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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Carbon Monoxide-Induced N−N Bond Cleavage of Nitrous Oxide That Is Competitive with Oxygen Atom Transfer to Carbon Monoxide As Mediated by a Mo(II)/Mo(IV) Catalytic Cycle

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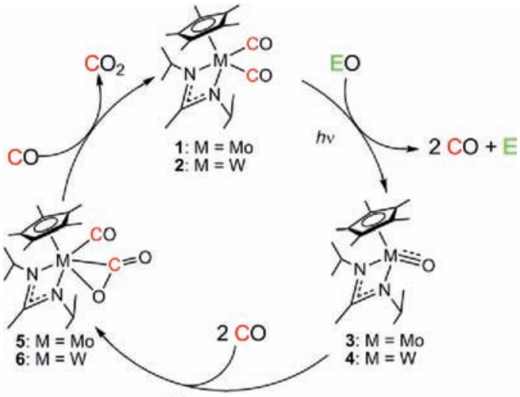
Supporting Information

ABSTRACT: In the presence of CO, facile N−N bond cleavage of N_2O occurs at the formal Mo(II) center within coordinatively unsaturated mononuclear species derived from $\mathrm{Cp^*Mo[N(^iPr)C(Me)N(^iPr)](CO)_2}$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) (**1**) and $\{\mathrm{Cp^*Mo[N(^iPr)C(Me)N(^iPr)]}\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}\mathrm{N_2})$ (**9**) under photolytic and dark conditions, respectively, to produce the nitrosyl, isocyanate complex $\mathrm{Cp^*Mo[N(^iPr)C(Me)N(^iPr)]}$($\kappa$-*N*-NO)($\kappa$-*N*-NCO) (**7**). Competitive N−O bond cleavage of N_2O proceeds under the same conditions to yield the Mo(IV) terminal metal oxo complex $\mathrm{Cp^*Mo[N(^iPr)C(Me)N(^iPr)](O)}$ (**3**), which can be recycled to produce more **7** through oxygen-atom-transfer oxidation of CO to produce CO_2.

Nitrous oxide (N_2O) is a greenhouse gas that has 310 times greater global warming potential than carbon dioxide (CO_2) on a weight-to-weight basis.[1] Nonselective catalytic reduction (NSCR) is a proven abatement technology for efficiently removing 90−99% of the N_2O in industrial flue gases associated with adipic and nitric acid production. However, it is an energy-intensive, high-temperature process.[2] The principal pathway for N_2O destruction in NSCR involves transition-metal-catalyzed decomposition to N_2 and O_2, both of which are attractive, environmentally benign end products. On the other hand, the discovery of alternative bond-breaking mechanisms for N_2O, and in particular N−N bond cleavage, could provide new opportunities for the development of more energy-efficient abatement technologies as well as new commercial processes that employ N_2O as an abundant commodity feedstock reagent.[3]

In 1995, Cummins and co-workers[4] reported that selective low-temperature N−N bond cleavage of N_2O could be achieved upon reaction with the Mo(III) trisamido complex $\mathrm{Mo[N(^tBu)Ar]_3}$ ($\mathrm{Ar} = 3,5\text{-}\mathrm{C_6H_3Me_2}$), providing a 1:1 ratio of the nitrosyl and terminal nitrido products, $\mathrm{(ON)Mo[N(^tBu)Ar]_3}$ and $\mathrm{(N)Mo[N(^tBu)Ar]_3}$, respectively. While subsequent experimental investigation of this seminal discovery favors a mechanism for N−N bond cleavage that involves rate-determining N_2O coordination along a pathway involving formation of a μ-NNO dinuclear species, a theoretical computational study supports simple mononuclear N_2O activation followed by N−N bond cleavage.[5,6] Few other reports of N−N bond cleavage of N_2O have appeared in the literature, and these invariably involve less experimentally tractable transition-metal and main-group-element clusters or transition-metal cations in the gas phase; as a result, mechanisms for these transformations remain enigmatic.[7,8] Herein we now report that metal-mediated carbon monoxide (CO)-induced N−N bond cleavage of N_2O can be competitive with N−O bond cleavage in the case of a formal Mo(II) metal center supported by the cyclopentadienyl ($\eta^5\text{-}\mathrm{C_5R_5}$) amidinate ($\eta^2\text{-}\mathrm{[N(R^1)C(R^2)N(R^3)]}$) (CpAm) ligand environment. In addition, the terminal Mo(IV) oxo species derived from the latter process can be recycled through efficient oxygen-atom-transfer (OAT) oxidation of CO that ultimately provides an excellent yield of the N−N-bond-cleaved product.

