that the rapid second reaction is also a two-electron change. The failure of 1,4-dibromocyclohexane to yield any product other than the monorhodium adduct **2** (R = 4-bromocyclohexyl, X = Br) implies a cyclic intermediate in this neighboring group effect.

As far as we are aware, such a neighboring group effect by a d^6 center is unparalleled.[11] Experiments are in progress to further explore this remarkable effect.

Acknowledgment. This work was supported by the National Science Foundation grant GP20273X. We are indebted to J. Brauman for helpful discussions.

(11) An electrophilic neighboring group effect has been observed over *five* carbons: R. K. Summerbell and S. R. Forrester, *J. Org. Chem.*, **26**, 4834 (1961); P. E. Peterson, D. R. Bonazza, and P. M. Herichs, *J. Amer. Chem. Soc.*, **95**, 2222 (1973). A referee has brought to our attention a report of a similar result in the reaction between vitamin B_{12} and $Br(CH_2)_4Br$: E. L. Smith, L. Mervyn, and P. W. Muggleton, *Ann. N. Y. Acad. Sci.*, **112**, 565 (1964).

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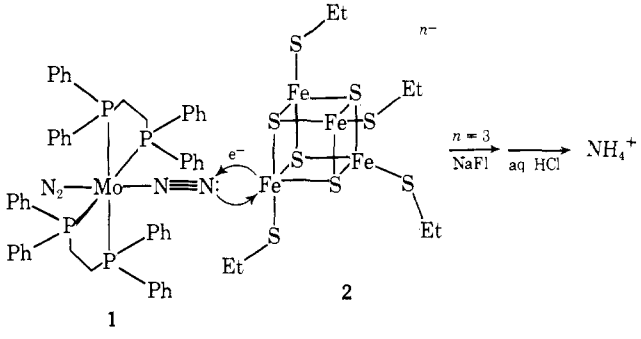
Biological and Abiological Nitrogen Fixation by Molybdenum-Bound N_2/4Fe–4S Cluster Systems

Sir:

Through study of the Mo–$^{15}N_2$ coordination compound **1**[1] and a new ferredoxin model, the 4Fe–4S cluster **2**,[2] we have discovered a biogenetic-type reaction



1 2

in which the cluster and reducing agent produce $^{15}NH_3$ from **1**, apparently by direct action on the N_2 ligand. This abiological reaction, although proceeding in small yield, is novel and carries distinct implications for the chemical nature of the biological N_2 fixation process.

In order to identify the particular reduced 4Fe–4S cluster species involved in the N_2 fixation process, the redox properties of the bis(tetrabutylammonium) salts were delineated by cyclic voltammetry.[3a] A reversible one-electron reduction of 2^{2-} to 2^{3-} was observed [CH_3CN, $E_{1/2}$ = −1.30 V *vs.* saturated calomel electrode (sce); DMSO, −1.28 V; 1-methyl-2-pyrrolidinone (NMP), −1.31 V]. Continued cathodic scanning revealed further conversion to 2^{4-}, which was completely reversible in NMP (−1.96 V).[3b] Irreversible oxidation of 2^{2-} was noted near −0.10 V on anodic sweeps.

For chemical generation of the 2^{n-} entities needed for fixation experiments, a series of homogeneous radical anion reductants were auditioned (standard oxidation potentials in 1,2-dimethoxyethane *vs.* sce):[4] sodium naphthalene (NaNp, 2.60 V), sodium phenanthrene (NaPh, 2.48 V), sodium pyrene (NaPy, 2.10 V), sodium anthracene (NaAn, 1.98 V), sodium fluoranthene (NaFl, 1.77 V), and sodium acenaphthylene (NaAc, 1.65 V). As inferred from the redox potentials and as evidenced by potentiometric and/or chemical data, stoichiometric amounts of NaNp or NaPh converted 2^{2-} completely to 2^{4-}. With NaPy or NaAn an equilibrium mixture of 2^{3-} and 2^{4-} was formed, while NaFl or NaAc served only to generate 2^{3-}. The reductions were carried out both in THF, in which 2^{3-} and 2^{4-} showed partial solubility, or under completely homogeneous conditions in NMP.[5]

As to the effect of a 4Fe–4S cluster itself, we note that 2^{2-}, 2^{3-}, and 2^{4-} separately and *per se* fail to produce NH_3 from excess or stoichiometric amounts of N_2 in THF.[6] Fixation experiments with 2^{3-} and 2^{4-} were also carried out by starting with THF suspensions of 2^{2-}, saturated and blanketed with $^{14}N_2$ or $^{15}N_2$, to which were added *ca.* 200 equiv of the desired radical anion. Yields (mol of NH_3/mol of 2^{2-}) thus obtained (NaNp, 0.275; NaPh, 0.163; NaPy, 0.015–0.000; NaAn, NaFl, NaAc, 0.000) reveal the involvement of 2^{4-} in the overall fixation process and the inability of 2^{3-} to fix excess N_2 under any conditions assayed.[7] Similarly, $^{15}N_2$ or ^{15}N-labeled **1** is converted by [$Fe_4S_4(S_2C_2Ph_2)_4$] (**3**) and *ca.* 200 equiv of NaNp to $^{15}NH_3$.[8] However, no $^{15}NH_3$ is produced from $^{15}N_2$ or ^{15}N-labeled **1** in the presence of 2 equiv of **3** pretreated with only 8–16 equiv of NaNp. Even in the presence of O_2, cluster 2^{4-} and excess NaNp effect NH_3 formation (0.070–0.120 mol) from free N_2.

