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The Tetrachloronitridomolybdate(VI) Species. An Intermediate in the Fixation of Azide to Ammonia

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It is well established that complexes of inorganic molybdenum salts with certain thiols catalyze the reduction of most substrates of nitrogenase in a manner very similar to the enzymatic reaction.[1] One of the striking properties of nitrogenase, the molybdenum-, iron-, and sulfide-containing nitrogen-fixing enzyme is its nonspecificity with regard to the reduction of substrates other than nitrogen. Azide is the only ligand other than nitrogen which is also reduced only to ammonia.[2] It is possible that the azide ion reacts at the active enzyme site in a manner analogous to nitrogen and intermediates which are formed *could be the same* as those in the reduction of nitrogen. For this reason, a study of the interaction of the azide ion with molybdenum pentachloride[3] and molybdenum tetrachloride was undertaken.

The reaction of chloroazide with molybdenum(V) chloride has been shown to yield $MoNCl_3$.[4] However, the presence of covalent azide and covalent chloride clouds the effective interaction between molybdenum(V) and the azide ion. Kolitsch and Dehnicke[5] have also isolated a triphenylphosphine adduct of $MoNCl_3$ and the pentachloronitridomolybdate(VI) ion as the tetramethylammonium and tetraphenylphosphonium salts. No chemistry of these complexes has been reported.

Experimental Section

Materials.—Molybdenum pentachloride and molybdenum tetrachloride were obtained from Research Organic-Inorganic Chemical Corp. Tetraethylammonium hydroxide was obtained from Eastman Organic Chemicals as a 10% aqueous solution. Sodium azide was reagent grade.

Chloroform and methylene chloride were continuously refluxed over calcium hydride and distilled as needed. Reagent grade ethyl ether was stored over freshly cut sodium.

Pure nitrogen or argon was obtained by passing the commercial dry gas through a 3-ft BTS[6] column and subsequently through calcium chloride and 4-A molecular sieve drying towers.

$(C_2H_5)_4NN_3$.—Tetraethylammonium azide was prepared by a method similar to that outlined by Gutmann, *et al.*[7] Hydrazoic acid, prepared in about 10% solution by passing a sodium azide solution over Amberlite IR-120 (H) ion-exchange resin, was passed directly into tetraethylammonium hydroxide until litmus paper showed the solution to be acidic. The resulting crude tetraethylammonium azide was purified by removing the water on a rotary evaporator at 100° for 10 hr and then repeated recrystallization from anhydrous chloroform. *Anal.* Calcd for $(C_2H_5)NN_3$: C, 55.80; H, 11.63; N, 32.55. Found: C, 55.08; H, 11.80; N, 30.93.

$(C_2H_5)_4NMoNCl_4$.—This complex can be prepared by the reaction of either molybdenum pentachloride or molybdenum tetrachloride with 1 equiv of tetraethylammonium azide in either chloroform or methylene chloride. For example, approximately 30 ml of anhydrous chloroform was cooled to $-78°$ and 0.515 g of $MoCl_5$ and 0.325 g of $(C_2H_5)_4NN_3$ were added. This mixture was stirred and allowed slowly to warm to room temperature over the period of 1 hr during which a yellow-brown product formed. The product was filtered, washed with anhydrous ether, and dried under vacuum for 1 hr at room temperature. *Anal.* Calcd for $(C_2H_5)_4NMoNCl_4$: C, 25.15; H, 5.23; N, 7.33; Mo, 25.11; Cl, 37.12. Found: C, 25.66, 25.74; H, 5.43, 5.32; N, 6.77, 6.44; Mo, 23.74; Cl, 37.40. The yield was 82%.

Hydrolysis of $(C_2H_5)_4NMoNCl_4$.—Typically, approximately 0.02 g of the nitrido complex was dissolved in dilute base and warmed while argon was passed over the reaction vessel into a standard sulfuric acid aliquot. The resulting sulfuric acid solution was titrated with a standard sodium hydroxide solution to determine the amount of ammonia given off. Runs averaged around 40% yield with the range of 26–50% yield.[8]

Analyses.—All analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Experimental Methods.—All reactions were carried out in inert atmospheres (dry nitrogen or argon) using standard Schlenk-tube techniques.

Magnetic Measurement.—Magnetic susceptibilities were measured by the Gouy method and corrected for diamagnetism with Pascal's constants.[9]

Spectroscopic Measurements.—The infrared spectra of the complexes were obtained by use of Nujol mulls and a Beckman IR-5A spectrophotometer and a Perkin-Elmer Model 457 spectrophotometer.

Results

Table I gives the important infrared features of the complex $(C_2H_5)_4NMoNCl_4$ and possible assignments. The magnetic moment of the complex was 0.30 BM which means the complex probably has some molybdenum(V) impurity, most likely $(C_2H_5)_4NMoOCl_4$, which would account for the low nitrogen analysis of the complex.

