Mechanistic Aspects of Molybdenum-Promoted Allylic Amination

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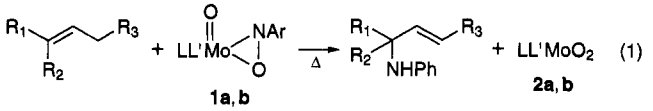
The mechanism of molybdenum-mediated allylic amination by phenylhydroxylamine has been probed through a variety of kinetics, trapping, and stoichiometric model reaction studies. Specifically, the amination of 2-methyl-2-hexene by (dipic)(HMPA)Mo(η^2-PhNO) (**1a**, dipic = 2,6-pyridinedicarboxylate; HMPA = hexamethylphosphoric triamide) is found to be first order in **1a** and zeroth order in olefin and HMPA. Evidence for dissociation of nitrosobenzene from **1a** is provided by trapping of the latter as a hetero-Diels–Alder adduct with 2,3-dimethylbutadiene and by exchange experiments of **1a** with free aryl nitroso compounds. A competing pathway involving extrusion of aryl nitrene from **1a** is also implicated by the production of carbazole from the thermolysis of (dipic)(HMPA)Mo(η^2-2-C_6H_5-C_6H_4NO) (**5**). The findings that (1) the ene reaction of nitrosobenzene with 2-methyl-2-hexene occurs readily (≤70 °C) and regioselectively to produce allyl hydroxylamine **7** and (2) that Mo(IV) complexes $(dedtc)_2MoO$ (**3b**, dedtc = *N,N*-diethyldithiocarbamate) and (dipic)(HMPA)MoO (**3a**) readily deoxygenate arylhydroxylamines (including **7**) support the involvement of these steps in the amination process. Control experiments and model reaction studies have identified some of the pathways for the formation of the byproducts, aniline and azoxybenzene. Together the above results indicate that the primary pathway for Mo-promoted olefin allylic amination involves: (1) reaction of LL'Mo(VI)O_2 with RNHOH to form a molybdooxaziridine **1** (and water); (2) dissociation of **1** to form RNO and LL'Mo(IV)O (**3**); (3) ene-reaction of RNO with the olefin to produce an *N*-allyl hydroxylamine; and (4) reduction of the allyl hydroxylamine by **3**, yielding the allyl amine and regenerating LL'Mo(VI)O_2 (**2**).

Introduction

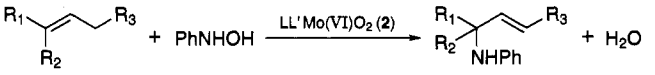
The direct, selective functionalization of hydrocarbons remains a continuing challenge for synthetic chemists. Although practical processes currently exist for the synthesis of α-oxygenated compounds by allylic oxidation of olefins,[1] direct methods for the production of the corresponding organonitrogen compounds, i.e. allyl amines, are few, with *stoichiometric* reactions of imido compounds (RN=X=NR; X = S,[2] Se[3]) being the most familiar. This being the case, we were intrigued by an early report of Sharpless and co-workers[4] in which formal imido transfer reactions of molybdooxoaziridine (or nitrosoarene) complexes LL'Mo(η^2-RNO), **1**, with some olefins were observed, producing allylic amines (eq 1).



1a,b **2a,b** (1)

a: L = 2,5 -pyridinedicarboxylate = dipic, L' = HMPA
b: L = L' = N,N-diethyldithiocarbamate = dedtc

The novelty of the above transformation, especially the striking, highly regioselective migration of the C–C double bond found in the initial examples, and the little explored reactivity of coordinated *C*-nitroso compounds[5] collectively piqued our interest in revisiting this chemistry with the intention of determining its synthetic potential and mechanistic features. Our initial efforts recently led to the successful development of a Mo-*catalyzed* process for olefin amination using phenylhydroxylamine as the stoichiometric aminating agent[6] (eq 2). These catalytic reactions exhibit the same ene-type reaction selectivity features[7a] as the stoichiometric coun-



$PhNH_2$ + PhN=N(O)Ph (2)

terparts, including double bond migration and decreasing olefin reactivity with decreasing degree of substitution, and hence are likely to be closely related mechanistically. A practical limitation of both the stoichiometric and the catalytic reactions is the low to moderate yields which result from competing formation of other N-containing byproducts, primarily aniline, azobenzene, and azoxybenzene. In a recent development Jørgensen and coworkers reported a survey of the catalytic efficiencies of several metal salts and complexes for allylic amination

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(2) Sharpless, K. B.; Hori,T. *J. Org. Chem.* **1976**, *41*, 176. Kresze, G.; Braxmeier, H.; Munsterer, H. *Org. Synth.* **1987**, *65*, 159.

(3) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. *J. Am. Chem. Soc.* **1976**, *98*, 269.

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(6) Srivastava, A.; Ma, Y.; Pankayatselvan, R.; Dinges, W.; Nicholas, K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 853.

(7) (a) General review: Snider, B. *Acc. Chem. Res.* **1980**, *13*, 426; RNO ene reactions. (b) Banks, R. E.; Hazeldine, R. N.; Miller, P. J. *Tetrahedron Lett.* **1970**, 4417. (c) Motherwell, W.; Roberts, J. S. *J. Chem. Soc., Chem. Commun.* **1972**. (d) Knight, G. T. *J. Chem. Soc., Chem. Commun.* **1970**, 1016. (e) Keck, G. E.; Webb, R. R.; Yates, J. B. *Tetrahedron* **1981**, *37*, 4007.