Scheme 1

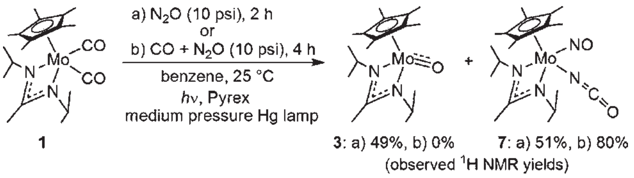


red text indicates ^{13}C (99%)-labeled reagent
for E = CO, see reference 10; for E = N_2, see this work

We recently reported that the group 6 CpAm bis(carbonyl) complexes $\mathrm{Cp^*M[N(^iPr)C(Me)N(^iPr)](CO)_2}$ [$\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$; M = Mo (**1**), W (**2**)][9] can serve as precatalysts for efficient reversible degenerate OAT between CO and CO_2 that proceeds according to the catalytic cycle involving a M(II)/M(IV) couple, as presented in Scheme 1 for the case where E = CO.[10] Importantly, except for the molybdenum η^2-CO_2 complex $\mathrm{Cp^*Mo[N(^iPr)C(Me)N(^iPr)](CO)(\eta^2\text{-}CO_2)}$ (**5**), which has only a transient lifetime under the conditions employed, all other intermediates and resting states (i.e., complexes **1**−**4** and **6**) are observable in solution and have been both isolated in analytically pure form and structurally characterized by single-crystal X-ray analyses. On the basis of these results, we reasoned that it should be possible to develop a similar catalytic OAT cycle for the oxidation of CO by N_2O that proceeds according to the reaction

Received: September 14, 2011
Published: October 25, 2011

Scheme 2



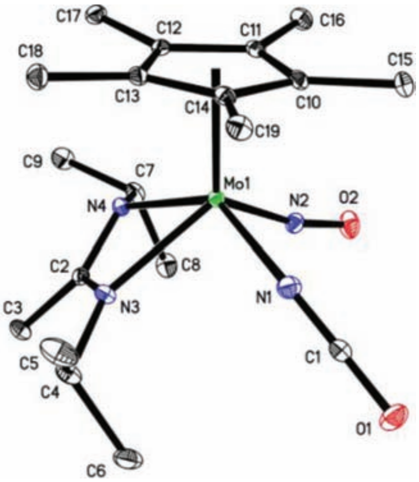


Figure 1. Molecular structure (30% thermal ellipsoids) of **7**. H atoms have been removed for clarity. Selected bond lengths (Å) and bond angles (deg): Mo1−N1, 2.1084(13); N1−C1, 1.1758(19); C1−O1, 1.2028(18); Mo1−N2, 1.7812(12); N2−O2, 1.2080(16); N2−Mo1−N1, 89.11(6); Mo1−N1−C1, 158.62(12); N1−C1−O1, 178.10(16), Mo1−N2−O2, 168.76(12).

CO + N_2O → CO_2 + N_2 (i.e., Scheme 1 for the case where E = N_2). In practice, a benzene-d_6 solution of **1** was found to be inert toward N_2O (10 psi) for an extended period of time (days) when kept in the dark. On the other hand, photolysis of the reaction mixture using a Rayonet carousel of medium-pressure Hg lamps did lead to partial conversion of **1** into the terminal oxo complex Cp*Mo[N(^{i}Pr)C(Me)N(^{i}Pr)](O) (**3**), thereby providing support for the general plausibility of the OAT cycle in Scheme 1.[11] However, the formation of **3** under these conditions proceeded alongside that of a single new coproduct that was painstakingly isolated in small amounts as an air-stable crystalline material for which spectroscopic and analytical characterization, including single-crystal X-ray analysis, are fully consistent with the identification of this species as the nitrosyl isocyanate complex Cp*Mo[N(^{i}Pr)C(Me)N(^{i}Pr)](*κ*-*N*-NO)(*κ*-*N*-NCO) (**7**), which is depicted in Scheme 2.[11] Figure 1 presents the solid-state molecular structure and selected bond lengths and bond angles of **7**. From these data, it can be noted that the molybdenum−nitrogen bond for the NO fragment is significantly shorter than that for the NCO moiety [cf., Mo1−N2 = 1.7812(12) Å and Mo1−N1 = 2.1084(13) Å, respectively], and the observed near-linearity of the nitrosyl group [i.e., Mo1−N2−O2 = 168.76(12)°] provides support for a formal metal−ligand bonding description consisting of a M(II, d^4) metal center interacting with a nitrosonium cation.[12] However, on the basis of the observed low NO stretching frequency (see below), an alternative formalization championed by Parkin[13] would be to consider the nitrosyl group as a trivalent NO^{3-} ligand, which would then mandate a M(VI, d^0) center for **7**.

