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RECENT TRENDS IN THE CHEMISTRY OF MOLECULAR COMPLEXES OF HETEROAROMATIC *N*-OXIDES

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Abstract – Literature review on molecular complexes of aromatic *N*-oxides with various electron acceptors published in the last decade is presented. Structure, chemistry, and new preparation methods of these complexes are discussed.

INTRODUCTION

Aromatic *N*-oxides are widely used as intermediates in the synthesis of pyridines, quinolines, and other nitrogen heterocycles.¹ This is due to increased reactivity of *N*-oxides in both electrophilic and nucleophilic reactions. The majority of the available data on preparation, structure, physical and chemical properties of the compounds has been reviewed previously.²⁻⁴ Publications on molecular complexes (MC) of aromatic *N*-oxides have been appearing in the literature since 1960s.⁵ *N*-Oxides are of interest as polydentate electron donors in reactions with various types of electron acceptors. Complexation is facilitated by relatively low ionization potentials of *N*-oxides, steric accessibility of reaction centers, and lability of the electron system. Several reviews describe donor-acceptor complexes of aromatic *N*-oxides.^{6,7} Continued interest in MC of *N*-oxides leads to development of the following new areas of their adduct chemistry:

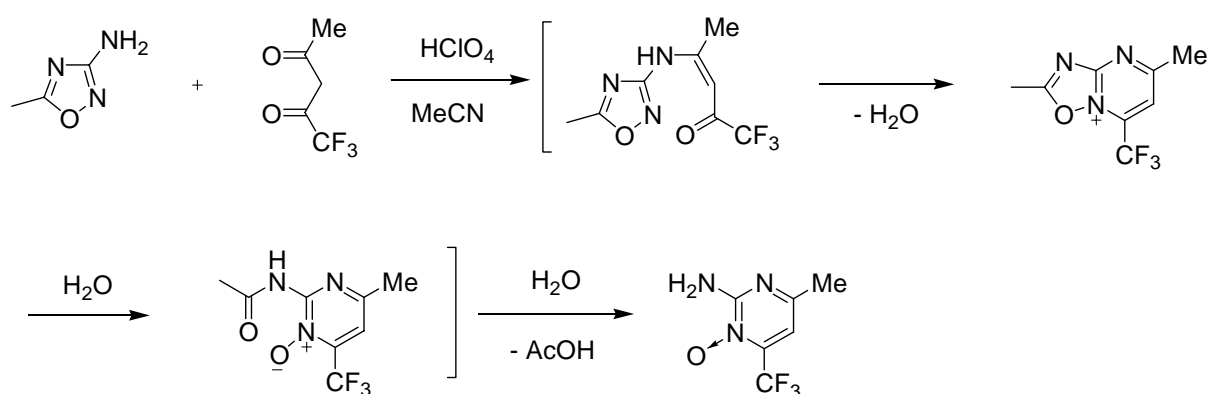
1. Expansion of the number of electron acceptors (d- and f-elements, π -acids) interacting with *N*-oxides.
2. Structural studies of the complexes (composition, stereochemistry, location of the donor center in an aromatic *N*-oxide molecule). Of particular interest is the information on new mixed complexes formed by extra-coordination of metals (e.g. zinc and copper tetraphenylporphyrines).

3. Synthesis and physical studies of products of further transformations of MC, radical-ion salts (RIS) that can serve as “organic metals” having high electrical conductivity.
4. Use of aromatic *N*-oxides and their MCs in organic synthesis, as effective catalysts and oxidizers.
5. Studies of biological properties of *N*-oxide MCs in comparison with *N*-oxides themselves.

In addition, new methods of preparation of aromatic *N*-oxides have been developed, with new oxidizing agents and catalysts. This review describes the literature on the above areas of chemistry of MCs of aromatic *N*-oxides in the last 10 years. This manuscript is based (in part) on the work in the author's group.