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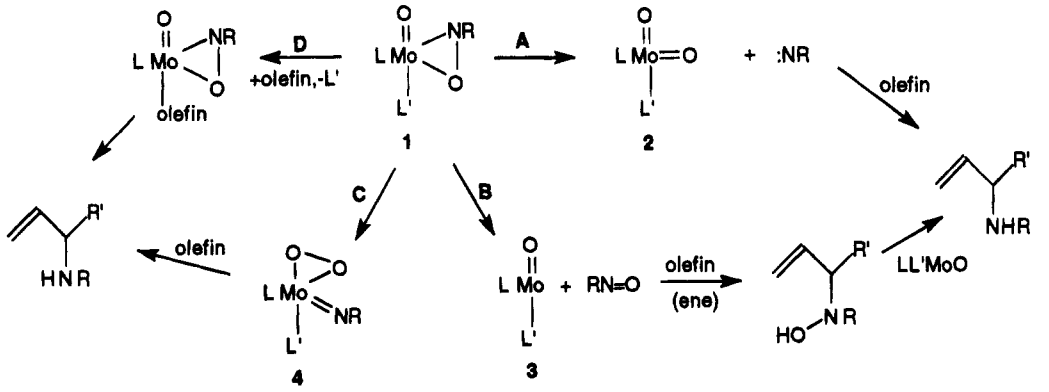
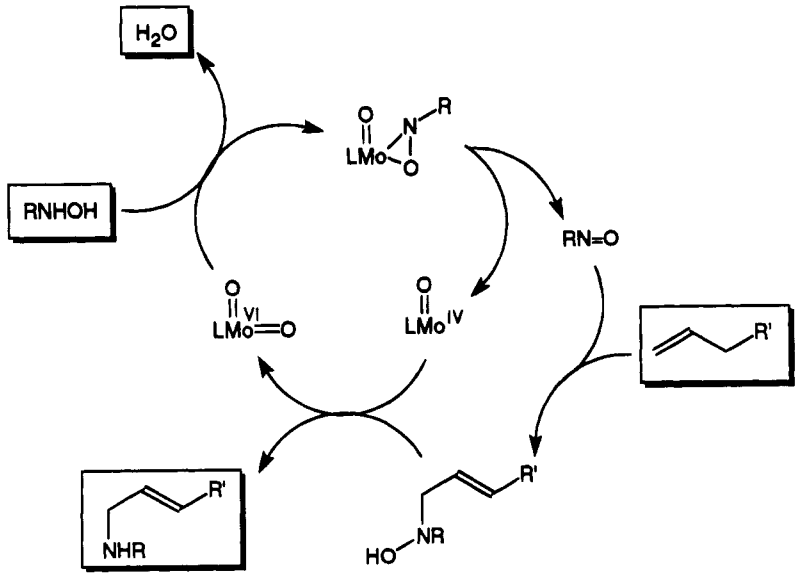
Scheme 1



Scheme 2

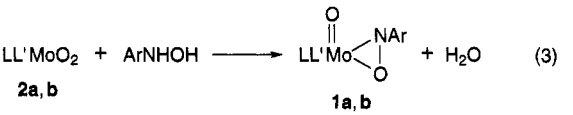


by phenylhydroxylamine, with an iron–phthalocyanine giving the best results.[8]

In order to elucidate the mechanistic pathway(s) of this new metal-mediated group transfer reaction[9] and to rationally improve its efficiency, we have conducted kinetics and model reaction studies. These experiments attempt to address the central question of how the NR group is transferred from the metal to the olefin. Secondarily, they seek to identify competing reaction pathways which may be manipulated to enhance catalyst activity while suppressing undesired side reactions. More generally, we hoped that these studies would contribute to defining the little known reactivity patterns of coordinated *C*-nitroso compounds and to identifying new pathways for metal-mediated group transfer reactions.

Results and Discusssion

From the preliminary studies of Sharpless[4] and Mares[10] involving the preparation of molybdooxaziridine complexes **1** and our own observations,[6] it was apparent that the initial step in the catalytic reaction mechanism is the generation of **1** from reaction of LL'Mo(VI)O_2 (**2**) with PhNHOH (eq 3). Thus, **1a,b** form within minutes and essentially quantitatively at 20 °C when PhNHOH and



(3)

LL'Mo(VI)O_2 (**2a,b**) are combined. Furthermore, as noted above, these compounds stoichiometrically aminate olefins with the same regioselectivity as found in the catalytic reaction and **1a** can be detected in the catalytic reaction mixtures spectroscopically (by IR). Indeed, the fact that both the stoichiometric reaction of **1** with olefins and the Mo-catalyzed reactions require temperatures in excess of 80 °C to proceed at a reasonable rate suggests that decomposition/conversion of **1** is rate-limiting. Conversely, no reaction or significant interaction can be detected between the catalysts LL'Mo(VI)O_2 (**2**) and olefin at or below typical reaction temperatures.

Given the initial formation of a molybdooxaziridine complex **1** in the catalytic reactions, establishing transfer of the NPh unit from the hydroxylamine to Mo, the central question then becomes how is this group transferred from Mo to olefin? Scheme 1 presents a number of alternatives which could account for the formation of allyl amine and regeneration of L_nMo(VI)O_2 and which provided a useful framework to guide our mechanistic probes. Pathway A involves fragmentation of Mo-ox-

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(9) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.
(10) Muccigrosso, D. A.; Jacobson, S. E.; Apgar, P. A.; Mares. F. *J. Am. Chem. Soc.* **1978**, *100*, 7063.

