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On the Origin of Selective Nitrous Oxide N−N Bond Cleavage by Three-Coordinate Molybdenum(III) Complexes

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Abstract: Reaction of $\mathrm{Mo(N[R]Ar)_3}$ (R = ^{t}Bu or $\mathrm{C(CD_3)_2CH_3}$) with $\mathrm{N_2O}$ gives rise exclusively to a 1:1 mixture of nitride $\mathrm{NMo(N[R]Ar)_3}$ and nitrosyl $\mathrm{ONMo(N[R]Ar)_3}$, rather than the known oxo complex $\mathrm{OMo(N[R]Ar)_3}$ and dinitrogen. Solution calorimetry measurements were used to determine the heat of reaction of $\mathrm{Mo(N[R]Ar)_3}$ with $\mathrm{N_2O}$ and, independently, the heat of reaction of $\mathrm{Mo(N[R]Ar)_3}$ with NO. Derived from the latter measurements is an estimate (155.3 ± 3.3 kcal·mol^{-1}) of the molybdenum−nitrogen bond dissociation enthalpy for the terminal nitrido complex, $\mathrm{NMo(N[R]Ar)_3}$. Comparison of the new calorimetry data with those obtained previously for oxo transfer to $\mathrm{Mo(N[R]Ar)_3}$ shows that the nitrous oxide N−N bond cleavage reaction is under kinetic control. Stopped-flow kinetic measurements revealed the reaction to be first order in both $\mathrm{Mo(N[R]Ar)_3}$ and $\mathrm{N_2O}$, consistent with a mechanism featuring post-rate-determining dinuclear N−N bond scission, but also consistent with cleavage of the N−N bond at a single metal center in a mechanism requiring the intermediacy of nitric oxide. The new 2-adamantyl-substituted molybdenum complex $\mathrm{Mo(N[2\text{-}Ad]Ar)_3}$ was synthesized and found also to split $\mathrm{N_2O}$, resulting in a 1:1 mixture of nitrosyl and nitride products; the reaction exhibited first-order kinetics and was found to be ca. 6 times slower than that for the *tert*-butyl-substituted derivative. Discussed in conjunction with studies of the 2-adamantyl derivative $\mathrm{Mo(N[2\text{-}Ad]Ar)_3}$ is the role of ligand-imposed steric constraints on small-molecule, e.g. $\mathrm{N_2}$ and $\mathrm{N_2O}$, activation reactivity. Bradley's chromium complex $\mathrm{Cr(N^{i}Pr_2)_3}$ was found to be competitive with $\mathrm{Mo(N[R]Ar)_3}$ for NO binding, while on its own exhibiting no reaction with $\mathrm{N_2O}$. Competition experiments permitted determination of ratios of second-order rate constants for NO binding by the two molybdenum complexes and the chromium complex. Analysis of the product mixtures resulting from carrying out the $\mathrm{N_2O}$ cleavage reactions with $\mathrm{Cr(N^{i}Pr_2)_3}$ present as an in situ NO scavenger rules out as dominant any mechanism involving the intermediacy of NO. Simplest and consistent with all the available data is a post-rate-determining bimetallic N−N scission process. Kinetic funneling of the reaction as indicated is taken to be governed by the properties of nitrous oxide as a ligand, coupled with the azophilic nature of three-coordinate molybdenum(III) complexes.

1. Introduction

Activation of N−N Bonds. Reactions involving the reductive cleavage of N−N bonds by metal atoms[1−14] or metal complexes constitute an intriguing and expanding facet of chemical science. Symmetrical substrates of interest include hydrazines,[15−17] diazenes (azo compounds),[18−21] and molecular nitrogen itself.[22−47] The latter substrate continues to present a dramatic and seductive challenge to chemistry, namely the development of new

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economical[37] systems for its conversion to ammonia and other nitrogen-containing feedstocks.[48] Unsymmetrical substrates include diazoalkanes,[49−57] organoazides,[16,17,20] which are known to be useful synthons for organoimido complexes,[58] and nitrosamines.[59−61]

Perhaps the most interesting unsymmetrical substrate for N−N bond activation is nitrous oxide,[62] most interesting precisely because it is not normally thought of as being susceptible to such activation.[63−68] Rather, the usual course of events upon reaction of nitrous oxide with reductants is the delivery of an oxygen atom and the liberation of molecular nitrogen.[68−76] In this respect the characteristic chemical behavior of nitrous oxide is analogous to that of organoazides[58] and accounts for the fact that N_2O has been touted as a thermodynamically potent[77,78] and environmentally friendly source of oxidizing equivalents.[69−73]

In view of the 1995 discovery that certain molybdenum complexes react with N_2O to effect *selective* cleavage of its N−N bond,[79] an imperative thus became a fuller understanding of the mechanism and energetics of said reaction,[80] for it is certain that any commercial implementation of N_2O as a clean oxidant would surely be augmented by a more complete knowledge of the coordination chemistry of this intriguing small molecule.

Note that *formation* of the nitrous oxide N−N bond has been observed recently in the reaction of a nitrido osmium complex with NO.[81]

Nitrous Oxide as a Ligand. Hoffmann and co-workers have studied nitrous oxide from a theoretical point of view and have concluded that N_2O should prefer to bind to metals at its nitrogen terminus.[82,83] A study of the interaction of N_2O with the Pt(111) surface likewise revealed a propensity for the small molecule to interact with the metal via its N terminus, as deduced primarily from an 80 cm^{-1} υ_{NN} blue shift for adsorbed N_2O versus the free gas ($\upsilon_{NN} = 2224$ cm^{-1}).[84]

Ruthenium(II) pentammine complexes of N_2O have provided the greatest wealth of experimental access to information concerning the properties of nitrous oxide as a ligand in coordination chemistry. Studied initially by Armor and Taube,[85−87]

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and by Diamantis and Sparrow,[88−92] salts of the $[Ru(NH_3)_5N_2O]^{2+}$ ion have been isolated as microcrystalline solids, but structural information, i.e., a single-crystal X-ray diffraction study, is not available. Much now is known about the vibrational spectra for bound nitrous oxide in complexes, the latter advances being largely to the credit of Bottomley,[93−96] who also devised a synthesis of $[Ru(NH_3)_5N_2O]^{2+}$ salts involving reaction of the nitrosyl derivative with hydroxylamine.[95] Access to the ion previously had involved reaction of the aquo derivative with N_2O gas, a method used also by Armor and Taube in the context of their study of linkage isomerism in $^{15}N_2$-labeled ruthenium(II) pentaammine complexes.[86]

To this day it appears that $[Ru(NH_3)_5N_2O]^{2+}$ remains the only well-characterized N_2O coordination complex, although transient infrared spectroscopy[97] and matrix isolation[98] studies have been carried out for the transient tungsten carbonyl adduct $W(CO)_5(N_2O)$. In contrast, the coordination chemistry of dinitrogen has undergone a dramatic evolution since its inception in the 1960s.[99] Perhaps the origin of this dichotomy rests in the inherent reactivity of bound nitrous oxide with respect to oxo transfer, it being the case oftentimes that bound dinitrogen is inert to further transformations. Much work has been conducted in which N_2O serves as an oxo source in transition metal and other systems,[69−76] but the observation of intermediate N_2O complexes typically is not documented.[72,73]

Three-Coordinate Complexes of Mo and Cr. Nitrous oxide N−N bond cleavage was one of the first reactions described for the unique three-coordinate molybdenum(III) complex, $Mo(N[R]Ar)_3$ (R = ^tBu, **1**; R = $C(CD_3)_2CH_3$, **1**-d_{18}; Ar = 3,5-$C_6H_3Me_2$).[79,80] Early characterization data showed **1** to be a monomeric species possessed of a quartet ground state, red in color, and readily soluble in hydrocarbon solvents. Particularly noteworthy vis-à-vis the class of well-characterized molybdenum(III) dimers exemplified by $Mo_2(NMe_2)_6$[100,101] is the monomeric nature of **1**, a characteristic enforced by the sterically encumbering nature of its amido nitrogen substituents.[44,102−104]

In view of the importance of steric considerations in fostering the monomeric nature of **1**,[44,102−104] variants have been sought that incorporate even larger substituents on their amido nitrogens.[42] Such variants include structurally characterized three-coordinate $Mo(N[1\text{-}Ad]Ar)_3$[42] (where 1-Ad is the 1-adamantyl substituent), which like **1** engages in mononuclear N_2 chemistry, but which unlike **1** is prevented sterically from engaging in the dinuclear N_2 chemistry required for dinitrogen reductive cleavage.[42,45−47] Another adamantyl-substituted derivative is $Mo(N[2\text{-}Ad]Ar)_3$, complex **2** of this work, a complex noteworthy in that its *secondary* adamantyl substituents present β-hydrogens to the Mo center without β-H elimination becoming manifest.[41] In contrast to this is the chemistry observed when ^iPr substituents are employed on the amido nitrogens: the complex of formula "$Mo(N[^iPr]Ar)_3$" has been shown to exist as its metallaziridine hydride tautomer.[41] In the present work the role of complex **2** is to provide a contrast with complex **1** in terms of reactivity with N_2O.

The first three-coordinate complexes of a trivalent group 6 element were the tris-diisopropylamide and the tris-hexamethyldisilazide complexes of chromium.[105−108] Bradley's $Cr(N^iPr_2)_3$[108] is complex **3** of this work, significant because in contrast to the Mo complexes it is shown to exhibit *no reaction* with N_2O. Coupled with its propensity to bind NO,[107,109,110] the lack of reaction of complex **3** with N_2O has rendered the complex invaluable as a mechanistic probe in the present study.

2. Results and Discussion

Kinetics with Toluene as Solvent. Bubbling of nitrous oxide through a sealed cuvette containing **1** (6×10^{-4} M in toluene) elicited a color change from orange to pale yellow over several minutes, corresponding to the conversion of 2 equiv of **1** to an equimolar mixture of nitride **1-N** and nitrosyl **1-NO** as indicated pictorially in Figure 1.

As displayed in Figure 2, spectrophotometric measurements revealed two wavelength regions suitable for stopped-flow experiments: 350−380 nm, where the optical absorbance was observed to increase, and 395−500 nm, where the optical absorbance was observed to decrease. An isosbestic point was located at 390 nm ($\epsilon = 2500$ M^{-1} cm^{-1}).

Kinetic data corresponding to the reaction between **1** and a large excess of N_2O (200−1300 equiv) was studied in detail in toluene solution over the temperature range from +5 to +25 °C. The spectral changes observed in stopped-flow experiments correspond well to those observed in the conventional spectrophotometric study (Figure 2). The observed pseudo-first-order rate constants measured in the regions both of increase and of decrease in optical absorbance agree to within 5%. Thus, the spectral changes observed in stopped-flow experiments may be taken to be indicative of the reaction of **1** with N_2O, as intended. It is worth noting that complex **1** is exceedingly air and water sensitive,[45,80] such that the stopped-flow measurements had to be carried out with rigorous exclusion of air and water from the system. As a control, the decomposition of complex **1** upon exposure to air was studied spectrophotometrically (spectrum c of Figure 5), with the result that air exposure causes a decrease in optical absorbance across the entire spectral window. The latter profile distinguishes the reaction of **1** with air as opposed to N_2O.

The kinetic curves, representing absorbance change as a function of time, at different wavelengths were fitted to a single-exponential equation, giving mean standard deviations within 2% over a period of five half-lives. No systematic changes in the value of the pseudo-first-order rate constant ($k_{obs} = 0.232 \pm 0.005$ s^{-1}) were observed as a function of varying the initial

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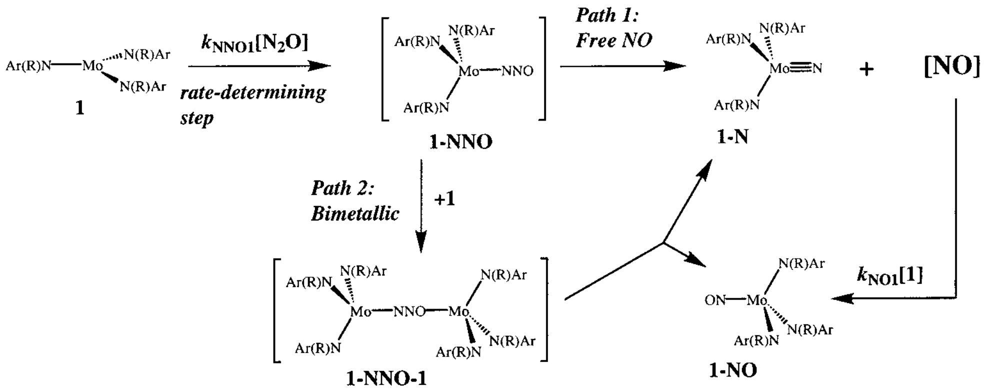

Figure 1. Reaction of **1** with N_2O to give equimolar amounts of nitrosyl **1-NO** and nitrido **1-N**. Mechanistic possibilities to be considered are path 1, a monometallic pathway with free NO as an intermediate, and path 2, a pathway involving the unobserved bimetallic intermediate **1-NNO-1**. Common to both pathways is the unobserved N_2O adduct, **1-NNO**. The second-order rate constant for reaction of **1** with N_2O is defined as k_{NNO1}, while the second-order rate constant for the binding of NO by **1** is defined as k_{NO1}.

