Nitrogen Atom Transfer Coupled with Dinitrogen Cleavage and Mo−Mo Triple Bond Formation

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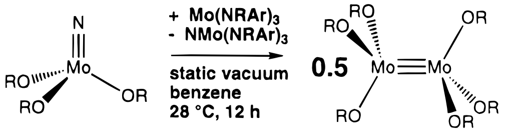
In principle, catalytic dinitrogen fixation[1] could be achieved by combining known dinitrogen cleavage[2] and intermetal nitrogen atom transfer[3] reactions in a single system. This would solve "the problem of regenerating the molybdenum(III) starting material to make a cyclic system".[4] In this report, we describe the first prototype of such a system. We show that the recently-reported[2] cleavage of dinitrogen by three-coordinate $Mo(NRAr)_3$ [R = $C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_3Me_2$, Figure 1, giving the terminal nitrido complex $NMo(NRAr)_3$,[5] is accelerated in the presence of Chisholm's[6] nitrido complex $NMo(OR)_3$ [R = $C(CH_3)_3$].

In the absence of dinitrogen (eq 1), $Mo(NRAr)_3$ reacts with $NMo(OR)_3$, giving $NMo(NRAr)_3$ along with 0.5 equiv of the known[7] dimer $Mo_2(OR)_6$. This reaction (benzene, 28 °C) is essentially quantitative (as determined by ^1H and ^2H NMR) and is complete in under 12 h. It was possible to separate $Mo_2(OR)_6$ and $NMo(NRAr)_3$ via fractional crystallization at −35 °C. Obtained as red-orange needles, a sample of dimer $Mo_2(OR)_6$ was characterized by elemental analysis, by EIMS, and by comparison of its ^1H and ^{13}C NMR spectra with those extant in the literature.[7] These results establish facile N atom transfer from $NMo(OR)_3$ to $Mo(NRAr)_3$ and demonstrate that the reaction can be coupled with Mo−Mo triple bond formation.



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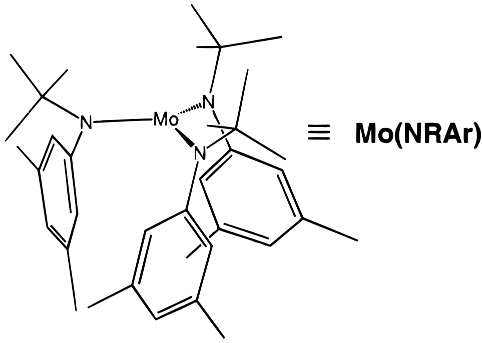
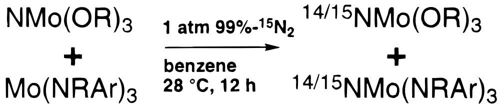


Figure 1. Reprinted with permission from ref 2. Copyright 1995 American Association for the Advancement of Science.

Under 1 atm of dinitrogen, the reaction of $Mo(NRAr)_3$ with $NMo(OR)_3$ (benzene, 28 °C, 3.5 mM in both metal complexes) again led to quantitative formation of nitrido $NMo(NRAr)_3$, a process requiring ∼6 h to reach completion. ^1H NMR analysis showed that under these conditions, only a small amount (∼7%) of dimer $Mo_2(OR)_6$ was produced. Pure $NMo(OR)_3$ was recovered via fractional crystallization in 74% yield, while pure $NMo(NRAr)_3$ was isolated in 83% yield. Control experiments show that the reaction of $Mo(NRAr)_3$ (benzene, 28 °C, 3.5 mM) with dinitrogen (1 atm) to give $NMo(NRAr)_3$ is quite slow, proceeding only to ≤5% in 12 h.[8] Thus, $NMo(OR)_3$ accelerates the reaction of $Mo(NRAr)_3$ with dinitrogen.

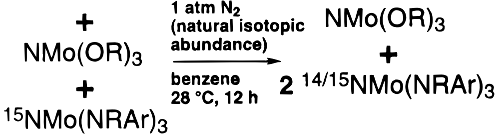
The reaction of $Mo(NRAr)_3$ with $NMo(OR)_3$ (benzene, 28 °C, 3.5 mM in both metal complexes) under an atmosphere of 99% $^{15}N_2$ was carried out next to substantiate dinitrogen cleavage (eq 2). The nitrido products $^{14/15}NMo(NRAr)_3$ and



$$\begin{matrix} NMo(OR)_3 \\ + \\ Mo(NRAr)_3 \end{matrix} \xrightarrow[\text{benzene}\\ 28\ ^\circ\text{C, 12 h}]{\text{1 atm 99\%-}^{15}\text{N}_2} \begin{matrix} ^{14/15}NMo(OR)_3 \\ + \\ ^{14/15}NMo(NRAr)_3 \end{matrix} \qquad (2)$$

$^{14/15}NMo(OR)_3$ (respectively 43% and 42% ^{15}N by EIMS) were separated and purified via fractional crystallization. IR[9] and ^{15}N NMR[10] spectroscopic data obtained for $^{14/15}NMo(NRAr)_3$ and $^{14/15}NMo(OR)_3$ were consistent with the level of ^{15}N-enrichment indicated by EIMS. Formation of a small amount (∼7% by ^1H NMR) of dimer $Mo_2(OR)_6$ in this reaction accounts for the less-than-quantitative (∼85%) incorporation of ^{15}N into the nitrido functions of $^{14/15}NMo(NRAr)_3$ and $^{14/15}NMo(OR)_3$.

