

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

References and Notes

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- (10) R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 1702 (1970).
- (11) Dioxo[*N*-(salicylidene)-2-hydroxybenzylamine](hexamethylphosphoramide)molybdenum(VI), **7**. *N*-(Salicylidene)-2-hydroxybenzylamine (21.3 g, 0.10 mol, prepared by mixing equimolar quantities of salicylaldehyde and *o*-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.
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- (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).
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- (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-*P*2₁2₁2₁ 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).
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- (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

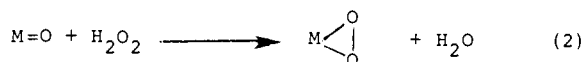
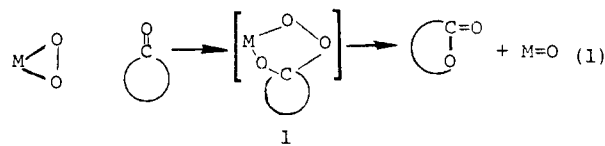
Robert D. Wilson, James A. Ibers*

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

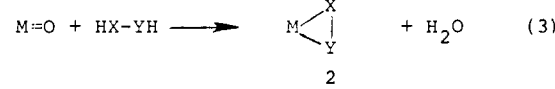
Group 6 Metalloxaziridines: Preparation, Characterization, and Reaction with Cyclohexanone

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 metalocycles **2** (eq 3). In the case of *N*-substituted hydroxylamines, the metalocycles **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.

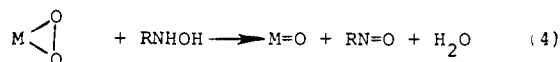
The metalocycles **2** stabilized by picolinato or pyridine-2,6-dicarboxylato ligands (subsequently called metalloxaziridines)⁴ were unknown. Therefore, our first objective was to demonstrate that they could be prepared. We are now pleased to report the successful preparation and characterization of complexes containing one or two three-membered metalocycles 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-

Table I. Spectral Properties of Metallooxaziridine Complexes^a

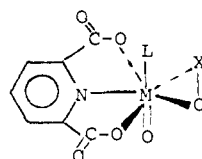
complex	Yield, %	¹³ C chemical shifts, ppm				¹³ C chemical shifts, ppm		IR, cm ⁻¹	
		phenyl ring				pyridine ring		C=O	M=O
		C(1)	C(2,6)	C(3,5)	C(4)	C(2)	C(4)		
3						148.5	1710, 1690	950	
4	94.0	148.3	116.6	128.6	126.4	145.7	1710, 1690	957	
5	93.6	146.7	115.8	128.3	126.0	147.8	1710, 1685	957	
6						149.7	1705, 1685	982	
7	63.2	148.0	116.2	128.2	124.5	146.1	1715, 1705	975	
pyridine-2,6-dicarboxylic acid						140.2	<i>b</i>		
8						141.4	1685	973	
9		149.4	116.9	129.4	125.2				
						138.8	1670, 1640	938	
					125.5				
picolinic acid						148.9	142.1	<i>b</i>	
PhNHOH		151.9	113.0	128.3	119.3				
PhNHOH·HCl		139.1	129.9	129.9	122.6				

^a All of the complexes gave satisfactory and complete elemental analysis as well as ¹H NMR. ^b Broad, not well-defined peak.

or tridentate ligands. In the second route the required oxo complex is formed as a transient species owing to the reduction of the peroxy complex by the *N*-substituted hydroxylamine (eq 4). Therefore, at least 2 mol of hydroxylamine are needed for every peroxy moiety present in the peroxy complex.



Thus, crystalline *N*-phenylhydroxylamine (10.10 g, 92.6 mmol) was added at 0 °C to a stirred mixture of hexamethylphosphoric triamide (HMPT) (17.05 g, 95.1 mmol), peroxy complex **3** (10.06 g, 30.9 mmol), and acetonitrile (300 mL).



- 3** M = Mo, L = H₂O, X = O
4 M = Mo, L = HMPT, X = PhN
5 M = Mo, L = Py, X = PhN
6 M = W, L = HMPT, X = O
7 M = W, L = HMPT, X = PhN

After 3 h partial evaporation of the solvent and treatment of the residue with ether yielded 16.29 g (94%) of metallooxaziridine **4**. Anal. Calcd: C, 40.50; H, 4.66; Mo, 17.03; N, 12.43; P, 5.50. Found: C, 40.58; H, 4.51; Mo, 17.15; N, 12.45; P, 5.59. The same compound has been prepared by the reaction of dioxo(pyridine-2,6-dicarboxylato)(HMPT)molybdenum(VI)⁵ (0.254 g, 0.484 mmol) with *N*-phenylhydroxylamine (0.072 g, 0.66 mmol) in acetonitrile (4 mL) at room temperature.