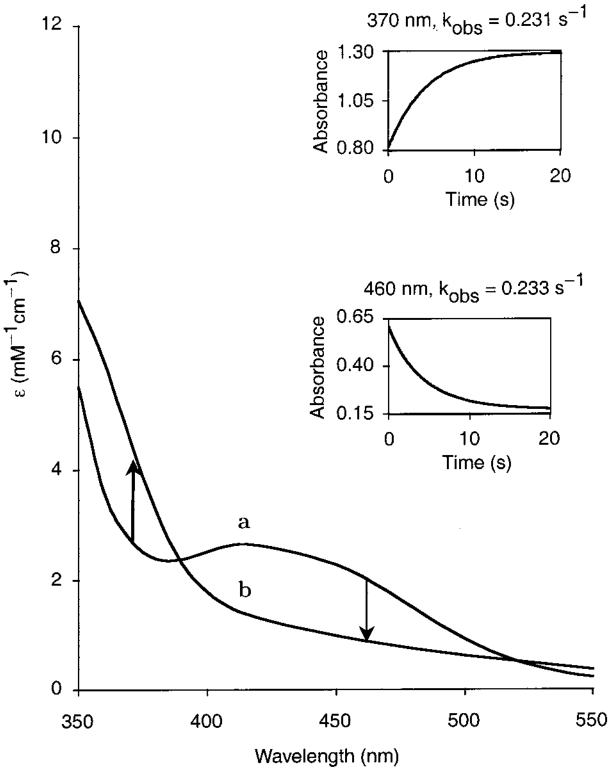

Figure 2. Visible spectra of Mo(N[R]Ar)$_3$ (**1**) in toluene before (a) and after (b) mixing with N_2O. Inset: kinetic traces of the reaction in typical stopped-flow shots at 25 °C. Initial concentration of **1**, 0.31 mM; initial concentration of N_2O, 66.5 mM (corresponding to a half-diluted saturated solution of the gas at 25 °C).

concentration of **1** in the range from 0.1 to 0.6 mM, using a saturated solution of N_2O in toluene ($[N_2O]_0$ = 66.5 mM) at 25 °C. Thus, the reaction clearly is first order in Mo(N[R]Ar)$_3$ (**1**).

A plot of the pseudo-first-order rate constant k_{obs} versus the initial concentration of N_2O is a straight line with practically zero intercept, as displayed in Figure 3. Such data were obtained both by using solutions prepared by saturation with calibrated N_2O/Ar gas mixtures, and with the use of the multimixing stopped-flow mode, the latter allowing the saturated N_2O solution to be diluted twice directly in the SF apparatus. This result shows that the reaction is first order in N_2O. The slope of the line gives the value of the second-order reaction rate constant $k_{NNO1} = 3.4 \pm 0.3$ M^{-1} s^{-1} for the reaction between **1** and N_2O at 25 °C.

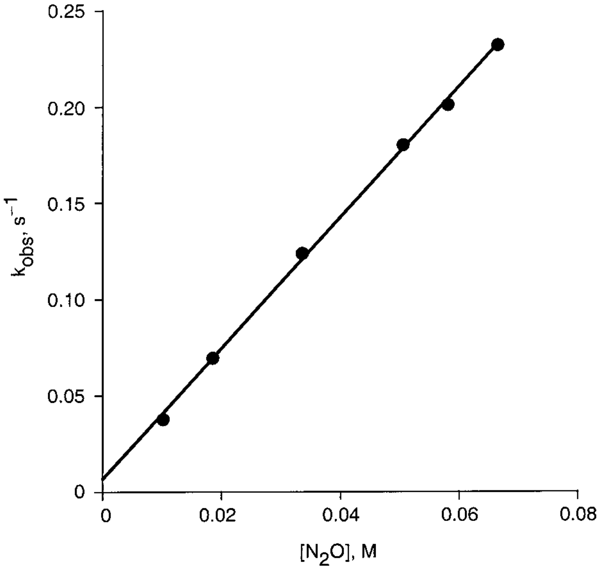

Figure 3. Dependence of the observed pseudo-first-order rate constant on N_2O concentration for the reaction between Mo(N[R]Ar)$_3$ (**1**) and N_2O in toluene at 25 °C. In each case the initial concentration of **1** was 0.3 mM. A least-squares fit of the data gives an intercept of 0.007 s^{-1} and a slope (corresponding to a second-order rate constant, see text) of 3.4 M^{-1} s^{-1}, with $R^2 = 0.999$.

The N_2O dependence of the reaction rate and the zero intercept representing no reaction in the absence of N_2O (Figure 3) together constitute a further confirmation that the process under scrutiny in the stopped-flow experiments is indeed the reaction of **1** with N_2O, as opposed to some undesired decomposition reaction. It should be borne in mind, however, that the observed second-order kinetic behavior is documented here under conditions involving a great excess of N_2O vis-à-vis complex **1**. One should refrain, therefore, from drawing conclusions as to what behavior to expect under conditions, for example, involving a great excess of complex **1**. Unfortunately, technical difficulties obviate kinetic study of the **1**/N_2O system under conditions involving an excess of complex **1**. At low N_2O concentrations the reaction becomes prohibitively slow, while instrumental limitations do not allow the use of inordinately high concentrations of chromophore **1**.

Activation Parameters. The reaction of complex **1** with N_2O in toluene was studied as a function of temperature (Figure 4), from +5 to +25 °C. Activation parameters obtained from fitting the data to the Eyring equation[111] are as follows: $\Delta H^{\ddagger} = 9.7 \pm 0.5$ kcal·mol^{-1}, and $\Delta S^{\ddagger} = -23.6$ eu. The observed activation

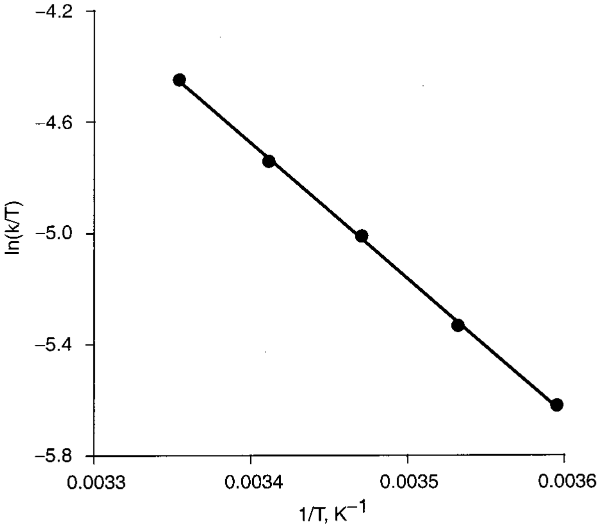

Figure 4. Plot of the temperature dependence of the second-order rate constant for the reaction of Mo(N[R]Ar)$_3$ (**1**) with N_2O in toluene. The fit is to the linear form of the Eyring equation, giving activation parameters of $\Delta H^{\ddagger} = 9.7$ kcal·mol^{-1}, $\Delta S^{\ddagger} = -24$ eu.

enthalpy is very close to values reported for other reactions of N_2O with transition metal complexes,[112,113] reactions which, however, give rise to oxygen atom transfer and dinitrogen formation rather than N−N bond scission. A negative activation entropy is typical for associative reactions, such as dioxygen binding to metal complexes.[114−116]

Below +5 °C the reaction between complex **1** and N_2O becomes too slow for reliable determination of its rate under our experimental conditions. In stopped-flow experiments at −40 °C, mixing the solutions of **1** and N_2O gave rise to approximately the same kinetic traces as diluting the solution of complex **1** with pure toluene. In both cases there were minor changes in absorbance on a relatively long time scale (≥100 s), which may be attributed to side reactions. Upon bubbling gaseous N_2O through a 6×10^{-4} M toluene solution of complex **1** at −78 °C in a Schlenk vessel, there was a slow fading of the orange color to pale yellow over 20−40 min, attributable to reaction with N_2O. In this way it was confirmed that no colored intermediates accumulate in any significant concentration when the reaction is carried out at low temperature.

Kinetics with Ether as Solvent. The pseudo-first-order rate constant for the reaction of **1** with saturated solutions of N_2O in diethyl ether at 25 °C was found to be $k_{obs} = 0.085 \pm 0.005$ s^{-1}. Under the assumption of second-order kinetics, this corresponds to a second-order rate constant, k_2, of 0.57 ± 0.05 M^{-1} s^{-1} for this, the case of diethyl ether as solvent. Thus, the nitrous oxide splitting by **1** is seen to be approximately 6 times slower in ether than in toluene. Weak coordination of a diethyl ether molecule to the three-coordinate Mo center in **1** is an unlikely explanation for the observed slower reactivity in this solvent, it being the case that Mo(N[R]Ar)$_3$ (**1**) crystallizes from ethereal solvents including THF without retaining solvent,[45] and the Lewis acidity of the complex is so weak that it fails to bind even strong donors such as pyridine. Furthermore, the visible spectrum of **1** is essentially identical in toluene to that in diethyl ether (Figure 2). Although it is possible that the broad features of the visible spectrum of **1** are insensitive to coordination of an ethereal solvent molecule, a more satisfying explanation of the reaction rate attenuation in ether stems from differential solvation of the putative polar intermediate nitrous oxide complex (ONN)Mo(N[R]Ar)$_3$ (**1-NNO**, see Figure 1). Such an explanation is, in effect, an argument based on dielectric strength considerations.[111] Undue attention need not be devoted to the relatively small observed difference in reaction rate in ether versus toluene.

Kinetics for Reaction of 1 with NO. One potentially important pathway (path 1, Figure 1) for the N_2O cleavage reaction involves fast trapping of NO after the N_2O binding and activation. Therefore, we investigated the kinetic parameters associated with NO binding by complex **1**.

Bubbling of nitric oxide through a sealed cuvette containing a 6×10^{-4} M concentration of complex **1** in toluene elicited an extremely rapid color change from orange to pale yellow, corresponding to the rapid binding of NO by **1** to form **1-NO**. This reaction has been shown to supply in quantitative fashion the diamagnetic nitrosyl **1-NO**.[79]

Spectrophotometric measurements revealed three wavelength regions suitable for stopped-flow experiments: below 360 nm, where an increase in optical absorbance was noted, 365−390 nm (increase), and 395 nm (decrease), divided by isosbestic points at 360 nm ($\epsilon = 3600$ M^{-1} cm^{-1}) and 395 nm ($\epsilon = 2550$ M^{-1} cm^{-1}).

The final spectral changes observed in stopped-flow experiments using complex **1** at 6×10^{-4} M and NO at 1.2×10^{-2} M in toluene correspond to those discerned upon bubbling NO through a solution of **1** in the conventional spectroscopic study.

According to the absorbance changes, the reaction was at least 90% complete in the “blind” mixing time of the stopped-flow apparatus (2 ms) at temperatures +25, −55, and −78 °C. In all cases (see Figure 5), the stopped-flow traces were horizontal straight lines with the absorption corresponding to the product, nitrosyl **1-NO**. No absorbance changes attributable to NO binding were seen even in the earliest period of stable detection.

For the purposes of estimating the rate of nitric oxide binding by **1**, we will assume the binding to be first order in complex **1**, first order in NO, and irreversible. The pseudo-first-order rate constant k'_{obs} can be evaluated as $>10^3$ s^{-1}. The second-order rate constant k_{NO1} then can be estimated at $>10^5$ M^{-1} s^{-1}. The observed fast reaction between **1** and nitric oxide is not surprising in view of the published data on the rates of NO binding by other transition metal complexes.[117−123]

The most detailed studies on the rate of NO binding by metal complexes have been carried out for iron(II) and iron(III) heme proteins and related phthalocyanine and porphyrin complexes.[117−123] Other systems having received scrutiny in this

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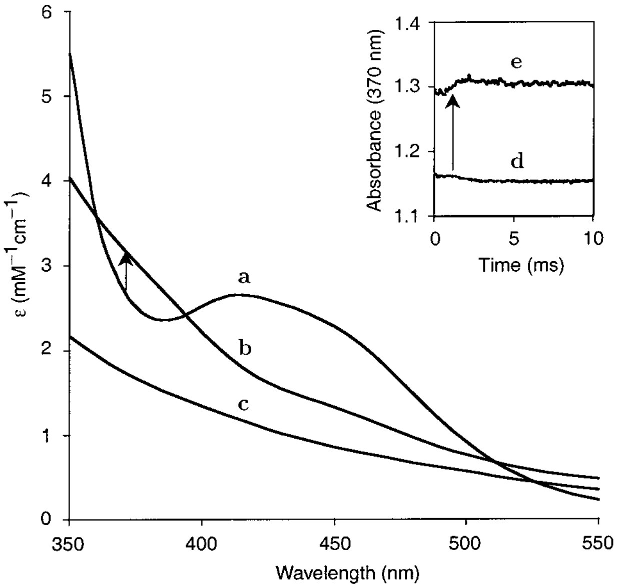

Figure 5. (a) Spectrum of Mo(N[R]Ar)$_3$ (**1**) in toluene solution. (b) Spectrum of **1** in toluene after exposure to NO. (c) Spectrum of a toluene solution of **1** after brief exposure to air. (d) Stopped-flow kinetic trace obtained on mixing a toluene solution of **1** with the pure solvent. (e) Stopped-flow kinetic trace obtained on mixing a toluene solution of **1** with a solution of NO in toluene. Initial concentrations (after mixing) for the latter experiment: [**1**], 0.33 mM; NO, 6 mM.

regard include the aqueous divalent ions of chromium[124] and iron,[125] a number of iron(II) complexonates,[126−128] and the ruthenium−edta system.[129] Association of NO with vacant coordination sites as in ferroheme proteins, and as in metalloporphyrins in nondonor solvents, has been identified with rate constants on the order of 10^9 M^{-1} s^{-1} at ambient temperature, close to the diffusion-controlled limit.[117−123] Such fast processes have been studied by flash photolysis techniques, due to the photoreversibility of NO coordination in the systems in question.

