

Communications to the Editor

The First d⁰ Metallooxaziridines. Amination of Olefins

Sir:

In 1975 we reported that d⁰ alkyl imido osmium compounds (**1**, X = NR; M = Os) react with olefins to produce vicinal amino alcohols^{1a} in a manner analogous to the vicinal diol forming reaction of the corresponding oxo compound (**1**, X = O; M = Os), osmium tetroxide. This observation suggested the possibility that a whole family of related atom-transfer reactions might be discovered by further permutation of X in multiply bonded metallic species of type **1**. To date, we have



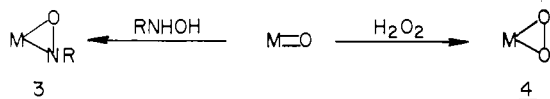
not succeeded in extending this concept beyond imido reagents (M = NR), but the imido concept has proven to be very general. Direct aminations of olefins can now be easily achieved with imido derivatives of sulfur,² selenium,³ and osmium.¹ These imido reagents are in most cases more effective than the oxo reagents (e.g., OsO₄ and SeO₂) which inspired their discovery.

In addition to metal oxo compounds there is one other class of metallic reagents which is known to transfer oxygen atoms to olefins. It is represented by the metal peroxides⁴ (**2**, X = Y = O) and the related metal complexes of alkyl hydroperoxides⁵ (**2**, X = OR; Y = O). We were naturally curious to know if the various permutations of O, N, C, and S for X and Y in the three-membered metalocycles **2** would lead to any useful new atom-transfer reactions with olefins.

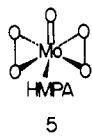
In light of the success of the imido reagents (M = NR) derived from the corresponding oxo reagents (M = O) by O → NR substitution, it seemed desirable to begin exploration of the three-membered metalocycles **2** with representatives bearing the structural unit shown in **3**. This type of complex (**3**) is formally derived by substitution of an NR moiety for one of the oxygen atoms of a peroxo complex (**4**); we have chosen the trivial name of metallooxaziridine⁶ for structure **3**. Since d⁰ metallooxaziridines **3** were apparently unknown,⁷ the first objective was to determine if they could be made.

Metal peroxo compounds are generally prepared by reaction of a metal oxo species with hydrogen peroxide⁴—Mimoun's reagent (**5**) being most familiar to organic chemists.⁸ It seemed likely that by using a hydroxylamine instead of hydrogen peroxide one might be able to form metallooxaziridines according to Scheme I, but attempts to prepare an aza analogue

Scheme I

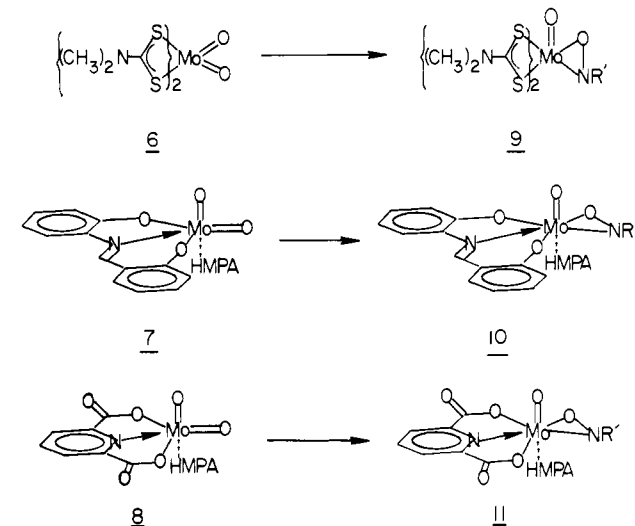


of **5** by such a procedure led only to uncharacterizable oils which generally decomposed to insoluble blue molybdenum species. However, the ability to manipulate one of the oxo

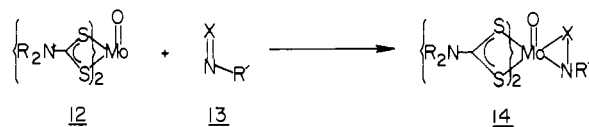


groups in certain *cis*-dioxomolybdenum(VI) complexes had previously been demonstrated,⁹ so we turned our efforts toward such species.