Table 1. Kinetic Data for the Reaction of (dipic)(HMPA)Mo(PhNO) (1a) with 2-Methyl-2-hexene[a]

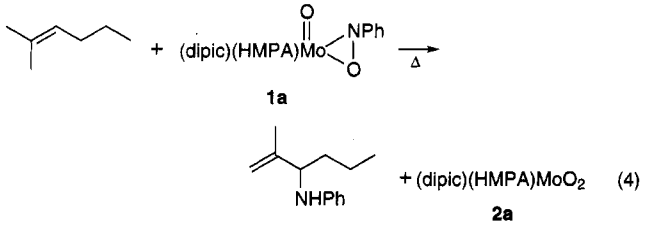
run	[1a] (M)	[olefin] (M)	[additive] (M)	k (s^{-1})
1[b]	0.0030	0.012		2.4×10^{-7}
2[b]	0.0059	0.012		4.7×10^{-7}
3[b]	0.0118	0.012		9.3×10^{-7}
4[b]	0.0030	0.025		2.2×10^{-7}
5[b]	0.0030	0.049		2.0×10^{-7}
6[c]	0.0059	0.012		5.5×10^{-7}
7[c]	0.0059	0.012	0.059 HMPA	5.9×10^{-7}
8[c]	0.0059	0.012	0.059 PhNO	3.1×10^{-5} [d]

[a] Carried out in refluxing 1,2-dichloroethane (83 °C). [b] Monitored by IR at 965 cm^{-1}. [c] Monitored by visible spectroscopy at 480 nm. [d] Second-order rate constant, L mol^{-1} s^{-1}.

aziridine **1** to produce the dioxo complex **2** and free phenyl nitrene; the latter then undergoes allylic C–H insertion to give the allyl amine. In pathway B, nitrosobenzene dissociates from **1** with cogeneration of L_n-Mo(IV)O (**3**); the free nitrosobenzene then undergoes an ene reaction with olefin producing an allyl hydroxylamine, which is subsequently reduced by **3** to the allyl amine with $LL'MoO_2$ regeneration. Pathway C involves valence isomerization of **1** to produce a Mo(VI) peroxoimido complex **4** which transfers the NPh unit to olefin by an undefined route, regenerating $LL'MoO_2$. Lastly, pathway D begins with olefin coordination to **1**, followed by NR transfer to olefin within the coordination sphere. Note that pathways A and B both involve dissociation of a reactive nitrogen fragment from Mo and a "metal-off" amination step whereas pathways C and D are associative, "metal-on" routes.

Our general approach to elucidating the mechanism of the Mo-promoted amination was (1) to examine the kinetics of the stoichiometric amination of 2-methyl-2-hexene by **1**; (2) to conduct trapping and crossover experiments to detect the presence of free nitrene and nitrosobenzene; and (3) to carry out stoichiometric model reactions to assess the feasibility and facility of the putative conversions elaborated in Scheme 1.

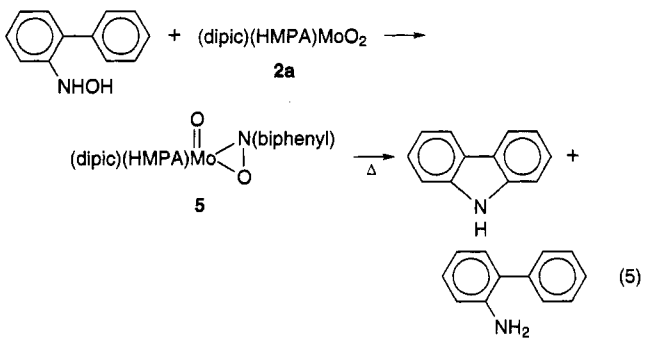
Kinetics of the Reaction of (dipic)(HMPA)MoO(η^2-PhNO) with Olefin. We sought to determine whether the initial step in the NPh group transfer reaction was dissociative or associative by examining the kinetics of the stoichiometric reaction of **1a** with 2-methyl-2-hexene in refluxing 1,2-dichloroethane (83 °C, eq 4). The Mo-concentration dependency was determined using



(4)

the initial rate method[11] (up to ca. 10% conversion) by monitoring the disappearance of the Mo=O IR absorption of **1a** at 965 cm^{-1} at three different concentrations (Table 1, runs 1–3). The resulting initial rate constants were linearly related to the concentration of **1a**, indicating a first-order dependence. A second set of kinetic runs was conducted by varying the olefin concentration. Over a 4-fold olefin concentration variation, the initial rates of reaction (runs 1, 4, 5) were unchanged, indicative of a zeroth-order olefin dependency. Finally, to assess the possibility of rate-determining HMPA dissociation, two runs were compared (entries 6, 7) differing only in the presence (or absence) of added HMPA (10 mol equiv); because of IR spectral interference from HMPA, the disappearance of **1a** was more conveniently monitored in the visible spectrum at 480 nm. The rates in these two cases were the same, within experimental error, showing the absence of inhibition and thus arguing against reversible, rate-limiting HMPA dissociation. In summary, the kinetics results demonstrate a first-order dependence of eq 4 on **1a** and zeroth-order behavior with respect to olefin and HMPA. Pathways A–C are consistent with these findings, but pathway D, which requires initial HMPA dissociation or olefin association, can be excluded.

