Anal.* Calcd for $Cl_2[N(CH_3)_2]B_3N_3H_3$: N, 29.11; Cl, 36.83. Found: N, 29.08; Cl, 36.28.

Preparation of $HCl_2B_3N_3H_3$. Reaction of $Cl_2[N(CH_3)_2]B_3N_3H_3$ with B_2H_6. The compound $HCl_2B_3N_3H_3$ was prepared by allowing $Cl_2[N(CH_3)_2]B_3N_3H_3$ to react with B_2H_6 in an appropriate solvent. The experimental conditions for the reaction were varied in order to optimize the yield of $HCl_2B_3N_3H_3$. The effects of changing the mole ratio of $Cl_2[N(CH_3)_2]B_3N_3H_3$ to B_2H_6 from 0.69 to 1.25, the reaction time from 1.5 to 24 hr, and the nature of the solvent (diethyl ether, *n*-pentane, or neat) were studied. The following experimental procedure maximized the yield of HCl_2B_3-

(1) O. T. Beachley, Jr., *Inorg. Chem.*, **12**, 2503 (1973).
(2) O. T. Beachley, Jr., *Inorg. Chem.*, **8**, 2665 (1969).
(3) R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, **6**, 575 (1967).
(4) O. T. Beachley, Jr., and T. R. Durkin, *Inorg. Chem.*, **12**, 1128 (1973)

(5) G. L. Brennan, G. H. Dahl, and R. Schaeffer, *J. Amer. Chem. Soc.*, **82**, 6248 (1960).
(6) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N. J. 1970, pp 492–496.
(7) W. Gerrard, H. R. Hudson, and E. F. Mooney, *J. Chem. Soc.*, 113 (1962).

N_3H_3 at 58% (based on the quantity of $Cl_2[N(CH_3)_2]B_3N_3H_3$ used). A 5.28-mmol sample of $Cl_2[N(CH_3)_2]B_3N_3H_3$ was dissolved in 25 ml of diethyl ether. Diborane (5.12 mmol) was condensed into the flask at $-196°$. The reaction was warmed to room temperature and stirred for 18 hr. The reaction mixture was then fractionated using trap temperatures of $-46, -63,$ and $-196°$, which separated HCl_2B_3-N_3H_3, $H_2ClB_3N_3H_3$, and a mixture of solvent and μ-$N(CH_3)_2B_2H_5$, respectively. These components were identified by their infrared spectra[3] and vapor pressures.[3]

Preparation of $Cl[N(CH_3)_2]_2B_3N_3H_3$. The new compound Cl-$[N(CH_3)_2]_2B_3N_3H_3$ has been prepared by two methods, the reaction of $Cl_3B_3N_3H_3$ with $N(CH_3)_2H$ and the reaction of $[N(CH_3)_2]_3B_3N_3$-H_3 with BCl_3. However, it should be noted that the compound is unstable at room temperature.

Reaction of $Cl_3B_3N_3H_3$ with $N(CH_3)_2H$. In a typical experiment 0.33 g (1.82 mmol) of $Cl_3B_3N_3H_3$ was dissolved in 25 ml of n-pentane in a flask equipped with a fritted-disk side arm. To this solution, 7.27 mmol of $N(CH_3)_2H$ was added by condensation at $-196°$ and then the mixture was warmed to room temperature. After stirring the mixture for 19 min, the white precipitate which had formed was removed by filtration. The solvent was immediately distilled from the filtrate. The resulting white crystalline solid (0.269 g, 73.1% yield based on $Cl_3B_3N_3H_3$) was identified as $Cl[N(CH_3)_2]_2$-$B_3N_3H_3$ by its spectral and analytical properties.