We were pleased to find that treatment of *cis*-dioxo-bis(*N,N*-dimethyldithiocarbamato)molybdenum(VI), **6**,¹⁰ as well as complexes **7**¹¹ and **8**,¹² with *N*-substituted hydroxylamines produced the desired molybdooxaziridines **9–11** in good to excellent yields (Table I).¹³



Assignment of the molybdooxaziridine structure, in addition to analogy to peroxo formation from H₂O₂, was based on the following observations. Complexes of dioxomolybdenum(VI) show two very strong infrared absorptions at ~900 and 940 cm⁻¹ indicative of a *cis* orientation of the oxo groups,¹⁴ while the molybdooxaziridines showed only one oxo absorption at higher frequency than either of the original bands.¹⁵ In addition, there was *no* evidence in the infrared region of any -OH or -NH absorption. This was corroborated by the NMR spectrum which clearly showed the addition of one -NR' group to the starting molybdenum complex and *no* exchangeable protons when the NMR sample was shaken with D₂O. Also, Schneider et al.¹⁶ had previously prepared similar complexes, **14** (X = NCOOEt; R' = COOEt), by reaction of oxo-bis(*N,N*-dialkyldithiocarbamato)molybdenum(IV), **12**, with diethyl azodicarboxylate, **13** (X = NCOOEt; R' = COOEt). Similarly, we reacted **12** (R = C₂H₅, generated from the



molybdenum(V) dimer¹⁷) with nitrosobenzene, **13** (X = O; R' = C₆H₅), which produced **14** (R = C₂H₅; X = O; R' = C₆H₅), identical with a sample prepared from *cis*-dioxo-bis(*N,N*-diethyldithiocarbamato)molybdenum(VI) and phenylhydroxylamine.

The expected seven-coordinate metal structure with η² bonding of the ONR group has been established for compound **11b** through a single-crystal X-ray diffraction study.¹⁸ The geometry about the molybdenum atom is pentagonal-bipyramidal with the planar, tridentate pyridine 2,6-dicarboxylate ligand occupying the equatorial positions along with the O and

Table I. Molybdooxaziridines

compd no.	R'	yield, %	color	mp, °C ^a	IR ^b
9a	<i>t</i> -C ₄ H ₉	32	purple	168 dec ^{c,d}	931 (940)
9b	C ₆ H ₅	78	purple-brown	189–190 ^d	933 (939)
9c	C ₆ H ₄ Cl	69	brown	182–183 ^{d,e}	942 (941) ^f
9d	C ₆ H ₄ CN	84	orange	198–198.5 ^{d,e}	941 (940) ^f
10a^g	<i>t</i> -C ₄ H ₉				
10b^h	C ₆ H ₅	53	red-purple		946 (957, 963 sh) ⁱ
10c^j	C ₆ H ₄ Cl	83	purple-brown		942 (959) ⁱ
10d	C ₆ H ₄ CN	85	red-brown	144–146 ^k	951 (955, 962) ⁱ
11a^g	<i>t</i> -C ₄ H ₉				
11b	C ₆ H ₅	94	purple-brown	193–195.5	952 (968) ⁱ
11c	C ₆ H ₄ Cl	94	purple-brown	209–211	959 (969) ⁱ
11d	C ₆ H ₄ CN	95	orange-brown	223.5–225.5	962 (969) ⁱ

^a Recrystallized from CH₂Cl₂/Et₂O unless otherwise noted. ^b Absorbance of oxo band in cm⁻¹ taken in KBr. Values in parentheses are from solution infrared taken in CHCl₃ unless otherwise noted. ^c Compound does not melt but begins to decompose slowly at indicated temperature. ^d Decomposes or melts with gas evolution. ^e Purified by trituration with Et₂O. ^f In CH₂Cl₂. ^g A reaction occurs between the hydroxylamine and dioxomolybdenum complex but no molybdooxaziridine is isolated. ^h This compound was crystallized from CH₂Cl₂-Et₂O to a constant mixture of ~80% molybdooxaziridine-20% dioxomolybdenum complex. The stated yield is calculated for pure product. ⁱ The oxo absorbance for these compounds appears as a sharp well-defined band in KBr, but in CHCl₃ solution the oxo band is broadened or split. ^j This compound was recrystallized from CH₂Cl₂-Et₂O to a constant mixture of ~90% molybdooxaziridine-10% dioxomolybdenum complex. The stated yield is calculated for pure product. ^k Solvated with 1/2 molecule of Et₂O.