In the multicomponent reaction, a 100 ml THF suspension of 0.03 mmol ^{15}N-labeled **1** and 0.45 mmol 2^{3-} was allowed to react for 12 hr under argon, after which 9 mmol of NaFl in 50 ml of THF was added. After

(1) (a) Prepared according to T. A. George and C. D. Seibold, *J. Organometal. Chem.*, **30**, C13 (1971), and labeled by subsequent exchange with $^{15}N_2$. (b) Structure: T. Uchida, Y. Uchida, M. Hidai, and T. Kodama, *Bull. Chem. Soc. Jap.*, 44, 2883 (1971).

(2) (a) Preparation: B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 3523 (1973). (b) X-Ray structure of $-SCH_2C_6H_5$ homolog: T. Herskovitz, B. A. Averill, R. H. Holm, J. H. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2437 (1972).

(3) (a) Measurements were conducted at room temperature at sweep rates from 60 to 220 mV/sec in 0.1 *M* tetraethylammonium perchlorate solutions using a Pt button indicator electrode. (b) Peak separations for the couples $2^{2-} \rightleftharpoons 2^{3-}$ and $2^{3-} \rightleftharpoons 2^{4-}$ were identical and the ratio of anodic to cathodic currents one, within experimental error.

(4) Prepared by mixing equimolar quantities of sodium and the hydrocarbon in THF. For the oxidation potential measurements, see G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, *Recl. Trav. Chim. Pays-Bas*, 75, 487 (1956).

(5) (a) Reduction of 2^{2-} with excess Na sand followed by filtration was found to be a superior procedure for the production of NMP solutions of 2^{4-}. (b) All fixation experiments employed the bis(tetraphenylarsonium) 2^{2-} species as starting material.

(6) (a) All experiments were conducted at room temperature for 12 hr to 3 days in a closed creased flask in which the appropriate blanketing gas continually recirculated through the reaction mixture. For design and details, see J. A. Gladysz, Ph.D. Thesis, Stanford University, 1974, in preparation. (b) All $^{14}N_2$ experiments were worked up as described in ref 8, employing a Kjeldahl-type distillation–titration followed by, after reconcentration of the sample, either a potentiometric determination using an Orion Model 95-10 NH_3 gas electrode or colorimetric analysis with Nessler's reagent. (c) Yields of $^{15}NH_4Cl$ were determined by cocrystallization with natural abundance NH_4Cl prior to the Kjeldahl work-up, followed by conversion to N_2 with alkaline NaOBr and precise mass spectrometric measurement of the $^{29}(N_2)/^{28}(N_2)$ peak ratio.

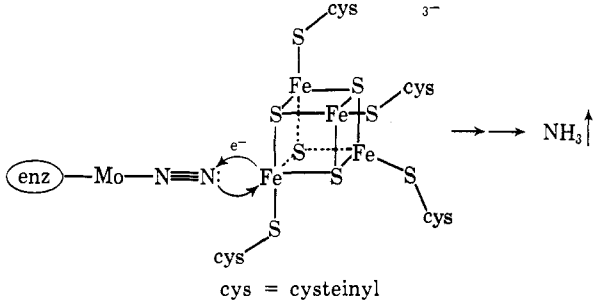
(7) (a) Gas absorption was noted in experiments with NaNp but not NaFl; upon titration of 2^{2-} with NaNp uptake usually commenced near the third equivalent added. Exhaustive controls have established that the cluster decomposition products formed in the presence of large excesses of NaNp are inactive in the fixation process. (b) Identical behavior was observed with $(Ph_4As)_2[Fe_4S_4(SCH_2C_6H_5)_4]$ in this type of experiment with NaNp. (c) Hydrazine was not observed in these or any other experiments.

(8) E. E. van Tamelen, J. A. Gladysz, and J. S. Miller, *J. Amer. Chem. Soc.*, **95**, 1347 (1973).

