Chemistry of Molybdenaoxaziridines. A Study of Oxo(*N*-phenylhydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) and Its Catalytic Properties

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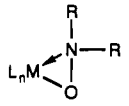
Abstract: The chemistry of molybdenaoxaziridines is investigated. Oxo(*N*-phenylhydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) complexes **3** are prepared in high yields by different procedures, either by a reaction between anilines and oxoperoxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**4**) or by an oxidative addition reaction of nitrosobenzenes to oxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(IV) (**6**). The kinetics of the reactions of a series of para-substituted anilines and **4** are studied, and a Hammett plot showed a correlation between $\log(k/k_o)$ and σ_p with a ρ value of −2.29. A mechanism for the formation of **3** is proposed. The electronic structure of **3** is investigated using extended-Hückel calculations. Based on the frontier orbitals of the system, a brief discussion of the chemical properties of **3** is presented. Complex **3** decomposes to mainly azoxybenzene and dioxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**5**). A variable-temperature study leads to an Arrhenius plot for this decomposition with a ΔG value of 16.1 kcal·mol^{-1}. Based on the detected decomposition products and on the observed nitroso ligand exchange reaction, a mechanism for the decomposition of **3** is proposed. Treatment of **3** with hydrogen peroxide leads to a selective formation of nitrosobenzenes and **4**. This reaction is further developed to a catalytic process for the selective oxidation of various substituted anilines to the corresponding nitrosobenzenes in high yields. The influences of different solvents and of the temperature on the yields of the oxidation are also examined. Based on the kinetic experiments, mechanisms for the stoichiometric and the catalytic oxidation reactions are suggested.

Introduction

Organotransition-metal complexes have been used for the activation of small as well as large molecules but can also provide a deeper insight into the reactions of enzymes. Compared to the considerable interest in understanding the activation and use of molecular oxygen and other oxygen-donating substrates by transition-metal complexes, the activation and use of molecular nitrogen and nitrogen-containing compounds has been offered only little attention. The chemistry of transition-metal peroxo and peroxide complexes is beginning to be well-understood from numerous studies,[1] and therefore it is tempting to take advantage of this knowledge from the oxygen–transition-metal chemistry and try to develop a similar nitrogen–transition-metal chemistry.

The mononitrogen-containing analogues of the studied transition-metal peroxo and peroxide complexes are the metallaoxaziridines, outlined in **1** and **2**, which are three-member ring systems, with formally one of the oxygen atoms of the similar peroxo/peroxide complexes replaced by a nitrogen fragment. A



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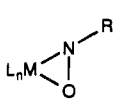

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main reason for the increasing interest in metallaoxaziridines **1** has been the discussion of the mechanism of the reduction of N-oxides.[2] Complex **1** can be viewed as a $[R_2NO]^-$ fragment bound to a transition metal in a bidentate fashion by an oxygen–metal bond and a nitrogen-to-metal lone-pair donation. This type of complex is isoelectronic with transition-metal peroxide complexes. Various examples of complexes **1** with different ligands and transition metals, and either one or two $[R_2NO]^-$ functionalities have been prepared and characterized.[2] In complex **2**, a $[RNO]^{2-}$ fragment is coordinated to a transition-metal center also in a bidentate fashion by an oxygen–metal bond and a nitrogen–metal bond. Complexes of type **2** have been prepared and characterized in very few cases,[3] and their chemistry is virtually unknown. The type **2** complexes are isoelectronic with transition-metal peroxo complexes, which are well-studied.[1]

The chemistry of molybdenaoxaziridines is described in this paper. New synthetic routes for the preparation of some type **2** complexes containing a molybdenum atom as the metal, as well as their chemical properties, are presented. Furthermore, a new synthetic methodology for selective oxidation of anilines to nitrosobenzenes is presented. The complex of concern is oxo(*N*-phenylhydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**3**) and its para-substituted phenyl counterparts.

Results and Discussion

I. Preparation of Oxo(*N*-phenylhydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (3). Oxo(*N*-phenylhydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**3**) can be prepared by different methods. To the best of our knowledge, the only procedure for the preparation of **3** has been the reaction of dioxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**5**) with phenyl hydroxylamine, route B in Scheme I.[3b,c] However, we have found

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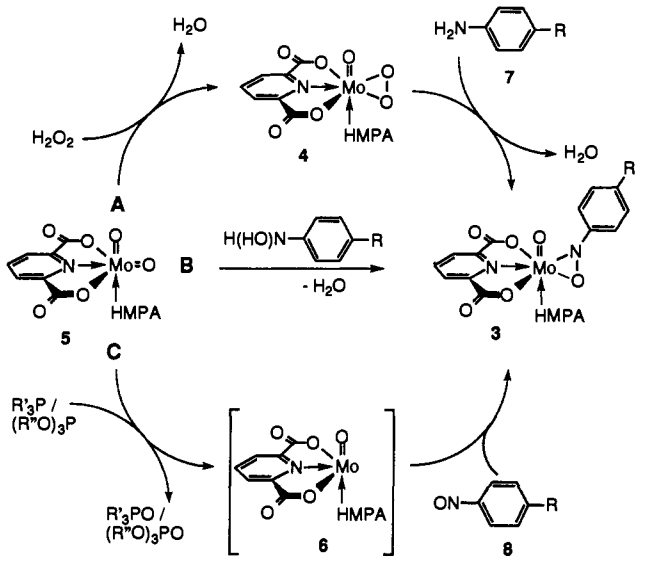
Scheme I



that **3** can be prepared either from anilines **7** and oxoperoxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) **4**[4] (route A in Scheme I) or by reaction of **5** with triphenyl phosphine or triethyl phosphite followed by an oxidative addition of the appropriate nitroso compound **8** as depicted in route C of Scheme I.

The procedure for the synthesis of **3** using route A in Scheme I is a convenient method compared to B or C, since substituted anilines are more accessible and stable than the substituted phenylhydroxylamines and the substituted nitrosobenzenes. Procedure A for formation of **3** involves an initial reaction of **5** with hydrogen peroxide, giving **4** in a high yield. Complex **4** reacts smoothly with **7** at room temperature, producing **3**, also in a good yield. The results for the formation of various molybdenaoxaziridines **3a–k** obtained by reaction of **4** with different para-substituted anilines **7a–k** are presented in Table I (for the experimental conditions, see the Experimental Section).

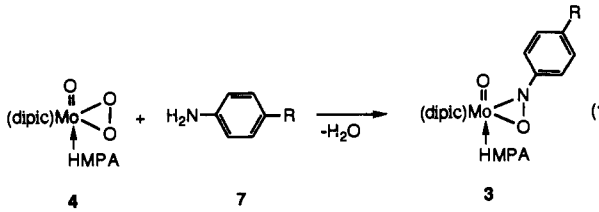
Table I. Results of the Reaction of Oxoperoxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**4**) with Para-Substituted Anilines **7a–k**, Giving Oxo(*N*-phenylhydroxyamine-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) **3a–k**

entry	*p*-R-C_6H_4-NH_2 (**7**), R	reaction time (h)	yields of **3** (%)
1	H, **7a**	22	87
2	CH_3O, **7b**	6	65
3	CH_3, **7c**	18	86
4	F, **7d**	24	86
5	Cl, **7e**	24	84
6	Br, **7f**	24	86
7	$C(O)OC_2H_5$, **7g**	45	91
8	$C(O)CH_3$, **7h**	45	74
9	CF_3, **7i**	48	88
10	CN, **7j**	90	74
11	NO_2, **7k**	115	68

It appears from the results in Table I that **3a–k** are obtained in high yields from **7a–k** with either electron-donating substituents, **7b,c**, or electron-withdrawing substituents, **7d–k**. The latter requires a longer reaction time than the former. The molybdenaoxaziridines **3a–k** are reasonably air-stable compounds and are characterized by spectroscopic methods (see the Experimental Section).

The formation of **3** can also be performed as a "one-pot reaction" by reacting **5** with hydrogen peroxide for 1 h, followed by addition of **7**. However, this method can cause trouble for some substrates due to unreacted hydrogen peroxide, which can further oxidize **3** (*vide infra*).