PREPARATION OF *N*-OXIDES

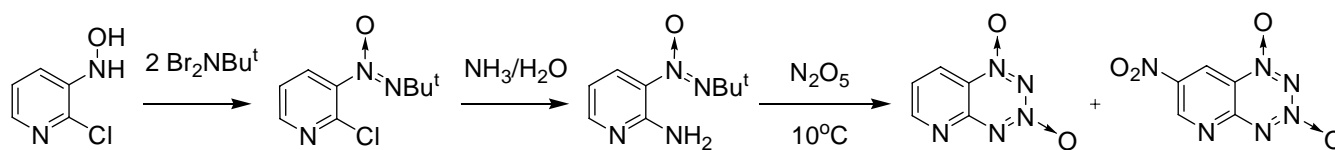
A very effective oxidizing agent for preparation of aromatic *N*-oxides from azines has been developed, $\text{HO}\cdot\text{MeCN}$ (I), which is prepared from molecular fluorine and acetonitrile. For example, I reacts with quinoxalines forming corresponding mono-oxides under mild conditions in good yields.⁸ Aminopyrimidine *N*-oxides are formed from oxadiazole amines and β -diketones upon cycloaddition and rearrangement with perchloric acid (Scheme 1).



Scheme 1

The reaction mechanism is discussed. 4-Methyl-6-(trifluoromethyl)-2-pyrimidinamine also gives monoxide upon direct oxidation.⁹

Treatment of 2- and 4-amino-3-(*tert*-butylazoxy)pyridines with nitrogen(V) oxide or NO_2BF_4 leads to 1,2,3,4-tetrazin-*N,N*-dioxide (Scheme 2), the first pyridoannulated oxide:

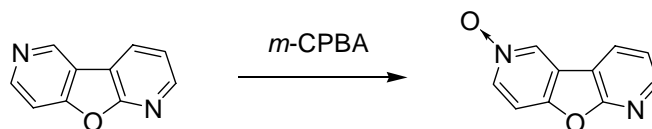


Scheme 2

Products of the reaction form 1:1 complexes with benzene, their structure being confirmed by X-ray analysis.¹⁰

Co(II) complexes with Schiff bases catalyze pyridine oxidation by molecular oxygen in water to form pyridine *N*-oxide.¹¹

Aromatic *N*-oxides can also be successfully prepared using a complex of H₂O₂ with urea. This reagent can be easily prepared, is commercially available, and has been used in a variety of solvents in the presence of carboxylic anhydrides. For example, this complex has been used to prepare *N*-oxides from diazine in high yields¹² and diethyl 3,4-pyridinedicarboxylic ester,¹³ very weakly basic substrates. In some cases, use of trifluoroacetic anhydride is necessary. New examples of *m*-chloroperbenzoic acid oxidation to aromatic *N*-oxides are reported. For example, furodipyridines have been oxidized to *N*-oxides (Scheme 3) with this reagent.¹⁴



Scheme 3

PROTON COMPLEXES OF AROMATIC *N*-OXIDES

The proton acceptor properties of *N*-oxides is an area of interest. Due to their ability to form hydrogen bonds, heteroaromatic *N*-oxides form stable complexes with H⁺, even with weak proton donors.

Solid 2:1 complexes of 2,6-lutidine, 2-picoline, and pyridine *N*-oxides with succinic acid were studied by IR, conductometry, and dielectrometry. It was shown that the complexes existed as an equilibrium between two crystal phases, with different enthalpies for their H⁺ bonds which were almost unaffected by methyl groups. The value and nature of electronic conductivity imply that these substances could be classified as proton semiconductors.¹⁵

The proton transfer reaction in complexes of pyridine-*N*-oxides with carboxylic and mineral acids were studied in organic solvents by IR, NMR, conductometric and vapor pressure osmometry methods. The constant of formation, homoconjugation and ionization were determined in polar aprotic solvents from potentiometric and conductance measurements.¹⁶

The physical characteristics of H^+ complexes of *N*-oxides with phenols were examined. Their stability is nearly independent of the charge on oxygen of the *N*-oxide group while the H^+ -bond polarity correlates well with charges on both the H atom of phenols and O atom of the proton acceptors.¹⁷ Pyridine-*N*-oxides form two types of crystal complexes with pentachlorophenol, in 1:1 and 1:2 base-to-acid ratios. The structure of 1:2 complex has been determined, with the oxygen atom of the *N*-oxide accepting H^+ -bonds from two molecules of pentachlorophenol. The two pentachlorophenol rings are nearly parallel to each and they are almost perpendicular to the pyridine ring.¹⁸