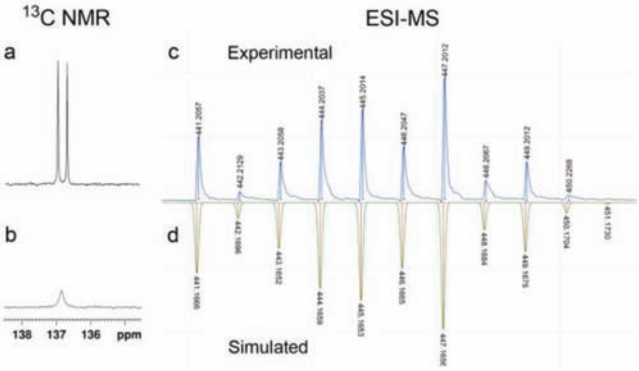


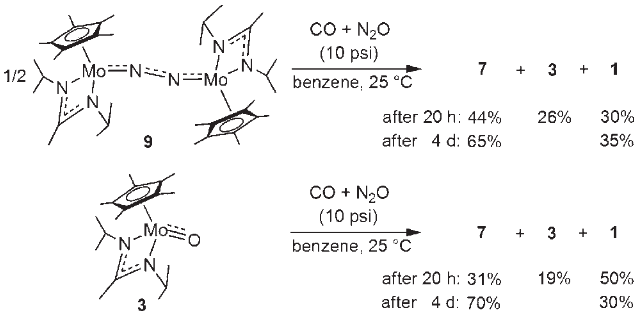
Figure 2. Partial $^{13}C\{^1H\}$ (125 MHz, benzene-d_6, 25 °C) NMR spectra for (a) the isocyanate chemical shift for isotopically labeled ($^{15}N^{13}CO$)(^{15}NO)-**7** and (b) ($N^{13}CO$)-**7**. (c) Experimental ESI-MS data for the parent ion, $[M + H]^+$, of unlabeled **7** and (d) the simulated MS isotopic distribution pattern for $[M + H]^+$ of unlabeled **7**.

As Scheme 2 and the partial ^{13}C NMR spectra in Figure 2a,b reveal, single (^{13}C) and double (^{13}C,^{15}N) isotopic labeling of the *κ*-*N*-NCO fragment of **7** were readily achieved by starting with bis(^{13}CO)-labeled (99%) **1** and conducting the photolysis in the presence of unlabeled N_2O and $^{15}N^{15}NO$ (99%), respectively. For the *κ*-*N*-$^{15}N^{13}CO$ group of the latter compound, a ^{13}C chemical shift of 136.8 ppm with $^1J(^{13}C-^{15}N)$ = 33.5 Hz was observed.[14] However, to date we have not been able to observe the expected longer-range coupling [i.e., $^3J(^{13}C-^{15}N)$] that might be expected between the ^{15}NO and $^{15}N^{13}CO$ moieties, nor have attempts to obtain ^{15}N NMR spectra for (*κ*-*N*-^{15}NO)-(*κ*-*N*-^{15}NCO)-labeled **7** (prepared from unlabeled **1** and $^{15}N^{15}NO$) been successful. Here, electrospray ionization mass spectrometry (ESI-MS) was used to provide unequivocal confirmation of the presence of the NO ligand through successful analysis of the high-resolution isotopic distribution pattern of the expected elemental composition of unlabeled **7**, as presented in Figure 2c,d. Finally, a solid-state IR spectrum (KBr) of unlabeled **7** displays strong vibrational absorption bands for ν_{NCO} at 2224 cm^{-1} and ν_{NO} at 1603 cm^{-1} that are shifted to 2150 and 1571 cm^{-1}, respectively, for (*κ*-*N*-^{15}NO)-(*κ*-*N*-$^{15}N^{13}CO$)-**7**.[15]