The kinetics of reaction 1, where **4** reacts with a series of para-substituted anilines, **7a–f, h, i, k**, have been investigated (in the remaining drawings, dipic will be used as an abbreviation for the pyridine-2,6-dicarboxylato ligand). The rates of the disappearance of **4** and **7a–f, h, i, k**, as well as the rate of formation of **3**, have been determined, and the reaction rate is found to be of second order, first order in each reactant.



R = H, OCH_3, CH_3, F, Cl, Br, $C(O)CH_3$, CF_3, NO_2

The variation of $\log(k/k_o)$ for the disappearance of **4** in the reaction with **7a–f, h, i, k** (reaction 1) correlates well with the Hammett σ_p values, as shown in Figure 1.

The ρ value for the Hammett plot in Figure 1 is calculated to be −2.29 with a correlation coefficient of 0.97. This shows that **7** having electron-donating substituents reacts faster with **4** than does **7** having electron-withdrawing substituents. Different mechanisms for the reaction of **7** with **4** can be envisaged; two

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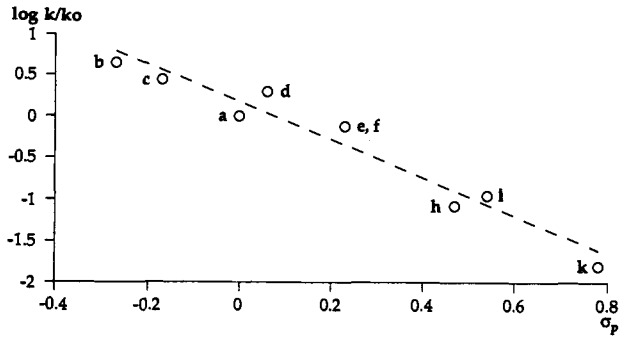
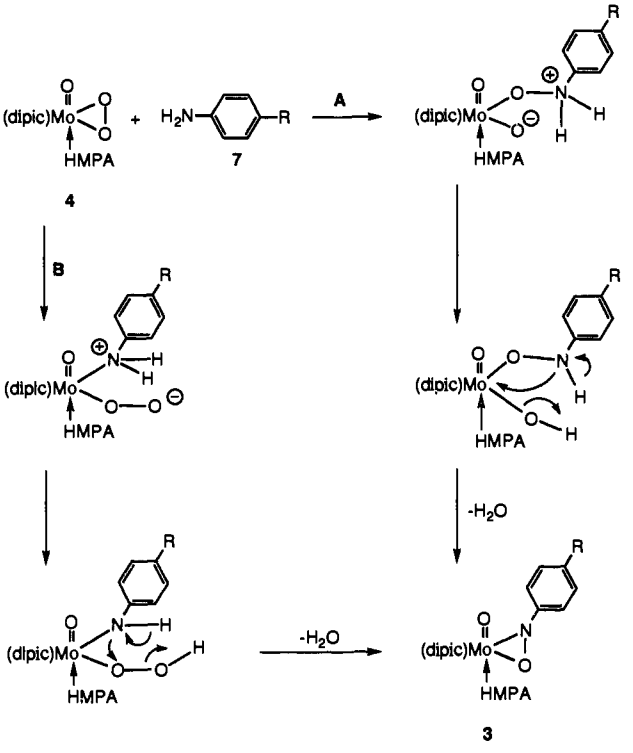


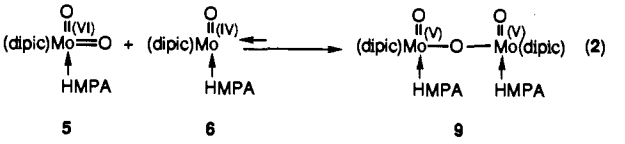
Figure 1. Hammett plot for the disappearance of **4** by the reaction with different para-substituted anilines **7a–f, h, l, k.**

Scheme II



approaches are outlined in Scheme II. The first step in mechanism A of Scheme II is a nucleophilic attack of the aniline nitrogen atom at one of the peroxygen atoms of **4** which are known to be electrophilic.[5] The peroxygen–peroxygen bond is broken by the attack. Proton transfer, followed by a nucleophilic attack of the aniline nitrogen atom on the molybdenum atom and elimination of water, leads to the formation of the **3**. In reaction mechanism B of Scheme II, the aniline nitrogen atom attacks the molybdenum atom, leading to a cleavage of the molybdenum–peroxygen bond,[6] followed by proton transfer. In the final step in path B, the aniline nitrogen atom attacks the α-oxygen atom of the hydroperoxide ligand, cleaving the peroxygen–peroxygen bond, and produces **3** and water. The ρ value (–2.29) is consistent with both reaction mechanisms. The similar oxidation of substituted anilines with peracetic acid gave a ρ value of –1.9,[7] which is comparable to the present ρ value. This similarity supports a direct attack of the aniline nitrogen atom at one of the oxygen atoms of the peroxygen unit (reaction mechanism A in Scheme II). It should also be noted that epoxidation of alkenes with early transition-metal peroxo complexes has been suggested to proceed via direct interaction between the alkene and one of the oxygen atoms of the peroxygen unit.[5]

The molybdenaoxaziridines **3** can also be prepared by a third method, as outlined in route C of Scheme I. If **5** is treated first with 1 equiv of phosphite or phosphine, the corresponding phosphate/phosphine oxide and probably oxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(IV) (**6**) are formed. Unfortunately, **6** seems to combine with **5**, giving a dimeric μ^2-oxomolybdenum(V) complex (**9**) (which we not yet have been able to characterize), as outlined in reaction 2.



Analogues of the proposed dimeric intermediate **9** are known from the literature.[8] The putative complex **9** or **6** then reacts with **8** in an oxidative addition reaction, giving a 1:1 mixture of **3** and **5**. The equilibrium of the dimerization reaction 2 must be to the right, since the use of several equivalents of phosphite/phosphine also afforded a 1:1 mixture of **3** and **5**.

A comparison of routes A and C in Scheme I reveals that the former represents the best methodology for the synthesis of **3**, as the latter procedure gives a maximum yield of 50% of **3**.

II. Electronic Structure of Oxo(*N*-phenylhydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (3a). The electronic structure of **3a** can be understood from an interacting diagram using a fragment molecular orbital analysis, where the fragments are [(dipic)MoO·HMPA]$^{2+}$ and [PhNO]$^{2-}$. The extended Hückel method is applied for this purpose.[9] An interaction diagram is shown in Figure 2, where the important orbitals of the molybdenum fragment are shown to the left and those of the nitrosyl fragment to the right.

The HOMO of the [(dipic)MoO·HMPA]$^{2+}$ fragment is found at the dipic part at –12.51 eV and is not shown in Figure 2. The [(dipic)MoO·HMPA]$^{2+}$ fragment to the left is a distorted square pyramid, which causes the well-known four-under-one splitting of the d orbitals at the metal. The LUMO of this fragment is the d_{yz} orbital at –9.87 eV, and the rest of the empty d-orbitals are the d_{xz}, d_{xy}, d_{z^2} and $d_{x^2-y^2}$, located at –9.37, –9.24, –8,51, and –5.45 eV, respectively. The interacting frontier orbitals of the [PhNO]$^{2-}$ fragment are outlined to the right of Figure 2, with the three shown orbitals being different combinations of the p_z orbitals. The HOMO, found at –11.78 eV, is antibonding between the nitrogen and oxygen atoms and also antibonding between the nitrogen atom and the carbon atom in the phenyl ring. An orbital, antibonding between the nitrogen and oxygen atoms but bonding between the nitrogen atom and the phenyl ring, is found at –13.49 eV. The bonding orbital between all three atoms is located at –15.54 eV. The result of the interaction of the two fragments is shown in the middle of Figure 2. The strongest interaction is between the LUMO of the [(dipic)MoO·HMPA]$^{2+}$ fragment, the d_{zy} orbital, and the two π^*_{N-O} orbitals of p_z character of the [PhNO]$^{2-}$ fragment. The d_{z^2} orbital of the [(dipic)MoO·HMPA]$^{2+}$ fragment interacts with an empty orbital on the [PhNO]$^{2-}$ fragment, not shown. It should be emphasized that the σ^*_{N-O} orbital in **3a** is located high in energy, as it is found