The stopped-flow technique in some cases can be applied to the study of near-diffusion-controlled reactions, by using very dilute reaction solutions at cryogenic temperatures.[114−116] Unfortunately, this approach is not applicable to the study of the reaction of **1** with NO, which most likely is nearly a diffusion-controlled process. Decreasing the reagent concentrations by several orders of magnitude will lead to the predominant registration of side reactions, due to the extreme air and water sensitivity of complex **1**. Moreover, comparing the low-temperature kinetic parameters with those obtained for the nitrous oxide reaction in the range from +5 to +25 °C is an endeavor of dubious merit. Since the major focus of the current study is the reaction of **1** with N_2O, further investigations into the kinetics of NO binding were not pursued. In any event, it is clear that the binding of NO by complex **1** is at least 5 orders of magnitude faster than its reaction with N_2O.

Thermochemistry of N_2O and NO: Literature Data. Bond dissociation enthalpies (BDEs) for N_2O have been given as follows: $D_{N-NO} = 114$ kcal·mol^{-1} and $D_{N_2-O} = 40$ kcal·mol^{-1}.[130−133] In a study on the reactions of nickel cluster ions, dioxygen was compared with nitrous oxide as an oxygen atom source, the conclusion being that N_2O is the more efficient O donor because it possesses a good leaving group, namely dinitrogen.[134] The D_{N-O} value for nitric oxide has been given as 151 kcal·mol^{-1}.[132]

Ab initio computational methods have been used to assess the binding energy between NO and first-row transition metal cations.[135]

All-electron ab initio calculations have been performed for the diatomic metal nitrides YN,[136] MoN,[137] and RhN,[138] said work serving to identify the ground states for these systems and serving also to provide a bonding description, spectroscopic constants, and bond dissociation energies. The calculated bond dissociation energies for these systems are 106, 119, and 40 kcal·mol^{-1}, respectively. This partial series of diatomic nitrides of second row transition metals illustrates the propensity of molybdenum to form a relatively strong triple bond to nitrogen. In addition, although the molybdenum and rhodium diatomic nitrides enjoy a description as triply bonded entities, the yttrium nitride molecule is indicated to have double bond character, consisting solely of two π bonds, with no σ component to the Y−N interaction.

Interestingly, what little information is available suggests that the uranium−nitride bond energy is similar to that for molybdenum: D_{U-N} for $[OUN]^+$ is ≈120 kcal·mol^{-1}, while D_{U-N} for $[UN]^+$ is ≈116 kcal·mol^{-1}.[139] The latter information may be useful in assessing the potential for dinitrogen splitting in heterodinuclear molybdenum/uranium dinitrogen complexes,[43] or in related diuranium systems.[140−143]

Thermochemistry. Solution calorimetry studies were carried out in order to assess enthalpic factors relevant to the selective splitting of the nitrous oxide N−N bond by complex **1**. The reactions in question, namely the N_2O splitting reaction and the NO binding reaction, both were particularly amenable to analysis by solution calorimetry because of their rapid and essentially quantitative nature.

Figure 6 displays the NO binding reaction as *C*, the enthalpy of which is found to be −82.5 ± 2.5 kcal·mol^{-1}, while the N_2O splitting reaction is indicated as *D*, the corresponding enthalpy change being −123.8 ± 0.8 kcal·mol^{-1}. As an aside, the latter two values in combination with *A*, the 114 kcal·mol^{-1} literature value for the N−NO bond dissociation enthalpy,[130−133] yield the value *B* for the Mo$\equiv$N BDE of 155.3 ± 3.3 kcal·mol^{-1}. Striking is the agreement of this value for *B* with values predicted using relativistic density functional theory calculations

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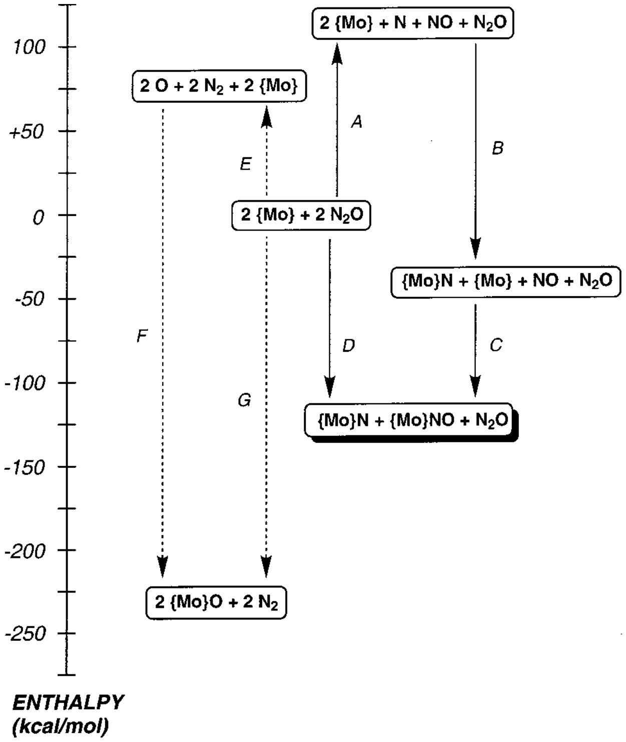

Figure 6. Thermodynamic parameters for the reaction between complex **1**, here represented as {**Mo**}, and N_2O. Note that 2 equiv of **1** and either 2 equiv (left branch) or 1 equiv (right branch) of N_2O are taken as the zero of energy. Quantities measured directly by solution calorimetry in this work correspond to *C* and *D*, respectively −82.5 ± 2.5 kcal·mol^{-1} (for **1** + NO) and −123.8 ± 0.8 kcal·mol^{-1} (for 2 equiv of **1** + N_2O). Using the literature value of 114 kcal·mol^{-1} for *A* in combination with *C* and *D* gives 155.3 ± 3.3 kcal·mol^{-1} for *B*, the Mo−N triple bond energy in **1-N**. Oxo transfer is calculated for 2 equiv of **1** to be downhill by twice the previously measured Mo−O BDE of 155.6 ± 1.6 kcal·mol^{-1} (*F*) offset by *E*, twice the literature value (40 kcal·mol^{-1}) for the nitrous oxide N−O BDE, giving *G* = −230 kcal·mol^{-1}.

(154 kcal·mol^{-1} for $N{\equiv}Mo(NH_2)_3$ and 157 kcal·mol^{-1} for $N{\equiv}Mo(NMe_2)_3$).[144] It appears that the calorimetrically determined Mo≡N BDE for nitride **1-N** is the first such value to be so obtained, and it is of interest further in that it indicates that the splitting of N_2 by 2 equiv of complex **1**, giving ultimately 2 equiv of **1-N**, is favored enthalpically by ca. 86 kcal·mol^{-1}. As has been surmised previously, therefore, the formation of two very strong Mo≡N triple bonds serves as the driving force for N_2 cleavage by complex **1**.[47,45,144−146]

Whereas reducing metal complexes typically effect oxo abstraction from N_2O,[68−76] with liberation of N_2 as a stable byproduct, the reaction of complex **1** with N_2O is completely selective for N−N bond cleavage.[79,80] It is of interest to determine if the latter observed outcome is in accord with thermodynamic considerations. It has been reported that the Mo−O BDE for the terminal molybdenum(V) oxo complex **1-O** is 155.6 ± 1.6 kcal·mol^{-1}, a value equal to *F*/2 in Figure 6. This fact, taken in conjunction with the knowledge that the NN−O BDE value is 40 kcal·mol^{-1},[130−133] permits the conclusion that the conversion of 2 equiv of complex **1** to 2 equiv of **1-O** (if effected by 2 equiv of N_2O) would be downhill by a quantity equal to *G*, namely 231.2 ± 3.2 kcal·mol^{-1}. Since the latter value is in excess of the value of *D* by 107.4 ± 4.0 kcal·mol^{-1}, one sees that oxidation of complex **1** by nitrous oxide would have been vastly preferable to N−N bond splitting, the pathway which prevails evidently for reasons that are entirely kinetic in origin.

Note that in Figure 6, the left branch considering the hypothetical oxidation of complex **1** requires 2 equiv of N_2O for comparison with the right branch, because in the right branch each molecule of N_2O effects conversion of 2 equiv of complex **1**. In other words, from the standpoint of bonds formed, one must compare the formation of two Mo−O bonds against the formation of one Mo≡N and one Mo−NO bond.

Synthetic and Structural Considerations for Mo(N[2-Ad]-Ar)$_3$ (2). The required aniline HN(2-Ad)Ar was synthesized according to the literature procedure for HN(2-Ad)Ph.[147] Simply heating 2-adamantanone with 2 equiv each of formic acid and 3,5-dimethylaniline using Lueckart conditions[148] resulted in the formation of the desired aniline in essentially quantitative yield, after accounting for the recovery of unreacted starting materials. Carrying out the synthesis using the published procedure with a 5 h reflux resulted in smooth product formation, but a substantial increase in conversion was realized when the reflux was extended to 24 h. Crystallization from pentane serves as an efficient purification for the aniline, HN(2-Ad)Ar. The signature ^{1}H NMR signal for HN(2-Ad)Ar in C_6D_6 is a resonance at 3.50 ppm assigned to the C−*H* moiety adjacent to nitrogen.

Deprotonation of HN(2-Ad)Ar using *n*-BuLi in a hydrocarbon solvent was found to result in clean, quantitative formation of Li(N[2-Ad]Ar), which precipitates directly from the reaction mixture. The lithium reagent is essentially insoluble in hydrocarbon solvents but has good solubility in ether and THF. The ^{1}H NMR spectrum of Li(N[2-Ad]Ar) in THF-d_8 features a signal at 3.31 ppm for the C−*H* moiety adjacent to nitrogen.

Complex **2** is synthesized straightforwardly. Treatment of $MoCl_3(THF)_3$[149] with a deficiency of Li(N[2-Ad]Ar) according to standard procedures[45] provided the desired three-coordinate molybdenum(III) complex in 64% recrystallized yield. The solubility properties of complex **2** are different enough from those for highly lipophilic **1** that crystallization was initiated upon storage of a concentrated solution at room temperature. The solubility properties of complex **2** are similar to those of the previously described *N*-1-adamantyl-substituted molybdenum(III) derivative.[43]

The ^{1}H NMR spectrum of complex **2** consists of several broad resonances, the most prominent of which is the signature resonance for the 18 benzylic hydrogens $C_6H_3(CH_3)_2$ appearing at −3.00 ppm. An Evans method[150,151] magnetic susceptibility measurement is consistent with assignment of complex **2** as having a quartet ground state ($\mu_{eff} = 3.88\ \mu_B$), as expected for three-coordinate molybdenum(III) complexes of this type.[45,144−146] The increased steric bulk of the 2-adamantyl substituent relative to the *tert*-butyl substituent of **1** manifests itself during recrystallization of *N*-2-adamantyl derivative **2**. Storage of the purified material at −35 °C under N_2 (1 atm) does *not* result in the formation of a bridging dinitrogen complex, which in the case of **1** is deep purple in color,[42,45,47] and the diamagnetic nitrido complex $NMo(N[2\text{-}Ad]Ar)_3$ (**2-N**) is *not* produced under these

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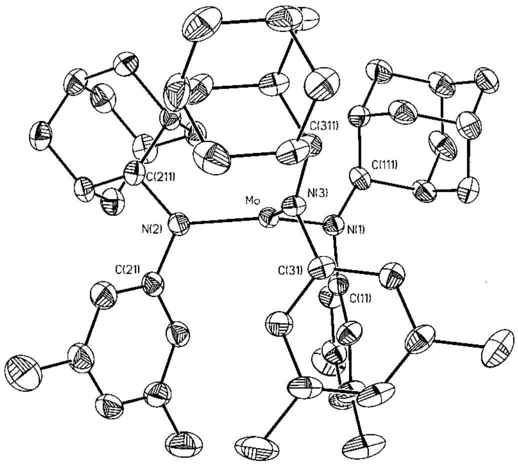

Figure 7. Structural diagram of Mo(N[2-Ad]Ar)$_3$ (**2**) with thermal ellipsoids drawn at the 30% probability level. Selected distances (Å): Mo−N1, 2.001(3); Mo−N2, 1.990(3); Mo−N3, 1.981(3); N1−C111, 1.473(4); N1−C11, 1.426(4); N2−C211, 1.482(4); N2−C21, 1.430(4); N3−C311, 1.479(4); N3−C31, 1.429(4). Selected angles (°): N1−Mo−N2, 121.24(11); N1−Mo−N3, 119.92(11); N2−Mo−N3, 118.79(11); Mo−N1−C111, 128.9(2); Mo−N1−C11, 112.2(2); C11−N1−C111, 116.6(3); Mo−N2−C211, 127.4(2); Mo−N2−C21, 111.2(2); C21−N2−C211, 117.8(3); Mo−N3−C311, 132.6(2); Mo−N3−C31, 108.0(2); C31−N3−C311, 116.1(3).

conditions. As has been expounded on in the case of the 1-adamantyl derivative,[41] Mo(N[1-Ad]Ar)$_3$, the sterically encumbering adamantyl substituents serve to inhibit formation of a dinuclear dinitrogen complex, thereby shutting down the dinitrogen cleavage reaction.[41]

