C−H Bond Activations by Metal Oxo Compounds

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Contents

Dr. Ahmet Gunay was born in Istanbul, Turkey in 1978. He received his Bachelor of Science degree in Chemistry from Bilkent University (Ankara, Turkey) in 2002. Then, he moved to the U.S.A. to pursue graduate studies at the University of Rochester, where he conducted research on "Carbon−Carbon Bond Activation of Acetylene Derivatives via Photolysis of Platinum Complexes" under the supervision of Prof William D. Jones and received his Ph.D degree in 2007. Since early 2008, he has been a Postdoctoral Researcher working on "Nitration of Alkanes with Nitric Acid by Polyoxometalates", at the University of Delaware under the joint supervision of Prof Klaus H. Theopold (Department of Chemistry & Biochemistry) and Prof Mark A. Barteau (Department of Chemical Engineering). Currently, he continues his Postdoctoral Researcher appointment with Prof Klaus H. Theopold and conducts research on "Small Molecule (O_2 and N_2) Activation by Low Valent Iron Complexes Supported with Highly Substituted Hydrotris(pyrazolyl)borate Ligands" at the University of Delaware.

1. Introduction

In an era dominated by the utilization of hydrocarbon mixtures (i.e., oil and natural gas) as feedstocks for the chemical industry, the functionalization of C−H bonds, particularly in a selective manner, remains one of the most fundamental problems of chemistry. This challenge is obviously not thermodynamic in nature because many transformations of alkanes are highly exergonic. Rather, the problem is a combination of attenuated reactivity and lack of selectivity of those processes able to overcome the kinetic restraints associated with breaking the strong and nonpolar covalent bond between carbon and hydrogen. While an "exhaustive" functionalization of hydrocarbons, producing, for example, CO_2 and H_2O, is performed so readily and on such a scale as to threaten climate change, selective transformations ranging from the chemoselective direct synthesis of methanol from methane to the enantioselective hydroxylation of camphor are beyond our current capabilities.

And yet, both of the latter reactions can be achieved under mild conditions via enzymatic catalysis using dioxygen as a reagent.[1,2] Our current understanding of the mechanisms of these highly selective reactions suggests that the reactive intermediates responsible for the hydroxylation of the C−H bonds are metal oxo species generated by the binding and "activation" of O_2. Accordingly, a survey of the reactivity of metal oxo complexes with C−H bonds is of interest; this is the topic of the present review. Although metal oxo species are strongly implicated as intermediates in transformations mediated by oxygenases, they are often of fleeting existence and thus not subject to detailed study. As we wish to focus on the reactions of the metal-oxo moiety with C−H bonds, we shall only consider reactions of stable, well-characterized compounds prepared by synthetic methods; enzymes are not considered here, except insofar as they provide the motivation for model studies. We also exclude reactions involving oxygen atom transfer without the cleavage of a C−H bond; thus epoxidations of alkenes and similar reactions are specifically excluded.

Oxo complexes of the transition metals are rather common, so much so that the classic text authored by Nugent and Mayer in 1988 devoted 20 pages to a tabulation of the then known ~650 structurally characterized representatives containing terminal metal oxo moieties.[3] However, their distribution over the d-block is by no means even; thus metal oxo complexes are apparently particularly stable/numerous for early metals in relatively high oxidation states; moreover, second and third row metals are more heavily represented.

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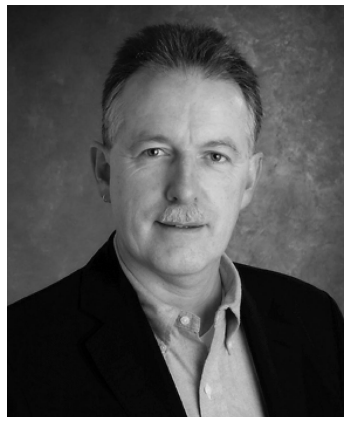


Klaus H. Theopold was born on Easter Sunday 1954 in Berlin, Germany, and grew up in Hamburg, where he received his "Vordiplom" in chemistry from the Universität Hamburg. In 1978, he moved to the U.S. for graduate work, receiving his Ph.D. from UC Berkeley in 1982 for work with Bob Bergman. After a year as a postdoctoral associate at MIT with Dick Schrock, he began his academic career as assistant professor at Cornell University. Since 1990, he has been on the faculty of the University of Delaware, where he is currently professor of chemistry and Chair of the Department of Chemistry and Biochemistry. Theopold's research interests include synthetic organometallic and inorganic chemistry of first row transition metals, with particular emphasis on reaction mechanisms and homogeneous catalysis. He prefers open shell molecules.