It should be noted that $Cl[N(CH_3)_2]_2B_3N_3H_3$ is a particularly unstable borazine derivative. The very short reaction time used in the preparative procedure is critical as $Cl[N(CH_3)_2]_2B_3N_3H_3$ decomposed to form a white nonvolatile solid which is insoluble in pentane. When a reaction time of several hours is used, only a trace of $Cl[N(CH_3)_2]_2$-$B_3N_3H_3$ can be isolated. In addition, the instability of the compound makes analytical experiments difficult. An accurately tared sample could not be obtained. However, a nitrogen:chlorine ratio was determined for a freshly prepared sample. The observed nitrogen to chlorine ratio for $Cl[N(CH_3)_2]_2B_3N_3H_3$ was 5.053:1.000 whereas the theoretical value is 5:1.

Reaction of $[N(CH_3)_2]_3B_3N_3H_3$ with BCl_3. In a typical experiment, 0.696 g (3.31 mmol) of $[N(CH_3)_2]_3B_3N_3H_3$ was allowed to react with 3.38 mmol of BCl_3 at room temperature in the absence of a solvent. The BCl_3 was rapidly taken up and a colorless solid and liquid were formed. After a 5-min reaction time, a volatile component was removed by vacuum distillation and identified as 2.36 mmol of $Cl_2BN(CH_3)_2$ by its infrared spectrum. In addition a small portion of the material remaining in the reaction flask sublimed at room temperature to a cold finger. This sublimate had an infrared spectrum identical with the sample of $Cl[N(CH_3)_2]_2B_3N_3H_3$ prepared by the other route. As the compound $Cl[N(CH_3)_2]_2B_3N_3H_3$ decomposes so readily, no attempt was made to optimize the preparative conditions.

Reaction of $Cl_2[N(CH_3)_2]B_3N_3H_3$ with BF_3. The reaction of $Cl_2[N(CH_3)_2]B_3N_3H_3$ with BF_3 was investigated in order to understand the chemical properties of $Cl_2[N(CH_3)_2]B_3N_3H_3$ and the potential products, the fluorochloroborazines. In a typical experiment, 5.237 mmol of BF_3 was allowed to react with 0.9502 g (4.873 mmol) of $Cl_2[N(CH_3)_2]B_3N_3H_3$ in a flask connected to the vacuum line. The mixture was stirred for 3.5 hr at room temperature. The reaction mixture was then fractionated using trap temperatures of $0, -23, -78,$ and $-196°$, which separated $Cl_3B_3N_3H_3$, $Cl_2FB_3N_3H_3$ (0.155 g, 19.5% based on $Cl_2[N(CH_3)_2]B_3N_3H_3$), $ClF_2B_3N_3H_3$ (0.064 g, 10.0%), and 1.163 mmol of BF_3. A nonvolatile residue (0.8616 g) remained in the reaction flask. The volatile products were identified according to their mass and infrared spectra.[8] The desired product of this reaction, $Cl_2FB_3N_3H_3$, rapidly disproportionates at room temperature as noted by changes in the mass and infrared spectra, to form $Cl_3B_3N_3H_3$ and $ClF_2B_3N_3H_3$. It should be noted that the presence of diethyl ether from $BF_3 \cdot O(C_2H_5)_2$ facilitates the decomposition and makes isolation of the products very difficult.

Infrared Spectra. The infrared spectra were recorded in the range 4000–400 cm^{-1} by means of a Perkin-Elmer 457 spectrometer. Gas-phase spectra were observed using a 10-cm cell equipped with KBr optics. Solid samples were prepared as Nujol mulls. Absorption intensities were measured using the method of Durkin, Glore, and De Hayes.[9]

The following give the spectra of $Cl_2[N(CH_3)_2]B_3N_3H_3$ and Cl-$[N(CH_3)_2]_2B_3N_3H_3$ [frequency, cm^{-1} (intensity: s, strong; m, medium; w, weak; sh, shoulder)]. $Cl_2[N(CH_3)_2]B_3N_3H_3$: 3450 (s,

Table I. Nuclear Magnetic Resonance Data (CH_3CN Solution)