Among strong acid proton donors, 4-toluenesulfonic acid forms a stable, salt-like adduct with 4-dimethylamino-2,6-dimethylpyridine *N*-oxide. It is noteworthy that the proton is transferred from acid to the *N*-oxide group but not to the amine nitrogen of the substituent.¹⁹

The co-crystal structure of the complex formed from 2,3,5,6-tetramethylpyrazine *N,N*-dioxide with pyromellitic dianhydride has been reported.²⁰ This complex displays both donor-acceptor bonding and $CH\cdots OH$ bonding between its components to yield a supramolecular layer domain in its composite crystal lattice. The emerging pattern of supramolecular chemistry of heterocyclic *N*-oxides based on their electron donor and H^+ -bond acceptor abilities is highlighted as a new set of tools for crystal engineering with this functional group.

The quantitative measure of the proton's complexation affinity is the pKa values of cationic acids conjugated to heterocyclic *N*-oxides. It was suggested that the affinity could be determined by direct measurements of pH in non-aqueous solutions of *N*-oxide salts. To prove this, the pKa values obtained have been compared with those resulting from potentiometric titration. The agreement between the results found by using both methods is very good.²¹

The *N*-oxide of 6-hydroxyquinoline is an interesting representative of super photoacids. The electronic effect of the oxidized nitrogen atom makes the excited state both less basic and more acidic than the parent molecule and adds hydroxyquinoline *N*-oxide to the class of high-acidity excited-state proton donors.²² A very informative method for studying of proton transfer complexes of heterocyclic *N*-oxides is ¹⁵N NMR spectroscopy. It was found that the chemical shifts of nitrogen atoms of *N*-oxide groups are strongly affected by substituents and hydrogen bond strength. For example, protonation of pyridine-*N*-oxides by dichloroacetic acid in CDCl₃ shifts the nitrogen signal ca 50 ppm to lower frequencies as compared with ca. 123 ppm for pyridine-*N*-oxides.²³ IR spectroscopy also gives useful information on hydrogen bond formation by *N*-oxides. For example, MC of *o*-nitraminopyridine *N*-oxide with methylamine (Figure 1) shows characteristic vibrational features in their IR spectra that are assigned to the $\nu(N-H\cdots O)$ stretching modes on Fermi resonance, with the overtone of the out-of-plane bending mode $2\gamma(N-H\cdots O)$.²⁴

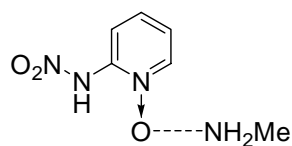


Figure 1

COMPLEXES OF S- AND P-ELEMENTS

The formation of weak MCs of pyridine *N*-oxides with the alkaline and alkaline-earth metal cations has been published recently.²⁵ The complexes are formed in aqueous solution with significant excess of complexing ions. Stability constants are small, from 0.11 (for KCl) to 0.58 (for MgCl₂) l·mol⁻¹ and slightly dependant on σ^+ -constants of substituents at the C4 position of pyridine. This ability to coordinate with such weak acceptors is evidence of the strong electron-donor properties of *N*-oxides.

A new type of donor-spacer-acceptor systems has been shown to be an efficient dual channel fluorosensor for Li⁺, Mg²⁺ and Ca²⁺. Formation of a new emitting charge-transfer excited state was discussed.²⁶ Mixed MCs of ethylenediamine with Mg, Ca, Sr, and Ba chelates and picoline and quinaldine *N*-oxides are more stable and have been characterized by elemental analysis, IR, and conductometry.²⁷

Complexes of 4-methylpyridine *N*-oxide with Lewis acids (e.g. BF₃) have been described.²⁸ Interestingly, in these MCs base-catalyzed α -deprotonation proceeds more readily than deprotonation of the active Me group of the heterocyclic ring. Reaction of the complexes with electrophiles also give 2-substituted 4-methylpyridine *N*-oxides.

