10. The chemical composition of antigorite from rock sample Mg159c (in percent by weight) is: SiO_2, 43.32; Cr_2O_3, 0.23; Al_2O_3, 1.30; Fe_2O_3, 0.50; FeO, 2.59; MnO, 0.04; MgO, 39.62; NiO, 0.08. The x_{Mg} (= molar MgO/MgO+FeO) = 0.965; $x_{Fe^{3+}}$ (= molar Fe^{3+}/Fe_{tot}) = 0.15 (determined by Mössbauer spectroscopy).
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Dinitrogen Cleavage by a Three-Coordinate Molybdenum(III) Complex

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Cleavage of the relatively inert dinitrogen (N_2) molecule, with its extremely strong N≡N triple bond, has represented a major challenge to the development of N_2 chemistry. This report describes the reductive cleavage of N_2 to two nitrido (N^{3-}) ligands in its reaction with $Mo(NRAr)_3$, where R is $C(CD_3)_2CH_3$ and Ar is $3,5-C_6H_3(CH_3)_2$, a synthetic three-coordinate molybdenum(III) complex of known structure. The formation of an intermediate complex was observed spectroscopically, and its conversion (with N≡N bond cleavage) to the nitrido molybdenum(VI) product $N{\equiv}Mo(NRAr)_3$ followed first-order kinetics at 30°C. It is proposed that the cleavage reaction proceeds by way of an intermediate complex in which N_2 bridges two molybdenum centers.

The relatively inert dinitrogen molecule (N_2) composes 78% of the Earth's atmosphere; the development of this molecule's chemistry is clearly desirable if this immense natural resource is to be utilized optimally. In this regard, the discovery of mild methods for scission of the N≡N triple bond represents a major challenge. Although the metalloenzyme nitrogenase constitutes a unique biological nitrogen-fixing system (*1*) and the Haber-Bosch ammonia synthesis is an example of industrial nitrogen fixation (*2*), little molecular-level detail is available concerning the critical N_2 cleavage processes operative for either of these processes. Well-characterized synthetic systems capable of splitting N_2 have been elusive (*3*), despite the multitude of known transition-metal complexes containing intact dinitrogen as a ligand (*4*). In connection with a study on cleavage of the N–N bond in nitrous oxide (N_2O), Laplaza *et al.* reported (*5*) the synthesis and structural characterization of the three-coordinate Mo(III) complex $Mo(NRAr)_3$ [**1**, where R = $C(CD_3)_2CH_3$ and Ar = $3,5-C_6H_3Me_2$ (Me, methyl), Fig. 1]. We now report the reductive scission of N_2 to two N^{3-} ligands in its reaction with **1**. The reaction occurs in hydrocarbon solution at low temperatures (−35° to 30°C) and pressures (1 atm).

Purification of red-orange **1** consisted of recrystallization under an Ar atmosphere (ethyl ether, 0.1 M, −35°C). When we attempted to purify **1** by recrystallization under an atmosphere of N_2, the solutions (ethyl ether, 0.1 M, −35°C) took on an intense purple color in less than 45 min. Examination of the purple solutions by ^2H nuclear magnetic resonance (NMR) spectroscopy (*6*) revealed that the signal at 64 parts per million (ppm) for **1** was being replaced by a single new peak at 14 ppm, attributable to the purple species (**2**, Fig. 2). When we carried out the reaction using pure **1** in toluene (leaving all other conditions unchanged), from which the complex crystallizes less readily, complete conversion to **2** took approximately 48 hours at −35°C. On warming to 30°C, the purple solutions of **2** gradually became gold and lost their paramagnetism. Removal of all volatile material in vacuo left an amber crystalline residue that dissolved readily in benzene-d_6 for ^1H NMR spectroscopic analysis. The ^1H NMR spectroscopy showed that a terminal nitrido Mo(VI) complex (**3**, Fig. 2), identical to the complex that we isolated

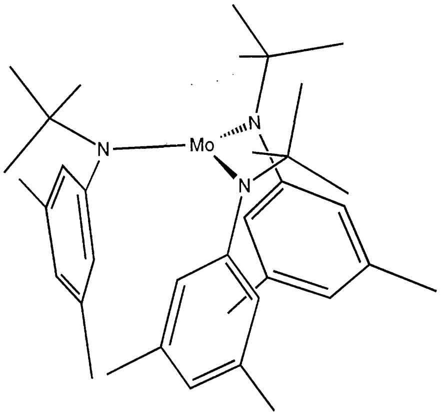

Fig. 1. Line drawing of the molecular structure of $Mo(NRAr)_3$ (**1**). The structure of **1** was determined by x-ray crystallography (*5*).