Figure 1 shows the current situation (i.e., in July 2009); while the numbers have increased significantly, there are now approximately 9000 terminal oxo complexes listed in the Cambridge Crystallographic Database, the overall picture remains the same.[4] The most heavily represented metals are vanadium, molybdenum (3345 complexes!), tungsten and rhenium. This skewed distribution is reasonably well understood, based on the bonding characteristics of the oxo ligand and the crystal field effects of various d^n configurations. In brief, strong π-donation from the oxygen lone pairs at short distances (1.6−1.8 Å) destabilizes the antibonding $p_\pi - d_\pi$ molecular orbitals; occupation of these π^* MOs becomes energetically unfavorable and restricts the electronic structure of the most stable oxo complexes to very low d-electron counts.[5] Thus it has been categorically stated that "M═O groups are stabilized at metal centers with an oxidation state of no less than 4+ and no more than four d-electrons".[6]

Considering the classic trade-off between stability and reactivity, it is then not surprising that the search for metal oxo reagents that can functionalize C−H bonds has focused on late transition metals. Many of nature's hydrocarbon functionalization schemes employ enzymes containing iron or copper, and the synthesis of oxo species of these and other late transition metals has been an exciting area of study, with some notable recent successes. Compounds such as $(mesityl)_3Ir{=}O$, $(alkyne)_2XRe{=}O$,[7] and Que's nonheme Fe(IV) oxo species made a start,[8] and more recently, the characterization of polyoxometallate stabilized metal oxo complexes of Pd, Pt, and Au has further pushed the boundaries.[9−12] This development was punctuated in 2008 with Milstein's report of a Pt(IV) oxo complex that displayed remarkable stability even in the presence of ancillary carbon and phosphine ligation.[13] These recent developments may herald new openings in the study of metal oxo mediated C−H bond functionalizations. In any event, a review of the known chemistry of C−H bonds mediated by metal oxo moieties is timely.

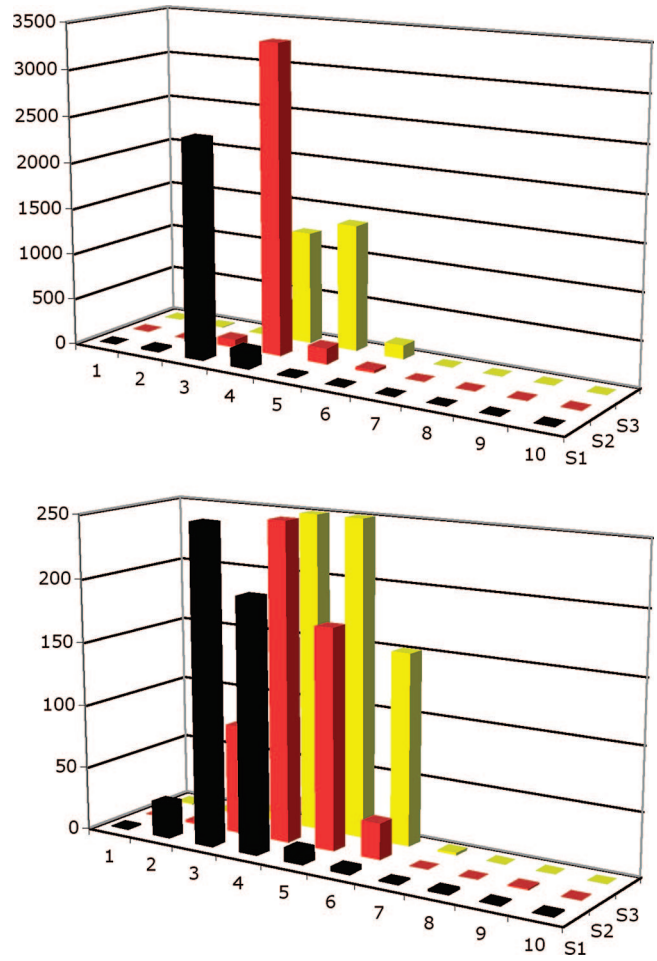


Figure 1. 3-D plot of the number of terminal metal oxo complexes of the transition metals listed in the Cambridge Crystallographic Database. Top: All compounds. Bottom: Expanded view.