The interaction of SiO₂ with pyridine *N*-oxides in aqueous media leads to unstable complexes of pentacoordinated silicon with O \cdots Si bond.²⁹ Formation of these complexes is responsible for the increased solubility of SiO₂ in water in the presence of *N*-oxides. The formation of these complexes is noteworthy since they arise from interaction with a weakly nucleophilic O center.

A series of MCs of *N*-oxides of isoquinoline, substituted quinolines, and 4-phenylpyridine with dimethyltin dichloride were described.³⁰ These adducts of (Me)₂SnCl₂-*N*-oxide (1:2 composition) are easily formed from the substrates in chloroform. *N*-Oxide oxygen atoms are coordinated to Sn atom, with a coordination number of 6. These adducts have been characterized by IR and ¹H, ¹³C and ¹¹⁹Sn NMR. Complexes of SbCl₅ and pyridine *N*-oxides (1:1) were proposed for oxidation of bezoins to benzyls. The reaction occurs upon reflux of the mixture in nitromethane and is accelerated by tertiary amines.³¹

Adducts of heteroaromatic *N*-oxides with iodine are important in the chemistry of MCs. They differ from one another in their composition, structure, stability, solubility, etc. These complexes, some existing only

in solution have been studied for over 50 years, were summarized in an earlier review.⁷ In recent years, these MCs have been studied in several publications.³²⁻³⁴ Molecular iodine forms solid adducts with polycyclic *N*-oxides of quinoline, isoquinoline, and acridine.³² As shown by IR and NMR spectroscopy, iodine coordinates with both the oxygen atom and with the aromatic π -system of quinoline and isoquinoline *N*-oxides (Figure 2).

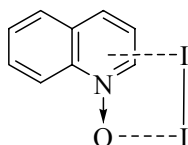


Figure 2

Acridine *N*-oxide forms σ , π -complexes exclusively with iodine, due to the substrate's extended aromatic system. Several publications^{32,33} have studied the complexation and MC structure of iodine with pyridine *N*-oxides. The complexes were prepared by either melting the starting materials or mixing their solutions in benzene or acetone. The MC's composition is 1:1 in solution, and 1:2 or 2:1 as a solid. Thermodynamic parameters were determined for "inner" and "outer" complexes that differ by the degree of orbital overlapping of the reacting molecules, and enthalpies of intermolecular bonding were calculated.

COMPLEXES WITH D- AND F-ELEMENTS

Nitro-substituted aromatic *N*-oxides are known to be carcinogenic, mutagenic, and cytotoxic compounds. MCs of 4-nitropyridine *N*-oxides with Cu ions were studied extensively.³⁵ Mono- and di-nuclear complexes with various coordination numbers were isolated and characterized with UV-vis and IR spectroscopies. MCs interconversion and their cytotoxicity were studied. Synthesis and bioactivity of (2-chlorophenoxyacetato) copper (II) adduct with 4-nitrosubstituted heteroaromatic *N*-oxides, 4-nitroquinoline, 4-nitropyridine, and 2-methyl-4-nitropyridine *N*-oxides were described in a publication by Slovenian researchers.³⁶ Complexation of 4-nitroquinoline *N*-oxide was shown to reduce its mutagenic activity by 9 times. However, in other complexes this phenomenon was not observed.

Isonicotinic acid *N*-oxide forms complexes with a polymeric structure with Cu (II) ions. The Cu(II) atom is coordinated by an elongated square pyramid geometry.³⁷ Picolinic and quinaldinic acid *N*-oxides form mixed complexes with copper glycinate, $[\text{CuL}_2] \text{L}^1$, where L = deprotonated glycine and L^1 = picolinic or quinolinic-*N*-oxide acids. Formation of these non-electrolyte mixed complexes occurs due to outer sphere coordination of $[\text{CuL}_2]$ with L^1 groups.³⁸ Pyridine and quinoline *N*-oxides form stable

complexes with CuL_2 and ZnCl_2 , of 1:1 or 2:1 composition depending on the ratio of the reagents and the nature of ligand and metal.³⁹ Polycrystalline 1:2 complexes of ZnCl_2 with pyridine and methylpyridines *N*-oxides exhibit temperature dependent polymorphism. Electronic effect of the methyl group exerts significant influence on the value of O...Zn bond enthalpy.⁴⁰