Crystals of complex **2** suitable for an X-ray diffraction study were obtained from a chilled ether solution. A representative $d_{\text{Mo-N}}$ value is 1.990(3) Å for the pseudo-three-fold-symmetric complex, while a representative $\angle_{\text{N-Mo-N}}$ value is 119.92(11)° (Figure 7). The sum of the three $\angle_{\text{N-Mo-N}}$ values is 359.95°, reflecting the trigonal planar coordination environment of the molybdenum center. A conformational feature of some interest involves the three C−*H* moieties adjacent to the nitrogen atoms. The three C−H vectors corresponding to these three β-hydrogens are roughly normal to the molecular pseudo-three-fold axis, and they also lie in a plane approximately coparallel with the MoN$_3$ plane. With the substituents disposed in such a manner, the conformational restrictions on the motions of the 2-adamantyl groups may be responsible for the absence of β-hydrogen elimination reactivity in the chemistry of **2**. By way of contrast, it should be recalled that the analogue of formula "Mo(N[^{i}Pr]Ar)$_3$" exists as its metallaziridine hydride tautomer and has a doublet rather than a quartet ground state.[41]

Insights from Reaction Chemistry of Complex 2. In the original report on complex **1**, it was shown that a terminal nitrido derivative, namely NMo(N[R]Ar)$_3$ (**1-N**), could be prepared by N atom abstraction from mesityl azide (MesN$_3$).[79] This reaction was unusual in that, normally, reducing metal complexes react with organic azides to give organoimido species with loss of dinitrogen.[58,152−154] Via a labeling experiment employing ^{15}NNN-*p*-tolyl as the source of the nitrido nitrogen atom, it was shown that the abstracted nitrogen originates from the terminal position.[79] From a mechanistic point of view, it is not known yet whether the reaction proceeds by [NNN] radical transfer[155,156] followed by N$_2$ loss, or by N atom abstraction followed by fast decomposition of the diazenyl radical [NNAr′] (Ar′ = mesityl or *p*-tolyl).[157,158]

The organoazide N atom abstraction reaction serves also as a convenient independent synthesis of nitride derivative NMo(N[2-Ad]Ar)$_3$ (**2-N**), the complex being obtained in 34% yield after an experiment performed in ether. Multiple recrystallizations from ether were required to provide **2-N** in pure form, accounting for the low isolated yield. In its proton NMR spectrum a characteristic resonance at 4.29 ppm (C$_6$D$_6$) is associated with the three amido β-hydrogens of diamagnetic **2-N**.

To characterize complex **2** chemically, its reaction with white phosphorus was investigated. A solution of complex **2** was treated with a large excess of P$_4$ to generate the diamagnetic phosphide complex, PMo(N[2-Ad]Ar)$_3$ (**2-P**), as a gold-brown solid, which was isolated in 54% yield (not optimized). Phosphide **2-P** exhibits a ^{1}H NMR resonance at 4.70 ppm for its three β-hydrogens, and in its ^{31}P NMR spectrum a single signal is located at 1215 ppm, the extremely large downfield shift being characteristic of terminal molybdenum(VI) and tungsten(VI) phosphide derivatives.[159−171] The significance of the reaction of **2** with P$_4$ rests in its indication that despite substantial crowding imposed by the 2-adamantyl substituents (Figure 7), sufficient space still is available at the molybdenum center to permit access to substrates at least as large as the tetrahedral P$_4$ molecule.

A crystal suitable for an X-ray diffraction study of phosphide **2-P** was obtained from a chilled ether solution. The Mo−P vector of the molecule (Figure 8) is coincident with a crystallographic three-fold axis of symmetry, and the $d_{\text{Mo-P}}$ value of 2.107(3) Å is in the expected range for molybdenum(VI) terminal phosphide complexes.[160−162] The $d_{\text{Mo-N}}$ value in the complex is 1.984(5) Å, not appreciably smaller than in the molybdenum(III) precursor, complex **2** (Figure 7). Phosphide **2-P** displays a pseudo-tetrahedral MoPN$_3$ core, with the $\angle_{\text{N-Mo-P}}$ value equal to 102.76(14)° and the $\angle_{\text{N-Mo-N}}$ value equal to 115.27(10)°. The observed compression of $\angle_{\text{N-Mo-P}}$

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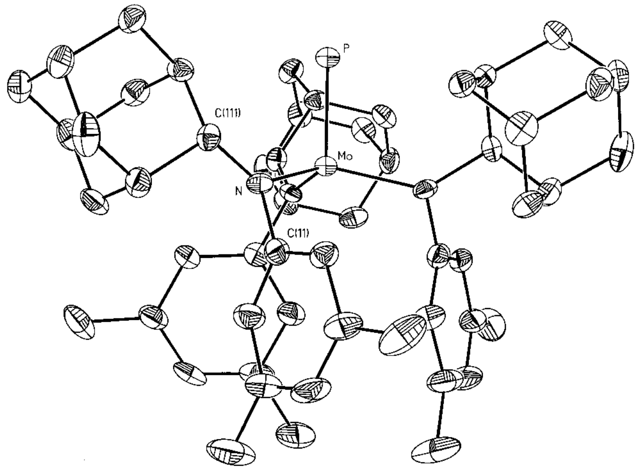

Figure 8. Structural diagram of PMo(N[2-Ad]Ar)$_3$ (**2-P**) with thermal ellipsoids drawn at the 30% probability level. Selected distances (Å): Mo−P, 2.107(3); Mo−N, 1.984(5); N−C11, 1.447(8); N−C111, 1.504(8). Selected angles (°): N−Mo−N′, 115.27(10); P−Mo−N, 102.76(14); Mo−N−C11, 110.4(4); Mo−N−C111, 135.8(4); C11−N−C111, 111.0(5).

relative to the tetrahedral angle allows for maximum orthogonality of the Mo−P π-bonds (axial) relative to the Mo−N π bonds (equatorial).

That the introduction of a phosphorus atom into the space bounded by the three 2-adamantyl groups requires substantial flexing of the molecular framework is indicated by the ca. 7° increase of the $\angle_{\mathrm{Mo-N-C}}$ (to the 2-adamantyl group) vis-à-vis precursor **2**. A complementary indication of this flexing to accommodate the phosphide phosphorus atom is a compressed value of $\angle_{\mathrm{C-N-C}}$ relative to precursor **2**, the decrease in this metric parameter being ca. 6°. Inspection of a space-filling model of phosphide **2-P** suggests that the metal atom is completely encapsulated by this complement of four ligands, such that the complex is expected not to undergo any reactions requiring coordination of a substrate to the metal center. A propellor-like arrangement of the three aryl paddles, an arrangement allowing for three edge-to-face interactions[172,173] which align one *ortho* hydrogen per ring with a proximal π cloud, is observed for both complexes **2** and **2-P**. The latter conformational attribute now is recognized to be a structural calling card for three-fold-symmetric molecules possessing an M(N[hydrocarbyl]Ar)$_3$ moiety.[45]

In view of the rapid reaction of complex **1** with N$_2$O, the reaction of 2-adamantyl derivative **2** with N$_2$O is noteworthy for being rather more sluggish. Accordingly, treatment of **2** in toluene solution with an excess of N$_2$O, added as a saturated toluene solution, resulted in consumption of complex **2** according to a smooth pseudo-first-order kinetic profile. Kinetic data for the reaction, carried out at 26 °C, were collected multiple times by conventional diode array spectrophotometric analysis at both of two initial concentrations of complex **2**. Suitable wavelengths for monitoring the decay of complex **2** were determined to be 427 or 500 nm, depending on the initial concentration of **2** employed. Simultaneous monitoring of the appearance of nitrosyl and nitrido products unfortunately was not possible due to spectral overlap. The pseudo-first-order rate constant k_{obs} obtained for the process was 0.031 ± 0.002 s^{-1}, for initial concentrations $[\mathbf{2}]_0$ of 0.6 and 2.4 mM. Dividing through by the constant concentration of nitrous oxide [N$_2$O] yields a corresponding second-order rate constant $k_{\mathrm{NNO2}} = 0.47 \pm 0.03$ M^{-1} s^{-1}. Thus it is seen that the splitting of N$_2$O by the *sec*-adamantyl-substituted derivative complex **2** is slower by approximately an order of magnitude than for *tert*-butyl-substituted complex **1**.

That the reaction in question leads to a 1:1 mixture of nitride **2-N** and nitrosyl **2-NO** was verified by proton NMR analysis of the crude mixtures stemming from the kinetic studies, and also by multiple independent experiments.

Competitive NO Binding by Complexes 1, 2, and 3. The binding of NO by three-coordinate metal complexes was investigated first by Bradley and co-workers in the context of the chromium derivative Cr(N^{i}Pr$_2$)$_3$, complex **3**.[107,109,110] Obtained smoothly upon treatment of complex **3** with 1 equiv of NO is the terminal nitrosyl derivative **3-NO**, a linear nitrosyl characterized by a low ν_{NO} of 1651 cm^{-1}, and serving as a chromium analogue of four-coordinate **1-NO**. Pseudo-tetrahedral chromium nitrosyls such as **3-NO** have been employed recently as intermediates in the synthesis of chromium(VI) terminal nitrido derivatives.[110,174] It was hoped in the present study that chromium complex **3** would be competitive with molybdenum complex **1** with respect to rate of NO binding, because control experiments showed **3** to be inert to N$_2$O. Subject to the criteria articulated below, complex **3** is to be used as an NO scavenger for the purpose of mechanistic discrimination. Also, **3-NO** showed no reactivity (i.e., NO or O transfer) with complexes **1** or **2**.

In the case of the 2-adamantyl-substituted three-coordinate complex **2**, the reaction with NO also proceeds smoothly, and, in a preparative experiment, nitrosyl (ON)Mo(N[2-Ad]Ar)$_3$ (**2-NO**) was obtained in 70% yield after recrystallization from THF. The proton NMR resonances of diamagnetic **2-NO** are similar to those for nitride **2-N**, but the diagnostic signal for the three β hydrogens of **2-NO** appears at 4.58 ppm (C$_6$D$_6$).

Prerequisite to the inclusion of Cr derivative **3** in the nitrous oxide reaction with **1**, information on the relative rates of NO binding by **3** and **1** was required. Accordingly, experiments were carried out in which a 1:1 mixture of **3** and **1** was treated with 1 equiv of NO, conditions under which the latter constitutes the limiting reagent. Thus, the product mixture is expected to contain nonzero concentrations of four components: Mo complex **1**, Cr complex **3**, and the two corresponding nitrosyls **1-NO** and **3-NO**. The experiment is designated schematically in Figure 9, the quantity of interest being the fraction H measured at t_∞.

Because of the complexity of the proton NMR spectra of such mixtures, ^{1}H NMR spectroscopy was used solely for verification of the presence of the four components, and to ascertain that the transformation had proceeded without side reactions. Quantification of the fraction H (Figure 9) was accomplished using ^{15}N NMR spectroscopy, to which end all experiments were carried out using the isotopomer ^{15}NO. ^{15}N NMR chemical shifts for **1-^{15}NO** and **3-^{15}NO** were determined to be 420.0 and 436.7 ppm, respectively, with relaxation times (T_1) measured at 3.38 ± 0.16 and 5.87 ± 0.26 s, respectively, as determined for the pure components. Analysis of the product mixture by ^{15}N NMR spectroscopy therefore is satisfactory since T_1 values in the presence of paramagnetic complexes generally are smaller than those for pure diamagnetic substances, and, in any event, the latter was shown by in situ measurement to be the case for the mixtures in question. Spectra for integration were acquired with

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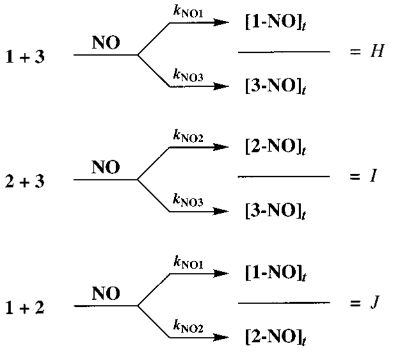

Figure 9. Schematic representation of three separate competition experiments in which 1:1 mixtures of **1** and **3**, **2** and **3**, and **1** and **2** were treated with NO (1 equiv). Experiments carried out with ^{15}NO were analyzed by ^{15}N NMR spectroscopy to determine the three ratios of product nitrosyls, the quantities *H*, *I*, and *J* as indicated, at a time *t* corresponding to complete reaction. An internal check is present since $H/I = J$.

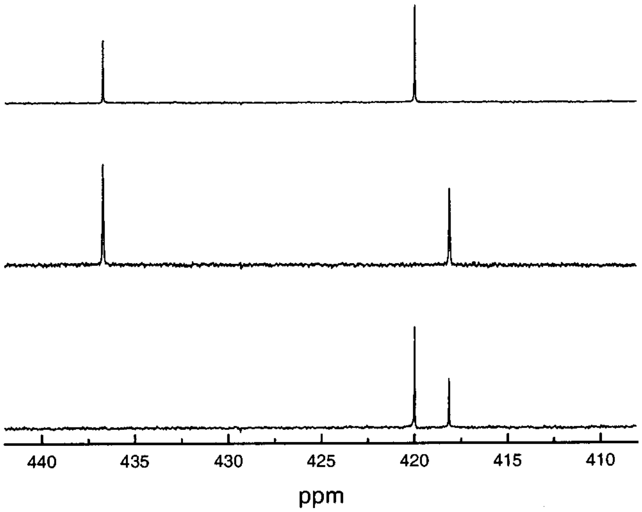

Figure 10. ^{15}N NMR data for three competition experiments in which 1:1 mixtures of **1** and **3**, **2** and **3**, and **1** and **2** were treated with ^{15}NO (1 equiv). The experiments serve to provide the quantities *H*, *I*, and *J*, as defined schematically in Figure 9.

delay times of at least 10 sec (45° pulse width), and measured values for the fraction *H* were found to be reproducible. Similar considerations apply for the quantities *I* and *J*, as discussed below.