Trapping Experiments. To assess the importance of dissociative pathways A and B (Scheme 1) involving free organonitrogen intermediates, we carried out experiments designed to trap these putative species, aryl nitrene and nitrosobenzene. Aryl nitrenes have been studied extensively[12] and one of the established diagnostic tests for their intermediacy is the intramolecular C–H insertion of biphenyl nitrenes to produce carbazole.[13] Accordingly, we prepared and characterized the nitrosobiphenyl complex **5** by reaction of *o*-(hydroxyamino)-biphenyl with dioxo complex **2b** (eq 5). When dark red



(5)

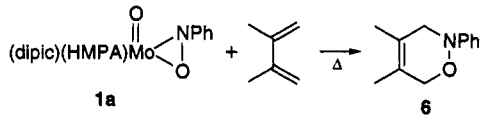
5 was thermolyzed in refluxing dioxane, dioxo complex **2** was produced along with *o*-aminobiphenyl as the primary organic product detected by GC/MS. However, heating **5** in chlorobenzene at the same temperature produced a mixture of carbazole and biphenylamine (ca. 1:1). This result provides evidence that nitrosobiphenyl complex **5** (and presumably **2a** as well), does (in part) serve as a source of free aryl nitrene, although formation of the noncyclized amine, even in the poor H-atom donating solvent chlorobenzene, suggests competitive operation of a second pathway. To our knowledge the result indicated in eq 5 provides the first example of free nitrene generation from a *C*-nitroso complex. Although not rigorously excluded, we believe that this pathway (**A**) does not contribute significantly to the formation of allyl amine since solvent H-atom abstraction, rearrangement, and dimerization pathways dominate over intermolecular C–H insertion reactions for phenyl nitrene (as required for allyl amine formation).[12]

(11) Moore, J. W.; Pearson, R. G. In *Kinetics and Mechanism*; Wiley, Inc.: New York, 1981; pp 65–66.

(12) Reviews: Smith, P. A. In *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984; pp 94–204. *Nitrenes–Reactive Intermediates in Organic Chemistry*; Lwowski, W., Ed.; Wiley and Sons: New York, 1970; Chap. 2, 3, 6, 7.

(13) (a) Sundberg, R. J.; Brenner, M.; Suter, S. R.; Das, B. P. *Tetrahedron Lett.* **1970**, 2715. Sundberg, R. J.; Heintzelmen, R. W. *J. Org. Chem.* **1974**, *39*, 2546.

C-Nitroso compounds are well known as participants in hetero-Diels–Alder reactions[14] and in ene-reactions.[7b–e] To evaluate the possibility that dissociative loss of nitrosobenzene from its intermediate Mo complex was operative in the Mo-promoted allylic amination, we examined the thermolysis of **1a** in the presence of excess 2,3-dimethylbutadiene (dioxane, 70 °C, eq 6). From this reaction the known adduct **6**[14b] was isolated (58%) along



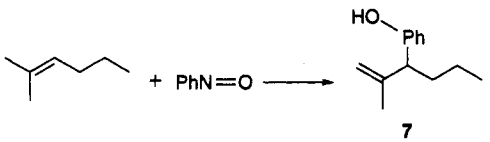
1a 6 (6)

with dioxo complex **2a**; aniline and azoxybenzene were detected by GC/MS. This result provides strong evidence for the generation of free nitrosobenzene via **1a** as a major process (pathway B). This conclusion is further bolstered by two other lines of evidence: (1) **1a** undergoes exchange of the *C*-nitroso ligand when heated with various free nitrosoarenes[6,8] and (2) $(dedtc)_2Mo(IV)O$[15] (**3b**) reacts with free PhNO rapidly and quantitatively at room temperature to give molybdooxaziridine complex **1b** (eq 7), suggesting that PhNO dissociation from **1** may be rate-limiting.

$$(dedtc)_2Mo(IV)O + PhN{=}O \longrightarrow (dedtc)_2MoO(\eta^2\text{-}PhNO) \quad (7)$$

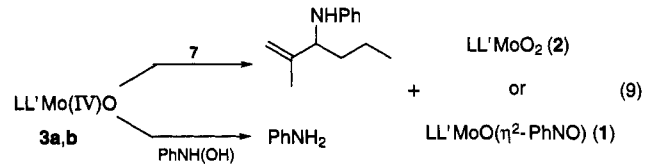
3b **1b**

Model Reactions Relevant to the PhNO Dissociation Pathway (B). The above trapping and exchange experiments demonstrate the dissociation of PhNO from **1a** under the conditions for stoichiometric and catalytic amination. To further evaluate the importance of the amination pathway B, model reactions for the second and third steps, the ene-reaction of PhNO and the Mo-effected hydroxylamine reduction were also examined. Accordingly, the direct reaction of PhNO with 2-methyl-2-hexene was carried out in dioxane at 70 °C (2.5 h, eq 8). Following chromatography and recrystallization the corresponding *N*-phenyl-*N*-allyl hydroxylamine **7** was isolated in moderate yield. The product (both before and after purification) was almost entirely a single regioisomer, that derived from the characteristic C=C transposition of the ene-reaction and found in the Mo-promoted reactions. Clearly, nitrosobenzene, generated by dissociation from **1a**, is capable of undergoing the ene-addition to olefins under typical amination conditions. Additionally, the correlation between olefin structure and efficiency of the Mo-catalyzed reactions (increasing yield with increasing degree of olefin substitution) follows the general reactivity trend of olefins in ene-type reactions.[7a]



7 (8)

To establish whether LL'Mo(IV)O species generated by PhNO dissociation from **1** (pathway B) were competent to reduce the allyl hydroxylamine generated via the ene-reaction, $(dedtc)_2Mo(IV)O$ (**3b**) was treated with allyl hydroxylamine **7** at room temperature (eq 9). After 5 h $(dedtc)_2Mo(VI)O_2$ (**2b**) was isolated upon precipitation with pentane; GC/MS analysis of the pentane-soluble



material indicated clean formation of the corresponding *N*-phenyl allyl amine **8**. This result establishes the feasibility of hydroxylamine reduction by Mo(IV) and demonstrates that each step of pathway B can occur readily under conditions of the stoichiometric and catalytic amination reactions. Moreover, this constitutes the first report of hydroxylamine reduction by Mo(IV), a new example of a large class of deoxygenation reactions promoted by Mo(IV) complexes and molybdoenzymes.[16,17]

Stoichiometric Model Reactions Relevant to Competing Side Reactions. A present limitation of the Mo-promoted amination reaction is the formation of N-containing byproducts, especially aniline and azoxybenzene. We have sought to identify the sources of these byproducts with the hope that an understanding of their modes of formation would aid in the development of more selective catalytic systems.