Compd	δ(NH),[a] ppm	δ(CH), ppm
$Cl_3B_3N_3H_3$	-6.08	
$Cl_2[N(CH_3)_2]B_3N_3H_3$	-4.81 (ortho)	-2.59
	-5.27 (para)	
$Cl[N(CH_3)_2]_2B_3N_3H_3$	-4.18	-2.59
$[N(CH_3)_2]_3B_3N_3H_3$	-3.06	-2.59

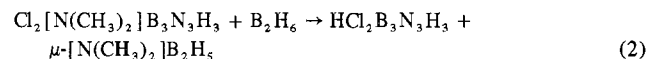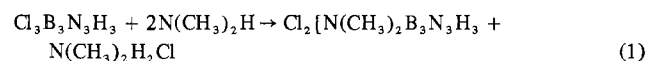[a] The ^{14}NH coupling constants could not be resolved.

sh), 3425 (vs), 2960 (s), 2805 (w), 1618 (m), 1520 (vs), 1430 (vs, br), 1062 (m, sh), 1042 (s), 963 (m), 850 (w), 765 (w, sh), 725 (s), 685 (s), 664 (vs), 650 (s, sh), 580 (w). $Cl[N(CH_3)_2]_2B_3N_3H_3$: 3475 (vs), 2920 (vs), 2800 (s), 1625 (w), 1530 (vs), 1430 (vs, br), 1327 (m), 1275 (vw), 1244 (vw), 1192 (vw), 1101 (s), 1073 (w), 1039 (s), 971 (m, sh), 959 (m), 907 (vw), 840 (w), 746 (m), 693 (s, sh), 680 (vs), 631 (vs), 592 (vw), 540 (vw).

Nuclear Magnetic Resonance Spectra. The ^1H nmr spectra were recorded at 100 MHz by means of a Jeolco HM-100 spectrometer. The reference compound was tetramethylsilane. The solvent for all samples was CH_3CN. The nmr data are tabulated in Table I.

Mass Spectra. The mass spectra were recorded by means of a Perkin-Elmer Hitachi Model RMU-6E spectrometer.

Results and Discussion

A synthetic route for the preparation of the compound $HCl_2B_3N_3H_3$ has been developed. The preparative reactions, as shown by eq 1 and 2, make use of readily available

$$Cl_3B_3N_3H_3 + 2N(CH_3)_2H \rightarrow Cl_2[N(CH_3)_2B_3N_3H_3 + N(CH_3)_2H_2Cl \quad (1)$$

$$Cl_2[N(CH_3)_2]B_3N_3H_3 + B_2H_6 \rightarrow HCl_2B_3N_3H_3 + \mu\text{-}[N(CH_3)_2]B_2H_5 \quad (2)$$

starting materials. Furthermore, the yield of $HCl_2B_3N_3H_3$ based on the initial quantity of $Cl_3B_3N_3H_3$ is very good. The reaction sequence makes use of the initial preparation of $Cl_2[N(CH_3)_2]B_3N_3H_3$. The reaction which leads to its preparation (eq 1) is essentially quantitative. It is of interest that significant quantities of $Cl[N(CH_3)_2]_2B_3N_3H_3$ are not formed and $Cl_3B_3N_3H_3$ does not remain unreacted. These observations suggest that a significant substituent effect, due to the $N(CH_3)_2$, influences the chemistry of Cl_2-$[N(CH_3)_2]B_3N_3H_3$. Apparently, the $N(CH_3)_2$ group alters the chemical properties of the borazine ring to make a boron atom bound to chlorine in $Cl_2[N(CH_3)_2]B_3N_3H_3$ much less acidic and, hence, less reactive to $N(CH_3)_2H$ than a boron atom in $Cl_3B_3N_3H_3$. It has been previously noted that the $N(CH_3)_2$ group is a strong electron-donating substituent[10] whereas chlorine has a very small substituent effect.[1,10] The second step of the sequence, the reaction of $Cl_2[N$-$(CH_3)_2]B_3N_3H_3$ with B_2H_6 (eq 2), occurs very readily if diethyl ether is used as solvent. The desired product, HCl_2-$B_3N_3H_3$, is easily separated from the reaction mixture. A very small amount of $H_2ClB_3N_3H_3$ ($<1\%$) but no $Cl_3B_3N_3$-H_3 is isolated. The yield of $HCl_2B_3N_3H_3$ depends on the reaction time and solvent. Short reaction times and neat conditions lead to decreased yields. If pentane is used as the solvent, only small amounts of $HCl_2B_3N_3H_3$ are obtained and $H_2BN(CH_3)_2$ is observed as a product. The nature of the reaction between B_2H_6 and a $N(CH_3)_2$ group and the possible intermediates in the reaction have been discussed.[4]