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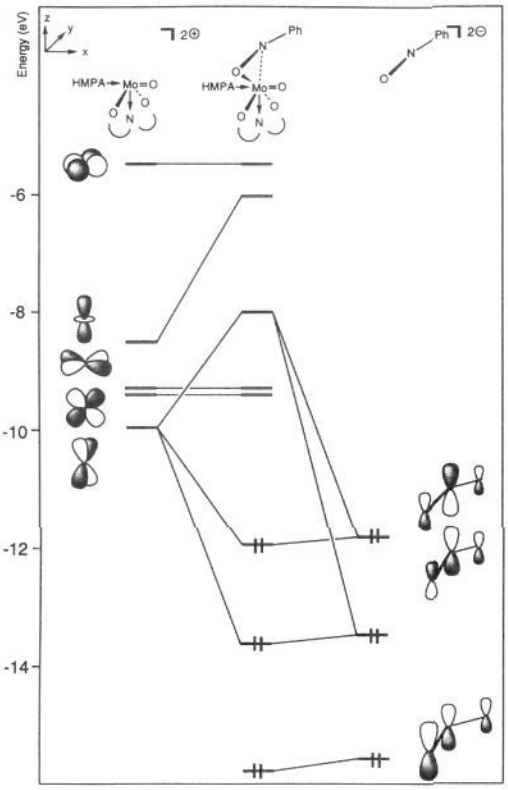


Figure 2. Interaction diagram for $[(dipic)MoO{\cdot}HMPA]^{2+}$ to the left interacting with $[PhNO]^{2-}$ to the right.

at –1.54 eV. If the energy of the σ^*_{N-O} orbital in **3a** is compared to the energy of the σ^*_{O-O} orbital of **4**, a significant difference is found: although the $[PhNO]^{2-}$ and $[O_2]^{2-}$ fragments can be considered isoelectronic, the σ^*_{N-O} orbital in **3a** is located at –1.25 eV, whereas in **4** the σ^*_{O-O} orbital is found 8 eV lower in energy, at –9.25 eV. This difference in energy could indicate a difference in the reaction patterns of **3a** compared with **4**, as **3a** is not as well set-up for interaction with a donor system as is **4** (*vide infra*).

In the interaction diagram outlined in Figure 2, only a small charge transfer (0.37 e) from the $[PhNO]^{2-}$ fragment to the $[(dipic)MoO{\cdot}HMPA]^{2+}$ fragment takes place. However, regarding the formation of **3a** as an oxidative addition reaction of **8a** to **6** (route C in Scheme I), nearly two electrons are transferred from **6** to the π^*_{N-O} orbital of nitrosobenzene, in principle leading to a two-electron reduction of the latter. The π^*_{N-O} orbital of nitrosobenzene has a larger amplitude at the nitrogen atom than at the oxygen atom; therefore a negative charge is accumulated on the nitrogen atom as a result of the addition. A negative charge (–0.45) on the nitrogen atom in the molybdenaoxaziridine ring in **3a** is calculated, compared to the calculated small positive charge (0.05) on the nitrogen atom for the free nitroso ligand.

III. Stability of Oxo(*N*-phenylhydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum-(VI) (3). An investigation of the stability of **3** in solution has been performed. At 25 °C, **3a** is reasonable stable and only a few percentage has decomposed after 100 h. However, increasing the temperature to 75 °C or higher causes decomposition of the complex. The kinetics of the decomposition of **3a** is found to be a second-order relation and has been studied as a function of temperature. An Arrhenius plot of the decomposition of **3a** is presented in Figure 3, and ΔG for the decomposition is calculated from the data to be 16.1 kcal·mol^{-1}.

The products obtained form the decomposition of **3** are investigated. The main organic product is azoxybenzene **11**. Interestingly, nitrosobenzene (**8**) is not detected, although it is

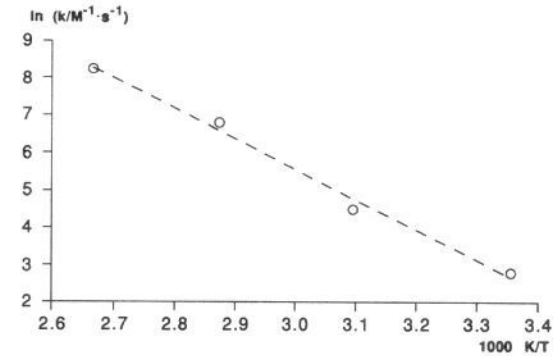
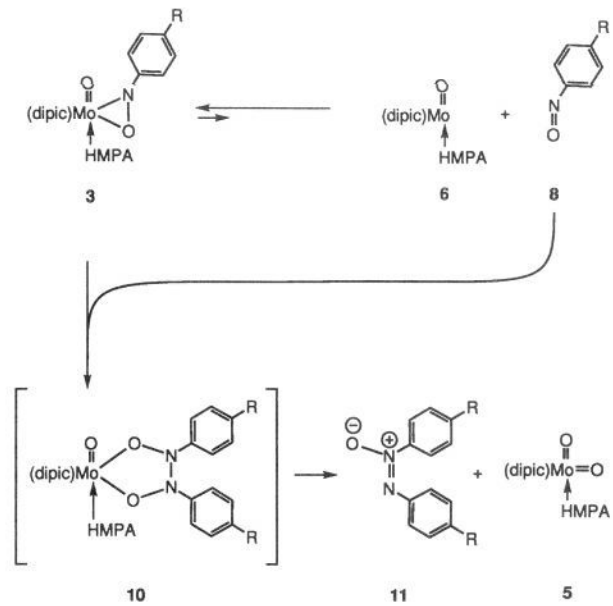


Figure 3. Arrhenius plot for the decomposition of **3a**.

Scheme III

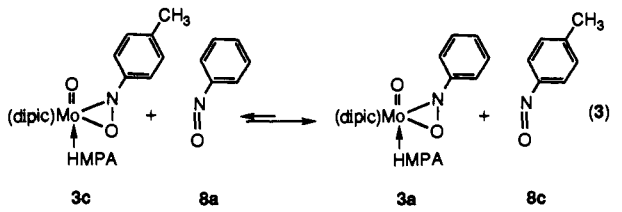


observed during the kinetics measurements. The dioxo complex **5** is the main detectable molybdenum complex. A proposed reaction pathway for the decomposition of **3** is shown in Scheme III.

The first step in Scheme III is a reductive elimination of nitrosobenzene (**8**) from **3**, forming **6**. Then, the nitrosobenzene formed reacts with another molybdenaoxaziridine complex (**3**), probably through an insertion of the nitroso functionality into the molybdenum–nitrogen bond, resulting in a 5-membered ring complex, (**10**). Extrusion of **11** from **10** gives the detected dioxo complex **5**. However, several attempts to isolate and characterize the proposed intermediate have unfortunately failed. Both the extended-Hückel calculation of **3** presented above and an *ab initio* calculation of $Pt(PH_3)_2CF_3NO$[10] have shown that the metal atom of the metallaoxaziridines possesses a partly positive charge, while the nitrogen atom is negatively charged. The N=O bond in nitrosobenzene has a positively charged nitrogen atom and a negatively charged oxygen atom,[11] and therefore an addition of the N=O bond across the molybdenum–nitrogen bond of the molybdenaoxaziridine ring sounds plausible. It should be noted that it has been proposed that alkenes can be inserted into the metal–nitrogen bond of a metallaoxaziridine[12] and that the reaction is suggested to take place via a 5-membered ring intermediate.

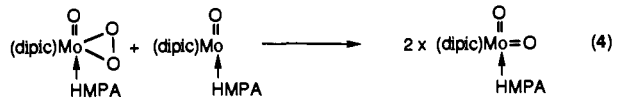
(10) Fantucci, P.; Pizzotti, M.; Porta, F. *Inorg. Chem.* **1991**, *30*, 2277.
(11) Wagnière, G. H. In *The Chemistry of the Nitro and Nitroso Groups;* Patai, S., Ed.; Wiley Interscience: New York, 1969; Chapter 1.
(12) Cenini, S.; Porta, F.; Pizzotti, M.; La Monica, G. *J. Chem. Soc., Dalton Trans.* **1984**, 355.

