attraction between cationic ester **2** and vesicles rendered anionic by the presence of **1**) likely augment hydrophobic association. Adjusted for the concentration differences, the intra-vesicular reaction rate is equivalent to that of the intermolecular reaction between monomeric species (Table 1, entry 2). An entropically favorable confinement of the reactants within the bilayer assembly must evidently compensate for any inhibitory rate effects inherent to the membrane environment.

With all the control runs suitably investigated, we were able to examine the vesicle/vesicle reaction (Table 1, entry 7). Its $t_{1/2}$ of 4.2 min indicates a much faster reaction than vesicular **2** plus *monomeric* acetohydroxamate (Table 1, entry 4, $t_{1/2} = 180$ min). This fact, plus the highly efficient intra-vesicular reaction evident in entry 6, suggests a reasonable mechanism for the vesicle/vesicle reaction: Collisions between vesicles containing **1** and vesicles containing **2** lead to a transfer of **2** from one vesicle population to the other.[18] (Potent steroidal anchoring of **1** has been shown previously to prevent a corresponding migration of the nucleophile within our time-scale).[10] A fast intra-vesicular catalyzed hydrolysis, depicted schematically in Figure 1, ensues.

A possible variation of the above vesicle-transfer mechanism was considered. Perhaps ester **2** departs from its vesicles, enters the water, and re-adsorbs into the vesicles containing nucleophile **1**. To test this idea, we studied the vesicle/vesicle reaction with an ester in which the dodecyl chain had been replaced by an octadecyl group. Adding six more carbon atoms should seriously impede any partitioning of the ester from the membrane into the free solution. Yet the vesicle/vesicle rates with the octadecyl analogue are only fourfold smaller than with the dodecyl ester **2**. This result is fully consistent with a collision-induced vesicle-to-vesicle transfer that is mildly retarded by the longer chain length.

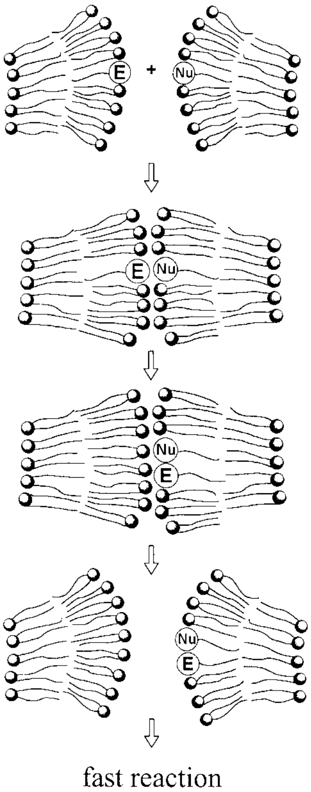

Figure 1. Proposed mechanism for a vesicle/vesicle reaction in which the vesicles collide, the electrophile gets transferred, and a fast intra-vesicular process ensues.

At the moment, organic reactivity among various colloidal particles is a scientific nursling. Further experimentation in the area, as colloid chemistry simulates and ultimately subsumes biology, is an easy call.

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Photochemical Activation of the $N\equiv N$ Bond in a Dimolybdenum–Dinitrogen Complex: Formation of a Molybdenum Nitride[**]

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Rosario Scopelliti, and Carlo Floriani*

Herein we describe a novel contribution to the developing field of $N\equiv N$ bond cleavage reactions,[1–3] in which we have for the first time cleaved the $N\equiv N$ bond by using light and transition metal complexes. Only two groups[1, 2] have so far given detailed information on the pathways leading to the six-electron reduction of dinitrogen. Such a reduction is a stepwise metal-assisted transformation consisting, usually, of a four-electron reduction of N_2, leading to a dimetallahydrazone, $L_nM{=}N{-}N{=}ML_n$, followed by a final, thermally induced reductive cleavage of the residual N–N bond. The present report focuses on the generation of the $d^3\text{-}[Mo(Mes)_3]$ frag-

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ment[4] (Mes ≡ 2,4,6-$Me_3C_6H_2$) as an active molecular species for achieving the four-electron reduction of dinitrogen in [$(Mes)_3Mo{=}N{-}N{=}Mo(Mes)_3$], which undergoes the photoinduced cleavage of the residual N–N bond. The wide occurrence of $L_nM{=}N{-}N{=}ML_n$ functionalities[5] that usually do not undergo further reduction to the corresponding metal nitrides makes the discovery of their potential photolability particularly interesting with regard to dinitrogen reduction.