TABLE I
IR SPECTROSCOPIC FEATURES AND POSSIBLE ASSIGNMENTS FOR $(C_2H_5)_4NMoNCl_4$ (cm^{-1})

1400 s		915 w	
1305 s		900 w	
1182 vs	$(C_2H_5)_4N^+$	793 vs	$(C_2H_5)_4N^+$
1052 s	$\nu(M-N)$	352 vs	$\nu_s(MCl_4)$
995 vs	$(C_2H_5)_4N^+$	347 vs	$\nu_{as}(MCl_4)$
951 m			

It is felt the azide ion coordinates with molybdenum in a manner similar to nitrogen in a nitrogenase system but reacts with molybdenum in a manner similar to the predicted intermediate in nitrogen fixation $[N_2^{2-}]$. That is, azide coordinates end on and forms an initial monomeric complex with molybdenum pentachloride (A). However, the combination of a good leaving group, in molecular nitrogen, and the ability of molybdenum to form retrodative π bonds with the azide ion locally weakens the bond between the first and second nitrogen in the azide (B).[10] The result is to leave be-

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[1] G. N. Schrauzer, *Advan. Chem. Ser.*, **No. 100**, 1 (1971).

[2] R. W. F. Hardy and R. C. Burns, *Ann. Rev. Biochem.*, **37**, 331 (1968).

[3] Molybdenum(V) is thought to be present in *clostridium pasteurianum* from electron spin resonance experiments.

[4] K. Dehnicke and J. Strähle, *Z. Anorg. Allg. Chem.*, **339**, 171 (1965).

[5] W. Kolitsch and K. Dehnicke, *Z. Naturforsch. B*, **25**, 1080 (1970).

[6] A. D. Broadbent, *J. Chem. Educ.*, **44**, 145 (1967).

[7] V. Gutmann, G. Hampl, and O. Leitman, *Monatsh. Chem.*, **95**, 1034 (1964).

[8] The mildness of the hydrolysis process is thought to be an important point here and the wide range of results probably results from some ammonia not being driven from the solution. More rigorous determinations of ammonia, such as the Kjeldahl technique, are not possible because of the presence of the tetraethylammonium cation.

[9] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 403.

[10] The tendency of the metal to furnish some electron density to the antibonding π orbitals and weaken the bonding in the azide must be of some importance since a similar niobium complex $(C_2H_5)_4NNbN_3Cl_5$ has been found to be *very* stable. The $[(C_2H_5)_4N]NbN_3Cl_5$ complex can be prepared by causing equimolar amounts of $(C_2H_5)_4NN_3$ and $NbCl_5$ to react under anhydrous conditions in chloroform at room temperature. The complex is bright yellow-orange and fairly air stable. *Anal.* Calcd for $[(C_2H_5)_4N]NbN_3Cl_5$: C, 21.72; H, 4.56; N, 12.66. Found: Cl, 22.09; H, 4.67; N, 12.09.

hind the very reactive N^- (C) species, which must behave chemically very much like $[N_2^{2-}]$

$$\mathrm{Mo^{V}Cl_5} + [|\underline{\mathrm{N}}{=}\mathrm{N}{=}\underline{\mathrm{N}}|]^- \longrightarrow \underset{\mathrm{A}}{[\mathrm{Cl_5Mo^{V}}{-}\overline{\mathrm{N}}{=}\mathrm{N}{=}\underline{\mathrm{N}}|]^-}$$

$$\underset{\mathrm{B}}{[\mathrm{Cl_5Mo^{V}}{-}\mathrm{N}\cdots\mathrm{N}{\equiv}\mathrm{N}]^-} \longrightarrow \underset{\mathrm{C}}{[\mathrm{Cl_5Mo^{V}N}]^-} + \mathrm{N_2}$$

The N^- species then is reduced by molybdenum and chloride to the N^{3-} species which remains strongly coordinated to the metal

$$[\mathrm{Mo^{V}NCl_5}]^- \longrightarrow \underset{\mathrm{D}}{[\mathrm{Mo^{VI}NCl_4}]^-} + {}^1/_2\mathrm{Cl_2}$$

In the case of the reaction of molybdenum(IV) chloride with azide, a similar initial product must be formed, *i.e.*, $MoCl_4N_3^-$. However, in this case the molybdenum(IV) intermediate $MoNCl_4^-$ can go to the molybdenum(VI) intermediate of the same formula without losing chlorine since two electrons can be transferred from the metal to the nitrogen.

Hydrolysis of the nitrido complex must proceed similarly to that of intermediates proposed by Van Tamelen[11] in the fixation of nitrogen by "titanocene." Nessel's reagent gives a strong positive test for ammonia and yields were around 40%.

No end products were isolated but they must contain MoO^{4+} or MoO_2^{2+} species. It is interesting to note that the ammonia produced by the hydrolysis of the molybdenum nitrido complex does not coordinate to the molybdenum even though there is a coordination position in the nitrido complex.

Further work with other nitrido complexes is presently under way. Similar preliminary results have been found for vanadium(III) and vanadium(IV).

[11] E. E. Van Tamelen, *Accounts Chem. Res.*, **3**, 361 (1970).