12 hr more, the reaction mixture was worked up, and $^{15}NH_3$ yields were determined mass spectrometrically (up to 0.012 mol/mol of **1**).[6c] In additional experiments involving 2^{3-} and **1**, yields of $^{15}NH_3$ produced through use of NaAc fell at much lower levels, and the stronger reducing agents NaAn and NaPy were even less effective. No $^{15}NH_3$ was generated by the action of NaAc, NaFl, NaAn, NaPy, 2^{2-}, 2^{3-}, or 2^{4-} alone on $^{15}N_2$ labeled **1**, but NaNp was effective, even in only a sixfold excess. When unlabeled, $^{14}N_2$ **1** was employed in various fixation experiments, larger (0.02–0.04 mol/mol of **1**) NH_3 yields were sometimes generated, presumably a consequence of an impurity present in the preparation of **1** utilized,[9,10]

In order to compare more fully with the biological N_2-fixation system, the action of 2^{n-} on nitrogenase substrates other than N_2 was studied. Whereas the enzyme converts alkyl cyanide to hydrocarbon,[11] 2^{2-}, 2^{3-}, and 2^{4-} were without action on this organic species. However, as in the biological system, 2^{3-} and 2^{4-} converted isocyanide ($C_{12}H_{25}NC$) to amine ($C_{12}H_{25}NH_2$) and 2^{4-} reduced alkyne (decyne-1) to alkene (decene-1, accompanied by some decyne-2). Interestingly, Δ^2-nonenylnitrile was also transformed by 2^{4-} in smaller yield to decene-1.

The body of results herein clearly points to the unique role of 2^{3-} in the abiological fixation of Mo-bound N_2. Assuming direct interaction of **1** and **2**, we believe it likely that the Mo-bound N_2 unit interacts at a corner of the cluster cube (as depicted), especially because of the available Fe coordination sites.[12] Whether the lone electron pair or the π-electrons (or both) of the N_2 ligand are involved in this binding cannot be said at this time. The subsequent radical anion reduction of Mo–Fe bound N_2 may be coordinated with electron transfer from 2^{3-}, possibly facilitated by involvement of the sulfide and/or mercaptide ligands. The biological relevance of these laboratory reactions is underscored by the electronic and structural identity of 4Fe–4S cubic cores in the reduced bacterial ferredoxins and these synthetic 2^{3-} systems.[2] Assuming that nature can avail itself of a chemical pathway of the type described herein, we propose that the enzymic N_2 fixation reaction proceeds as shown below.



cys = cysteinyl

(9) In the molybdenum series, the reported formation of $^{14}NH_3$ resulting from the action of 2 equiv of **3** pretreated with 8–16 equiv of NaNp[8] may be due to the presence of a non-nitride contaminant (reducible to the NH_3 level but not subject to $^{15}N_2$ exchange) generated during the preparation of **1**.[1]

(10) Lecture, 24th Congress of the International Union of Pure and Applied Chemistry, Hamburg, Sept 4, 1973.

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(13) National Science Foundation Fellow, 1971–1974.
(14) Deutsche Forschungsgemeinschaft Fellow, 1973.

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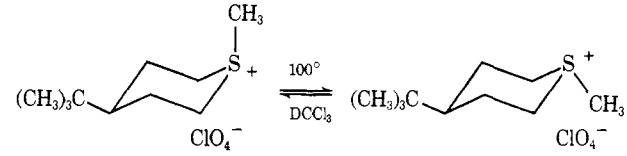
Conformational Equilibrium in *S*-Methylthianium Perchlorate

Sir:

The energy difference between equatorial and axial methyl in methyl-substituted cyclohexanes was determined very early in the development of conformational analysis and with high accuracy;[1,2] the equatorial conformation is preferred by 1.7 ± 0.1 kcal/mol in the liquid phase. For some time thereafter it was believed that equatorial substituents were, quite generally, more stable than axial ones; one of the earliest findings to dispel this notion was the discovery[3] that the preferred conformation in thiacyclohexane sulfoxide is the one with axial oxygen ($\Delta G°$ = 0.2–1.3 kcal/mol).[3] In recent years, quite a number of cases of preferential stability of axial conformations have come to light;[4] most of these involve heteroatoms as one of the interacting partners. One that does not and yet lacks equatorial preference of the methyl group is *P*-methylphosphacyclohexane in which $\Delta G°$ for the *P*-methyl group is near zero.[5] In contrast, it has been reported[6] that in thiacyclohexylmethylsulfonium salts the *S*-methyl group is largely equatorial; this claim is, however, based on possibly unsafe considerations of geminal coupling constants of the protons at C(2) and C(6).

Since, in connection with another problem,[7] we were vitally interested in the *S*-methylthianium equilibrium, we decided to synthesize the model 4-*tert*-butyl compounds (**1** and **2**) shown in Scheme I and to study their equilibration. The salts were easy to prepare in a *ca.*

Scheme I



(1) E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **39**, 173 (1947).
(2) *Cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley-Interscience, New York, N. Y., 1965.
(3) C. B. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **86**, 2935 (1964); **87**, 1109 (1965); J. C. Martin and J. J. Uebel, *ibid.*, **86**, 2936 (1964); J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).
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