N atoms of the ONPh group (see Figure 1). Some important structural parameters follow: Mo-O(1) = 1.668 (4), Mo-O(3) = 2.127 (4), Mo-N(1) = 2.036 (5), Mo-O(2) = 1.944 (4), N(1)-O(2) = 1.416 (7) Å. The phenyl ring of the ONPh group does not lie in the equatorial plane; rather, the torsion angle Mo-O(2)-N(1)-C(11) is 111.4 (4)°.

The N atom of the molybdooxaziridine ring displays bond angles consistent with sp³ hybridization (e.g., O(2)-N(1)-C(11) = 112.6 (4)°), and the N-O distance of 1.416 (7) Å agrees well with the single bond distance of 1.46 Å in hydroxylamine.¹⁹ These metric values around atom N(1) are in contrast with the related distances and angles about the N atoms in dichlorobis(nitrosobenzene)palladium²⁰ which contains N-bound ONPh ligands. In this palladium complex all bond angles around the N atoms are within 3° of 120°, the Pd, N, O, and C(α-phenyl) atoms are essentially planar, and the N-O distance (1.209 (3) Å) is that expected for a double bond.

Table I demonstrates the generality of the molybdooxaziridine synthesis.²¹ Most of the complexes gave high yields of well-defined crystals. A comparison of the oxo infrared absorption in solution and in the solid state points to a consistent difference between the bisdentate complex **9** and the tridentate-monodentate complexes **10** and **11**. While the former showed sharp oxo absorptions in both solution and KBr, the latter showed sharp bands in the solid state but broadened or split oxo bands in solution. This may be due to some degree of HMPA dissociation and/or isomerization of complexes **10** and **11** when they are in solution.²²

A typical preparation of molybdooxaziridine **11c** follows. To a stirred slurry of dioxo(pyridine 2,6-dicarboxylato)-(hexamethylphosphoramido)molybdenum(VI), **8**¹² (4.72 g, 10 mmol), in 50 mL of methylene chloride in a 125-mL Erlenmeyer flask was added *p*-chlorophenylhydroxylamine (1.72 g, 12 mmol) in one portion. All solids rapidly dissolved giving a purple solution within seconds. After 30 min, MgSO₄ (3 g) was added and stirring was continued an additional 15 min. The solution was then filtered with the aid of additional methylene chloride and the filtrate was concentrated on a rotary evaporator giving a crude purple solid. Trituration with 100 mL of diethyl ether and filtration gave 5.58 g (94%) of pure **11c**, mp 206–208 °C (recrystallization from methylene chloride-ether raised the melting point to 209–211 °C).

Recent experiments have shown that molybdooxaziridines do indeed transfer an -NR group to certain olefins; however, allylic amines rather than the anticipated aziridines were

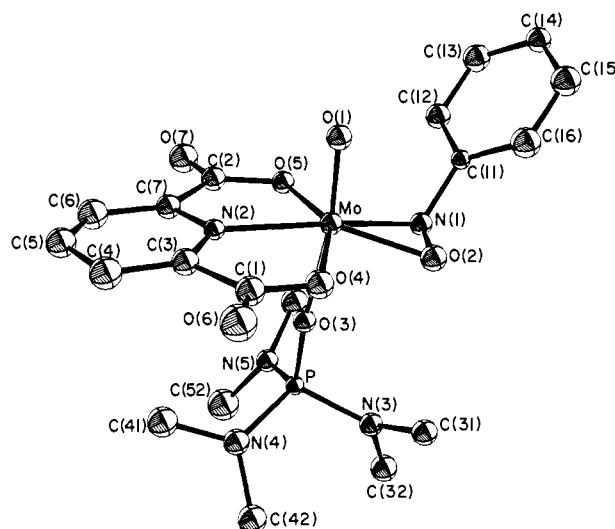
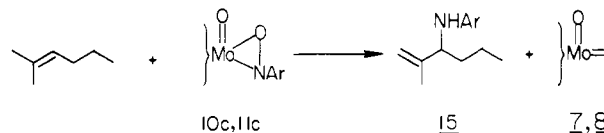