Polycrystalline 1:2 complexes of ZnI_2 with pyridine and methylpyridine *N*-oxides exist as an equilibrium of several solid phases with different intermolecular bond formation enthalpies and a different mechanism of transfer of electronic effect via these bonds. Complexes with ZnI_2 , like ZnCl_2 complexes, are ionized in a cumulative mode on rapid heating from 18 to 26-45 °C.⁴¹

The reaction of Zn-tetraphenylporphine with nitrogen heterocycles and their *N*-oxides in water, methanol, acetonitrile, nitromethane or acetone leads to solid extra-coordinated complexes. The adducts can add solvent molecules, increasing the Zn coordination number to 6. Composition of the complexes and their stability constants were determined, and IR and UV spectral data were obtained. Weaker, outer-sphere complexes with hemin exist only in solution in equilibrium with their components. They are detected by shifts in the absorption bands of the starting materials.⁴²

Methyl sulfonates of La(III), Gd(III), Lu(III), upon reaction with 2 moles of pyridine and methylpyridine *N*-oxides form 1:1, 1:2, or 1:1.5 adducts with inclusion of water molecules. Thermal stability of these complexes has been studied. The rupture of the metal-*N*-oxide bond is promoted by heating, along with fragmentation of the *N*-oxide molecule.^{43,44} Mixed complexes of lanthanides and pyridine *N*-oxide with β -enolate co-ligands demonstrate important luminescent properties.⁴⁵ Mixed complexes of pyridine carboxylic acids-*N*-oxides with La(III), Nd(III), Eu(III) and 2,2-bipyridine or 1,10-phenanthroline were characterized using luminescence (conventional and laser-induced) spectroscopy. The Effect of various substituents and solvents on luminescence intensity and the complex lifetime were studied.⁴⁶⁻⁴⁸ Vibrational properties and the structure of the poly-coordinated Pr(III) complexes with 2,6-lutidine-*N*-oxide derivatives were studied by IR and Raman spectroscopies.⁴⁹ More than 20 ternary complexes of Nd(III), Gd(III) and Er(III) with pyridine, quinoline and isoquinoline *N*-oxides have been described.⁵⁰ Complexing lanthanides are part of the adducts with 3,5-di-*tert*-butyl- γ -resorcylic acid. Their interaction with *N*-oxides occurs due to extracoordinating properties of the metals. Those complexes were characterized by elemental analysis, electronic conductivity, thermal analysis and IR spectroscopy. The coordination geometries of metal ions can be described as a distorted octa-coordinated bicapped trigonal prism.

Polycrystalline MCs of pyridine and methylpyridine *N*-oxides with MnCl_2 contain tightly bound water as a third component due to hydrogen bond formation. These MCs are light and temperature sensitive, their crystal structure and conductivity changing upon irradiation or heating.⁵¹ These *N*-oxides also form 2:1 MCs with FeCl_3 . In the solid state, the complexes exist as three crystal phases in equilibrium with each

other each having different enthalpies of formation of coordination bonds.⁵² The reaction of molecules of RhCIL (where L is cycloocta-1,5-diene or bicyclo[2,2,1]heptadiene) with quinoline or 4-phenylpyridine *N*-oxides (L^1) leads to the formation of complexes $RhCIL \cdot L^1$, which can coordinate with an additional molecule of triphenylphosphine. These complexes were characterized by elemental analysis and spectroscopic data.⁵³

N-OXIDES AND THEIR COMPLEXES IN ORGANIC SYNTHESIS

Heteroaromatic *N*-oxides and their MCs are widely used as catalysts, nucleophilic reagents, and oxidizing agents in organic synthesis. In many cases, their catalytic effect is superior to that of non-oxidized heterocyclic bases. There are many examples of the catalytic activity of *N*-oxides in the literature. Their application to asymmetric catalysis has been described.⁵⁴ Their activity is often explained by MC formation with ions of metals, non-metals, or π -electron acceptors.