To test for reversibility of N atom transfer, we investigated the reaction of $Mo(NRAr)_3$ with $NMo(OR)_3$ (benzene, 28 °C, 3.5 mM in both metal complexes) in the presence of $^{15}NMo(NRAr)_3$[5] (3.5 mM, ∼99% ^{15}N) under dinitrogen (natural abundance N_2, eq 3). ^1H and ^2H NMR monitoring showed that



$$\begin{matrix} Mo(NRAr)_3 \\ + \\ NMo(OR)_3 \\ + \\ ^{15}NMo(NRAr)_3 \end{matrix} \xrightarrow[\text{benzene}\\ 28\ ^\circ\text{C, 12 h}]{\text{1 atm N}_2\\ \text{(natural isotopic}\\ \text{abundance)}} \begin{matrix} NMo(OR)_3 \\ + \\ 2\ ^{14/15}NMo(NRAr)_3 \end{matrix} \qquad (3)$$

the reaction proceeded with quantitative conversion of $Mo(NRAr)_3$ to its nitrido counterpart $^{14/15}NMo(NRAr)_3$. Dimer

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[1] *Catalytic Ammonia Synthesis*; Jennings, J. R., Ed.; Plenum: New York, 1991.

[2] Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.

[3] (a) Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125. (b) Woo, L. K.; Goll, J. G.; Czapla, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478. (c) Woo, L. K.; Goll, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3755. (d) Neely, F. L.; Bottomley, L. A. *Inorg. Chim. Acta* **1992**, *192*, 147. (e) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1989**, *111*, 5955. (f) Mayer, J. M. *Chemtracts: Inorg. Chem.* **1992**, *4*, 380. (g) Bakir, M.; White, P. S.; Dovletoglou, A.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2835. (h) Evans, D. A.; Bilodeau, M. T.; Faul, M. M. *J. Am. Chem. Soc.* **1994**, *116*, 2742. (i) Jitsukawa, K.; Hata, T.; Yamamoto, T.; Kano, K.; Masuda, H.; Einaga, H. *Chem. Lett.* **1994**, *7*, 1169. (j) Svastits, E. W.; Dawson, J. H.; Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1985**, *107*, 6427.

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[5] Laplaza, C. E.; Odom, A. L.; Davis, W. M.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 4999. $NMo(NRAr)_3$ has been structurally characterized via an EXAFS study: $d(MoN_{nitrido})$ = 1.66 Å, $d(MoN_{amido})$ = 1.98 Å. Results to be published in an upcoming full paper (Laplaza, C. E.; Cummins, C. C.; Pickering, I.; George, G., manuscript in preparation). In addition, we have determined via single-crystal X-ray diffraction that $NMo[N(^tBu)Ph]_3$ is a discrete, three-fold-symmetric monomer in the solid state: Johnson, M. J. A.; Cummins, C. C., unpublished results. The structure of $NMo[N(^tBu)Ph]_3$ is very similar to that of the recently-reported terminal phosphido complex $PMo(NRAr)_3$: Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2042. A single-crystal X-ray diffraction study has been carried out for $NMo(NPh_2)_3$: Gebeyehu, Z.; Weller, F.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1991**, *593*, 99.

[6] Chan, D. M.-T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Marchant, N. S. *Inorg. Chem.* **1986**, *25*, 4170.

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[8] Note that our original report on dinitrogen cleavage by $Mo(NRAr)_3$ (ref 2 above) involved its conversion to purple $(\mu\text{-}N_2)[Mo(NRAr)_3]_2$ at low temperature (−35 °C, 1 atm of N_2) for ∼76 h. Subsequent warming to 30 °C gave $NMo(NRAr)_3$ ($t_{1/2}$ = 35 min).

[9] We assign the MoN stretching frequency for $NMo(OR)_3$ (pentane solution/KBr plates) as follows: $\nu_{Mo^{14}N} = 1052\ cm^{-1}$; $\nu_{Mo^{15}N} = 1024\ cm^{-1}$.

[10] We find the ^{15}N NMR shift for $^{15}NMo(OR)_3$ to be +811 ppm relative to liquid ammonia (0 ppm). The corresponding shift for $^{15}NMo(NRAr)_3$ is +840 ppm; see ref 2 above.

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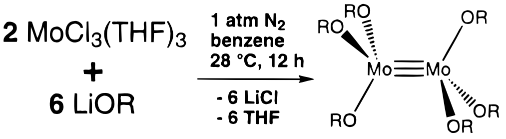
$Mo_2(OR)_6$ formed only to a small extent (~7%). EIMS analysis of the $NMo(OR)_3$ recovered from this reaction mixture indicated negligible ^{15}N-enrichment. We conclude that N atom transfer from $NMo(OR)_3$ to $Mo(NRAr)_3$ is irreversible on the time scale and under the conditions of the reactions studied here. This means that the ^{15}N label in $^{14/15}NMo(OR)_3$ (eq 2) cannot have come by way of $^{14/15}NMo(NRAr)_3$. Thus, it appears that the $Mo(OR)_3$ fragment plays an active dinitrogen-splitting role in the present reaction system.