Figure 1. A perspective drawing of the oxo(*N*-phenylhydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphoramido)molybdenum(VI) molecule showing the atom labeling scheme. Hydrogen atoms are not included. The atoms are drawn at their 50% probability ellipsoids of thermal vibration at -158 °C.

isolated. For example, reaction of molybdooxaziridine **10c** or **11c** with excess 2-methyl-2-hexene (dichloroethane, 100 °C, 24 h) gave allylic amine **15** in 55 and 57% yields, respectively, along with high yields of the parent dioxomolybdenum complexes **7** and **8**. It is of interest that formation of **15** involves a



shift of the double bond from its original position. This ene-like selectivity has been observed for four other olefins to date (β,β -dimethylstyrene, methylenecyclohexane, 1-octene, tetramethylethylene); however, the complete absence of other isomers has not yet been rigorously proven. The scope and mechanism of this new reaction is currently under investigation and will be the subject of a future publication.

Acknowledgments. K.B.S. is grateful to the National Science Foundation (CHE77-14628), Hoffmann-La Roche, and Eli

Lilly for financial assistance and J.A.I. thanks the National Science Foundation (CHE76-10335) for financial support.

References and Notes

- (1) (a) K. B. Sharpless, D. W. Patrick, L. K. Truesdale, and S. A. Biller, *J. Am. Chem. Soc.*, **97**, 2305 (1975); (b) K. B. Sharpless, A. O. Chong, and K. Oshima, *J. Org. Chem.*, **41**, 177 (1976); (c) A. O. Chong, K. Oshima, and K. B. Sharpless, *J. Am. Chem. Soc.*, **99**, 3420 (1977); (d) E. Herranz, S. A. Biller, and K. B. Sharpless, *ibid.*, **100**, 3596 (1978); (e) D. W. Patrick, L. K. Truesdale, S. A. Biller, and K. B. Sharpless, *J. Org. Chem.*, **43**, 2628 (1978); (f) E. Herranz and K. B. Sharpless, *ibid.*, **43**, 2544 (1978).
- (2) K. B. Sharpless and T. Hori, *J. Org. Chem.*, **41**, 176 (1976); S. P. Singer and K. B. Sharpless, *ibid.*, **43**, 1448 (1978).
- (3) K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, *J. Am. Chem. Soc.*, **98**, 269 (1976).
- (4) J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Radiochem.*, **6**, 279 (1964).
- (5) J. Kollar (to Halcon International), U.S. Patent 3 360 584 (1967); A. O. Chong and K. B. Sharpless, *J. Org. Chem.*, **42**, 1587 (1977), and references cited therein.
- (6) This trivial name is derived from the fact that three-membered heterocycles containing carbon, oxygen, and nitrogen in the ring are called oxaziridines. It is noteworthy that certain oxaziridines have been reported to transfer their nitrogen to olefins producing aziridines: E. Schmitz and K. Janisch, *Chem. Heterocycl. Compounds*, **10**, 1432 (1974).
- (7) (a) Low-valent metal complexes of nitrosoaryls are known. For examples see M. J. Barrow and O. S. Mills, *J. Chem. Soc. A*, 864 (1971), and S. Otsuka, Y. Aotani, Y. Tatsuno, and T. Yoshida, *Inorg. Chem.*, **15**, 656 (1976). (b) An interesting lower valent protonated metalloxaziridine of vanadium has just been described: K. Wieghardt, U. Quilitzsch, B. Nuber, and J. Weiss, *Angew. Chem.*, **90**, 381 (1978).
- (8) H. Mimoun, I. Seree de Roch, and L. Sajus, *Tetrahedron*, **26**, 37 (1970). It has been demonstrated that a peroxy oxygen and not the oxo oxygen atom is transferred to the olefin: K. B. Sharpless, J. M. Townsend, and D. R. Williams, *J. Am. Chem. Soc.*, **94**, 295 (1972).
- (9) (a) J. Dirand, L. Ricard, and R. Weiss, *J. Chem. Soc., Dalton Trans.*, 278 (1976); (b) J. Dirand, L. Ricard, and R. Weiss, *Inorg. Nucl. Chem. Lett.*, **11**, 661 (1975); (c) M. W. Bishop, J. Chatt, and J. R. Dilworth, *J. Organomet. Chem.*, **73**, C59 (1974); (d) D. Westlake, R. Kergoat, and J. E. Guerschais, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **280**, 113 (1975); (e) S. Current and K. B. Sharpless unpublished results.
- (10) R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 1702 (1970).