Initial control experiments[18] indicated that aniline and azoxybenzene are partly derived (in the catalytic reactions) from thermal disproportionation/condensation of phenylhydroxylamine. This is clearly not the complete picture, however, since the stoichiometric reaction of **1a** with olefin (*op cit*), wherein no hydroxylamine is present, also produces aniline and azoxybenzene.[6]

Having shown that LMo(IV)O complex **3b** readily deoxygenates the *N*-phenyl allyl hydroxylamine **7**, it seemed likely that this and other Mo(IV) species could reduce PhNHOH to $PhNH_2$. Indeed, the reaction of **3b** with PhNHOH proceeds rapidly at room temperature giving both aniline and the corresponding dioxo derivative **2b** (eq 9). In order to assess the potential for hydroxylamine reduction by the corresponding dipicolinate Mo(IV) complex **3a**, the latter was prepared as a brown air-sensitive solid by reduction of dioxo derivative **2a** with $P(OMe)_3$. The shifted NMR resonances of **3a** relative to **2a**, a Mo=O IR absorption at 952 cm^{-1}, a molecular ion (457 for $C_{13}H_{21}{}^{96}MoN_4O_6P$) observed by FAB MS, and its chemical properties supported the formulation. When treated with PhNHOH in CH_2Cl_2 at 20 °C, **3a** was rapidly converted to dioxo complex **2a** with coproduction of aniline (by GC/MS). Although not the focus of the present investigation, this reaction may have considerable generality as a method for efficient hydroxylamine reduction.[19]

Given the evidence for (partial) aryl nitrene generation from thermolysis of the Mo-oxaziridine complexes (*op cit*), another likely route to aniline appeared to be via H-atom abstraction from solvent by the nitrene.[12] Consistent

(14) (a) Boger, D. L.; Weinreb, S. N. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic Press: New York, 1987; Chap. 3, pp 71–93. (b) Taylor, E. C.; Tseng, C.-P.; Rampal, J. B. *J. Org. Chem.* **1982**, *47*, 552. (c) Taylor, E. C.; McDaniel, K.; Giam, C. S. *Can. J. Chem.* **1980**, *58*, 2447.

(15) Chen, J.-J. G.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612.

(16) Holm, R. H. *Chem. Soc. Rev.* **1987**, *87*, 1411.

(17) Review: Steifel, E. I.; Coucouvanis, D.; Newton, W. E. In *Molybdenum Enzymes, Cofactors and Model Systems*, ACS Symposium Series 535; American Chemical Society: Washington, D.C., 1993.

(18) Srivastava, A. S. M.S. Thesis. University of Oklahoma, 1992.

(19) March, H. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 1218.

with this hypothesis was the absence of aniline when **1a** was pyrolyzed in the solid state and the predominant formation of carbazole from thermolysis of **5** in chlorobenzene (a poor H-atom donor) vs the dominance of biphenyl amine from the reaction in dioxane. Surprisingly, however, thermolysis of **1a** in d_8-dioxane produced only $PhNH_2$ (by MS). Considering that this result might be clouded by H/D exchange with adventitious moisture during or after the reaction, efforts to maintain rigorously dry reaction and workup conditions were applied, but these still led to no appreciable D-incorporation into the aniline. We did find that somewhat more $PhNH_2$ was produced when water was intentionally added (12.5%, 2:1 H_2O/**1a**) and somewhat less formed under "dry" conditions (10.7%), suggesting a more direct role for water in the formation of aniline.

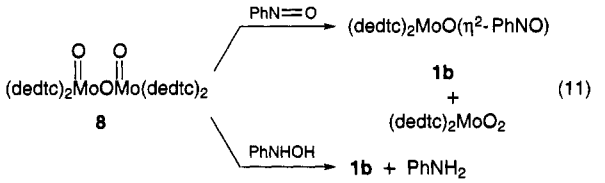
Together, these findings, though neither completely definitive nor quantitative, provide evidence for the likely involvement of several pathways for amine production including: (1) nitrene reaction with solvent and/or water; (2) direct reaction of water with Mo-oxaziridine **1a**; (3) LMo(IV)O reduction of PhNHOH; and (4) thermal disproportionation of PhNHOH (under catalytic conditions).