The observed value for *H* after nitrosylation of a 1:1 mixture of **1** and **3** was 1.65, a value corresponding to the following ratio of second-order rate constants for NO binding: $k_{NO1}/k_{NO3} = 2.06$. Numerical integration of the differential equations describing this kinetic system was employed to obtain the value of k_{NO1}/k_{NO3}, given the observed product ratio *H* and the stated initial conditions. Importantly, the same value within error for *H* was obtained regardless of whether the NO was predissolved and introduced as a solution, or added in gaseous form to the headspace in the reaction vessel.[175]

It was possible also to gauge the efficiency of NO binding by Cr complex **3** relative to the more sterically encumbered three-coordinate molybdenum(III) complex **2**. Accordingly, treatment of a 1:1 mixture of **2** and **3** with 1 equiv of ^{15}NO led to an observed ratio of nitrosyls $I = 0.73$, corresponding to a ratio of second-order rate constants $k_{NO2}/k_{NO3} = 0.64$. Thus it is seen that the NO binding efficiencies for the three complexes considered here are in the order **1** > **3** > **2**. It is consistent with chemical intuition that the most hindered system, namely the 2-Ad-substituted complex **2**, should be less competitive in its ability to scavenge NO than its ^{t}Bu-substituted congener, complex **1**. Less obvious is that the chromium(III) complex **3** should be intermediate in reactivity, but this outcome is dramatic in its illustration of the ability of ligands to attenuate reactivity.[176,177]

Internal consistency in the above-determined numbers was obtained by carrying out a third competition experiment, namely the treatment with ^{15}NO (1 equiv) of a 1:1 mixture of the two molybdenum complexes, **1** and **2**. Measured in this case was a ratio of nitrosyls $J = 2.29$, a value in very good agreement with that obtained indirectly by dividing the results of the two foregoing experiments that involve chromium (i.e., 1.65/0.73 = 2.26). Since $J = 2.29$, the corresponding ratio of second-order rate constants $k_{NO1}/k_{NO2} = 3.28$ is also in good agreement with dividing the respective independent calculations (i.e., 2.06/0.64 = 3.22).

Competition Experiments Involving N_2O. Knowing the relative rate constants for NO binding by the three-coordinate molybdenum(III) and chromium(III) complexes, it is possible to generate expectation values for the ratio of nitrosyls to be produced in experiments involving nitrous oxide splitting (Figure 12), assuming a mechanism that involves molecular NO as a post-rate-determining intermediate (e.g., path 1, Figures 1 and 11).

Accordingly, kinetic simulations for the treatment of a 1:1 mixture of molybdenum complex **1** and chromium complex **3** with an excess (10 equiv) of $^{15}N_2$-labeled nitrous oxide led to a predicted value for the ratio of nitrosyls $K = 0.89$, whereas the observed value (^{15}N NMR analysis) after complete consumption of complex **1**, the limiting reagent, was 27.7. This striking result implies that the capture of molecular NO by the metal complexes is *not* the dominant mechanism of metal nitrosyl formation in the nitrous oxide N−N bond cleavage reaction. Given the system proposed in Figure 11, one can account for the formation of small amounts of **3-^{15}NO** by either the heterobimetallic pathway or by some linear combination of path 2 and path 1. Either way, the conclusion may be drawn firmly that path 1, the pathway involving free NO in a post-rate-determining step, is *not* dominant.

Introduction of chromium complex **3** into the relatively slow N_2O splitting reaction system involving the bulkier 2-Ad-substituted Mo complex **2** again led to the observation of far smaller amounts of the chromium nitrosyl **3-^{15}NO** than expected if molecular NO were important as an intermediate. Accordingly, treatment of a 1:1 mixture of **2** and **3** with 10 equiv of $^{15}N_2$-labeled nitrous oxide led after complete reaction to the ratio of nitrosyls $L = 1.24$, whereas the expected value, assuming NO capture as the sole mechanism of nitrosyl formation, was 0.34. The observation indeed revealed a greater percentage of **2-^{15}NO** formation than expected if NO capture were the dominant nitrosylation mechanism. Furthermore, if the dominant nitrosylating agent in the present case is the putative adduct **2-NNO**, then the observed value of *L* indicates that Cr complex **3** is competitive with Mo complex **2** for interception of this intermediate. Consideration of steric factors indicates that this should be so, inasmuch as it ought to be relatively difficult to pack two molecules of 2-adamantyl-substituted **2** around a single N_2O molecule. In line with such reasoning is the observed value of *K*, which suggests complex **3** to be less efficient at scavenging putative **1-NNO** than is complex **1** itself.

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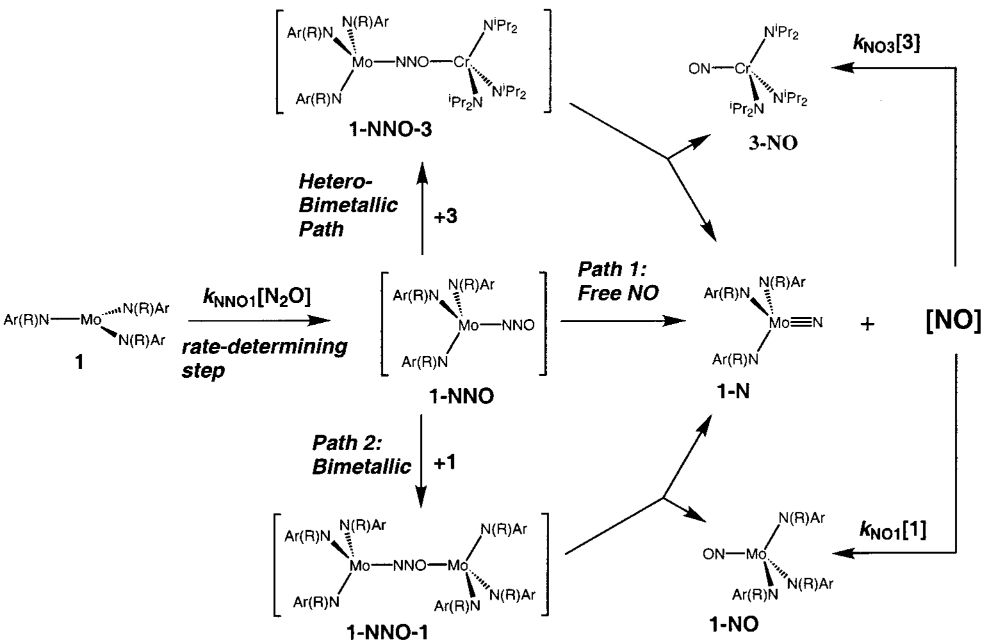

Figure 11. Reaction of **1** with N_2O in the presence of **3** ($Cr(N^iPr_2)_3$, 1 equiv) to give a mixture of Mo and Cr nitrosyls **1-NO** and **3-NO**, along with the Mo nitrido **1-N**. Known Cr nitrido **3-N** is not observed among the products. Formation of **3-NO** may occur by NO capture with second-order rate constant k_{NO3} if path 1 is the dominant N_2O cleavage pathway, or via an unobserved heterobimetallic adduct **1-NNO-3** if path 1 is not operative.

$$\mathbf{1}+\mathbf{3}\xrightarrow{N_2O}\frac{[\mathbf{1\text{-}NO}]_t}{[\mathbf{3\text{-}NO}]_t}=K$$

$$\mathbf{2}+\mathbf{3}\xrightarrow{N_2O}\frac{[\mathbf{2\text{-}NO}]_t}{[\mathbf{3\text{-}NO}]_t}=L$$

$$\mathbf{1}+\mathbf{2}\xrightarrow{N_2O}\frac{[\mathbf{1\text{-}NO}]_t}{[\mathbf{2\text{-}NO}]_t}=M$$

Figure 12. Definition of the quantity *K* as the ratio of nitrosyls produced upon treatment of a 1:1 mixture of complexes **1** and **3** with 10 equiv of N_2O. Implicit in this experiment is that for every nitrosyl formed, also formed is an equivalent of the molybdenum nitride **1-N**. If the mechanism of nitrosyl formation were NO capture (path 1 of Figure 11), then the value of *K* would be predictable based on the independently determined quantity *H*; see Figures 9 and 10 and the text. Similar considerations apply to the quantities *L* and *M*.

Also examined was the competition experiment involving addition of 0.5 equiv of $^{15}N_2O$ to a solution containing a 1:1 mixture of the two molybdenum complexes **1** and **2** (Figure 12). Determination of the ratio *M* of nitrosyls produced after complete reaction was effected by ^{15}N NMR spectroscopy, the value obtained being too large to measure accurately because of the extremely small amount of **2-NO** produced. Using the values determined above for k_{NO1}/k_{NO2} and k_{NNO1}/k_{NNO2}, it was predicted via simulation that the value for *M* would have been 1.75 if NO capture were the sole means of nitrosyl formation. This final competition experiment serves to underscore further the inconsistency of path 1 (Figure 11), the monometallic bond cleavage pathway, with the collective competition experiments.

3. Concluding Remarks

First reported in 1995,[79] and elaborated upon in 1998,[80] the intriguing and counterintuitive observation of nitrous oxide N−N bond cleavage by a three-coordinate molybdenum(III) complex[44,102] has been difficult mechanistically to unravel due to the absence of observable intermediates. Only very recently has the reverse reaction been observed, namely the *formation* of nitrous oxide upon treatment of a nitrido−metal complex with NO.[81]

The present work has shed light on the thermodynamic considerations involved in the cleavage reaction, it being most striking that the observed reaction is enthalpically far less favorable than a plausible alternative scenario that would involve nitrous oxide deoxygenation. A thermodynamic quantity derived from the present work is a value for the molybdenum−nitrogen triple bond dissociation energy for nitrido derivative **1-N**, this quantity (155.3 ± 3.3 kcal•mol^{-1}) being relevant also to another important reaction of complex **1**, namely the splitting of dinitrogen via a well-defined bimetallic intermediate.[40−47] Computational studies have devoted effort to prediction of the Mo≡N bond energy,[144−146] and from the present work an experimental value now is available for comparison.

Given that the nitrous oxide N−N bond cleavage reaction is *not* under thermodynamic control, kinetic parameters were investigated. The reaction of complex **1** with an excess of N_2O was studied by stopped-flow techniques, while the reaction of the more hindered three-coordinate Mo(III) derivative complex **2** with N_2O, which proceeds similarly to give a 1:1 mixture of nitrosyl and nitride products, was amenable to monitoring by conventional diode array spectrophotometric techniques. In both cases it was determined that the reaction is first order in the starting molybdenum complex, mandating that if the N−N bond cleavage process is bimetallic in nature, then the relevant bimetallic intermediate is post-rate-determining in nature. That N_2O binding is the slow step may reflect attendant structural changes, e.g., the bending of N_2O upon complexation, along with a change in spin state from quartet to doublet.[178−183] Complexation of N_2O by the molybdenum complexes of

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relevance here is expected to be a reductive process akin to the binding of organic azides at their nitrogen terminus by group 5 metal complexes.[152−154] Activation parameters were determined for the reaction system featuring N_2O cleavage by complex **1**, said parameters being indicative of the energetics for N_2O reductive complexation.

One mechanistic scenario consistent with the information summarized in the preceding paragraphs implicates free nitric oxide as a post-rate-determining intermediate. To investigate this possibility, Bradley's three-coordinate chromium(III) complex[107,109,110] was used as an in situ NO scavenger in the nitrous oxide N−N bond cleavage reactions. Appropriate control and competition experiments revealed the formation of Bradley's nitrosyl in quantities far less than predicted by post-rate-determining NO capture. The simplest mechanism consistent with all the data is a post-rate-determining bimetallic scission of the nitrous oxide molecule. This conclusion is particularly intriguing when juxtaposed with the contrary results of a recent computational study, a study suggesting that a bimetallic mechanism ought to lead to deoxygenation rather than N−N bond cleavage.[184]

Perhaps most telling vis-à-vis the kinetically driven *selectivity* of the nitrous oxide N−N bond cleavage reaction is the observation that the N_2O binding event represents the rate-determining step. Corresponding to this key binding event is a transition state that appears thus far to have defied description via computational methods.[184] Evidently the putative adduct, e.g. **1-NNO**, is a potent nitrosylating agent. It is predicted that if steric considerations can be so arranged as to preclude the formation of a post-rate-determining bimetallic intermediate, then other chemistries of the mononuclear N_2O adduct might be realized.