Several observations further support the mechanism proposed in Scheme III: (i) the decomposition or equilibrium that produces nitrosobenzene has been observed for other types of nitroso complexes;[13] (ii) identification of a complex with a 5-membered ring structure by X-ray crystallography similar to **10** supports this intermediate;[14] and (iii) addition of **8a** to the methyl-substituted molybdenaoxaziridine **3c** at room temperature caused a ligand exchange, as outlined in reaction 3.



3c **8a** **3a** **8c**

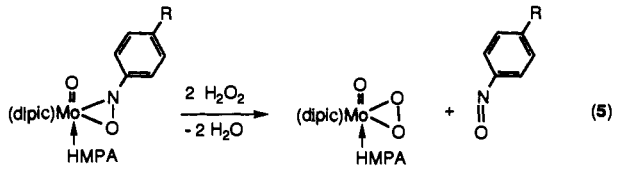
Addition of **8a** to **3h**, which has a trifluoromethyl substituent, at room temperature did not cause any ligand exchange. This observation, together with reaction 3, indicate that electron-withdrawing substituents stabilize **3**, whereas electron-donating substituents destabilize it. Furthermore, small amounts of **5** are observed in reaction 1 when aniline is substituted with an electron-donating substituent. The formation of **5** can be explained as follows: complex **3** decomposes to **6** and **8** according to Scheme III, followed by reaction of **6** with **4**, the substrate in reaction 1, to give **5** as outlined in reaction 4.



4 **6** **5**

We have tried to take advantage of the higher stability of molybdenaoxaziridines **3** with electron-withdrawing substituents relative to those with electron-donating substituents in the synthesis of unsymmetric azoxybenzenes from nitrosobenzene and **3** with a different nitroso ligand. The reaction is performed using **3h** and **8a** in refluxing dioxane, as it has been observed that the *p*-(trifluoromethyl)phenyl nitroso ligand is not replaced by nitrosobenzene at room temperature. Based on GC–MS and the typical MS patterns of azoxybenzenes,[15] it is concluded that the reaction leads to all four possible azoxybenzenes in a ratio of about 1:1:1:1. The formation of four azoxybenzenes can only be explained by ligand-exchange reactions.

IV. Stoichiometric and Catalytic Oxidations of Para-Substituted Anilines. Reaction of **3** with 1 equiv of hydrogen peroxide leads to the formation of nitrosobenzenes **8** and a 1:1 mixture of **3** and **4**, reaction 5. This indicates that hydrogen peroxide reacts



3 **4** **8**

more willingly with **5** than with **3**. A complete conversion of **3** to **8** and **4** can be achieved using 2 equiv of hydrogen peroxide, as outlined in reaction 5.

The reaction taking place in route A of Scheme I can be combined with reaction 5, leading to a new selective method for

(13) Watkins, J. J.; Balch, A. L. *Inorg. Chem.* **1975**, *14*, 2720.
(14) Fochi, G.; Floriani, C.; Chiesi-Villa, A.; Gaustini, C. *J. Chem. Soc., Dalton Trans.* **1986**, 445.
(15) Tam, S. W. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley Interscience: London, 1975; Chapter 5.

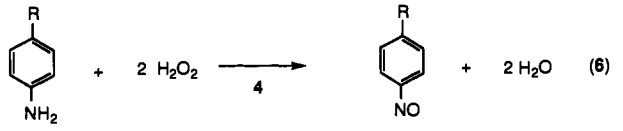
Table II. Results of the Stochiometric Oxidation of Oxo(*N*-phenylhydroxylamido-*O*,*N*)(pyridine-2,6-dicarboxylato)-(hexamethylphosphortriamide)molybdenum(VI) **3a** and Its Para-Substituted Counterparts **3c**, **e**, **g**, **h–j** to Para-Substituted Nitrosobenzenes **8a**, **c**, **e**, **g**, **h–j** and the Molybdenum–Peroxo Complex **4**

entry	3, R	reaction time (min)	yields of *p*-R-C_6H_4-NO (**8**) (%)
1	H, **3a**	20	80
2	CH_3, **3c**	20	90
3	Cl, **3e**	20	73
4	$C(O)OC_2H_5$, **3g**	25	57
5	$C(O)CH_3$, **3h**	35	60
6	CF_3, **3i**	25	47
7	CN, **3j**	45	30

stoichiometric oxidation of different anilines to the corresponding nitrosobenzenes via **3**. In the first step, **4** is converted to **3** by reaction with the appropriate aniline, **7**. Step 2 is reaction between **3** and hydrogen peroxide with formation of nitrosobenzene (**8**) and re-formation of **4**. One advantage of using the stoichiometric oxidation of anilines via **3** is that the condensation reaction of phenylhydroxylamine with **7** or **8** is excluded,[16] though small amounts of azoxybenzene are still detected, which might be accounted for by the mechanism outlined in Scheme III, Table II shows the results of the stoichiometric oxidations of **3a**, **c**, **e**, **g**, **h–j**, to **8a**, **c**, **e**, **g**, **h–j** using hydrogen peroxide.

The results in Table II reveal that the method works best for **3** with an electron-donating substituent attached to the phenyl ring compared to the complexes substituted with electron-withdrawing groups. This observation may be explained by weaker binding of the electron-rich nitroso ligands to the molybdenum atom, compared to the electron-poor nitroso compounds, as described above. It should also be mentioned that small amounts of aniline are detected for reaction of **3** substituted with electron-donating groups. Finally, it should be pointed out that the reaction is fast and easy to perform; the reaction conditions are mild, and the reaction is performed in organic solvents.

Since the molybdenum–peroxo complex **4** is reproduced in the stoichiometric oxidation reactions (see reaction 5), it was tempting to make a catalytic analogue of the oxidation reaction of anilines **7a–j** using **4** as the catalyst, as outlined in reaction 6.



7 **8**

R = H, OCH_3, CH_3, F, Cl, Br, $C(O)OC_2H_5$, $C(O)CH_3$, CF_3, CN

The catalytic oxidation turned out to be a very good potential reaction, which has been tested for various para-substituted anilines. As for the stoichiometric reaction, different substituents may be present on the phenyl ring without interfering with the oxidation reaction of the amine. The results for the catalytic oxidation of a series of para-substituted anilines are presented in Table III.

It is seen from Table III that anilines, substituted with either electron-donation or electron-withdrawing groups, can be oxidized to the corresponding nitroso compounds in moderate to good yields. The variation in the yields of nitrosobenzenes is less pronounced in the catalytic oxidation than in the stoichiometric oxidations, indicating that the catalytic oxidations might proceed differently than the stoichiometric oxidations. The reaction time is a further indication of the existence of two different reaction

(16) (a) Boyer, J. H. In *The Chemistry of the Nitro and Nitroso Groups*; Patai, S., Ed.; Wiley Interscience: New York, 1969; Chapter 5. (b) Sollenberg, P. Y.; Martin, R. B. In *The Chemistry of the Amino Group*; Patai, S., Ed.; Wiley Interscience: London, 1968; Chapter 7.

Table III. Results of the Catalytic Oxidation of Para-Substituted Anilines **7a–j** to Para-Substituted Nitrosobenzenes **8a–j** Using Oxoperoxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)-molybdenum(VI) (**4**) as Catalyst

entry	*p*-R-C_6H_4-NH_2 (**7**), R	reaction time (h)	yield of *p*-R-C_6H_4-NO (**8**), (%)
1	H, **7a**	4	54
2	CH_3O, **7b**	0.5	62
3	CH_3, **7c**	2	77
4	F, **7d**	2	61
5	Cl, **7e**	2	65
6	Br, **7f**	2	63
7	$C(O)OC_2H_5$, **7g**[a]	2	60
8	$C(O)CH_3$, **7h**[a]	2	43
9	CF_3, **7i**[a]	2	40
10	CN, **7j**[a]	2	55

[a] Using a 75/25 mixture of petroleum ether/dichloromethane as solvent.

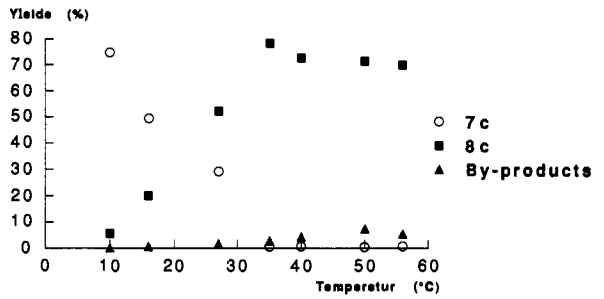


Figure 4. Temperature dependence of catalytic oxidation of *p*-toluidine (**7c**).

mechanisms, as the reaction time for the catalytic processes is short compared to the reaction time for the formation of **3** (see Table I).