As to the mechanism(s) of formation of axozybenzene, we have gathered evidence for the involvement of a direct, "on the metal" pathway. The first indication of this possibility came while assessing nitrosobenzene dissociation from **1a**. We reasoned that if nitrosobenzene dissociation were rate-limiting in the amination of olefins by **1a**, addition of excess nitrosobenzene should inhibit the reaction by suppressing dissociation. Experimentally, exactly the opposite was found! In fact, the rate of disappearance of **1a** and appearance of azoxybenzene, in the presence or absence of olefin, was found to *increase* with added nitrosobenzene (Table 1). These results suggest the intervention of an associative pathway involving nitrosobenzene and the Mo-oxaziridine complex **1a** (eq 10). Additional support for such a process has been reported recently by Jorgensen and co-workers[20] to

$$\underset{\textbf{1a}}{(dipic)(HMPA)MoO(\eta^2\text{-}PhNO)} + PhN{=}O \longrightarrow (dipic)(HMPA)MoO_2 + \underset{\textbf{2a}}{PhN{=}N(O)Ph} \quad (10)$$

explain the fact that the rate of thermolysis of **1a** (in the absence of olefin or nitrosobenzene) is *second order*. This finding, when contrasted with the *first-order* dependence on **1a** in the presence of olefin or nitrosobenzene, may be reconciled in terms of a competition between olefin and **1a** for the available nitrosobenzene. Thus, in the presence of olefin the nitrosobenzene partially dissociated from **1a** is primarily trapped via the relatively fast ene reaction (independent of [**1a**]) rather than reacting with undissociated **1a**, giving overall first-order behavior in **1a**.

The Role of Dinuclear Mo(V) Complexes. Dinuclear Mo(V) complexes **8** can play an important role in Mo(VI)/Mo(IV) atom-transfer reactions,[16] sometimes limiting catalytic activity. No spectroscopic evidence (by IR, NMR) for the intermediacy of such species in the stoichiometric or catalytic aminations could be found, but low concentrations could have eluded us. We sought therefore to assess what the effects of **8** present under catalytic conditions would be by examining relevant reactions of the representative complex **8b** (eq 11). Treatment of **8b** with 1 mol equiv of PhNHOH at room temperature gave a mixture of Mo-oxaziridine complex



(11)

1b, dioxo complex **2b**, and aniline. This result showed that if **8** is formed in the catalytic reaction it would be recycled back to catalytically active complexes, but that the presence of **8** could also contribute to undesired aniline production.

Since free nitrosobenzene has been implicated in the catalytic process, we also examined its interaction with dinuclear **8b**. At room temperature **8b** and PhNO reacted over 1.5 h to produce Mo-oxaziridine complex **1b** together with dioxo derivative **2b** (eq 11). Both of these results are consistent with (but do not require) the existence of an equilibrium between dinuclear Mo(V) species **8b** and the corresponding Mo(IV) and Mo(VI) complexes **3b** and **2b**, the former of which reacts both with PhNHOH (eq 9) and with PhNO (*op cit*) and the latter of which reacts with PhNHOH (eq 3). It is perhaps also significant that deliberate attempts to prepare a Mo(V) derivative of the type (dipic)Mo(O)OMo(O)(dipic) (**8a**), either by partial reduction of **2a** or by direct combination of the corresponding Mo(VI) and Mo(IV) derivatives **2a** and **3a** were inconclusive, suggesting that **8a** may be unstable with respect to dissociation. Although the involvement of dinuclear Mo(V) species has not been established in the olefin amination process, the above experiments indicate both the oxidizing and reducing capabilities of the representative Mo(V) complex **8b** and its recyclability to catalytically involved Mo-dioxo and Mo-oxaziridine derivatives.

Summary and Conclusions

In summary, the primary pathway for Mo-promoted olefin amination involves (1) reaction of $LMo(VI)O_2$ with RNHOH to form Mo-oxaziridine **1** (and water); (2) dissociation of **1** to form RNO and LMo(IV)O **3**; (3) ene-reaction of RNO with the olefin to produce an *N*-allyl hydroxylamine; and (4) reduction of the allyl hydroxylamine by **3** producing the allyl amine and regenerating $LMo(VI)O_2$. The molybdenum catalyst thus serves as a Mo(VI)/Mo(IV)/(Mo(V)?) redox shuttle, a familiar role which is played out in both Mo-containing enzymes[17] and synthetic catalysts.[21] In the present system, however, the end result is not direct O-atom transfer but rather a group transfer, i.e. of the isoelectronic NR unit. Studies are underway to extend the scope of the reaction and to enhance its efficiency and selectivity through systematic variation of catalyst, cocatalysts, aminating agent, and reaction conditions and by applying some of the lessons learned from the present mechanistic study.

Experimental Section

General Methods and Materials. All reactions were performed in an atmosphere of prepurified dinitrogen (99.997%) using standard Schlenk tube or dry box techniques. Reagent

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grade solvents were dried, distilled, and stored under N_2 and were used in all manipulations. 2,6-Pyridinedicarboxylic acid, diethyldithiocarbamic acid sodium salt trihydrate, nitrosobenzene, triethylphosphine, triethyl phosphite, HMPA, and 2-methyl-2-hexene were purchased and used as received without further purification. MoO_2(dipic)(HMPA),[4] MoO(dipic)(HMPA)-(η^2-nitrosobenzene),[4] $(dedtc)_2MoO_2$,[22] $(dedtc)_2MoO(\eta^2$-nitrosobenzene),[4] $Mo_2O_3(dedtc)_4$,[15] PhNHOH,[23] 2′-C_6H_5-C_6H_4NHOH,[24] and $MoO(O_2)$(dipic)(HMPA)[20] were prepared following literature procedures. IR spectra were measured with a Bio-Rad 3240-SPC FT-IR instrument, ^{1}H NMR spectra on a Varian XL-300 spectrometer at 300 MHz, mass spectra on VGZAB-E or Kratos HRMS-25 mass spectrometers, and UV-vis spectra on a Hewlett-Packard 8452 A diode array spectrophotometer. GC analysis was performed with a HP 5790 A gas chromatograph with FI detection using a 6 ft. glass column packed with OV 101; GC/MS analyses were obtained on a HP 5985 mass spectrometer with a SE-54 (30 m) capillary column.