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and characterized in conjunction with our N_2O study (*5*), had formed in essentially quantitative yield.

In a preparative-scale experiment, the nitrido complex **3** was isolated in 76% recrystallized yield from the reaction of **1** (300 mg in 6 ml of toluene) with N_2 (1 atm) and was identical in all spectroscopic and physical properties to samples of **3** prepared by other means (*7*). To verify unequivocally that the source of the nitrido nitrogen atom was indeed N_2, we carried out the procedure under $^{15}N_2$ (1 atm). Infrared spectroscopy showed that $^{15}N{\equiv}Mo(NRAr)_3$ (**3**-^{15}N, frequency $\nu_{Mo\equiv{}^{15}N}$ = 1014 cm^{-1}) formed to the exclusion of unlabeled **3** ($\nu_{Mo\equiv N}$ = 1042 cm^{-1}), and a signal for **3**-^{15}N was located at +840 ppm in the ^{15}N NMR [with reference (*8*) to external nitromethane at +380.2 ppm]. Identical spectral properties were found for **3**-^{15}N prepared independently (*5*) by treatment of **1** with selectively labeled $^{15}NNN(p\text{-}C_6H_4Me)$.

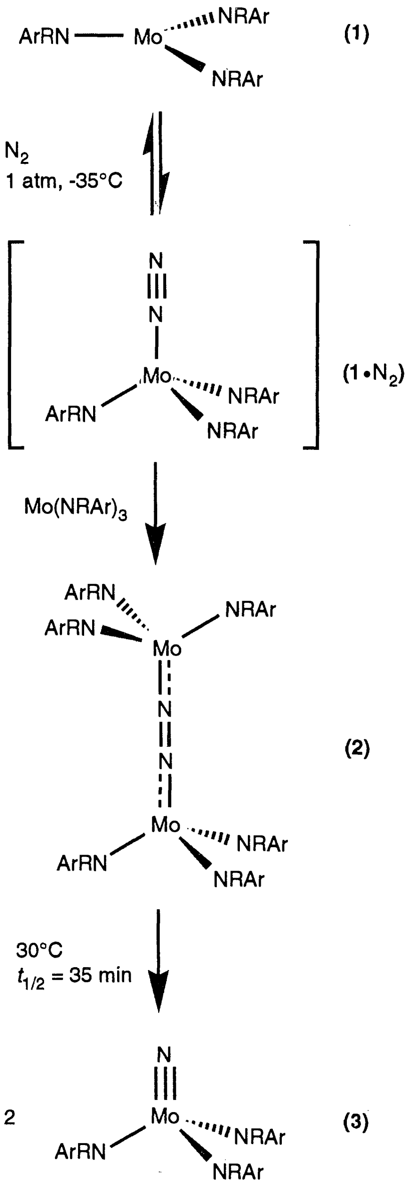

Fig. 2. Proposed sequence of reactions for the conversion of $Mo(NRAr)_3$ (**1**) to $N{\equiv}Mo(NRAr)_3$ (**3**) in the presence of N_2 by way of the intermediate complex **2**; $t_{1/2}$ is the half-life for the conversion of **2** to **3**.

A reasonable supposition is that the purple intermediate **2** is a dimolybdenum complex with a bridging dinitrogen ligand, as depicted in Fig. 2. Schrock and coworkers have observed the formation of purple paramagnetic dinuclear dinitrogen complexes containing Mo(III) in a triamidoamine coordination environment and have verified their structural assignment by x-ray crystallography in one case (*9*). Symmetry considerations (*10*) indicate that dinuclear systems of this sort should be paramagnetic, with the two unpaired electrons located in a degenerate pair of delocalized Mo–N–N–Mo π orbitals. As yet we have been unable to isolate purple **2** to verify its structure by x-ray crystallographic means, in part because of its thermal instability with respect to **3**.