Arylation of [$MoCl_4 \cdot DME$] in DME by using precisely four equivalents of MesMgBr led to a blue-green solution which slowly absorbs dinitrogen until a N_2:Mo molar ratio of 1:2 is reached. The solution turns red at the end of the N_2 absorption. The reaction solvent was evaporated to dryness, then the solid was extracted with benzene. The extraction, which can be equally well run either under N_2 or Ar, gave **1** in 60% yield as a red crystalline solid. The overall reaction producing **1** can be viewed as a reductive arylation of [$MoCl_4 \cdot DME$], leading formally to [$Mo(Mes)_3$], which performs the dinitrogen fixation. The proposed structure of **1** is supported by the results of an X-ray structure analysis (Figure 1).[6, 9b] The three mesityl groups and the nitrogen atoms around each Mo center display a trigonal-pyramidal arrangement; Mo1 and Mo2 are displaced by 0.384(1) and 0.480(1) Å, respectively, from the basal plane towards the nitrogen atoms. The $Mo{-}N_{av}$ (1.806(9) Å) and N–N distances (1.243(13) Å) support the cumulene structure and a significant degree of reduction of dinitrogen. Complex **1** is paramagnetic, with a μ_{eff} value of 1.54 μ_B at 298 K. This value is quite unusual,[1] and might be explained by population of both the singlet and the triplet state of the [$Mo^V{-}N_2{-}Mo^V$] skeleton.[7]

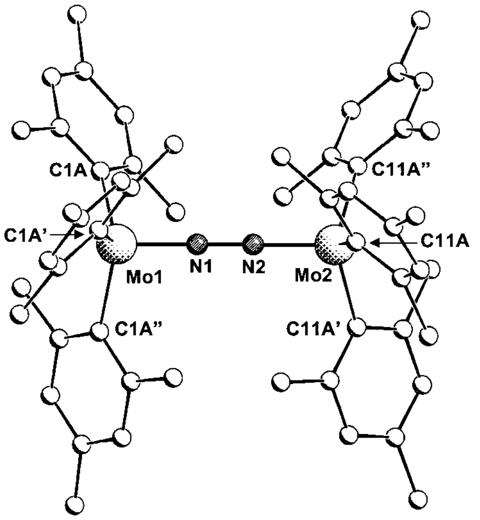
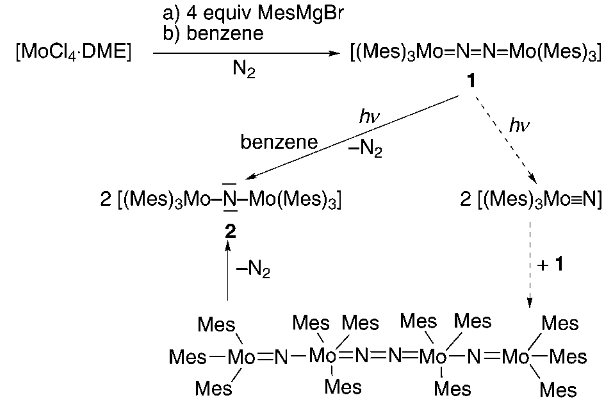


Figure 1. Structure of complex **1** (SCHAKAL drawing). Selected bond lengths [Å] and angle [°]: Mo1-N1 1.794(9), Mo2-N2 1.818(9), Mo1-C1A 2.131(7), Mo2-C11A 2.136(5), N1-N2 1.243(13); Mo1-N1-N2 = Mo2-N2-N1 180.0(-). Symmetry transformations: ': $-y, x-y, z$; ": $-x+y, -x, z$.