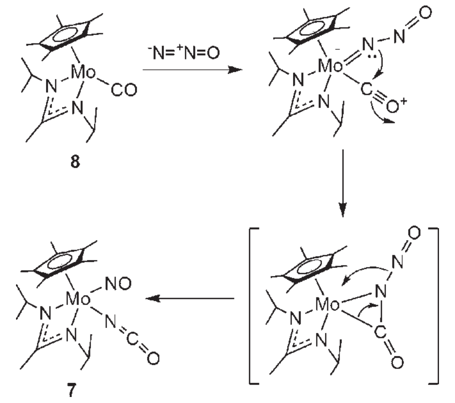
As previously mentioned, coproduction of the terminal oxo complex **3** along with **7** suggested that the catalytic OAT cycle of Scheme 1 is viable. Indeed, when a preformed gas mixture consisting of a 1:1 ratio of ^{13}CO (99%) and N_2O was employed, an 80% yield of **7**, as assessed by ^{1}H NMR spectroscopy, was obtained after photolysis of **1** according to Scheme 2 (condition b). Observation of the concomitant formation of $^{13}CO_2$ under these conditions provided unequivocal confirmation of the ability to recycle the terminal oxo coproduct **3** through metal-mediated CO oxidation involving OAT from N_2O.[11]

A key question to address is whether N−N bond cleavage of N_2O requires a population of an excited-state species that is generated under photolytic conditions. For the OAT cycle of Scheme 1, we originally proposed that the purpose of the photolysis was to promote loss of CO from **1** and thereby generate the more electron-deficient, coordinatively unsaturated, transient intermediate Cp*Mo[N(^{i}Pr)C(Me)N(^{i}Pr)](CO) (**8**), which could then engage in complexation of either CO_2 or N_2O.

Scheme 3



Scheme 4



Since **1** can be prepared in quantitative yield through carbonylation of the dinuclear “end-on-bridged” dinitrogen complex $\{Cp^*Mo[N(^iPr)C(Me)N(^iPr)]\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ (**9**) using CO (10 psi) at room temperature,[9] it was reasoned that kinetic trapping of transient **8** generated from **9** in the presence of both CO and N_2O might also lead to the production of **7**. It is important to note that reaction of **9** with N_2O (10 psi) alone provides a near-quantitative yield of only the terminal oxo complex **3**.[10] However, as Scheme 3 reveals, when a benzene solution of **9** was pressurized with a 1:1 mixture of ^{13}CO and N_2O (10 psi), a mixture of the N−O-bond-cleaved product **3** (26%) and the N−N-bond-cleaved product **7** (44%) was obtained along with a 30% yield of **1** after 20 h in the dark; after 96 h, complete conversion of the oxo species **3** occurred, providing a final product ratio of **1** (35%) and **7** (65%). Interestingly, a similar result was obtained by starting with pure **3** as the precursor under identical conditions, which yielded **1** (30%) and **7** (70%) after 96 h in the dark as the only observable products (see Scheme 3). These results provide conclusive proof that N−N bond cleavage of N_2O is a thermal process that most likely involves **8** as a common intermediate in either the photolytic or dark reactions. Finally, when bis(carbonyl) **2** containing the third-row transition metal tungsten was employed in place of **1** under the photolytic conditions of Scheme 2, or when the analogous ditungsten dinitrogen complex $\{Cp^*W[N(^iPr)C(Me)N(^iPr)]\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ (**10**)[9] was treated according to the conditions of Scheme 3, no evidence for a similar N−N bond cleavage of N_2O was obtained in either case.

CO-induced N−N multiple-bond cleavage at a metal center has been documented previously for dinitrogen,[14] azobenzene,[16] and an aryldiazoalkane.[17] To account for the present results, we currently favor the mechanism shown in Scheme 4, which is similar to that previously proposed by Bergman and co-workers[16] for CO-induced N−N bond cleavage of a diazoalkane by the Cp^*_2Ti fragment. Further precedent exists for end-on *κ-N* coordination of N_2O to a vanadium center,[18] and for isocyanate formation via intramolecular attack on a metal-bound CO group is provided by related metal azide chemistry.[19]

Additional investigations are currently in progress to establish key mechanistic details for the **1** → **7** and **9** → **7** transformations and to probe the potential for developing new catalytic cycles involving **7** and related derivatives to extend the utility of N_2O as a “green” commodity reagent.[3,20]

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details, including crystallographic analysis for compound **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We are grateful for the funding of this work provided by the Department of Energy, Office of Basic Energy Sciences (Grant DE-SC0002217).

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