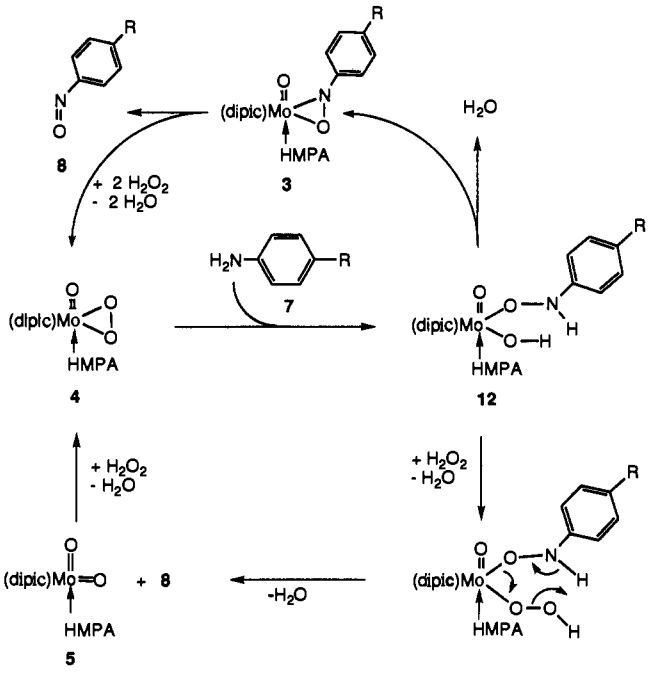
To optimize the catalytic reaction, the oxidation of *p*-toluidine (**7c**) has been performed in different solvents. A smooth reaction is found in petroleum ether, although the catalyst **4** is insoluble in this solvent. Within 2 h at room temperature, more than 40% of **8c** is formed. Furthermore, it is observed that decomposition of the catalyst is less pronounced in petroleum ether than in other solvents. Changing the solvents to, *e.g.*, acetonitrile, THF, or dioxane leads also to an oxidation of **7c** to **8c**, but a more rapid decomposition of the catalyst takes place in these solvents.

The reaction temperature is found to be a critical parameter for the formation of nitrosobenzene in the catalytic oxidation, reaction 6. The product distribution observed for the catalytic oxidation of **7c** after 2 h at different temperatures in petroleum ether is shown in Figure 4.

The temperature study in Figure 4 shows that the formation of *p*-nitrosotoluene (**8c**) increases significantly when the temperature is increased from 15 °C to 35 °C. At 35 °C, nearly 80% of **8c** is formed, whereas only 20% is formed at 15 °C. The byproducts are small amounts of the overoxidized compound *p*-nitrotoluene and the condensation products *p,p'*-dimethylazobenzene and *p,p'*-dimethylazoxybenzene.

It was first assumed, that the catalytic reaction 6 proceeds in two steps as the stoichiometric oxidation first by formation of a molybdenaoxaziridine (**3**) from the molybdenum–peroxo complex **4** and aniline (**7**), followed by reaction of **3** with hydrogen peroxide, producing nitrosobenzene (**8**) and **4**. Furthermore, it was taken for granted that the formation of **3** is the rate-determining step, because it has been found that the reaction of **3** with hydrogen peroxide (reaction 5) is fast compared with the formation of **3** (reaction 1). If the formation of **3a** is rate-determining, further simplifying assumptions can be made: (i) the concentration of the catalyst **4** is constant and equal to $[\mathbf{4}]_{t=0}$ (a steady-state approximation), (ii) the amount of reacted **7a** is equal to the amount of **8a** formed; and (iii) the sum of the concentration of **7a** and **8a** is equal to the starting concentration of **7a** ($[\mathbf{7a}]_t + [\mathbf{8a}]_t = [\mathbf{7a}]_{t=0}$). When assumptions (i) and (ii) are applied to the rate expression for the disappearance of **7a**, eq I, the result is eq II. From equation II and assumption (iii), an expression for the formation of **8a** can be found (eq III).

Scheme IV



$$\frac{d[\mathbf{7a}]}{dt} = (-1 \times 10^{-3}\ M^{-1}\ s^{-1})[\mathbf{7a}]_t[\mathbf{4}]_t = \left(-\frac{d[\mathbf{3a}]}{dt}\right) \quad \text{(I)}$$

$$\frac{d[\mathbf{7a}]}{dt} = (-1 \times 10^{-3}\ M^{-1}\ s^{-1})[\mathbf{7a}][\mathbf{4}]_{t=0} \quad \text{(II)}$$

$$[\mathbf{8a}]_t = [\mathbf{7a}]_{t=0}(1 - \exp((-1 \times 10^{-3}\ M^{-1}\ s^{-1})[\mathbf{4}]_{t=0})) \quad \text{(III)}$$

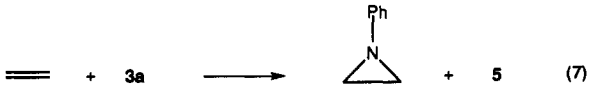
From eq III, the theoretical amount of produced **8a** has been calculated and compared with the measured amounts of experimentally formed **8a** from reaction 6 at different reaction times. It is found that the formed amount of **8a** is much greater than the theoretically calculated amount of **8a**. This observation is in accordance with a rate of formation of **8a** that is about 100 times faster than expected. For anilines with electron-withdrawing substituents, the difference in expected and obtained yields was even more pronounced. It can thus be concluded that **3** is an unlikely intermediate in the catalytic oxidations of **7** to **8**. Based on a kinetic analysis, it is also found that the catalytic reaction probably proceeds via complex **5**. These observations motivated us to propose two different mechanisms for the stoichiometric and the catalytic oxidations, as shown in Scheme IV.

The upper cycle in Scheme IV explains the stoichiometric oxidation, while the lower accounts for the catalytic one. The stoichiometric cycle consists of two steps, a combination of reactions 1 and 5, as described previously. The first step in the catalytic cycle is identical to the stoichiometric mechanism, route A in Scheme I, with a nucleophilic attack of the aniline nitrogen atom at one of the peroxygens in **4** to give **12**. The next step is proposed to be a ligand-exchange reaction of the hydroxyl with a peroxide substituent. This step is followed by an extrusion of **8** and water from the molybdenum complex, producing **5**. The last step in the catalytic cycle is a reoxidation of **5** by hydrogen peroxide to **4**.

Very few methods have been developed for direct oxidation of anilines to the corresponding nitroso compounds. The oxidation of anilines to the nitroso analogues can be achieved by Caro's

acid and can be used for the oxidation of a variety of substrates, although overoxidation often is observed.[16,17] Recently dimethyldioxirane was also used as an oxidation reagent for primary aromatic amines. This method generally leads to formation of the corresponding nitro compounds and oximes. The nitroso compounds are only observed in very low yields.[18] Transition-metal-catalyzed oxidations of primary aromatic amines have only been studied sparsely for a few systems. To our knowledge, no selective catalytic oxidation of primary amines to the corresponding nitroso compounds has been achieved. Oxidation of different anilines using molybdenum and vanadium complexes as catalysts and *tert*-butyl hydroperoxide as the oxidant leads to formation of the corresponding nitrobenzene as the only detectable product.[19] Similar results are obtained using hydrogen peroxide under phase-transfer conditions in the presence of some ruthenium complexes, where azo and azoxy compounds are formed in combination with the nitro compounds.[20] A Cu(I)–O_2 complex can accomplish the oxidation of 3,4-dimethylaniline to 3,4-dimethylnitrosobenzene under stoichiometric conditions.[21] A combination of peroxytungsten phosphate and hydrogen peroxide can catalyze the oxidation of anilines, but the nitroso as well as the nitro compounds were identified.[22] It should also be noted that $Mo(O)(O_2)_2(H_2O)$(HMPA), a related molybdenum–peroxo complex, recently was shown to oxidize primary benzylamines to the corresponding oximes and/or Schiff bases.[23] The present method for the oxidation of substituted anilines to the corresponding nitroso compounds seems to be superior compared to those recently published, as (i) the oxidation stops with the nitroso compound, (ii) only minor overoxidation to the nitro compounds is observed, (iii) only very small amounts of azo and azoxy products are formed, and (iv) this methodology can be used for anilines substituted with both electron-withdrawing and electron-donating substituents.