Although N_2O adducts have not in this work been directly observed, it seems nevertheless that the activation pathway followed ultimately is dictated by the properties of N_2O as a ligand,[82,83] in conjunction with the unique N-atom-accepting propensity demonstrated for tris-amido molybdenum(III) complexes.[44]

4. Experimental Procedures

General Considerations. Solvents were dried and deoxygenated according to procedures detailed elsewhere.[80] Diethyl ether was dried according to a literature procedure.[185] White phosphorus (Monsanto) was purified by recrystallization from toluene. $MoCl_3(THF)_3$[149] and $Mo(N[^tBu]Ar)_3$[43] were prepared via published procedures. Other chemicals were purified via standard procedures or used as received. Magnetic susceptibilities were measured by NMR spectroscopy.[150,151] NMR spectra were recorded on Varian XL-300, Varian Unity-300, Varian Mercury-300, or Varian VXR-500 spectrometers. ^1H and ^{13}C NMR chemical shifts were reported with reference to solvent resonances (C_6D_6, 7.15, 128.0; $CDCl_3$, 7.24, 77.0; C_4D_8O, 3.58 and 1.73, 67.6 and 25.4). ^{15}N NMR spectra were referenced as reported previously.[110] CHN analyses were performed by Oneida Research Services (Whitesboro, NY), Microlytics (South Deerfield, MA), or Mikroanalytisches Labortorium (Mülheim, Germany). Melting points were obtained in sealed glass capillaries and are uncorrected. ^{15}NO, $^{15}N_2O$, and $N^{15}NO$ gas as well as C_6D_6, $CDCl_3$, and C_4D_8O were purchased from Cambridge Isotope Laboratory and used as is. Infrared spectra were recorded on a Bio-Rad 135 Series FTIR spectrometer. UV−visible spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. X-ray diffraction data were collected on a Siemens Platform goniometer with a charge-coupled device (CCD) detector.

Stopped-Flow Kinetic Measurements. Nitrous oxide (99.99%, Electronic Gases, The BOC Group, Inc.), nitric oxide (99.9%, Airgas), and argon (ultra-high-purity grade, Airgas) were used as received. Solutions of $Mo(N[R]Ar)_3$ in toluene or diethyl ether (0.3−1.2 mM) were prepared in a Vacuum Atmospheres glovebox filled with argon. Solutions of nitric oxide were prepared at 25 °C by bubbling the gas through the degassed dry solvent in a Hamilton gastight 10 mL syringe furnished with a Kontes three-way stopcock in a gas-bag filled with argon. Solutions of nitrous oxide of various known concentrations were prepared in the same way from N_2O and Ar gas mixtures generated using Bel-Art Products flowmeters calibrated for these gases. The solubilities of the gases at 25 °C are 133 ± 4 mM N_2O in toluene, 30 ± 1 mM N_2O in diethyl ether, and 12 ± 1 mM NO in toluene (see Supporting Information for details).

Caution! *The solutions containing N_2O must be bubbled through with an inert gas before disposal! A nonchemical explosion happened during the storage of a tightly closed bottle with such wastes, probably due to the slow reaction of N_2O with organic substances to form much less soluble N_2.*

Visible spectra were recorded on a Hitachi U-2000 UV−vis spectrophotometer. Kinetic measurements were performed at temperatures from −78 to +25 °C using a Hi-Tech Scientific (Salisbury, Wiltshire, UK) SF-43 Multi-Mixing CryoStopped-Flow instrument equipped with stainless steel plumbing, a stainless steel mixing cell with sapphire windows, and an anaerobic gas-flushing kit. The instrument was connected to an IBM computer with IS-2 Rapid Kinetics software by Hi-Tech Scientific. The temperature in the mixing cell was maintained to ±0.1 K, and the mixing time was 2 ms. The driving syringe compartment and the cooling bath filled with hexanes (Fisher) were flushed with argon before and during the experiments, using anaerobic kit flush lines. All flow lines of the SF-43 instrument were extensively washed with degassed anhydrous solvent before charging the driving syringes with reactant solutions. Most of the experiments were performed in a single-mixing mode of the instrument, with a solution of $Mo(N[R]Ar)_3$ being directly mixed with a N_2O solution in 1:1 ratio. A multimixing mode was used in some experiments to dilute N_2O stock solution 2 times with the solvent directly in the stopped-flow apparatus, before the $Mo(N[R]Ar)_3$ was added. These measurements were designed in order to avoid any possible contact of N_2O solutions with air upon dilution. In all kinetic experiments, series of 8−12 shots gave standard deviations within 5%, with overall reproducibility (established by repeated preparation and mixing of starting solutions) within 10%.

Synthesis of HN(2-Ad)Ar. 3,5-Dimethylaniline (33.4 mL, 268 mmol, 2.01 equiv), formic acid (10.4 mL of a 95−98% solution, ca. 2 equiv), and 2-adamantanone (20.06 g, 133.5 mmol) were heated at 95−100 °C for 24 h. Concentrated HCl (70 mL) was then added, and the solution was heated at 95 °C for 1 h. A copious amount of white solid appeared. The reaction mixture was diluted with water (100 mL), and the white solid was collected on a frit. The filtrate contained the hydrochloride of 3,5-dimethylaniline. The filter cake was washed with water (100 mL), and 3,5-dimethylaniline was recovered from the filtrate by adding concentrated NaOH solution (ca. 5 M) until the pH was ca. 14, at which point a yellow oil appeared. The aqueous layer was washed with ether (2 × 150 mL), and the solvent was removed in vacuo to yield a yellow oil (22 mL, 176 mmol). The filter cake was then washed with ether (2 × 100 mL), removing unreacted 2-adamantanone, which was recovered by removing the ether in vacuo (9.82 g, 73.5 mmol). The filter cake was slurried in water (200 mL) and ether (200 mL), and NaOH (12 g) was added to neutralize the hydrochloride. The organic layer was separated, and the aqueous layer was washed with ether (2 × 200 mL). The combined organics were washed with saturated aqueous sodium chloride (200 mL) and saturated aqueous sodium bicarbonate (200 mL). The combined aqueous layers were then extracted with ether (200 mL). The combined organics were evaporated, resulting in a white solid (14.9 g, 58.3 mmol, 43.7%). The solid was recrystallized from pentane at −35 °C in five crops (13.67 g, 53.54 mmol, 40%). Mp: 57−58 °C. ^1H NMR (500 MHz, C_6D_6): $\delta = 6.412$ (s, 1H, para), 6.252 (s, 2H, ortho), 3.636 (s, 1H, NH), 3.502 (s, 1H), 2.222 (s, 6H, ArMe), 1.948 (s, 2H), 1.614−1.802 (m, 10H), 1.4 (d, 2H). ^{13}C NMR (76 MHz, $CDCl_3$): $\delta = 147.41$ (s), 138.73 (q), 118.63 (d), 110.82 (d),

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56.60 (d), 37.68 (t), 37.37 (t), 31.65 (d), 31.54 (t), 27.43 (d), 27.30 (d), 21.43 (q). MS (70 eV): *m/z* (relative intensity) 255 (100) [M$^+$]. Anal. Calcd for $C_{18}H_{25}N$: C, 84.65; H, 9.87; N, 5.48. Found: C, 84.94; H, 10.03; N, 5.52.

Synthesis of LiN(2-Ad)Ar. HN(2-Ad)Ar (10.30 g, 40.33 mmol) was dissolved in pentane (50 mL) and cooled to −35 °C. *n*-Butyllithium (28 mL of a 1.6 M solution, 44.8 mmol, 1.1 equiv) was added via syringe over about a 5 min period, causing the precipitation of a fine white powder. The solid was collected on a frit and dried in vacuo to a constant weight (10.19 g, 38.99 mmol, 97%). ^{1}H NMR (500 MHz, C_4D_8O): $\delta = 5.590$ (s, 2H, ortho), 5.349 (s, 1H, para), 3.306 (s, 1H), 2.150 (m, 2H), 1.962 (s, 6H, ArMe), 1.87 (s, 2H), 1.83 (m, 4H), 1.716 (s, 3H), 1.38 (d, 2H), 1.28 (m, 1H). ^{13}C NMR (126 MHz, C_4D_8O): $\delta = 161.87$ (s, aryl ipso), 137.09 (s, meta), 110.63 (br d, ortho), 107.74 (d, para), 62.32 (d), 39.84 (t), 39.23 (t), 34.02 (t), 33.97 (d), 29.72 (d), 22.56 (q).

Synthesis of Mo(N[2-Ad]Ar)$_3$ (2). LiN(2-Ad)Ar (3.8001 g, 14.541 mmol, 2.02 equiv) was slurried in ether (100 mL), and the slurry was then chilled until frozen. The frozen slurry was allowed to thaw, and when magnetic stirring was just possible, $MoCl_3(THF)_3$ (3.0200 g, 7.2145 mmol) was added. The reaction mixture was stirred vigorously for 4.5 h, during which time the solution turned dark brown. The reaction mixture was filtered through Celite, and the filter cake was washed with ether (2 × 20 mL) until the washings were colorless. The filtrate was evaporated in vacuo, redissolved in ether (35 mL), and allowed to stand at room temperature overnight. A dark precipitate was removed by filtration, and the filtrate was reduced in volume and stored at room temperature until crystallization initiated. The saturated solution was then stored overnight at −35 °C. The solid powdery material was collected on a frit and washed with cold pentane (3 × 5 mL), yielding a dark orange material. A second crop was obtained by a similar crystallization from pentane (15 mL) (2.279 g, 2.653 mmol, 64%). Mp: 211−212 °C. ^{1}H NMR (300 MHz, C_6D_6): $\delta(\Delta\nu_{1/2}) = 12.818(71)$, 6H; 9.288(148), 6H; 5.299(ca. 300); 3.534(109); 1.962(ca. 300); −2.995(124), 18H, ArMe; −47.64(193), 3H. MS (70 eV): *m/z* (relative intensity): 861.1 (6.6) [M$^+$]. μ_{eff} (300 MHz, C_6D_6): 3.875 μ_B. Anal. Calcd for $C_{54}H_{72}MoN_3$: C, 75.49; H, 8.45; N, 4.89. Found: C, 74.96; H, 8.63; N, 4.70.

Synthesis of NMo(N[2-Ad]Ar)$_3$ (2-N). Complex **2** (0.4747 g, 0.5525 mmol) was dissolved in ether (10 mL) and chilled to −35 °C. Mesityl azide (90 μL, 0.6186 mmol, 1.1 equiv) was dissolved in ether (15 mL) and chilled to −35 °C. The solution of **2** was added to the azide solution over 15 min. The reaction mixture turned purple and then changed to brown over 5 min. After 1 h of stirring, the solvent was removed in vacuo. Two crops of tan-brown powder were obtained from a concentrated ether solution at −35 °C (0.1648 g, 0.1887 mmol, 34%). Mp: 235−240 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.730$ (s, 3H, para), 6.708 (s, 6H, ortho), 3.898 (s, 3H), 2.490 (s, 6H), 2.082 (s, 18H, ArMe), 2.000 (d, 6H), 1.84 (d, 12 H), 1.72 (m, 6H), 1.36 (d, 6H), 1.273 (6H). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 6.886$ (s, 3H, para), 6.031 (s, 6H, ortho), 4.29 (s, 3H), 2.96 (s), 2.35 (m), 2.097 (s, 18H, ArMe), 1.851 (s), 1.682 (s), 1.52 (m). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.951$, 137.731, 127.268, 127.125, 72.733, 38.414, 38.215, 32.327, 30.921, 28.540, 27.677, 21.632. Anal. Calcd for $C_{54}H_{72}MoN_4$: C, 74.28; H, 8.31; N, 6.42. Found: C, 74.21; H, 8.38; N, 6.49.

Synthesis of (ON)Mo(N[2-Ad]Ar)$_3$ (2-NO). Complex **2** (0.6658 g, 0.7750 mmol) was dissolved in ether (10 mL), and NO (21 mL, 0.8594 mmol, 1.1 equiv) was then added via syringe. The reaction mixture was stirred for 20 min, and the solution turned light brown-orange in color. The solvent was removed in vacuo, and the remaining solid was dissolved in ca. 10 mL of THF with stirring. Two crops of a powdery solid were collected (0.4800 g, 0.5399 mmol, 70%). Mp: 280−285 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.770$ (s, 3H, para), 5.779 (s, 6H, ortho), 4.190 (s, 3H), 2.162 (s, 6H), 2.100 (s, 18H, ArMe), 1.902−1.697 (m, 30 H), 1.40 (d, 6H). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 6.884$ (s, 3H, para), 6.092 (s, 6H, ortho), 4.579 (s, 3H), 2.638 (s, 6H), 2.10 (m, 9H), 2.080 (s, 18H, ArMe), 1.866 (s, 12H), 1.7−1.5 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.943$ (s), 137.929 (q), 128.119 (d), 127.515 (d), 75.536 (d), 38.361 (t), 38.194 (t), 33.835 (d), 31.019 (d), 28.260 (d), 27.897 (d), 21.714 (q). IR (benzene, 2 cm^{-1}): 1604 cm^{-1}. Anal. Calcd for $C_{54}H_{72}MoN_4O$: C, 72.95; H, 8.16; N, 6.30. Found: C, 72.63; H, 8.43; N, 5.80.

Synthesis of PMo(N[2-Ad]Ar)$_3$ (2-P). Complex **2** (0.5212 g, 0.6067 mmol) was dissolved in toluene (10 mL), and P_4 (0.0861 g, 0.695 mmol, 4.58 equiv) was added. The reaction mixture was stirred for 1 h, at which point the solvent was removed in vacuo. The solids obtained were dissolved in ether (20 mL) and filtered, removing a dark brown-orange solid (ca. 90 mg). The filtrate was evaporated to dryness and dissolved in methylene chloride (5 mL). Acetonitrile (10 mL) was added, causing precipitation of a brown solid, which was collected on a frit. This process was repeated with the filtrate, resulting in a second crop of material (0.2896 g, 0.3254 mmol, 54%). Mp: 223−224 °C (dec). ^{1}H NMR (500 MHz, C_6D_6): $\delta = 6.654$ (s, 3H, para), 5.987 (s, 6H, ortho), 4.700 (s, 3H), 3.129 (s, 6H), 2.086 (s, 18H, ArMe), 1.937 (m, 12H), 1.800 (br m, 6H), 1.651 (s, 12H), 1.413 (d, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 149.94$ (s), 137.06 (q), 128.33 (d), 127.15 (d), 79.40 (d), 38.68 (t), 38.21 (t), 35.32 (d), 30.83 (t), 28.11 (d), 27.83 (d), 21.57 (q). ^{31}P NMR (203 MHz, $CDCl_3$): $\delta(\Delta\nu_{1/2}) = 1215.46(86)$. MS (70 eV): *m/z* (relative intensity) 891.8 (0.72) [M$^+$]. HRMS (EI, 70 eV): calcd mass, 891.451793; found mass, 892.451(2). Anal. Calcd for $C_{54}H_{72}MoN_3P$: C, 72.87; H, 8.15; N, 4.72. Found: C, 73.64; H, 7.92; N, 4.34.