Kinetic Studies. Dependence on 1a and Olefin. In a three-necked round-bottom flask fitted with a condenser, nitrogen inlet, and a silicone septum stopper were added molybdooxaziridine complex **1a** (0.025 g, 0.044 mmol), 2-methyl-2-hexene (26 μL, 0.184 mmol), and 1,2-dichloroethane (15 mL). The flask was placed in a thermostated oil bath at 83 °C. After 5 min for thermal equilibration, aliquots were withdrawn every 5 min and, after cooling, the samples were analyzed by FT-IR in a 1.0 mm cell (NaCl windows with solvent reference) according to the decrease in absorbance (10–12% conversion, initial rate method[11]) of the Mo=O stretching band at 965 cm^{-1}. Absorbance was converted into concentration from an absorbance/concentration working curve and initial rates were determined by a plot of the concentration of **1a** vs time.

Dependence on HMPA and PhNO. Rate dependencies on HMPA and PhNO concentration were determined by UV/vis spectroscopy because of interference from bands of the these substances in the 965 cm^{-1} region. Analyses were carried out in thermostated cuvettes by monitoring the decrease in the 480 nm absorption of **1a**. As above, **1a** (0.05 g, 0.0886 mmol), 2-methyl-2-hexene (52 μL, 37 mmol), and 1,2-dichloroethane (15 mL) were stirred at reflux in the absence and presence of HMPA (10 equiv) in a flask immersed in a thermostated oil bath (Table 1). Aliquots were withdrawn (5 min), diluted with 1,2-dichloroethane (0.4 mL/2 mL), and introduced into the cuvette. The reaction of **1a** with PhNO was carried out similarly but in the absence of olefin (because of competing olelfin/PhNO reaction).

Thermolysis of (dipic)(HMPA)MoO(η^2-nitrosobenzene) (1a). Compound **1a** (0.50 g, 0.89 mmol) in dioxane (20 mL) was heated at reflux for 22 h. The solvent was removed by rotary evaporation and the residue was washed with pentane several times to remove the organic product. The solid thus obtained was recrystallized from a mixture of dichloromethane and pentane to obtain white (dipic)(HMPA)MoO_2 (**2a**, 57%). GC-MS analysis of the pentane extract indicated the presence of aniline, azoxybenzene, and free HMPA. No other molybdenum complex was detected.

Solid state thermolysis of **1a** was carried out in an evacuated, closed flask at 120 °C for 24 h and worked up/analyzed following the above procedure. Azoxybenzene was detected as the only organic product.

Thermolysis of (Diethyldithiocarbamate)$_2$MoO(η^2-nitrosobenzene) (1b). The thermolysis of **1b** was carried as with **1a** above. $Mo_2O_3(dedtc)_4$ (72%) was obtained as a precipitate and aniline was detected by GC/MS of the pentane extracts.

Preparation of (dipic)(HMPA)MoO(η^2-2-nitrosobiphenyl) (5). To a solution of dioxo complex **2a** (0.48 g, 1.0 mmol) in 50 mL of CH_2Cl_2 was added *o*-(hydroxyamino)-biphenyl (0.22 g, 1.2 mmol) and the solution was stirred for 30 min. Anhydrous $MgSO_4$ (1 g) was added and stirring continued for another 15 min. The $MgSO_4$ was filtered off and the solvent was removed by rotary evaporation. The resulting dark red sticky solid was dried overnight and recrystallized from THF/diethyl ether to produce dark red crystalline **5** (66%). IR (KBr): ν (MoO) 958 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.13 (d, J = 9.9 Hz, 18), 7–8.5 (m, 9). MS (FAB, 3-nitrobenzyl alcohol matrix) *m/e* 639 (M + H$^+$). Anal. Calcd for $C_{25}H_{30}MoN_5O_7P$: C, 46.96; H, 4.73; N, 10.95. Found: C, 47.57; H, 5.04; N, 10.46.

Thermolysis of 5: Nitrene Trapping. A solution of (dipic)(HMPA)MoO(η^2-nitroso-2-biphenyl) (**5**) (0.05 g, 0.08 mmol) in dioxane (10 mL) was refluxed for 24 h. MoO_2(dipic)-(HMPA) (**2a**) was obtained as a precipitate following dioxane evaporation and pentane trituration. *o*-Aminobiphenyl was detected as the sole product by GC/MS analysis of the pentane soluble fraction. When chlorobenzene was used as the solvent, **2a** was again formed and *o*-aminobiphenyl (49%) and carbazole (51%) were detected in the pentane extracts.

Reaction of 1a with 2,3-Dimethylbutadiene. A solution of molybdooxaziridine complex **1a** (0.10 g, 0.18 mmol) and 2,3-dimethyl-1,3-butadiene (0.26 mL, 2.3 mmol) in dioxane (10 mL) was heated at 70 °C for 24 h. The resulting dark red solution was evaporated and dried under vacuum for about 30 min. Trituration with pentane left unreacted **1a** and dioxo complex **2a** as a minor product. Aniline and 3,6-dihydro-4,5-dimethyl-*N*-phenyl-1,2-oxazine (**6**) were detected by ^{1}H NMR and GC-MS analysis of the pentane-soluble fraction. The ^{1}H NMR and GC-MS of the latter was compared with an authentic sample prepared as described previously.[7]