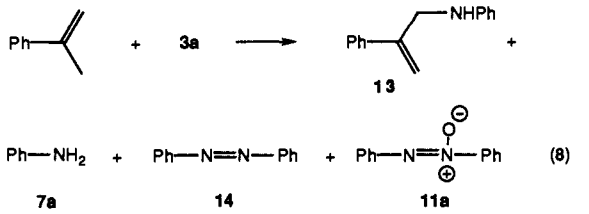
V. **Reaction of 3 with Alkenes.** The molybdenaoxaziridines **3** are isoelectronic with the molybdenum–peroxo complex **4**. Transition-metal–peroxo complexes can transfer one of the peroxygen atoms to an alkene under formation of an epoxide,[24] and transition-metal complexes catalyze the alkene epoxidation with hydrogen peroxide or alkyl peroxides as the oxidant.[1c,d,24] Based on the similarity of **3** and **4**, it could thus be expected that, *e.g.*, **3** would react with alkenes to form aziridines:



(7)

The reaction of **3a** with alkenes has been tested with, *e.g.*, α-methylstyrene as the substrate, but *no* aziridine product is formed. The difference in reactivity between **3a** and **4** can probably be accounted for by the difference in the frontier orbitals of **3a**, as discussed in Section II. However, another reaction takes place when **3a** reacts with α-methylstyrene in dioxane at 80 °C, as shown in reaction (8).

The reaction, which can by viewed as an ene reaction, leads to the formation 2-phenyl-3-(phenylamino)-1-propene (**13**) in about 10% yield. Unfortunately, the major products are aniline (**7a**, 1–2%), azobenzene (**14**, 15%), and azoxybenzene (**11a**, 5%).



(8)

The formation of these byproducts is consistent with the decomposition of **3a** under the applied reaction conditions. Other substrates did not lead to better yields of the allylic amine. Very recently, attempts to turn the allylic amination reaction into a catalytic reaction have been performed, using **5** as the catalyst and with phenylhydroxylamine as the nitrogen-fragment donor.[25] The observed yields of the allylic amines was not increased in the catalytic reaction compared to the stoichiometric reaction.[3b,25] It has also been found that the allylic amination reaction (reaction 8) depends on the nature of the organic ligand at the molybdenum center, as an exchange of the dipic ligand with the *N*-salicylidene-2-aminophenolato ligand leads to a significant increase in the yield of **13**,[26] but also here the major products were **7a**, **14**, and **11a**. Changing the catalytic system to various iron complexes leads to a straight formation of the allylic amines.[26]

Summary

In this paper a new synthetic procedure for the preparation of a series of molybdenaoxaziridines from a molybdenum–peroxo complex and anilines is presented. A kinetic study of the reaction between the molybdenum–peroxo complex and para-substituted anilines showed correlation between the Hammett σ_p and $\log(k/k_o)$ and gave a ρ value equal to −2.29. As a result of the Hammett plot, two possible reaction mechanisms for the formation of the molybdenaoxaziridine were suggested, the most plausible suggestion starting with a nucleophilic attack of the aniline nitrogen atom at one of the peroxygen atoms of the molybdenum–peroxo complex. The molybdenaoxaziridines decompose to mainly azoxybenzenes with an activation energy of 16.1 kcal·mol^{-1}. A new synthetic methodology for either stoichiometric or catalytic selective oxidation of para-substituted anilines to the corresponding nitrosobenzenes using hydrogen peroxide is also presented. The oxidations have been performed with anilines substituted with either electron-donating or electron-withdrawing substituents in the para position with good yields. Comparison of the rate of formation of nitrosobenzene in the catalytic reaction with the rate of formation of the molybdenaoxaziridine excludes the molybdenaoxaziridine as a predominant intermediate in the catalytic reaction. The reaction of the molybdenaoxaziridine with alkenes is briefly discussed and compared with the reaction of the isoelectronic molybdenum–peroxo complex and alkenes. Differences in reactivity of the isoelectronic complexes are understood from an extended-Hückel study.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer. All spectra were recorded in $CDCl_3$. Tetramethylsilane (TMS) was used as an internal standard. For **4** and **5**, H_A and H_B refer to the protons of the pyridine-2,6-dicarboxylato ligand which make up a typical A_2B spin system. For **3a–k** H_A, H_B, and H_C refer to the protons of the pyridine-2,6-dicarboxylato ligand which make an ABC spin system. In ^{13}C NMR, C_i, C_o, C_m, and C_p refer to the ipso, ortho, meta, and para carbons of the N-phenyl ring, and C_{1-7} refer to the carbons of the pyridine-2,6-dicarboxylato ligand.

GC was recorded on an HP 5890; column, OV-10.1. GC–MS was recorded on an HP 5890 VG-trio 2; column, OV-101.

Materials. *p*-Methoxyaniline, *p*-toluidine, *p*-fluoroaniline, *p*-chloroaniline, *p*-bromoaniline, ethyl *p*-aminobenzoate, *p*-aminoacetophenone,

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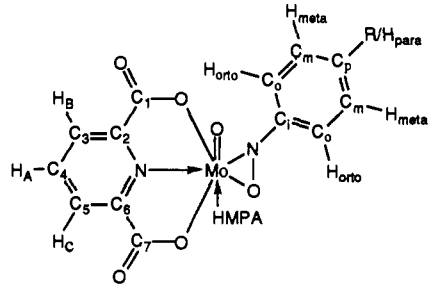

p-(trifluormethyl)aniline, *p*-cyanoaniline, *p*-nitroaniline, $MoO_2(acac)_2$, HMPA, hydrogen peroxide (35%), CH_2Cl_2, petroleum ether, diethyl ether, dioxane, $CHCl_3$, THF, acetonitrile, and $CDCl_3$ are commercially available and were used as received, except for the solvents, which were dried before use according to standard methods. Aniline was distilled prior to use. The decomposition experiments and the formation of **6** were performed under nitrogen, using Schlenk techniques, where the solvents had been distilled over Na/benzophenone and degassed prior to use.

Preparations. Dioxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**5**) was prepared according to literature methods.[3b] ^1H NMR δ: 2.44 (d, J_{HP} = 9.8 Hz, 18H), HMPA; 8.42 (J = 7.74 Hz, 1H), H_B; 8.30 (J = 7.74 Hz, 2H), H_A. ^{13}C NMR δ: 36.3, 36.4 (HMPA); 127.5 (C_3, C_5); 144.6 (C_4); 147.3 (C_2, C_6); 166.7 (C_1, C_7). The X-ray structure of **5** has been determined.[27]

Oxoperoxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)-molybdenum(VI) (**4**) was prepared as follows. (a) Pyridine-2,6-dicarboxylic acid (9,78 g $MoO_2(acac)_2$, 30 mmol) and HMPA (5.38 g, 5.22 mL, 30 mmol) were stirred at 25 °C in CH_2Cl_2 (200 mL) for 23 h. Hydrogen peroxide (3.0 mL, 35% aqueous solution, 34 mmol) was added, and the solution was stirred for another hour. The solution was filtered, and most of the solvent was removed by rotary evaporation. After addition of diethyl ether and filtration, **4** was isolated (13.32 g, 91%). (b) **5** (4.72 g, 10 mmol) was dissolved in CH_2Cl_2 (75 mL), and hydrogen peroxide (1 mL, 35% aqueous solution, 11 mmol) was added. After 1 h, the solution was treated as above; yield, 84%. ^1H NMR δ: 2.33 (d, J = 9.9 Hz, 18H), HMPA; 8.54 (J = 7.71 Hz, 1H), H_B; 8.40 (J = 7.71 Hz, 2H), H_A. ^{13}C NMR δ: 36.2, 36.3 (HMPA); 128.8 (C_3, C_5); 145.4 (C_4); 148.1 (C_2, C_6); 167.7 (C_1, C_7). The X-ray structure of **4** has been determined.[27]

General Procedure for the Preparation of the Molybdenaoxaziridine Complexes 3. Oxoperoxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**4**) (488 mg, 1 mmol) was dissolved in CH_2Cl_2 (5–10 mL). Aniline (**7**) (1.1–2.0 mmol) was added, and the solution was stirred at room temperature for the times listed in Table I. When the reaction was completed, the solvent was removed on a rotary evaporator, and petroleum ether or diethyl ether (20 mL) was added to the residue. Filtration gave the desired molybdenaoxaziridine.