For example, the interaction of quinoline *N*-oxides with chloranil initially leads to charge transfer complexes (CTC) that quickly hydrolyze to salts of the corresponding *N*-hydroxyazines and 2,5-dihydroxy-5,6-dichloro-*p*-benzoquinone (chloranil acid, Figure 3: X=H, Me, OMe, Cl).⁵⁵

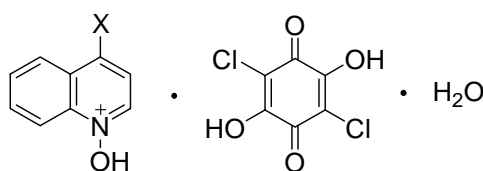
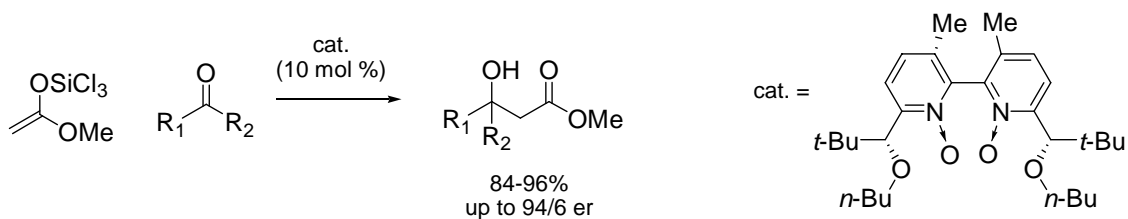


Figure 3

Pyridine *N*-oxides catalyze aldol condensation of methyl trichlorosilyl ketene acetal $Cl_3SiOC(OMe)=CH_2$ with various ketones. Chiral 3,3'- and 6,6'-substituted 2,2-pyridil bis-*N*-oxides provide the aldol products with variable enantioselectivities ranging from 94/6 enantiomeric ratio for aromatic ketones to nearly racemic for aliphatic ketones (Scheme 4).⁵⁶



Scheme 4

The reaction results in the *anti*-adduct from (*E*)-enol ethers and the *syn*-adduct from the (*Z*)-isomer.⁵⁷ CTC of *N*-oxides with π -acceptors often form as intermediates in the process of formation of species with complete electron transfer, radical-ion salts (Figures 4,5: X=H, Me, OMe, Cl).⁵⁸⁻⁶⁰ The process is

observed in the reactions with the strongest π -acids, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone or 7,7,8,8-tetracyanoquinodimethane.

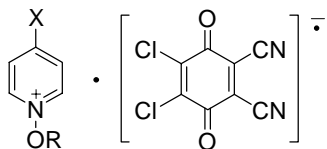


Figure 4

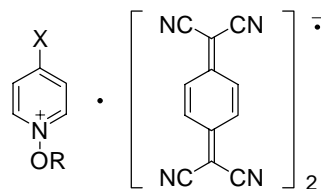
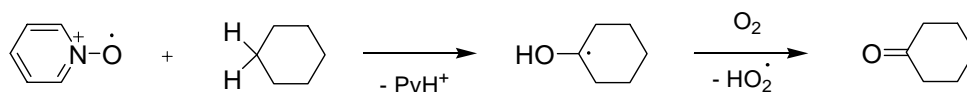


Figure 5

The rate of transformation and yields of RIS depend on substitution in the aromatic ring. The resulting salts of *N*-hydroxy and *N*-alkoxy azines with ion-radicals of π -acids are highly electroconductive (organic metals). Their conductivity is significantly higher than that of the corresponding unoxidized nitrogen bases.^{61,62} Reaction of pyridine *N*-oxide with a strong oxidizer, lead tetraacetate, gives unstable short-lived cation-radicals $\text{PyO}^{\bullet+}$.⁶³ These species are unique in their ability to oxidize alkanes predominantly at secondary carbon atoms, forming ketones. For example, cyclohexane forms cyclohexanone upon action of $\text{PyO}^{\bullet+}$ (Scheme 5).⁶⁴