- (11) Dioxo [*N*-(salicylidene)-2-hydroxybenzeneamine](hexamethylphosphoramide)molybdenum(VI), **7**. *N*-(Salicylidene)-2-hydroxybenzeneamine (21.3 g, 0.10 mol, prepared by mixing equimolar quantities of salicylaldehyde and α -aminophenol in methanol and collecting the orange crystals which formed) and MoO₂(acac)₂ (32.6 g, 0.10 mol) were stirred together in 400 mL of methylene chloride for 30 min to form an insoluble brown precipitate. Hexamethylphosphoramide (17.9 g, 0.10 mol) was then added and the mixture was stirred for 20 min during which time the brown precipitate disappeared and a bright orange solution formed. The solution was filtered to remove a trace of insoluble matter and the solvent was then removed on a rotary evaporator. This left a crude orange-red product which was purified by trituration with 100 mL of diethyl ether. Filtration gave 48.5 g (94%) of **7** as orange crystals: mp 201–205 °C. IR (KBr) 898, 925 cm⁻¹ (oxo). Recrystallization from CH₂Cl₂-Et₂O raised the melting point to 203.5–206 °C. Anal. Calcd for C₁₉H₂₇MoN₄O₅P: C, 44.02; H, 5.26; N, 10.81. Found: C, 44.14; H, 5.30; N, 10.89. A similar complex with H₂O as the sixth ligand instead of HMPA has been prepared: K. Chjo, *Daehan Hwahak Hwojee*, **17**, 169 (1973); *Chem. Abstr.*, **79**, 38088 (1973).
- (12) Dioxo(pyridine-2,6-dicarboxylato)(hexamethylphosphoramide)molybdenum(VI), **8**. Pyridine-2,6-dicarboxylic acid (5.01 g, 30 mmol), MoO₂(acac)₂ (9.68 g, 30 mmol), and HMPA (5.37 g, 30 mmol) were stirred at 25 °C in 200 mL of methylene chloride for 24 h. Filtration removed 0.5 g of a blue impurity. Most of the solvent was removed on a rotary evaporator and the residue was trituated with diethyl ether. Filtration gave 12.55 g (89%) of **8** as white crystals which exhibited a very faint blue tinge but were of sufficient purity for further reaction. If desired the product can be recrystallized from CH₂Cl₂-Et₂O: mp 240–243 °C dec; IR (KBr) 912, 935 cm⁻¹ (oxo). Anal. Calcd for C₁₃H₂₁MoN₄O₇P: C, 33.06; H, 4.49; N, 11.87. Found: C, 33.08; H, 4.50; N, 11.96. A similar complex with H₂O instead of HMPA as the sixth ligand has been prepared.^{9d}
- (13) Satisfactory spectra were obtained for all compounds reported. Representative complexes from each group in Table I gave satisfactory elemental analyses and molecular weight determinations.
- (14) F. A. Cotton, "Structure and Bonding in Molecular Oxo-molybdenum Compounds", from the Proceedings of the International Conference on the Chemistry and Uses of Molybdenum, P. C. H. Mitchell, Ed., Clima Molybdenum, London, 1974.
- (15) Other seven-coordinate monooxomolybdenum(VI) complexes are spectroscopically similar. (See complexes described in ref 9a, 9b, 9d, and 9e.)
- (16) P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, **94**, 8640 (1972).
- (17) W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, **13**, 1100 (1974).
- (18) Crystals of oxo(*N*-phenylhydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(HMPA)molybdenum(VI), obtained from methylene chloride-diethyl ether, crystallize in the orthorhombic space group *D*_{2h}²-P2₁2₁2₁ with four molecules in a cell of dimensions *a* = 13.079 (12), *b* = 13.898 (12), *c* = 12.511 (12) Å at -158 °C. Data were collected to a limiting 2θ angle of 69.6° on a Picker FACS-1 diffractometer using monochromatized Mo Kα radiation and with the crystal maintained at -158 ± 2 °C. The structure was solved and refined by standard procedures (see, for example, J. M. Waters and J. A. Ibers, *Inorg. Chem.*, **16**, 3273 (1977)). The present stage of refinement is for an isotropic model with hydrogen atoms; the *R* index is 0.059 for 4827 unique data having *F*_o² > 3σ(*F*_o²).
- (19) P. A. Giguère and I. D. Liu, *Can. J. Chem.*, **30**, 948 (1952).
- (20) R. G. Little and R. J. Doedens, *Inorg. Chem.*, **12**, 537 (1973).
- (21) *N*-Substituted hydroxylamines were necessary for formation of the molybdoxaziridines. Hydroxylamine itself gave molybdenum nitrosyls and this will be reported in more detail in the future. We have also isolated high yields of crystalline complexes using *N*-hydroxybenzenesulfonamide and *N*-hydroxyurethane, but at present we are uncertain of their structures.
- (22) The NMR spectra of these complexes (at 33 °C) did not show evidence of HMPA dissociation; however, this could be attributed to rapid exchange of free and bound HMPA on the NMR time scale. We have observed facile exchange of HMPA with other donor ligands.
- (23) National Science Foundation Energy-Related Postdoctoral Fellow, 1976–1977; National Institutes of Health Postdoctoral Fellow, 1977–1978.
- (24) The early stages of this research were carried out in the Department of Chemistry of the Massachusetts Institute of Technology.