The amount of each of the anilines, solvent used for precipitation, and ^1H and ^{13}C NMR spectra data are given below.

3a: 1,1 mmol of aniline; petroleum ether; red-brown crystals. ^1H NMR δ: 2.36 (d, J = 9.9 Hz, 18H), HMPA; 7.02 (t, J = 7.3 Hz, 1H), H_p; 7.38 (dd, J = 8.6, 7.3 Hz, 2H), H_m; 7.71 (d, J = 8.6 Hz, 2H) H_o; 8.33–8.52 (m, 3H, H_A, 8.38; H_B, 8.47; H_C, 8.36, J_{AB} = 7.72 Hz, J_{AC} = 1.08 Hz, J_{BC} = 7.76 Hz). ^{13}C NMR δ: 36.3, 36.3 (HMPA); 116.4 (C_o); 126.3 (C_p); 128.2, 128.3 (C_3, C_5); 128.3 (C_m); 144.9 (C_4); 148.3, 148.6 (C_2, C_6); 159.6 (C_i); 168.1, 168.9 (C_1, C_7). The X-ray structure of **3a** has been determined.[3b]

3b: 1.1 mmol of *p*-methoxyaniline; diethyl ether; purple crystals. ^1H NMR δ: 2.36 (d, J = 9.9 Hz, 18H), HMPA; 3.81 (s, 3H), R = OCH_3; 6.90 (d, J = 9.0 Hz, 2H), H_m; 7.64 (d, J = 9.0 Hz, 2H), H_o; 8.32–8.52 (m, 3H, H_A, 8.38; H_B, 8.46; H_C, 8.35, J_{AB} = 7.71 Hz, J_{AC} = 1.03 Hz, J_{BC} = 7.79 Hz). ^{13}C NMR δ: 36.4, 36.5 (HMPA); 55.5 (OCH_3); 113.3 (C_m); 117.7 (C_o); 128.2, 128.2 (C_3, C_5); 145.0 (C_4); 148.2 148.6 (C_2, C_6); 154.1 (C_i); 158.5 (C_p); 168.1, 169.0 (C_1, C_7).

3c: 1.1 mmol of *p*-toluidine; petroleum ether; red-brown crystals. ^1H NMR δ: 2.36 (d, J = 9.9 Hz, 18H), HMPA; 2.44 (s, 3H), R = CH_3; 7.19 (d, J = 8.4 Hz, 2H), H_m; 7.61 (d, J = 8.4 Hz, 2H), H_o; 8.32–8.52 (m, 3H, H_A, 8.38; H_B, 8.46; H_C, 8.35, J_{AB} = 7.70 Hz, J_{AC} = 1.06 Hz, J_{BC} = 7.80 Hz). ^{13}C NMR δ: 20.8 (R = CH_3); 36.4, 36.5 (HMPA); 116.1 (C_o); 128.1, 128.1 (C_3, C_5); 128.6 (C_m); 135.9 (C_p); 144.8 (C_4); 147.9, 148.3 (C_2, C_6); 157.6 (C_i); 167.8, 168.7 (C_1, C_7).

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3d: 1.1 mmol of *p*-fluoroaniline; petroleum ether; orange-brown crystals. ^1H NMR δ: 2.36 (d, J = 9.9 Hz, 18H), HMPA; 7.06 (dd, J = 9.0 Hz, J_{HF} = 8.5 Hz, 2H), H_m; 7.67 (dd, J = 9.0 Hz, J_{HF} = 5.0 Hz, 2H), H_o; 8.34–8.53 (m, 3H, H_A, 8.39; H_B, 8.48; H_C, 8.37, J_{AB} = 7.71 Hz, J_{AC} = 1.06 Hz, J_{BC} = 7.78 Hz). ^{13}C NMR δ: 36.4, 36.5 (HMPA); 114.8 (d, J_{CF} = 22.8 Hz, C_m); 117.7 (d, J_{CF} = 8.1 Hz, C_o); 128.2, 128.2 (C_3, C_5); 145.0 (C_4); 147.8, 148.2 (C_2, C_6); 157.7 (d, J_{CF} = 2.8 Hz, C_i); 161.2 (d, J_{CF} = 242 Hz, C_p); 167.7, 168.6 (C_1, C_7).

3e: 1.2 mmol of *p*-chloroaniline; petroleum ether, orange-brown crystals. ^1H NMR δ: 2.35 (d, J = 9.9 Hz, 18H), HMPA; 7.33 (d, J = 8.8 Hz, 2H), H_m; 7.64 (d, J = 8.8 Hz, 2H), H_o; 8.35–8.54 (m, 3H, H_A, 8.40; H_B, 8.50; H_C, 8.37, J_{AB} = 7.74 Hz, J_{AC} = 1.05 Hz, J_{BC} = 7.77 Hz). ^{13}C NMR δ: 36.4, 36.5 (HMPA); 117.7 (C_o); 128.2, 128.2 (C_3, C_5/C_m); 131.3 (C_p); 144.9 (C_4); 147.9, 148.2 (C_2, C_6); 157.8 (C_i); 167.7, 168.6 (C_1, C_7).

3f: 1.2 mmol of *p*-bromoaniline; petroleum ether; orange-brown crystals. ^1H NMR δ: 2.35 (d, J = 9.9 Hz, 18H), HMPA; 7.48 (d, J = 8.6 Hz, 2H), H_m; 7.59 (d, J = 8.6 Hz, 2H), H_o; 8.35–8.54 (m, 3H, H_A, 8.40; H_B, 8.49; H_C, 8.37, J_{AB} = 7.73 Hz, J_{AC} = 1.06 Hz, J_{BC} = 7.76 Hz). ^{13}C NMR δ: 36.4, 36.5 (HMPA); 118.0 (C_o); 119.3 (C_p); 128.2, 128.3 (C_3, C_5); 131.2 (C_m); 144.9 (C_4); 147.9, 148.2 (C_2, C_6); 158.3 (C_i); 167.7, 168.6 (C_1, C_7).

3g: 2.0 mmol of ethyl *p*-aminobenzoate; diethyl ether; brown crystals. ^1H NMR δ: 1.37 (t, J = 7.1 Hz, 3H), R = $C(O)CH_2CH_3$; 2.36 (d, J = 10.0 Hz, 18H), HMPA; 4.35 (q, J = 7.1 Hz, 2H), R = $C(O)CH_2CH_3$; 7.73 (d, J = 8.6 Hz, 2 H) H_o; 8.08 (d, J = 8.6 Hz, 2H), H_o; 8.35–8.54 (m, 3H, H_A, 8.40; H_B, 8.49; H_C, 8.37, J_{AB} = 7.78 Hz, J_{AC} = 0.83 Hz, J_{BC} = 7.79 Hz). ^{13}C NMR δ: 14.4 (R = $C(O)OCH_2CH_3$); 36.4, 36.5 (HMPA); 60.6 (R = $C(O)OCH_2CH_3$); 116.0 (C_o); 127.6 (C_p); 128.2, 128.3 (C_3, C_5); 130.1 (C_m); 145.0 (C_4); 147.9, 148.2 (C_2, C_6); 162.6 (C_i); 166.1 (R = $C(O)OCH_2CH_3$); 167.6, 168.4 (C_1, C_7).