We sought independent access to "$Mo(OR)_3$", in order to determine whether N_2 cleavage by $Mo(OR)_3$ alone [i.e., in the absence of $Mo(NRAr)_3$] is competitive with formation of dimer $Mo_2(OR)_6$. Treatment of $MoCl_3(THF)_3$[11] (benzene, 3.5 mM, 28 °C, 1 atm of N_2) with 3 equiv of LiOR led only to clean formation of dimer $Mo_2(OR)_6$ (70% isolated yield, eq 4).[12]



(4)

$NMo(OR)_3$ was not detected (^1H NMR) in the crude reaction mixture. This result suggests that both $Mo(NRAr)_3$ and $Mo(OR)_3$ are required for dinitrogen cleavage in the reaction system of eq 2. Since the dinitrogen-splitting reaction described previously for $Mo(NRAr)_3$ is known to proceed via the bimetallic intermediate $(\mu\text{-}N_2)[Mo(NRAr)_3]_2$,[13] we propose that an analogous intermediate $(RO)_3Mo(\mu\text{-}N_2)Mo(NRAr)_3$ (not observed) is responsible for dinitrogen cleavage in the reaction system of eq 2.

This work unites well-defined dinitrogen cleavage and nitrogen atom-transfer reactions. Preliminary experiments indicate that the system reported here (eq 2), although cyclic, is not efficient enough to become truly catalytic.[14] The finding that alkoxide-ligated molybdenum(III) may participate in dinitrogen cleavage chemistry is in line with reports on catalytic dinitrogen fixation by molybdenum(III) and vanadium(III) in protic media.[15] In future reports, we will seek to more brightly illuminate mechanistic aspects of the chemistry described here.[16]

Acknowledgment. For funding, C.C.C. is grateful to the National Science Foundation (CAREER Award CHE-9501992), to DuPont (Young Professor Award), to the Packard Foundation, and to the MIT Department of Chemistry. C.E.L. thanks MIT's UROP (Undergraduate Research Opportunities Program) for funding.

Supporting Information Available: Experimental details for all procedures described in the text (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[11] We prepare orange $MoCl_3(THF)_3$ according to: Dilworth, J. R.; Zubieta, J. *Inorg. Synth.* **1986**, *24*, 193. For a paramagnetic ^1H NMR study of the solution stability of monomeric *mer*-$MoCl_3(THF)_3$, see: Poli, R.; Mui, H. D. *J. Am. Chem. Soc.* **1990**, *112*, 2446. For the single-crystal X-ray structure of *mer*-$MoCl_3(THF)_3$, see: Hofacker, P.; Friebel, C.; Dehnicke, K.; Bäuml, P.; Hiller, W.; Strähle, J. *Z. Naturforsch.* **1989**, *44b*, 1161.

[12] This route to $Mo_2(OR)_6$ appears to be simpler and higher-yielding than the original literature route involving treatment of $Mo_2(NMe_2)_6$ with ROH (ref 7a); another improved route to $Mo_2(OR)_6$ compounds has recently appeared: Gilbert, T. M.; Landes, A. M.; Rogers, R. D. *Inorg. Chem.* **1992**, *31*, 3438.

[13] A recent EXAFS investigation confirmed the proposed linear structure for the MoNNMo core of $(\mu\text{-}N_2)[Mo(NRAr)_3]_2$; these results will be published in an upcoming full paper (Laplaza, C. E.; Cummins, C. C.; Pickering, I.; George, G., manuscript in preparation) along with activation parameters for the first-order conversion of $(\mu\text{-}N_2)[Mo(NRAr)_3]_2$ to $NMo(NRAr)_3$. For the single-crystal X-ray structure of a complex related to $(\mu\text{-}N_2)[Mo(NRAr)_3]_2$, see: Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804.

[14] For example, treatment of $Mo(NRAr)_3$ (benzene, 0.05 M, 28 °C, 1 atm of N_2) with 10, 2, or 1 mol % $NMo(OR)_3$ led to $\leq$20% conversion to $NMo(NRAr)_3$ over a 12 h period as determined by ^1H NMR.

[15] (a) Antipin, M.; Struchkov, Y.; Shilov, A.; Shilova, A. *Gazz. Chim. Ital.* **1993**, *123*, 265. (b) Luneva, N. P.; Mironova, S. A.; Shilov, A. E.; Antipin, M. Y.; Struchkov, Y. T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1178. (c) Shilov, A. E. *Pure Appl. Chem.* **1992**, *64*, 1409.

[16] For example, we are currently attempting to characterize an observable blue intermediate, presumably $(RO)_3Mo(\mu\text{-}N)Mo(NRAr)_3$, in the N atom abstraction from $NMo(OR)_3$ by $Mo(NRAr)_3$.