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Rearrangement of Dimethylchloromethylborane with Nucleophiles

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Previous work from this laboratory reported[1] that treatment of dimethylchloromethylborane (I) with water or lithium azide yields hydroxymethyldimethylborane and azidomethyldimethylborane, respectively. It was also reported that catalytic hydrogenation of the product from the reaction of I with lithium azide yields aminomethyldimethylborane. We have found that these compounds were incorrectly formulated and that the actual structures are ethylated trigonal boranes, $XB(CH_3)C_2H_5$, with the substituent bonded to boron. These arise from an alkyl rearrangement similar to those encountered by other workers.[2,3] Further, isomerization of I in the presence of $SbCl_5$ leads cleanly to methylethylboron chloride (II). In order to clarify the earlier results, the reactions of I and II with several nucleophiles were studied.

Experimental Section

Apparatus and Materials.—All reactions were performed using standard high-vacuum techniques described elsewhere.[4] The ^1H nmr spectra were recorded on a Varian Associates A-60 or HR-220 spectrometer. The ^{11}B nmr spectra were measured on a Varian Associates HA-100 spectrometer at 32.1 MHz. Mass spectra were measured on a Varian Associates MAT CH-7 mass spectrometer. Dimethylamine, trimethylamine, and methyl mercaptan were purchased from the Matheson Co. in cylinders and used without further purification. Lithium azide (Eastman) was dried under vacuum. Dimethylarsine, dimethylphosphine, trimethylphosphine, and dimethylchloromethylborane were prepared by literature procedures.[5-7]

Preparations.—In a typical reaction I or II (1.5–3.0 mmol) and a nucleophile were sealed into a Pyrex tube equipped with a break-seal. Equimolar quantities of reactants were used in all cases except for the reactions of I with dimethylamine or potassium iodide wherein twofold and tenfold excesses of nucleophile were used, respectively. After reaction the tube was opened to a vacuum line and the products were separated by trap to trap distillation or fractional sublimation. Reaction conditions and products are summarized in Table I.

Table I

Reaction Conditions and Product Data

Reactants	Reaction conditions	Product	Yield, %	0° vapor pressure, mm
I + $(CH_3)_2NH$	*a*	$CH_3(C_2H_5)BN(CH_3)_2$	89	14
I + CH_3OH	*a*	$CH_3(C_2H_5)BOCH_3$	84	67
I + SbF_3	*a*	$CH_3(C_2H_5)BF$	91	21[e]
I + $SbCl_5$	*a*	$CH_3(C_2H_5)BCl$	98	115
I + KI	*b*	$(CH_3)_2BCH_2I$	40	11
I + $(CH_3)_2PH$	*c*	$(CH_3)_2BCH_2P(CH_3)_2$	62	*f*
I + $(CH_3)_2AsH$	*c*	$(CH_3)_2BCH_2As(CH_3)_2$	68	*f*
I + CH_3SH	*c*	$(CH_3)_2BCH_2SCH_3$	80	*f*
II + LiN_3	*d*	$CH_3(C_2H_5)BN_3$	94	4
II + H_2O	*a*	$CH_3(C_2H_5)BOH$	90	16

[a] At 80° for 30 min. [b] At 0° for 60 min; acetone solvent. [c] At 100° for 90 min. [d] At 50° for 180 min. [e] At −63°. [f] Solid of low vapor pressure.

Results and Discussion

Treatment of I with nucleophiles yields B-substituted methylethylboranes by alkyl rearrangement or α-substituted methylboranes without rearrangement. The methylethylboranes were identified by comparison of their proton and boron chemical shift values (Table II) with those of analogous dimethyl- and diethyl-substituted boranes. In all cases agreement was found with literature values.[8] The rearranged compounds were also identified by their mass spectral fragmentation patterns. Intense peaks at masses corresponding to CH_3BX and C_2H_5BX fragments (where X is derived from the nucleophile) occurred as expected in each case. Supporting chemical evidence for the rearranged structures of the azido-[9] and hydroxo-substituted boranes is given by their preparations from either I or II.[10] The proton nmr spectra (Table II) of the α-substituted

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[1] R. Schaeffer and L. J. Todd, *J. Amer. Chem. Soc.*, **87**, 488 (1965).

[2] H. Jagger and G. Hesse, *Chem. Ber.*, **95**, 345 (1962).

[3] D. S. Matteson and R. W. H. Mah, *J. Amer. Chem. Soc.*, **85**, 2599 (1963).

[4] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, N. Y., 1948.

[5] R. D. Feltham and W. Silverthorn, Inorg. *Syn.*, **10**, 160 (1967).

[6] G. W. Parshall, *ibid.*, **11**, 157 (1968).

[7] L. Zeldin and P. R. Girardot, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 15N.

[8] H. Noth and H. Vahrenkamp, *J. Organometal. Chem.*, **12**, 23 (1968).

[9] The previously reported aminoo compound was prepared from this azide and is therefore also rearranged.

[10] Hydrogen peroxide causes rearrangement of I prior to oxidation and therefore is not a useful reagent for distinguishing rearranged and unrearranged structures.