Exposure of Mo(N[2-Ad]Ar)$_3$ (2) to N$_2$. Several hundred milligrams of complex **2** was dissolved in ether (ca. 10 mL), and the solution was stored at −35 °C overnight. No color change was observed. A ^{1}H NMR spectrum of the sample indicated that complex **2** was pure and had undergone no net reaction.

^{15}N NMR General Considerations. For all experiments involving ^{15}NO, $^{15}N_2O$, or N^{15}NO, the amount of gas employed was measured using a gastight syringe. Manipulations involving the transfer of labeled gases were carried out inside an N_2-filled glovebox as follows. A septum was fitted over the open end of the commercially obtained glass vessel containing the appropriate ^{15}N-labeled gas (100 mL, 1 atm). The headspace between the septum and the break-seal was evacuated by using a needle connected to a source of vacuum. An amount of mercury equivalent in volume to the just-evacuated headspace was then introduced. Next, the break-seal was broken. To maintain a constant pressure of 1 atm inside the vessel containing the labeled gas, each time a desired quantity of gas was withdrawn, an equal volume of mercury was simultaneously added.

^{15}N NMR Chemical Shifts of Relevant Species. The nitrido and nitrosyl derivatives considered in the present study were found to have the following ^{15}N NMR chemical shifts (C_6D_6, shifts given in ppm downfield of $^{15}NH_3$): **1-^{15}N**, 837.9; **1-^{15}NO**, 420.0; **2-^{15}N**, 839.8; **2-^{15}NO**, 418.4; **3-^{15}NO**, 436.7. The ^{15}N NMR chemical shift for the chromium nitrido derivative **3-^{15}N** has been reported previously as 929 ppm.[110]

^{15}N NMR Integration Standards. The T_1 value for each ^{15}N-labeled nitrosyl complex was determined prior to employing ^{15}N NMR integration as the method for determining relative concentrations. Said T_1 values are as follows: **1-^{15}NO**, 3.38 ± 0.16 s; **2-^{15}NO**, 3.34 ± 0.29 s; **3-^{15}NO**, 5.87 ± 0.26 s. In view of the latter values and taking into account the acquisition time (0.810 s) and delay time (10.000 s) used for the collection of the ^{15}N NMR spectra, integration of the NMR spectrum is expected to be a reliable measure of concentration. This was done through the use of integration standards.

During the NO competition experiments, paramagnetic material was present; therefore, the T_1 characteristics obtained for this and other competition reactions would have a lower magnitude of T_1. The values determined by ^{15}N NMR were as follows: **1-^{15}NO**, 2.44 ± 0.16 s; **2-^{15}NO**, 1.23 ± 0.12 s; **3-^{15}NO**, 4.05 ± 0.26 s.

To a 100 mL Schlenk flask were added complexes **1** (24 mg, 3.89×10^{-5} mol, 1.0 equiv) and **2** (33 mg, 3.89×10^{-5} mol, 1.0 equiv), along with 5 mL of toluene solvent. Also added to the flask was a magnetic, Teflon-coated stir bar, and then the flask was fitted with a septum. The mixture was degassed and placed under partial vacuum while stirring, following which the gas ^{15}NO (2.2 mL, 8.56×10^{-5} mol, 2.2 equiv) was added via syringe. After the reaction mixture was stirred for 20 min at 25 °C, the solvent and all volatile material were removed in vacuo. The red-orange solid residue was dissolved in C_6D_6 (750 μL), and the solution was transferred into an NMR tube. Proton

NMR spectra indicated that the starting materials had been consumed completely and that **1-^{15}NO** and **2-^{15}NO** had been produced in essentially quantitative fashion. Integration of the ^{15}N NMR spectrum of the mixture indicated the ratio [**1-^{15}NO**]/[**2-^{15}NO**] to be 0.94.

A standard integration sample for a mixture of **1-^{15}NO** and **3-^{15}NO** was prepared similarly as follows. A 100 mL Schlenk flask was charged with complexes **1** (24 mg, 3.89 × 10^{-5} mol, 1.0 equiv) and **3** (14 mg, 3.89 × 10^{-5} mol, 1.0 equiv), along with 5 mL of toluene solvent and a Teflon-coated magnetic stir bar. The experiment was conducted as in the preceding paragraph. Upon workup, ^{1}H NMR spectra verified that the starting materials had been consumed quantitatively and that **1-^{15}NO** and **3-^{15}NO** had been produced in essentially quantitative fashion. Integration of the ^{15}N NMR spectrum of the mixture indicated the ratio [**1-^{15}NO**]/[**3-^{15}NO**] to be 0.98.

A third integration standard for the mixture of complexes **2-^{15}NO** and **3-^{15}NO** was prepared similarly as follows. A 100 mL Schlenk flask was charged with complexes **2** (33 mg, 3.89 × 10^{-5} mol, 1.0 equiv) and **3** (14 mg, 3.89 × 10^{-5} mol, 1.0 equiv), along with 5 mL of toluene solvent and a Teflon-coated magnetic stir bar. The experiment involving the addition of ^{15}NO was conducted as described above. Upon workup, ^{1}H NMR spectra indicated that the starting materials had been converted completely to the corresponding nitrosyls **2-^{15}NO** and **3-^{15}NO**. Integration of the ^{15}N NMR spectrum of the mixture indicated the ratio [**2-^{15}NO**]/[**3-^{15}NO**] to be 1.03.

Competitive ^{15}NO Binding by 1 and 2. A 100 mL Schlenk flask was charged with complex **1** (24 mg, 3.89 × 10^{-5} mol, 1.0 equiv), complex **2** (33 mg, 3.89 × 10^{-5} mol, 1.0 equiv), 5 mL of toluene solvent, and a Teflon-coated magnetic stir bar. The flask then was fitted with a septum, attached to a Schlenk line, and the mixture degassed. With stirring was introduced ^{15}NO (1.0 mL, 3.89 × 10^{-5} mol, 1.0 equiv) via syringe. After 20 min all volatile material including the toluene solvent was removed under reduced pressure. The residual red-orange solid was dissolved in C_6D_6 (750 μL), and the solution was transferred into an NMR tube for analysis. Proton NMR spectra revealed the presence of precursor complexes (**1** and **2**), along with the product nitrosyl complexes (**1-^{15}NO** and **2-^{15}NO**). Integration of the ^{15}N NMR spectrum showed the [**1-^{15}NO**]/[**2-^{15}NO**] ratio to be 2.22. Repetition of this experiment gave a value of 2.38 for the quantity of interest.

Competitive ^{15}NO Binding by 1 and 3. A 100 mL Schlenk flask was charged with complex **1** (24 mg, 3.89 × 10^{-5} mol, 1.0 equiv) and complex **3** (14 mg, 3.89 × 10^{-5} mol, 1.0 equiv), 5 mL of toluene solvent, and a Teflon-coated magnetic stir bar. The experiment was conducted as described above, using 1.0 equiv of ^{15}NO. Upon workup, ^{1}H NMR analysis indicated the presence of starting complexes **1** and **3** in addition to the product nitrosyls, complexes **1-^{15}NO** and **3-^{15}NO**. Integration of the mixture's ^{15}N NMR spectrum revealed the [**1-^{15}NO**]/[**3-^{15}NO**] ratio to be 1.82. Repetition of this experiment gave a value of 1.80 for the quantity of interest.

Competition between 1 and 3 with ^{15}NO Toluene Solution. In a 20 mL vial, **1** (24 mg, 3.89 × 10^{-5} mol, 1.0 equiv) and **3** (14 mg, 3.89 × 10^{-5} mol, 1.0 equiv) were dissolved in toluene (3 mL). The vial was equipped with a Teflon-coated magnetic stir bar and a septum. A saturated ^{15}NO toluene solution (3.3 mL of solution containing 1.0 mL of ^{15}NO, 3.89 × 10^{-5} mol, 1.0 equiv) was added via a syringe over a period of 5 min. The solution was rapidly stirred for 30 min. The solvent then was removed in vacuo. A second reaction was performed following the same protocol. For both samples, ^{1}H NMR spectra verified a mixture of **1**, **3**, **1-^{15}NO**, and **3-^{15}NO**. The ^{15}N NMR spectrum was integrated and revealed the **1-^{15}NO**:**3-^{15}NO** ratio to be 1.64 and 2.12, respectively for the two runs.

Competitive ^{15}NO Binding by 2 and 3. A 100 mL Schlenk flask was charged with complex **2** (33 mg, 3.89 × 10^{-5} mol, 1.0 equiv) and complex **3** (14 mg, 3.89 × 10^{-5} mol, 1.0 equiv), 5 mL of toluene solvent, and a Teflon-coated magnetic stir bar. The experiment was conducted as above with 1.0 equiv of ^{15}NO. Upon workup, ^{1}H NMR analysis indicated the presence of starting complexes **2** and **3**), in addition to product nitrosyls **2-^{15}NO** and **3-^{15}NO**. Integration of the mixture's ^{15}N NMR spectrum revealed the [**2-^{15}NO**]/[**3-^{15}NO**] ratio to be 0.82. Repetition of this experiment gave a value of 0.65 for the quantity of interest.

Control Experiment: Exposure of Complex 3 to N_2O. A 100 mL Schlenk flask was charged with complex **3** (20 mg, 5.56 × 10^{-5} mol), 5 mL of toluene solvent, and a Teflon-coated magnetic stir bar. The flask was fitted with a septum and attached to a vacuum line, and the mixture was degassed. Gaseous N_2O (95 mL, 3.89 mmol, 70 equiv) then was introduced. The mixture was stirred at 25 °C for 90 min, at which point the solvent was removed in vacuo. The solid residue was dissolved in C_6D_6 (750 μL) for analysis. Proton NMR spectroscopy verified that complex **3** had undergone no net reaction, since peaks attributable to it (very broad peak at 30 ppm) were the only peaks observed in the spectrum.

Control Experiment: Exposure of Complex 3-NO to 1. To a 20 mL vial were added complex **3-NO** (24 mg, 6.16 × 10^{-5} mol, 1.0 equiv), **1** (41 mg, 6.16 × 10^{-5} mol, 1.0 equiv), 10 mL of ether, and a Teflon-coated magnetic stir bar. The mixture was stirred at 25 °C for 45 min, at which point the solvent was removed in vacuo. The solid residue was dissolved in C_6D_6 (750 μL) for analysis. Proton NMR spectroscopy verified that complex **3-NO** and **1** had undergone no reaction.

$^{15}N_2O$ Reaction with a Mixture of Complexes 2 and 3. A 100 mL Schlenk flask was charged with complex **2** (33 mg, 3.89 × 10^{-5} mol, 1.0 equiv) and complex **3** (14 mg, 3.89 × 10^{-5} mol, 1.0 equiv), 5 mL of toluene solvent, and a magnetic Teflon-coated stir bar. The flask then was fitted with a septum and attached to a vacuum line, and the mixture was outgassed. Gaseous $^{15}N_2O$ (10.0 mL, 3.89 × 10^{-4} mol, 10.0 equiv) was then introduced via syringe, and the mixture was stirred vigorously for 90 min, at which point the solvent was removed in vacuo. The brown-orange residual solid was dissolved in C_6D_6 (750 μL), and transferred into an NMR tube for analysis. Proton NMR spectra revealed the presence of starting complex **3** in addition to product nitrosyls **2-^{15}NO** and **3-^{15}NO**, along with the product nitrido derivative **2-^{15}N**. The chromium nitrido species **3-^{15}N** was not observed to be present among the products. The ^{15}N NMR resonances were integrated and revealed the [**2-^{15}NO**]/[**3-^{15}NO**] ratio to be 1.25. Also, the integrated intensity for the **2-^{15}N** signal was equal to the sum of integrated intensities for the **2-^{15}NO** and **3-^{15}NO** signals. Repeating this experiment produced similar results, with a value for [**2-^{15}NO**]/[**3-^{15}NO**] of 1.22 being obtained.

$^{15}N_2O$ Reaction with a Mixture of Complexes 1 and 3. To a 100 mL Schlenk flask was added complex **1** (24 mg, 3.89 × 10^{-5} mol, 1.0 equiv), complex **3** (14 mg, 3.89 × 10^{-5} mol, 1.0 equiv), 5 mL of toluene solvent, and a Teflon-coated magnetic stir bar. The flask was fitted with a septum and attached to a vacuum line, and the mixture was outgassed. $^{15}N_2O$ (10.0 mL, 3.89 × 10^{-4} mol, 10.0 equiv) was added to the vessel via syringe, and the mixture was stirred vigorously for 90 min, at which point the solvent was removed in vacuo. The brown-orange residual solid was dissolved in C_6D_6 (750 μL), and the solution was transferred into an NMR tube for analysis. Proton NMR spectra revealed the presence of starting complex **3**, along with product nitrosyls **1-^{15}NO** and **3-^{15}NO** and product nitrido derivative **1-^{15}N**. Integration of the ^{15}N NMR resonances showed the [**1-^{15}NO**]/[**3-^{15}NO**] ratio to be 26.1. Also, the integrated intensity for the signal corresponding to complex **1-^{15}N** was equal to the sum of those corresponding to nitrosyls **1-^{15}NO** and **3-^{15}NO**. Repetition of this experiment was carried out similarly and yielded a value for [**1-^{15}NO**]/[**3-^{15}NO**] of 29.3.