3h: 2 mmol of *p*-aminoacetophenone; diethyl ether; orange crystals. ^1H NMR δ: 2.36 (d, J = 9.9 Hz, 18H), HMPA; 2.58 (s, 3H) R = $C(O)CH_3$; 7.76 (d, J = 8.8 Hz, 2H), H_o; 8.02 (d, J = 8.8 Hz, 2H), H_m; 8.36–8.57 (m, 3H, H_A, 8.41; H_B, 8.52; H_C, 8.39, J_{AB} = 7.71 Hz, J_{AC} = 1.03 Hz, J_{BC} = 7.77 Hz). ^{13}C NMR δ: 26.5 (R = $C(O)CH_3$); 36.4, 36.5 (HMPA); 116.2 (C_o); 128.2, 128.3 (C_3, C_5); 129.1 (C_m); 134.6 (C_p); 145.1 (C_4); 147.9, 148.2 (C_2, C_6); 162.7 (C_i); 167.6, 168.7 (C_1, C_7); 196.9 (R = $C(O)CH_3$).

3i: 2.0 mmol of *p*-(trifluoromethyl)aniline; diethyl ether; orange crystals. ^1H NMR δ: 2.36 (d, J = 9.9 Hz, 18H), HMPA; 7.63 (d, J = 8.6 Hz, 2H), H_m; 7.78 (d, J = 8.6 Hz, 2H), H_o; 8.36–8.55 (m, 3H, H_A, 8.40; H_B, 8.50; H_C, 8.38, J_{AB} = 7.70 Hz, J_{AC} = 0.90 Hz, J_{BC} = 7.83 Hz). ^{13}C NMR δ: 36.3, 36.4 (HMPA); 116.4 (C_o); 124, 0 (q, J_{FCF_3} = 271 Hz, R = CF_3); 125.5 (q, J_{FC_m} = 3.7 Hz, C_m); 127.4 (q, J_{FC_p} = 32 Hz, C_p); 128.3, 128.3 (C_3, C_5); 145.1 (C_4); 147.8, 148.1 (C_2, C_6); 161.4 (C_i); 167.6, 168.4 (C_1, C_7).

3j: 2.0 mmol of *p*-cyanoaniline; diethyl ether; orange crystals. ^1H NMR δ: 2.36 (d, J = 10.0 Hz, 18H), HMPA; 7.67 (d, J = 8.9 Hz, 2H), H_m; 7.77 (d, J = 8.9 Hz, 2H) H_o; 8.37–8.56 (m, 3H, H_A, 8.41; H_B, 8.52; H_C, 8.39, J_{AB} = 7.71 Hz, J_{AC} = 1.00 Hz, J_{BC} = 7.80 Hz). ^{13}C NMR δ: 36.3, 36.4 (HMPA); 108.6 (C_p); 116.9 (C_o); 118.9 (R = CN); 128.3, 128.4 (C_3, C_5); 132.6 (C_m); 145.3 (C_4); 147.8, 148.0 (C_2, C_6); 162.1 (C_i); 167.5, 168.3 (C_1, C_7).

3k: 2.0 mmol of *p*-nitroaniline; diethyl ether; orange crystals. ^1H NMR δ: 2.37 (d, J = 10.0 Hz, 18 H), HMPA; 7.79 (d, J = 9.0 Hz, 2H), H_o; 8.27 (d, J = 9.0 Hz, 2H), H_m; 8.37–8.58 (m, 3H, H_A, 8.42; H_B, 8.53; H_C, 8.40, J_{AB} = 7.57 Hz, J_{AC} = 1.04 Hz, J_{BC} = 7.90 Hz). ^{13}C NMR δ: 36.3, 36.4 (HMPA); 116.6 (C_o); 124.5 (C_m); 128.4, 128.5 (C_3, C_5); 145.3 (C_4); 145.4 (C_p); 147.8, 148.1 (C_2, C_6); 163.8 (C_i); 167.5, 168.2 (C_1, C_7).

Oxo(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)-molybdenum(IV) (6). Complex **5** (472 mg, 1 mmol) was dissolved CH_2Cl_2 (10 mL) in a Schlenk flask. Triethyl phosphite or triphenyl phosphine (1–5 mmol) was added, and the solution turned brown. The solvent was removed in vacuo after 1 h, and the phosphorus compounds were sublimated using a cold finger with liquid nitrogen as coolant or extracted with petroleum ether. The materials on the cold finger were analyzed by NMR, and the residue was dissolved in CH_2Cl_2 (10 mL) and nitrosobenzene (1 mmol) added. After 1 h, petroleum ether was added, and the solution was filtered. The residue was analyzed by NMR, which showed a 1:1 mixture of **5** and **3a**.

Kinetic Measurements. A 0.05 M $CDCl_3$ solution of oxoperoxo-(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum-(VI) (**4**) (600 μL) was mixed with a 0.2 M $CDCl_3$ solution of the appropriate substituted aniline (150 μL) in an NMR tube. NMR spectra

were recorded after these reaction times: R=OCH_3, 0, 8, 15, 25, 45, 90, and 160 min; R = CH_3, 0, 10, 20, 35, 30, 110, 200, and 240 min; R = H, 0, 30, 120, 280, 772, and 1500 min; R = F, 0, 30, 70, 140, 180, 320, 820, and 1400 min; R = Cl, 0, 60, 150, 230, 450, 880, and 1740 min; R = Br, 0, 60, 180, 380, 880, and 1760 min; R = $C(O)CH_3$, 0, 360, 1120, 2030, and 4560 min; R = CF_3, 0, 30, 1620, and 2580 min; R = NO_2, 0, 1400, 4500, and 5770 min.

Decomposition Measurements. These experiments were performed under an inert N_2 atmosphere using Schlenk techniques. Dioxane (5 mL) was added to oxo(*N*-phenylhydroxylamido-*O*,*N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**3**) (0.25 mmol). Samples (0.5 mL) were taken and analyzed. The solvent was removed in vacuo, and the crude was analyzed by ^1H NMR. Sample times were as follows: 25 °C, 4, 12, 48, and 98 h; 50 °C, 4, 12, 22, 48, 54, and 97 h; 75 °C, 3, 11, 24, 48, 73, and 101 h; 102 °C, 2, 4, 6, 9, and 24 h.

Cross-Coupling Experiments. **3i** (0.5 mmol) and **8a** (0.5 mmol) were dissolved in dioxane (10 mL) and refluxed for 6 h. The solvent was removed on a rotary evaporator, and the residue was washed with petroleum ether and filtered. The filtrate was analyzed by GC–MS and found to contain 23% of *p*,*p*′-bis(trifluormethyl)azoxybenzene, 20% of *p*-(trifluormethyl)azoxybenzene, 30% of *p*′-(trifluormethyl)azoxybenzene, and 27% of azoxybenzene. An NMR spectrum of the residue showed 58% of **5**, 24% of **3i**, and 18% of **3a**.

Stoichiometric Oxidation. Oxo(*N*-phenylhydroxylamido-*O*,*N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphortriamide)molybdenum(VI) (**3**) (0.5 mmol) was dissolved in CH_2Cl_2 (5 mL). Hydrogen peroxide (91 μL, 35% aqueous solution, 1.1 mmol) was added. When the red-purple color disappeared, petroleum ether (15 mL) was added. This caused precipitation of the oxoperoxo(pyridine-2,6-dicarboxylato)-(hexamethylphosphortriamide)molybdenum(VI) (**4**), which was removed by filtration. The solvents were removed from the filtrate by rotary evaporation. The residue was analyzed by GC–MS and/or ^1H NMR.

Catalytic Oxidation. Petroleum ether (10 mL) was added to **4** (0.1 mmol) at 35 °C. The appropriate aniline (1 mmol) and hydrogen peroxide (192 μL, 35% aqueous solution, 2.2 mmol) were added. When the reaction had finished, the molybdenum complex was filtered off, and the solvent was removed by rotary evaporation. The residue was analyzed by GC–MS or NMR.

Solvent Screening. The experiments were performed as described above for the catalytic oxidation.

Temperature Dependence. *p*-Toluidine (**7c**) (1 mmol) was added to a slurry of **4** (0.1 mmol) in 10 mL of petroleum ether. Hydrogen peroxide (192 μL, 35% aqueous solution, 2.2 mmol) was added, and the reaction mixture was stirred for 2 h. The reaction mixture was filtered, and the solvent was removed from the filtrate in vacuo. The residue was analyzed by GC–MS. Temperatures studied: 10, 16, 27, 35, 41, 50, and 56 °C.

Note Added in Proof: After submission of this manuscript two papers have appeared dealing with oxidations of aromatic amines to the corresponding nitroso compounds.[28]

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