Previous research has shown that $BF_3 \cdot O(C_2H_5)_2$ reacts with an $N(CH_3)_2$ group on a borazine ring to form fluoroborazines.[10] In an analogous reaction, $Cl_2[N(CH_3)_2]B_3N_3$-H_3 also reacts with $BF_3 \cdot O(C_2H_5)_2$ to form $Cl_2FB_3N_3H_3$. However, the presence of ether in the reaction mixture makes isolation of the products very difficult. If gaseous

(8) H. Beyer, H. Jenne, J. B. Hynes, and K. Niedenzu, *Advan. Chem. Ser.*, No. 42, 267 (1963).

(9) T. Durkin, J. Glore, and L. De Hayes, *J. Chem. Educ.*, 48, 452 (1971).

(10) O. T. Beachley, Jr., *J. Amer. Chem. Soc.*, 92, 5372 (1970).

BF$_3$ is used instead, Cl$_2$FB$_3$N$_3$H$_3$ is obtained in 20% yields according to eq 3. The low yield of Cl$_2$FB$_3$N$_3$H$_3$ is proba-

$$BF_3 + Cl_2[N(CH_3)_2]B_3N_3H_3 \rightarrow Cl_2FB_3N_3H_3 +$$
$$F_2BN(CH_3)_2 \tag{3}$$
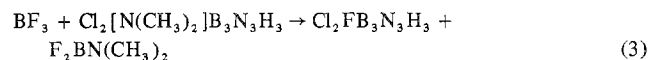
bly related to the disproportionation of the product to form Cl$_3$B$_3$N$_3$H$_3$ and ClF$_2$B$_3$N$_3$H$_3$. Both the infrared and nmr spectra of Cl$_2$FB$_3$N$_3$H$_3$ vary with time. Similar results[8] have been previously observed for the compound.

The ^{1}H nmr data for the series of compounds Cl$_{3-x}$[N-(CH$_3$)$_2$]$_x$B$_3$N$_3$H$_3$ (x = 0-3) are given in Table I. The chemical shift of the NH protons is dependent on the nature and the degree of substitution. In contrast, the chemical shift of the CH protons of the N(CH$_3$)$_2$ group is constant throughout the series. As the number of N(CH$_3$)$_2$ groups bound to the borazine ring increases, the NH resonance moves to higher field. However, it should be noted that an "additivity effect"[1] for each N(CH$_3$)$_2$ group is not observed. There is no regular change in the NH chemical shift with the degree of substitution. Similar results[1] have been noted for the series H$_{3-x}$[N(CH$_3$)$_2$]$_x$B$_3$N$_3$H$_3$. The chemical shift of the CH proton in the N(CH$_3$)$_2$ group remains constant throughout the series Cl$_{3-x}$[N(CH$_3$)$_2$]$_x$B$_3$N$_3$H$_3$. This observation might imply that the electron pair on the exocyclic nitrogen is delocalized into the ring to the same extent in all the derivatives. A second explanation, meta N(CH$_3$)$_2$ groups have little effect on each other, can also be offered. There are even oth-

er possible interpretations. Probably, very little use should be made of these observations. However, it should be noted that similar results are observed for C$_6$H$_5$[N(CH$_3$)$_2$] and C$_6$H$_4$[N(CH$_3$)$_2$]$_2$.