The formation of purple **2** appears to proceed more rapidly at −35°C than at room temperature (~28°C); solutions of **1** (ethyl ether, 0.1 M) do not turn purple when stored under N_2 (1 atm) at room temperature for 2 to 8 hours, and conversion to **3** is not appreciable (≤5%) under these conditions. The more rapid N_2 uptake at −35°C is likely to be a manifestation of the greater solubility of N_2 in organic solvents with decreasing temperature (*11*), which would lead to greater equilibrium concentrations of a mononuclear N_2 adduct $(N_2)Mo(NRAr)_3$ (**1**•N_2), the logical immediate precursor to **2**. Because the conversion of dinuclear **2** to nitrido **3** could be monitored by ^{2}H NMR, we were able to verify that the disappearance of **2** at 30°C is a first-order process [rate constant k = (3.32 ± 0.13) × 10^{-4} s^{-1}; four runs]. This result is expected for direct dissociation of a dimeric entity into two monomeric units, as postulated in Fig. 2 (**2** → **3**). The rate constant at 30°C for conversion of **2**-$^{15}N_2$ to **3**-^{15}N was indistinguishable [k = (3.16 ± 0.32) × 10^{-4} s^{-1}; four runs] from the value for unlabeled **2**.

Four-coordinate molybdenum nitrido complexes have been known for some time (*12*), and the tris(amido) molybdenum nitrido complex $N{\equiv}Mo(NPh_2)_3$ (Ph = phenyl), closely related to **3**, has been shown by x-ray crystallography to be monomeric in the solid state (*13*). It is thought that the M≡N triple bond is one of the strongest metal-ligand bonds (*14*), and its formation clearly provides the thermodynamic driving force for the N_2 cleavage reaction elucidated here. A lower limit for the Mo≡N dissociation enthalpy of ~472 kJ mol^{-1} is suggested by the overall transformation **1** + 0.5 N_2 → **3**, in view of the enthalpy of dissociation of N_2 (944 kJ mol^{-1}) (*15*). Monomeric $Mo(NRAr)_3$ (**1**) is formally related to the well-known dimeric Mo(III) complexes $X_3Mo{\equiv}MoX_3$ (X = alkyl, amide, alkoxide), which have unbridged metal-metal triple bonds (*16*). Severe steric constraints (see Fig. 1) apparently render **1** immune to dimerization, endowing the complex with the stored energy required for the observed reactivity toward N_2.

Our work establishes the reductive cleavage of N_2 to two nitrido (N^{3-}) ligands, mediated by a soluble transition-metal complex of known structure. This system has permitted a spontaneous transition-metal–mediated N_2 cleavage process (**2** → **3**) to be studied (*17*, *18*).

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7. We conducted the preparative-scale reaction between **1** and N_2 by storing the toluene solution of **1** at −35°C for about 76 hours. The reaction's progress was monitored occasionally by ^{2}H NMR. When conversion to **2** was judged complete, the reaction mixture was allowed to warm to room temperature (~28°C) over a period of 5 hours, during which time the mixture turned amber. Analysis by ^{1}H NMR revealed that the nitrido complex **3** had formed cleanly. This complex was recrystallized from ethyl ether at −35°C. Because $Mo(NRAr)_3$ (**1**) is extremely sensitive to air and water, in all experiments involving **1** we used appropriately dried and deaerated solvents. The nitrido complex **3** is less sensitive to air and water and may be handled for brief periods in the air without extensive decomposition.
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18. In our investigations of the N_2 cleavage reaction, we are attempting to isolate and investigate the intermediates depicted in Fig. 2.
19. Financial support for C.C.C. was provided by the Department of Chemistry of the Massachusetts Institute of Technology (MIT) and for C.E.L. by the MIT Undergraduate Research Opportunities Program. C.C.C. thanks R. R. Schrock for many stimulating discussions.

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CD1 Recognition by Mouse NK1$^+$ T Lymphocytes

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Rare major histocompatibility complex (MHC) class I–like CD1-specific T cells have been isolated from human blood, but it has not been determined whether these clones are part of a defined subset of CD1-specific T cells selected during T cell development, or whether their recognition of CD1 is a fortuitous cross-reaction. In mice, an entire subset of αβ thymocytes with a unique phenotype was found to be CD1-specific. This particular subset, and its human counterpart, provide evidence that CD1 has a general role in selecting and interacting with specialized αβ T cells.