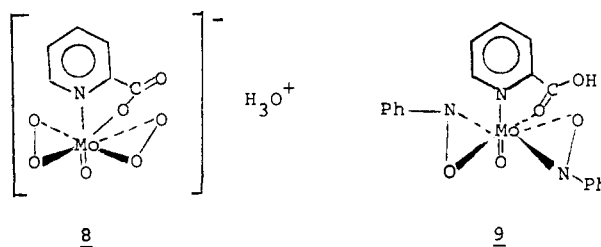
A solution of this complex in acetonitrile shows no conductivity suggesting a covalent complex. There is no evidence of either OH or NH bands in the IR spectra.⁶ Comparison of the IR spectra (shape and position of both C=O and Mo=O bands) and ¹³C NMR chemical shifts⁷ of mainly C(4) of the pyridine ring in **3** and **4** (Table I) strongly suggests that the bonding of the pyridine-2,6-dicarboxylato and oxo ligands in peroxy complex **3**² and metallooxaziridine **4** are analogous. Then the position of the metallooxaziridine ring in **4** should correspond to that of the peroxy moiety in **3**. This close similarity between **3** and **4** is proven by preliminary single-crystal X-ray data.⁸ The key parameters of the metallooxaziridine

ring⁹ are as follows: Mo-N, 2.05 (2), Mo-O, 1.95 (2), and N-O, 1.45 (3) Å. As in **3** where the O-O distance corresponds to that in peroxides² the N-O distance in **4** is in agreement with that in hydroxylamine (1.47 Å).¹⁰

Catalytic activity of peroxy complexes of the type **3** is drastically affected by the lability of the ligand L.¹¹ Therefore, preparation of metallooxaziridines with ligands more labile than HMPT was desirable. This objective can be accomplished by a reaction of peroxy complex **3** with at least 3 mol of *N*-phenylhydroxylamine in acetonitrile. A yellow precipitate of unknown structure is formed which can be easily converted to **4** or **5** by treatment with HMPT or pyridine. Similar analogues of **4** are formed when the yellow precipitate is treated with other oxygen or nitrogen ligands such as DMF, Me₂SO, and alcohols in organic solvents.

Tungsten metallooxaziridines of the type **7** can be prepared from tungsten peroxy complexes² in analogy to the chemistry described for molybdenum. Again, zero conductivity in CH₃CN, no presence of OH or NH bands in IR spectra, and the similarity of IR, ¹H NMR, and ¹³C NMR of **4**, **6**, and **7** (Table I) clearly suggest that the structures of molybdenum and tungsten metallooxaziridines are analogous.¹²

In an attempt to make the analogy between peroxy complexes and metallooxaziridines complete and possibly find a more reactive species, complexes containing two metallooxaziridines per molybdenum (spiro-metallooxaziridines) were synthesized. Spiro-metallooxaziridines, so far, could be prepared only from the corresponding peroxy complexes since the required trioxo complexes are unstable and cannot be isolated. Thus, reaction of peroxy complex **8** with at least 4 mol of *N*-phenylhydroxylamine in acetonitrile at room temperature yields metallooxaziridine **9**. ¹³C NMR of **9** (Table I) leads us



to the assumption that the bonding of the PhNO moiety in **9** is similar to that in **4** and that the bonding of the pyridine ring of picolinic acid in **9** corresponds to that in **8**. However, the structural similarity of **8** and **9** cannot be complete since complex **9** exhibits zero conductivity in Me₂SO while peroxy complex **8** is a two-ion conductor.² Therefore, covalent nonionic structure **9** with picolinic acid as a neutral bidentate ligand is

preferred for the spirometallooxaziridine.

Reaction of either **3** or the corresponding dioxo complex with either *N*-methylhydroxylamine or benzohydroxamic acid so far has not yielded pure metallooxaziridine complexes.^{1,3}

The metallooxaziridines do behave as "nitrenoids". This is suggested by thermal decomposition of **4** to azobenzene and by the formation of a mixture of 2-(*N*-phenyl)iminocyclohexanone and azobenzene when **4** is treated with cyclohexanone in chlorobenzene at 80 °C. The scope and mechanism of the reaction of metallooxaziridines of the type **4** containing ligands more labile than HMPT or spirometallooxaziridine **9** with ketones, esters, and nitriles is under investigation and will be reported in the future.

Acknowledgment. We thank Mr. G. E. Babbitt for measurement of ¹³C NMR spectra.