It should be mentioned that there is a major difference between the [$Mo(Mes)_3$] fragment and the [$Mo(NRAr)_3$] (R = *t*Bu; Ar = 3,5-$Me_2C_6H_3$) fragment from the work by Cummins and co-workers.[1] In the latter case, the σ- and π-donor properties of the ligand induce the spontaneous thermal cleavage of the N–N bond. Complex **1** is thermally resistant (refluxing benzene), so that the cleavage of the residual N–N bonds was not achieved by such a pathway. In contrast, when a solution of **1** in benzene was exposed to UV light (λ = 365.0 nm), **2** was formed in good yield (79%). This finding supports the proposed pathway shown in Scheme 1. The photochemically induced cleavage of the N–N bond presumably produces the monomeric nitride [$(Mes)_3Mo{\equiv}N$],[8] which acts as a Lewis base on the as yet unreacted **1**, thus forming **2** and leading to the observed 50% loss in the dinitrogen content. The reaction of [$(Mes)_3Mo{\equiv}N$], synthesized according to the literature,[8] with **1** is consistent with the proposed mechanism given in Scheme 1. The reaction led quantitatively to **2**, with the complete loss of N_2. Complex **2** is paramagnetic (μ_{eff} = 1.68 μ_B at 298 K), as expected for a doublet configuration, and its structure is displayed in Figure 2.[9] Both metal atoms have a slightly distorted tetrahedral coordination. The Mo–N bond lengths in **2** (Mo1–N1 1.952(5), Mo2–N1 1.936(5) Å) are much longer than those in the analogous dimolybdenum-bridged nitrido complexes.[1c, 1e] Such long distances come close to Mo–N single bonds,



Scheme 1. The combined metal- and light-assisted cleavage of the N≡N bond. Mes = 2,4,6-$Me_3C_6H_2$.

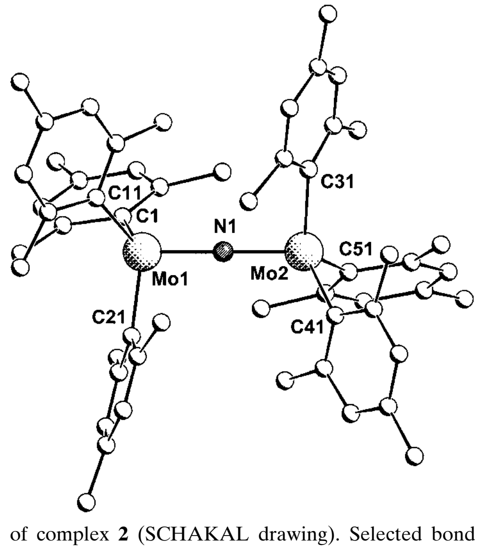


Figure 2. Structure of complex **2** (SCHAKAL drawing). Selected bond lengths [Å] and angle [°]: Mo1-N1 1.952(5), Mo1-C1 2.104(6), Mo1-C11 2.143(7), Mo1-C21 1.996(6), Mo2-N1 1.936(5), Mo2-C31 2.058(8), Mo2-C41 2.105(5), Mo2-C51 2.090(7); Mo1-N1-Mo2 179.1(3).

though the Mo-N-Mo angle (179.1(3)°) is in agreement with a bridging sp nitrogen atom.[10] We believe that in the present case the structural parameters are the consequence of a particularly congested structure.

The photochemically induced cleavage of the N−N bond in a dimetalladinitrogen complex is a quite unique finding in this field and should provide new stimulus on how to achieve dinitrogen activation by the use of metals and light.[11]

Experimental Section

1: A solution of MesMgBr (177.6 mL, 1.01 M, 179.4 mmol) in THF was added dropwise to a suspension of [$MoCl_4 \cdot$DME] (14.70 g, 44.83 mmol) in DME (300 mL) cooled at $-20\,^{\circ}C$. The brown suspension, which was allowed to warm to 20 °C under stirring, turned blue-green in about 3 h. At this stage the N_2 absorption started and continued for 3 days. The gas-volumetric measurements showed the absorption of N_2 had taken place in a N_2:Mo molar ratio of 1:2. The final red suspension was evaporated to dryness; all traces of THF were removed completely. The red residue, which was extracted with benzene, gave a purple solution. This solution was evaporated to dryness to give **1** (60 %) as a powder containing very small amounts of magnesium salts. Further purification was achieved by extracting the solid with *n*-hexane. Dark red crystals of **1** suitable for X-ray analysis were obtained from a C_6H_6/*n*-hexane mixture, as **1** · 1.5 THF. ^1H NMR ([D_6]benzene, 400 MHz, 25 °C): $\delta = 66.98$ (s, 18 H; CH_3), 46.26 (s, 36 H; CH_3), 25.63 (s, 12 H; ArH); μ_{eff} (298 K) = 1.54 μ_B; elemental analysis calcd (%) for $C_{54}H_{66}Mo_2N_2$ (935.0): C 69.37, H 7.11, N 3.00; found: C 69.58, H 7.23, N 2.81. Complex **1** is thermally stable, but not photochemically stable in benzene.