$^{15}N_2O$ Reaction with a Mixture of Complexes 1 and 2. To a 100 mL Schlenk flask were added complex **1** (24 mg, 3.89 × 10^{-5} mol, 1.0 equiv) and complex **2** (33 mg, 3.89 × 10^{-5} mol, 1.0 equiv), along with 5 mL of toluene solvent and a magnetic Teflon-coated stir bar. The flask was fitted with a septum and attached to a vacuum line, and the mixture then was outgassed. Gaseous $^{15}N_2O$ (1.0 mL, 3.89 × 10^{-5} mol, 0.5 equiv) was then introduced via syringe, and the mixture was stirred vigorously for 90 min, at which point the solvent was removed in vacuo. The brown-orange solid residue was dissolved in C_6D_6 (750 μL), and the solution was transferred into an NMR tube for analysis. Proton NMR spectra revealed the presence of starting complex **2**, in addition to product nitrosyl **1-^{15}NO** and nitride **1-^{15}N** and a trace amount of nitrosyl **2-^{15}NO**. The ^{15}N NMR resonances were integrated, but the [**1-^{15}NO**]/[**2-^{15}NO**] ratio was deemed too large for accurate determination. No nitride **2-^{15}N** was observed in the ^{15}N NMR spectrum of the mixture.

$N^{15}NO$ Reaction with Complex 1. Complex **1** (24 mg, 3.89×10^{-5} mol, 1 equiv) was dissolved in 5 mL of toluene solvent in a 100 mL Schlenk flask. The flask was then equipped with a magnetic Teflon-coated stir bar and a septum. After attachment of the flask to a vacuum line, the mixture was outgassed. Gaseous $N^{15}NO$ (5.0 mL, 1.95×10^{-5} mol, 5.0 equiv) was then introduced via syringe. The mixture was stirred for 2 h, at which point the solvent was removed in vacuo. The brown-orange solid residue was dissolved in C_6D_6 (750 μL), and the solution was transferred into an NMR tube for analysis. Proton NMR spectra showed the presence of only two products, nitrosyl **1-^{15}NO** and nitride **1-N**, in an approximate equimolar ratio. The ^{15}N NMR spectrum of the mixture was found to consist solely of the signal for **1-^{15}NO**, showing that the nitrous oxide N−O bond remains unbroken during the course of N−N bond cleavage.

Kinetic Data for Reaction of Complex 2 with N_2O. Kinetic experiments were carried out in a vessel having a 5 mL quartz cell connected via a graded seal and 5 mm diameter glass tube to a 50 mL glass Schlenk reaction vessel. The cell and associated reaction vessel were equipped with Teflon stopcocks such that they could be mutually isolated and independently addressed. Both compartments were equipped with a Teflon-coated magnetic stir bar.

Toluene solvent (50 mL) was added to complex **2** (50.8 mg, 59.1 mmol) to provide a 1.2 mM stock solution. The solution of complex **2** was freeze−pump−thawed and stored under an argon atmosphere at −35 °C. The stock solution was twice the desired concentrated for the kinetic measurements, since the addition of the N_2O solution leads to dilution, giving an initial concentration of complex **2** of 0.6 mM at the start of data collection.

A second stock solution containing complex **2** (41.3 mg, 48.0 mmol) in 10 mL of toluene solvent also was made following the above protocol. This 4.8 mM solution was employed to achieve an initial concentration of 2.4 mM in complex **2** at the start of data collection.

A typical kinetic run was carried out by addition of 2.50 mL of either stock solution to the quartz cell, under an argon atmosphere. The cell was then attached to a vacuum system and outgassed. Toluene (2.50 mL) was then added to the 50 mL glass compartment and was subjected to three freeze−pump−thaw cycles. Into the 50 mL glass compartment was then introduced 1 atm of N_2O. After 90 min of stirring, it was assumed that a saturated solution of N_2O solution had been produced. The solution of complex **2** was stirred at 1000 rpm while in the spectrometer, and the solution was allowed to equilibrate at the desired temperature for 5 min prior to the start of each kinetic run. Runs were started by opening the stopcocks, allowing the two compartments to communicate, and permitting the solutions of complex **2** and N_2O to be mixed. The reaction mixture was quickly transferred to the quartz cell for observation. After 1 h of data collection, the reaction mixture was transferred to the glass compartment, and the solvent removal in vacuo was effected. Proton NMR spectroscopy was used to examine the reaction mixture, confirming that a 1:1 ratio of **2-N** and **2-NO** indeed had been produced.

Kinetic data were collected on a Hewlett-Packard 8453 diode array spectrophotometer equipped with a built-in magnetic stirrer. The reaction temperature for all runs was set to 26.4 ± 0.5 °C using an HP 89090A Peltier temperature control accessory. The decay of **2** was monitored at 427 nm (λ_{max}) and at 500 nm. In a typical run, 40 data points were collected at 90 s intervals. Plots of $\ln[(A - A_\infty)/A_0]$ vs time were linear through three half-lives. Rate constants were determined using the Kaleidagraph least-squares curve-fitting routine with the equation $A_t = A_\infty + A_0\, e^{-kt}$. At least three runs were carried out at each initial concentration of complex **2**, 0.6 and 2.4 mM. The data from these runs were determined to be 0.031, 0.028, and 0.034 s^{-1} for the 0.6 mM experiments and 0.034, 0.029, and 0.030 s^{-1} for the 2.4 mM experiments.

X-ray Structural Determination for Mo(N[2-Ad]Ar)$_3$ (2). A dark orange needle of approximate dimensions 0.57 × 0.37 × 0.19 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 183 K using Mo Kα radiation (λ = 0.71073 Å). The total data collected were 20 644 reflections ($-13 \le h \le 13$, $-21 \le k \le 11$, $-24 \le l \le 25$), of which 7395 were unique ($R_{int} = 0.0300$). Corrections applied: semiempirical from Ψ-scans. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon F^2 converged with residuals of $R_1 = 0.0448$, w$R_2 = 0.1178$, and GOF = 1.255 based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated ($d_{C-H} = 0.96$ Å) positions except for solvent molecules. The largest residual peak and hole electron density was 0.463 and −0.270 e·Å^{-3}. Crystal data: monoclinic, $a = 11.761(3)$ Å, $b = 19.737(5)$ Å, $c = 22.761(5)$ Å, $V = 5170(2)$ Å^3, $\beta = 101.89(2)°$, space group $P2_1/n$, $Z = 4$, $\mu = 0.294$ mm^{-1}, $M_r = 923.13$ for $C_{58}H_{72}MoN_3O$, ρ(calcd) = 1.186 g·cm^{-3}, and $F(000) = 1964$.

X-ray Structural Determination for PMo(N[2-Ad]Ar)$_3$ (2-P). A yellow parallelepiped of approximate dimensions 0.31 × 0.25 × 0.22 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 183 K using Mo Kα radiation (λ = 0.71073 Å). The total data collected were 14 332 reflections ($-37 \le h \le 36$, $-37 \le k \le 36$, $-37 \le l \le 37$), of which 1697 were unique ($R_{int} = 0.0352$). Corrections applied: semiempirical from Ψ-scans. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. The unit cell contains 1/3 of a disordered C_6H_6 molecule; the disorder was not modeled, the C_6H_6 carbons were refined isotropically and hydrogens were not included. Least-squares refinement based upon F^2 converged with residuals of $R_1 = 0.0661$, w$R_2 = 0.1830$, and GOF = 1.307 based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated ($d_{C-H} = 0.96$ Å) positions. The residual peak and hole electron density was 1.053 and −0.510 e·Å^{-3}. Crystal data: rhombohedral, $a = b = c = 38.3067(6)$ Å, $V = 5033.71(14)$ Å^3, $\alpha = \beta = \gamma = 18.6720(10)°$, space group $R\bar{3}c$, $Z = 3$, $\mu = 0.334$ mm^{-1}, $M_r = 1282.82$ for $C_{80}H_{96}Mo_{1.33}N_4P_{1.33}$, ρ(calcd) = 1.270 g·cm^{-3}, and $F(000) = 2040$.

Thermochemistry: General Considerations. All manipulations involving organomolybdenum complexes were performed under an inert atmosphere of argon in a Vacuum Atmospheres glovebox containing less than 1 ppm oxygen and water. Nitric oxide was obtained from Matheson Gas and handled in a stainless steel manifold following passage through a coiled copper tubing trap at −78 °C. Toluene was distilled from sodium benzophenone ketyl, stored over Na/K alloy, and vacuum transferred prior to calorimetric use. Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[186] or the enthalpy of solution of KCl in water.[187] The experimentally determined enthalpies for these two standard calibration reactions were the same within experimental error as literature values. The calorimeter has been described previously,[188] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

^{1}H NMR Titrations. Prior to the calorimetric experiments, an accurately weighed amount (ca. 0.1 mg) of the molybdenum complex was placed in an NMR tube, and toluene was subsequently added. The solution was titrated with a solution of the ligand of interest. The reactions were monitored by ^{1}H NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative under the experimental calorimetric conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for the organomolybdenum reactions investigated.

Calorimetric Measurement for Reaction of Mo(N[R]Ar)$_3$ (1) with N_2O. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20−30 mg sample of **1** was accurately weighed into the lower vessel, which was then closed and sealed with 1.5 mL of mercury. Four milliliters of a N_2O-saturated stock toluene solution was added, and the remainder of the cell was assembled, removed from the glovebox,

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and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that complex **1** was not added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 1.5 h), the calorimeter was inverted, thereby allowing the reactants to mix. After reaching thermal equilibrium, the vessels were removed from the calorimeter, taken into the glovebox, opened, and analyzed using NMR spectroscopy. Conversion to nitride **1-N** and nitrosyl **1-NO** in a 1:1 ratio was found to be quantitative under these reaction conditions. The enthalpy of reaction, 53.0 ± 0.3 kcal·mol^{-1}, of **1** represents the average of five individual calorimetric determinations. The enthalpy of solution of **1** was then added to this value to obtain a value of -61.9 ± 0.4 kcal·mol^{-1} for all species in solution.

Calorimetric Measurement of Enthalpy of Solution of Mo(N[R]-Ar)$_3$ (1). To consider all species in solution, the enthalpies of solution of **1** had to be directly measured. This was performed by using a procedure similar to the one described above with the exception that no ligand was added to the reaction cell. This enthalpy of solution represents the average of three individual determinations and is 8.9 ± 0.2 kcal·mol^{-1} in toluene.

General Considerations for the Calorimetry with Nitric Oxide. Deuteriobenzene and toluene were obtained from Aldrich Chemical Co. and were purified by distillation from sodium benzophenone ketyl under an argon atmosphere. Nitric oxide was obtained from Matheson Gas and handled in a stainless steel manifold following passage through a coiled copper tubing trap at −78 °C. Nitrous oxide (99.9995%) and argon (99.999%) were obtained from Praxair and used as received. Calorimetric measurements were made in either a Setaram C-80 or a Guild isoperibol calorimeter. FTIR spectra were obtained on a Perkin-Elmer system 2000 using solution cells obtained from Harrick Scientific using CaF_2 windows. ^{1}H NMR spectra were measured in C_6D_6 using a Bruker 300 MHz NMR spectrometer.

Enthalpy of Reaction of Mo(N[R]Ar)$_3$ (1) with NO in the Guild Calorimeter. Glass ampules containing between 0.12 and 0.23 g of solid **1** were loaded in the glovebox and sealed under an inert atmosphere. The solution calorimeter of approximate volume 500 mL was evacuated for 2 h prior to loading with 400 mL of freshly distilled toluene under an argon atmosphere. The atmosphere was switched to nitric oxide, which was bubbled through the stirred calorimeter for a sufficient time to ensure displacement of the argon atmosphere by one of nitric oxide. Excess nitric oxide was vented through a bubbler and to an exhaust hood.

Caution! Nitric oxide, and in particular its oxidation product nitrogen dioxide, are hazardous materials and should be handled with care.

Two ampules containing a total of approximately 0.4 g of complex **1** were broken into the solution to remove any residual water contained in the calorimeter or solution. Before and after breaking an ampule, a series of electrical calibrations were performed. Ampules were broken by depressing a Pyrex rod fitted with a Teflon holder such that only glass and Teflon were in contact with the calorimetry solution. Ampules were changed under a flow of argon from a port above the calorimeter in such a way that the initially saturated solution did not lose any significant amount of NO. The value of -73.6 ± 2.3 kcal·mol^{-1} is the average of four measurements. Analysis of the FTIR of a small-scale reaction in C_6D_6 done under analogous conditions shows a peak at 1602 cm^{-1}, in agreement with the literature value of 1604 cm^{-1}, and also with that obtained from the reaction with N_2O.

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Supporting Information Available: Differential equations used for kinetic simulations, evaluation of the solubility of N_2O and NO in organic solvents, plots of simulated kinetic traces for interpretation of competition experiments, raw UV−visible data for reactions of molybdenum complexes with excess N_2O, and crystal structure data and tables (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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