Lanny S. Liebeskind,²³ K. Barry Sharpless*

Department of Chemistry, Stanford University²⁴
Stanford, California 94305

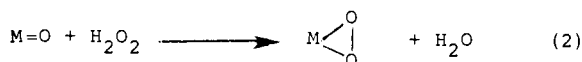
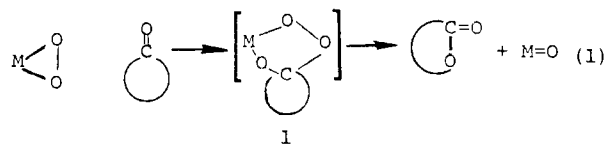
Robert D. Wilson, James A. Ibers*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201
Received May 30, 1978

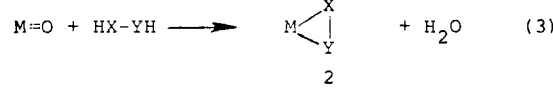
Group 6 Metalloxaziridines: Preparation, Characterization, and Reaction with Cyclohexanone

Sir:

We have previously demonstrated that peroxy complexes of group 6 metals catalyze oxidation of cyclic ketones by hydrogen peroxide.¹ This reaction represents the first example of an oxygen transfer from molybdenum and tungsten peroxy complexes² to ketones. The peroxy complexes are reduced to the corresponding oxo complexes via metallozone **1** (eq 1). Reaction of hydrogen peroxide with the oxo complex regenerates the peroxy complex and completes the catalytic cycle³ (eq 2).



We have attempted to generalize the results by postulating that oxo complexes may react with different HX-YH species to form three-member metallocycles **2** (eq 3). In the case of *N*-substituted hydroxylamines, the metallocycles **2** (X = RN;



Y = O) were expected to transfer the R-N moiety to cyclic ketones and form either lactams in analogy to eq 1 or behave as "nitrenoids" and produce derivatives of α -amino ketones.

The metallocycles **2** stabilized by picolinato or pyridine-2,6-dicarboxylato ligands (subsequently called metalloxaziridines)⁴ were unknown. Therefore, our first objective was to demonstrate that they could be prepared. We are now pleased to report the successful preparation and characterization of complexes containing one or two three-membered metallocycles per metal consisting of the group 6 metal, oxygen, and nitrogen. These complexes are prepared by a reaction of *N*-substituted hydroxylamines with either dioxo complexes in analogy to eq 3 or with peroxy complexes stabilized by di-