The relative thermal stability of the compounds in the series is Cl$_3$B$_3$N$_3$H$_3$ $\sim$ [N(CH$_3$)$_2$]$_3$B$_3$N$_3$H$_3$ > Cl$_2$[N(CH$_3$)$_2$]-B$_3$N$_3$H$_3$ >> Cl[N(CH$_3$)$_2$]$_2$B$_3$N$_3$H$_3$. A similar order was observed for the simple dimethylamino derivatives.[3] This order might be related to the strengths of the boron-chlorine and boron-nitrogen (exocyclic) bonds, considering the substituent effects. The electron-donating ability of the N(CH$_3$)$_2$ group could weaken the boron-chlorine bond, thus increasing the possibility of producing HCl and eventually N(CH$_3$)$_2$H$_2$Cl, an observed decomposition product. When two N(CH$_3$)$_2$ groups are present, Cl[N(CH$_3$)$_2$]$_2$B$_3^-$N$_3$H$_3$ is so unstable that one can monitor the decomposition using successive infrared scans. There is no doubt that the instability of Cl[N(CH$_3$)$_2$]$_2$B$_3$N$_3$H$_3$ limits its usefulness as a synthetic intermediate.

Notes

Contribution from The Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Conformations of the 3,10-*meso*- and (3R,10R)-3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) Complexes

Tasuku Ito[1] and Daryle H. Busch*

Complex I, 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) ion, exists as the non-interconvertible 3,10-meso and 3,10-racemic isomers, since the complex has two asymmetric carbons at the 3 and 10 positions.[2,3] In this study the stereochemistry of the 3,10-meso and 3R,10R complexes has been elucidated by detailed analyses of their pmr spectra.[4]

I II
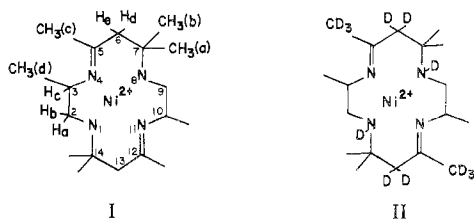
(1) On leave from the Department of Chemistry, Fukushima University, Fukushima, Japan.
, (2) (a) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1204 (1962); (b) N. F. Curtis, D. A. Swann, T. N. Waters, and I. E. Maxwell, *J. Amer. Chem. Soc.*, 91, 4588 (1969).
(3) H. Ito and J. Fujita, *Bull. Chem. Soc. Jap.*, 44, 741 (1971).

It is known that the imine methyl protons and the methylene protons adjacent to the imine bonds in analogous macrocyclic nickel(II) complexes are easily deuterated in basic D$_2$O solutions[5-7] and the appropriate deuterated (-d_{12}) derivatives (II) have been prepared for these studies. Spectra 1 and 2 in Figure 1 are those of the 3,10-meso complex and its deuterated derivative, respectively. Spectral parameters for both complexes are summarized in Tables I and II.

Direct evidence has not been previously reported on the positions of the methyl groups on the diaminopropane residues for the meso ligand (2,9 or 3,10). We have observed two kinds of couplings between the amine proton and the methylene protons of the five-membered chelate ring for the *trans*-dichloro- and *trans*-dicyanocobalt(III) complexes containing this ligand, indicating that the diaminopropane residue methyl groups must be located at the 3 and 10 positions.[8]

Methyl Protons. The pmr spectrum of each isomer shows three singlets and one doublet of equal intensity in the high-field region. These are due to the eight pairwise-equivalent methyl groups within each isomer. This suggests that the 3,10-meso and 3R,10R complexes have C_i and C_2 symmetry, respectively. The imine methyl protons are easily assigned

(4) Though the pmr data of these complexes were reported by Curtis, *et al.*,[2b] their results were limited to the methyl proton resonances. Some of their assignments are shown to be incorrect by this study.
(5) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, 90, 6938 (1968).
(6) E. K. Barefield and D. H. Busch, *Inorg. Chem.*, 10, 108 (1971).
(7) V. L. Goedken and D. H. Busch, *Inorg. Chem.*, 10, 2679 (1971).
(8) T. Ito and D. H. Busch, to be submitted for publication.