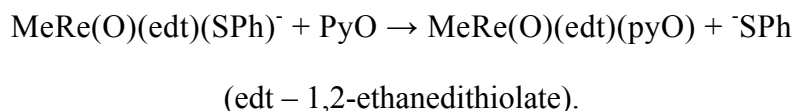


Scheme 5

The reaction of *N*-oxides with tantalum complexes has been described in the literature.⁶⁵ The benzamidinate Ta methylenide complex $[(4\text{-Tol})\text{C}(\text{NSiMe}_3)_2]\text{Ta}(\text{CH}_2)\text{Me}$ reacts with pyridine-*N*-oxides to form Ta oxo-complexes $[(4\text{-Tol})\text{C}(\text{NSiMe}_3)_2]\text{Ta}(\text{O})\text{Me}$ and methylpyridines. Thus, double group transfer reactions were observed. Mechanistic studies show that the reaction proceeds via regioselective methylene group transfer to the pyridine-*N*-oxides.

Bonding of 4-nitropyridine and 4-nitroquinoline *N*-oxides into CTC with Lewis acids and π -acceptors sharply increases their activity towards nucleophilic reagents. Nitro group substitution with weak nucleophiles proceed much easier than in free *N*-oxides, under mild conditions and high yields.⁶⁶ This expands the synthetic utility of *N*-oxides.

Mixed complexes of *N*-oxides with rhenium compounds have been studied extensively in the literature.⁶⁷⁻⁶⁹ These adducts were used for oxidation of various organic compounds. The Re atom (in methyl(oxo)rhenium complexes with sulfur-containing ligands) exists in a five-coordinated distorted square pyramid. Upon reaction of Re complexes with S-ligands and aromatic *N*-oxides, partial replacement of the ligand with *N*-oxide occurs:



The Re complex, $\text{Re}_2\text{O}_2(2\text{-mercaptomethylthiophenol})_3$, catalyzes oxidation of tertiary phosphines, arsines, stibines, sulfides and dienes by pyridine *N*-oxides. The kinetics and mechanism of the oxidation were studied.^{70,71} The reaction is proposed to go through a Re(VII) intermediate with pyridine-*N*-oxide as one of the ligands. The N-O bond was activated through coordination to Re, and the O atom was abstracted by an organic compound.

N-Oxides, in their complexes with methyltrioxorhenium (VII), are used as co-oxidants with H_2O_2 for oxidation of olefins to epoxides. Adducts of aromatic *N*-oxides are more stable than those of aliphatic *N*-oxides.⁷² The use of different oxidizing agents in organic synthesis is reviewed in the literature⁷³ including aromatic *N*-oxides in the complexes with MeReO_3 .

Intermediates in the Ru(IV)porphyrine catalyzed epoxidation of olefins by pyridine-*N*-oxides are *N*-oxide-coordinated Ru-*N*-oxides complexes.⁷⁴

Heteroaromatic *N*-oxides are the oxygen atom transfer reagents that have been routinely used in the synthesis of high-valence transition metal complexes. For example, pyridine-*N*-oxides form uranium (IV) bis(alkyl)complexes $(\text{C}_5\text{Me}_5)_2\text{UR}_2$ (R=Me, CH_2Ph) which unexpectedly result in activation of an sp^2 hybridized C-H bond. This C-H activation also takes place with the thorium bis(alkyl) derivatives. It is in contrast to the known oxygen atom transfer reactivity patterns of pyridine-*N*-oxides with oxophilic complexes and constitutes a new mode of reactivity for pyridine-*N*-oxides.⁷⁵

The data discussed above indicate that heteroaromatic *N*-oxides are interesting objects in reactions of MCs formation with various types of acceptors. Complexation of *N*-oxides changes considerably the physical and chemical properties of *N*-oxides and the complexing agent. In some cases this allows reactions to occur in MC that are not possible in free *N*-oxides. Their behavior in biological systems also changes upon complexation. The new directions in the research of *N*-oxide MCs reviewed demonstrate perspectives in pure and applied science of these heterocyclic compounds and their complexes with electron-deficient systems.

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