2: A purple solution of **1** (2.12 g, 2.27 mmol) in benzene (125 mL) was irradiated with a high-pressure mercury lamp ($\lambda = 365.0$ nm) for 18 h. The purple solution turned green. The solvent was evaporated to dryness, and *n*-hexane (30 mL) was added to give a green powder which was collected and dried in vacuo (1.65 g, 79 %). Recrystallization of the powder from C_6H_6/*n*-hexane gave crystals of **2** · THF suitable for X-ray analysis. Elemental analysis calcd (%) for $C_{54}H_{66}Mo_2N$ (920.0): C 70.42, H 7.22, N 1.52; found: C 70.23, H 7.09, N 1.57; μ_{eff} (298 K) = 1.68 μ_B. A by-product of the photochemical reaction is a small amount of mesitylene, as confirmed by NMR spectroscopy and GC-MS. When the reaction was carried out in a gas-volumetric apparatus, 50 % of the N_2 content was evolved.

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[6] Crystal data for **1**: $C_{54}H_{66}Mo_2N_2 \cdot 1.5\,C_4H_8O$, $M_r = 1043.2$, hexagonal, space group $R\bar{3}$, $a = 14.418(2)$, $c = 45.856(9)$ Å, $V = 8255(2)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.259$ g cm^{-3}, $F(000) = 3288$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $\mu(Mo_{K\alpha}) = 4.83$ cm^{-1}: crystal dimensions $0.18 \times 0.25 \times 0.30$ mm. The structure was solved by the heavy-atom method and anisotropically refined only for the Mo and N atoms. Both the symmetry-independent mesityl ligands were found to be statistically distributed over two orthogonal positions (called A and B), which were isotropically refined with site occupation factors of 0.5. The THF solvent molecule, which lies about a center of symmetry, was found to be affected by disorder. The best-fit was obtained by splitting the carbon atoms over two positions (called A and B), which were isotropically refined with site occupation factors of 0.25. The oxygen atom of the THF molecule was isotropically refined with a site occupation factor of 0.5. All the hydrogen atoms were put in geometrically calculated positions and introduced as fixed contributors in the last stage of refinement ($U_{iso} = 0.08$ Å^2). For 1900 unique observed reflections [$I > 3\sigma(I)$] collected at $T = 143$ K on a Mar345 IPDS diffractometer ($5 < 2\theta < 55°$) the final R value is 0.058 ($wR2 = 0.147$).[9b]

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[9] a) Crystal data for **2**: $C_{54}H_{66}Mo_2N \cdot 2\,C_4H_8O$, $M_r = 1065.2$, triclinic, space group $P\bar{1}$, $a = 12.870(4)$, $b = 14.520(6)$, $c = 16.520(6)$ Å, $\alpha = 65.84(2)$, $\beta = 73.91(3)$, $\gamma = 78.40(2)°$, $V = 2692.8(18)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.314$ g cm^{-3}, $F(000) = 1122$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $\mu(Mo_{K\alpha}) = 4.95$ cm^{-1}: crystal dimensions $0.15 \times 0.18 \times 0.21$ mm. The structure was solved by the heavy-atom method and anisotropically refined for all the non hydrogen atoms except for the O2, C63, C65 – C68 disordered atoms of THF molecules which were split over two positions (called A and B), which were isotropically refined with a site occupation factor of 0.5. All the hydrogen atoms were put in geometrically calculated positions and introduced as fixed contributors in the last stage of refinement ($U_{iso} = 0.08$ Å^2). For 7480 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 143$ K on a Rigaku AFC7S diffractometer equipped with a Rigaku Mercury CCD ($5 < 2\theta < 60°$) the final R value is 0.063 ($wR2 = 0.148$). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-165487 (**1**) and CCDC-165488 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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