Reaction of MoO(dedtc)$_2$ (3b) with PhNO. To a solution of **3b** (0.072 g, 0.17 mmol) in dichloromethane (15 mL) was added nitrosobenzene (0.019 g, 0.17 mmol) in one portion. The solution immediately turned brown and was then stirred for 30 min. The solvent was evaporated and the resiude triturated with several portions of petroleum ether. The ^{1}H NMR spectrum of the residue (90%) was identical to that of authentic $(dedtc)_2MoO(\eta^2$-nitrosobenzene).[4]

3-(*N*-Phenylhydroxyamino)-2-methylhex-1-ene (7a). This compound was prepared using the general method of Knight[7d] by stirring nitrosobenzene (0.54 g, 5.0 mmol) and 2-methyl-2-hexene (5.0 g, 35 mmol) in dioxane (25 mL) at 70 °C for 2.5 h. After solvent evaporation, the product was isolated by column chromatography under N_2 on neutral alumina using mixed petroleum ether (bp 35–60 °C) and diethyl ether as eluants. The product was recrystallized several times from petroleum ether (bp 35–60 °C) at −60 °C to produce the allyl hydroxylamine **7** (25%) as a white solid. ^{1}H NMR (CDCl3): δ 0.85 (t, J = 7.3 Hz,3H), 1.2 (bm, 2H), 1.7 (s, 3H), 1.9 (s, 2H), 5.1 (d, J = 6.9 Hz, 1H), 6.2 (bm, 1H), 7–7.7 (m, 5H); MS (12 eV, EI) *m/e* 205.

Reaction of MoO(S$_2$CNEt$_2$)$_2$ (3b) with Allyl Hydroxylamine 7a. To a solution of **3b** (0.072 g, 0.18 mmol) in dichloromethane (10 mL) was added **7a** (0.036 g, 0.18 mmol) and the solution was stirred for 5 h at room temperature. The solvent was evaporated and the residue triturated with pentane to remove the organic products. ^{1}H NMR analysis of the residue indicated the formation of $(dedtc)_2MoO_2$ (**2b**) and GC-MS of the pentane extract showed the presence of 3-*N*-phenylamino-2-methylhex-1-ene, M$^+$ = 189 (100% *of base peak*), identical to an authentic sample.[6]

Reaction of MoO(S$_2$CNEt$_2$)$_2$ (3b) with PhNHOH. The reaction of **3b** with excess PhNHOH (1.6 equiv), conducted as above, gave Mo-oxaziridine complex **1b** (61%) and aniline. The reaction of this complex with equimolar PhNHOH under the same conditions gave Mo(V) dimer **8b** and aniline.

(Dipic)(HMPA)Mo(IV)O (3a). To a solution of triethyl phosphite (0.80 mL, 4.1 mmol) in CH_2Cl_2 (15 mL) was added dropwise 0.48 g (1.0 mmol) of dioxo derivative **1a** in CH_2Cl_2 (15 mL) over a period of 2 h. After stirring for another 2 h at room temperature, the dark brown solution was reduced to half volume and kept in the refrigerator overnight. The resulting dark brown air-sensitive precipitate was collected by filtration and washed with a mixture of CH_2Cl_2/hexane several times and dried in vacuo (80%). IR (KBr): ν (MoO) 952 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.42 (d, J = 9.9 Hz, 18H), 8.05 (br d, J = 7.7 Hz, 2H), 8.12 (m, 1H). MS (FAB, matrix: 3 nitrobenzyl alcohol) 458 (M + H$^+$).

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Reaction of (dipic)(HMPA)MoO (3a) with PhNHOH. Mo(IV) complex **3a** (0.032 g, 0.070 mmol) was dissolved in THF (5 mL) and solid PhNHOH (0.028 g, 0.25 mmol) was added. The mixture was stirred at room temperature for 2 h, producing a reddish-brown solution. Evaporative solvent removal and ^{1}H NMR ($CDCl_3$) analysis of the residue indicated quantitative (>90%) formation of Mo-oxaziridine complex **1a**.

Reaction of $Mo_2O_3(S_2CNEt_2)_4$ (8b) with PhNO. To a solution of **8b** (0.20 g, 0.24 mmol) in dichloromethane (20 mL) was added solid nitrosobenzene (0.070 g, 0.65 mmol) in one portion. The solution color changed immediately to brown. After stirring at room temperature for 1.5 h, the solvent was pumped off and the residue triturated with diethyl ether followed by pentane, producing a brick red solid (88%). IR and ^{1}H NMR were identical to an authentic sample of $(dedtc)_2MoO(\eta^2$-nitrosobenzene). The pentane extracts were found to contain aniline, azobenzene, and azoxybenzene (GC-MS). The reaction with equimolar nitrosobenzene gave the same result.

Reaction of $Mo_2O_3(S_2CNEt_2)_4$ (8b) with PhNHOH. Similarily the reaction of **8b** with equimolar and excess PhNHOH was carried out as above (2 h). In the case of the 1:1 reaction, Mo-oxaziridine complex **1b**, dioxo complex **2b**, and some remaining **8b** were obtained as the pentane-insoluble material and aniline was detected by GC/MS analysis of the pentane-soluble fraction. When an excess of PhNHOH was employed (2.7 equiv), Mo-oxaziridine complex **1b** was isolated as the sole Mo-containing product in >90% yield along with aniline as the organic product.

Reaction of (dipic)(HMPA)MoO_2 (1a) with PhNO. A solution of **1a** (0.10 g, 0.21 mmol) and nitrosobenzene (0.23 g, 0.21 mmol) in dichloromethane (10 mL) was stirred at room temperature for 5 h. The solvent was evaporated from the faint brown homogeneous solution and dried in vacuum. ^{1}H NMR analysis indicated the presence only of **1a** and nitrosobenzene.

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