Mouse NK1$^+$ T cells constitute up to 20% of the mature compartment of the thymus and are also found in most peripheral tissues, with particular frequency in bone marrow and liver (*1–7*). They consist of CD4$^+$ and CD4$^-$8$^-$ double-negative (DN) cells. Unlike other T cells, NK1$^+$ T cells express the surface receptors normally associated with natural killer (NK) cells, including NKR-P1 and Ly-49, and they can lyse NK-sensitive target cells (*8*). In addition, they have the unique ability to secrete large amounts of cytokines, especially interleukin-4 (IL-4), upon primary stimulation through their αβ T cell receptors (TCRs) in vitro (*1, 5, 7*) and in vivo (*9*). Because this secretion of IL-4 is rapid, NK1$^+$ T cells are likely to promote the differentiation and recruitment of T helper 2 (T_H2) cells over T_H1 cells in immune responses in which they are engaged (*10*). Elucidating the contribution of these specialized T cells thus depends on the identification of their TCR ligands.

Several findings have suggested that the ligand is a nonpolymorphic MHC class I molecule that is conserved in different species. First, thymic selection of NK1$^+$ T cells depends on the expression of β_2-microglobulin (β_2M) (*2, 4*) and thus, by implication, on the expression of class I molecules. Second, the TCR repertoire of both CD4$^+$ and DN NK1$^+$ T cells is largely restricted to TCRs comprising a single, invariant TCRα chain, $V_\alpha14$-$J_\alpha281$, paired with $V_\beta8$, $V_\beta7$, or $V_\beta2$ TCRβ chains (*11*). Third, the same TCR repertoire exists in different strains of mice, regardless of MHC haplotype (*11*). Fourth, a human counterpart to this subset exists that uses TCRs comprising an invariant TCRα chain, $V_\alpha24$-$J_\alpha Q$ (the homolog of mouse $V_\alpha14$-$J_\alpha281$), paired with $V_\beta11$ TCRβ chains (homologs of mouse $V_\beta8$) (*11, 12*).

A clue to the identity of the NK1$^+$ T cell ligand is the ligand's tissue distribution. Expression of β_2M on bone marrow–derived cells, but not on thymic epithelium, enables thymic selection of NK1$^+$ T cells (*2, 4*). The relevant bone marrow–derived cell is probably a thymocyte rather than a dendritic cell or macrophage, because mice with severe combined immunodeficiency disease that were inoculated with β_2M-deficient fetal liver cells did not generate NK1$^+$ T cells (although they developed mainstream T cells), even though their thymic dendritic cells were largely β_2M-positive (*13*). In addition, NK1$^+$ T cells induce cytolysis of cortical thymocytes (*14*). These findings suggest that immature thymocytes express the NK1$^+$ T cell ligand, whereas thymic epithelial cells and professional antigen-presenting cells (APCs) do not. This pattern fits that of the *TL* and *CD1* gene families, which, in contrast to classical MHC class I molecules, are mainly expressed by immature CD4$^+$8$^+$ thymocytes (*15, 16*).

Table 1. Recognition of an MHC class I ligand by DN32.D3, a NK1$^+$ T cell–derived hybridoma. Duplicate samples of DN32.D3 hybridoma cells (3 × 10^4) were cultured with 5 × 10^5 cells from the thymus, spleen, or bone marrow of the indicated mouse strains in 96-well flat-bottom microplates for a period of 20 to 24 hours. IL-2 released in the supernatant was measured in units per milliliter, where 1 U/ml corresponds to 3 pM recombinant human IL-2 as measured by CTLL indicator cells (*1*). Mean values for duplicate samples are given. Standard errors were less than 20% of this value. Purified F23.2 mAb to $V_\beta8.2$ was used at 1 μg/ml, versus the same concentration of 28.8.6S, an isotype-matched mAb to H-2K^{b}D^b. These results were confirmed in two to five separate experiments.

Tissue source	Stimulator cell strains and IL-2 production (U/ml)				
	B6	B10.A	BALB/c	129	B6.β_2M^{-}*
		Experiment 1			
Thymus	27	20	44	32	<1
		Experiment 2			
Thymus + anti-H-2K^{b}D^b mAb	32				
Thymus + anti-$V_\beta8.2$ mAb	<2				
		Experiment 3			
Thymus	29				
Spleen	0.5				
Bone marrow	0.2				

*B6.β_2M$^-$ mice bear a homozygous inactivation of their gene encoding β_2M and were backcrossed eight times to C57BL/6.

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