References and Notes

- S. E. Jacobson, R. Tang, and F. Mares, presented at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978; *J. Chem. Soc., Chem. Commun.*, in press.
- The best catalysts proved to be peroxo complexes stabilized by picolinato and pyridine-2,6-dicarboxylato ligands. The X-ray single-crystal structures of these complexes were determined.¹
- Formation of oxoperoxo(pyridine-2,6-dicarboxylato)(HMPT)molybdenum(VI) from dioxo(pyridine-2,6-dicarboxylato)(HMPT)molybdenum(VI) and H₂O₂ is fast at room temperature.
- When we obtained indications of the existence of *N*-methyl metallooxaziridines in solution, Sharpless reported his findings on the preparation of *N*-phenyl-substituted metallooxaziridines stabilized by *N,N*-dialkyl dithiocarbamate and by *N*-(salicylidine)-2-hydroxyaniline ligands (19th Industrial Symposium, Stanford, Calif., Jan 1978).
- Dioxo(pyridine-2,6-dicarboxylato)(HMPT)molybdenum(VI) can be prepared by a reaction of oxoperoxo(pyridine-2,6-dicarboxylato)(HMPT)molybdenum(VI) with suitable reducing agents. Thus peroxo complex **3** (2.1 g, 6.44 mmol) was reacted with *N*-methylhydroxylamine (0.47 g, 10 mmol) in acetonitrile (80 mL) at 25 °C overnight. Small amounts of a white precipitate was removed by filtration. The filtrate was concentrated under vacuum at 25 °C to about one third of its volume. About the same amount of ether was added to the concentrate and the mixture was placed in the freezer. On the next day, orange crystals (1.28 g, 62%) were collected: IR (Nujol mull) 913, 937 (Mo=O); 1710 cm⁻¹ (C=O). Anal. Calcd for C₁₃H₂₂MoN₄O₇P: C, 33.06; H, 4.49; Mo, 20.31; N, 11.86; P, 6.56. Found: C, 33.14; H, 4.52; Mo, 20.55; N, 11.91; P, 6.44. Complexation of pyridine rings to high valent group 6 metals exhibits a large (5–7 ppm) and characteristic chemical shift for C(4).²
- IR spectra were taken in Nujol mulls and fluorocarbon mulls.
- Complexation of pyridine type ligands results in strong ¹³C NMR shifts, often in opposite directions, depending on the type of bonding between the metal and the ligand.
- Crystal data and refinement results: orthorhombic; *a* = 13.165 (8), *b* = 13.898 (6); *c* = 12.555 (8) Å; space group P2₁2₁2₁; *z* = 4; *R*₁ = 0.097, *R*₂ = 0.096; 1333 observed reflections. No hydrogens were located. The complete structure will be published later.
- The N–O bond distances of nitrosobenzene η² bound to Pd(0) (1.35 Å) or to Fe(0) (1.40 Å) are significantly shorter than in **4**: M. Calligaris, T. Yoshida, and S. Otsuka, *Inorg. Chim. Acta*, **11**, L15 (1974); M. J. Barrow and O. S. Mills, *J. Chem. Soc. A*, 864 (1971). This fact may suggest π bonding in the Pd and Fe complexes in contrast to a typical σ bonding in the Mo and W metallooxaziridines described in this report. Notice that the O–O distance in peroxo complexes is practically insensitive to the type of metal (*d⁰ → d¹⁰*) involved: M. Laing, *J. Chem. Soc., Chem. Commun.*, 660 (1975); P. J.-M. Le Carpentier, R. Schlupp, and R. Weiss, *Acta Crystallog. Sect. B*, **28**, 1278 (1972); P. J.-M. Le Carpentier, A. Mitschler, and R. Weiss, *ibid.*, **28** (1972); ref 2.
- International Tables for X-ray Crystallography, Vol. III, The Kynoch Press, Birmingham, England, 1968, p 270.
- The aquo ligand in **3** can be readily displaced by compounds such as ketones. The ketone complexes were isolated and characterized by elemental analyses, ¹H NMR, and ¹³C NMR. The easy displacement of H₂O by ketones may be the reason why complex **1** is an active catalyst for oxidation of cyclic ketones to lactones by H₂O₂. When the aquo ligand in **3** is displaced by less labile ligands such as HMPT, the catalytic activity of **1** is drastically decreased: S. E. Jacobson and F. Mares, unpublished results.
- Structures of the corresponding Mo and W peroxo complexes are also equivalent.²
- Benzohydroxamic acid displaces pyridine-2,6-dicarboxylato ligand in **3** as well as in the corresponding dioxo complex. As a result only Mo(O)₂(PhC(O)NHO)₂ is isolated in high yields. This fact has been demonstrated by elemental analysis and by comparison of IR spectra with that of an authentic sample prepared from benzohydroxamic acid and Mo(O)₂(acac)₂.

D. A. Muccigrosso, S. E. Jacobson
P. A. Apgar, F. Mares*

Corporate Research Center, Allied Chemical Corporation
Morristown, New Jersey 07960

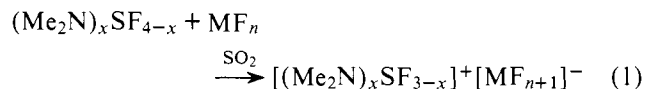
Received July 18, 1978

Amino-Substituted Sulfonium Salts. Synthesis and Stereochemistry

Sir:

Amino-substituted sulfonium cations, [(R₂N)_xSF_{3-x}]⁺ (*x* = 1, 2, 3), are isoelectronic with aminophosphines and, consequently, their stereochemistry, reactivity, and ligand behavior are of significant potential interest.¹

We find that the syntheses of the [Me₂NSF₂]⁺ (**1**) and [(Me₂N)₂SF]⁺ (**2**) cations can be accomplished in high yields by treatment of the appropriate fluorosulfurane with a fluoride ion acceptor such as BF₃, PF₅, or AsF₅ in SO₂ solutions at –60 to –65 °C:



This is a similar approach to that used² for the synthesis of [SF₃]⁺[BF₄][–]. However, since the fluorosulfurane, (Me₂N)₃SF, is unknown it was necessary to develop a novel synthesis for the completely amino-substituted cation, [(Me₂N)₃S]⁺ (**3**). After several unsuccessful attempts to prepare the latter by treating **1** or **2** with dimethylamide anion, we discovered that the reaction of SF₄ with B(NMe₂)₃ affords high yields of **3** as its tetrafluoroborate salt:



Typically, an equimolar mixture of SF₄ and (Me₂N)₃B in SO₂ solution is allowed to warm slowly from –196 to +10 °C. Removal of the SO₂ and trace quantities of volatiles in vacuo produces white, solid [(Me₂N)₃S]⁺[BF₄][–], mp 110 °C dec.³ The reaction of SF₄ and (Me₂N)₃B can be followed by NMR spectroscopy. Immediately after warming to –60 °C, ¹H peaks corresponding to **1** (triplet,⁴ δ 3.18, *J*_{FSNCH} = 7.5 Hz), **2** (doublet, δ 2.95, *J*_{FSNCH} = 7.0 Hz), and **3** (singlet, δ 2.55) and (Me₂N)₃B are clearly discernible. The resonances corresponding to **1**, **2**, and (Me₂N)₃B decrease with time and that of **3** increases until, after 20 min at ambient temperature, all that remains is the singlet resonance of **3**. ¹⁹F spectra⁵ taken in the early stages of the reaction confirm the presence of SF₃⁺ (singlet, –19 ppm), **1** (septet, –16.0 ppm, *J*_{FSNCH} = 7.5 Hz), and **2** (multiplet, +15.6 ppm, *J*_{FSNCH} = 7.0 Hz) and, in addition, exhibit four poorly resolved "quartet" resonances which we attribute to BF₄[–] (143.5 ppm, *J*_{11BF} = 2 Hz), [Me₂NBF₃][–] (153 ppm, *J*_{11BF} = 20 Hz), [(Me₂N)₂BF₂][–] (155 ppm, *J*_{11BF} = 18 Hz), and [(Me₂N)₃BF][–] (156 ppm, *J*_{11BF} = 17 Hz).⁶ As time elapses the resonance due to BF₄[–] grows at the expense of the other three. To accommodate the foregoing observations we postulate that the initial step in the reaction is F[–] abstraction by (Me₂N)₃B to form [(Me₂N)₃BF][–] and SF₃⁺, the latter undergoing F[–]/Me₂N[–] exchange with either (Me₂N)₃B or [(Me₂N)_xBF_{4-x}][–]. In support of this postulate we find that (a) the AsF₆[–] salts of SF₃⁺, **1**, and **2** undergo rapid reaction with (Me₂N)₃B to afford **3**, and (b) the sulfurane (Me₂N)₂SF₂ does not react with (Me₂N)₃B in this temperature range.

The stereochemistry of aminosulfonium cations has been investigated by dynamic NMR spectroscopy. For example, below –30 °C the ¹H spectrum of **1** consists of two overlapping triplets which we attribute to two Me environments (Me_a, δ 3.06, *J*_{FSNCH_a} = 9.5 Hz; Me_b, δ 2.98, *J*_{FSNCH_b} = 5.5 Hz).⁷ This deduction is confirmed by the presence of two singlets in the ¹³C spectrum (Me_a, 41.2, and Me_b, 36.7 ppm).^{5,7} Under the same conditions the ¹⁹F spectrum comprises a 16-line spectrum which is due to the coupling of the two Me groups to two equivalent F ligands. Taken collectively, the low-temperature NMR data establish structure **4** for **1**, and thereby demonstrate that aminosulfonium cations and aminophosphines are isosteric.⁸ Upon warming to –15 °C the ¹H spec-