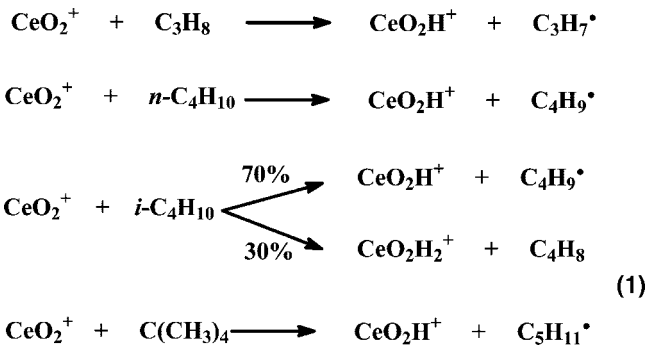
Historically, the cleavage of C−H bonds by oxo complexes had been considered a radical reaction, similar to the autoxidation of hydrocarbons. The abstraction of hydrogen atoms was thought to require radical character in the metal oxo species. However, beginning in the 90s, Mayer et al. showed that unpaired electrons or spin density (i.e., radical character) was not a requirement for such hydrogen atom transfer (HAT) reactions. Rather, a sufficient thermodynamic driving force was recognized as the crucial factor in determining reactivity. Linear energy relationships like the Polanyi correlation between C−H bond strength and the rate constant for hydrogen atom abstraction were shown to apply to these reactions.[14] At the same time, it was recognized that metal complexes are more flexible and varied in their electronic structure than a simple monatomic radical (e.g., $Cl^\bullet$). Thus the two constituents of a hydrogen atom, namely, a proton and an electron can be transferred simultaneously but to (and from) different locations. This gave rise to the designation as "proton coupled electron transfer" (PCET), that is, the current theoretical framework in which the reactions of interest here are often discussed.[15,16]

In keeping with the distinct trend shown in Figure 1, the review of C−H bond activation reactions by transition metal oxo compounds will be organized by groups, progressing from the left to the right of the periodic table.

2. C−H Bond Activations by Group III Metal Oxo Compounds

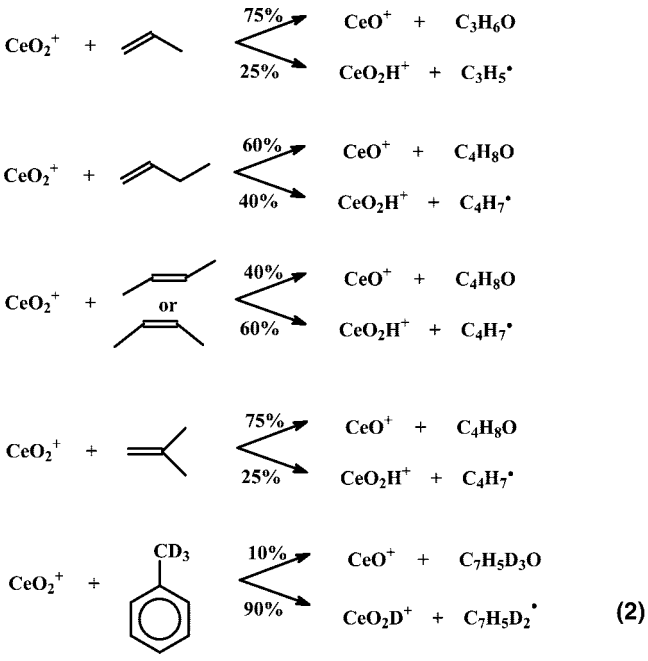
By consecutive oxidation of Ce^+ with O_2 and NO_2, "bare" CeO_2^+ ions were prepared in the gas phase and reacted with saturated and unsaturated hydrocarbons to investigate C−H bond activation by use of Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR) (Scheme 1).[17]

Almost exclusive C−H bond activation was observed in the reaction of linear and branched alkanes with CeO_2^+ (eq 1).



(1)

However, the reaction of "thermalized" (i. e., brought to thermal equilibrium with the bath gas, here pulsed-in argon) CeO_2^+ with simple alkenes and aromatic compounds showed both oxygen-atom transfer and C−H bond activation (eq 2).



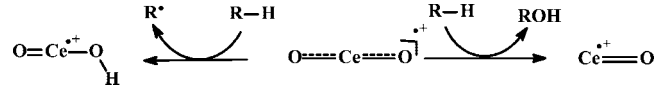
(2)

Carbon−carbon bond activation was not observed in these reactions.

3. C−H Bond Activations by Group IV Metal Oxo Compounds

Although there are many titanium[18] and zirconium[19,20] oxo compounds reported in the literature, there is no example of C−H bond activation by Group IV metal oxo compounds.

Scheme 1. C−H Bond Activations by Bare CeO_2^+ Ions



4. C−H Bond Activations by Group V Metal Oxo Compounds

Gas phase reaction of VO_2^+ with straight chain alkanes was studied via the FT-ICR technique.[21] Reactivity differences of alkanes with increasing carbon number were reported. While the reaction of VO_2^+ with ethane produced 100% $[VO_2H_2]^+$ and ethene, that of VO_2^+ with propane showed 92% $[VC_3H_6O_2]^+$, H_2, 6% $[VC_3H_4O_2]^+$ and $2H_2$, and 2% $[VO_2H_2]^+$ and C_3H_6. However, the reaction of *n*-butane with VO_2^+ resulted in an additional reaction pathway, namely, a C−C bond activation and combined loss of H_2 and H_2O. This reaction gave 31% of $[VC_4H_6O]^+$, H_2 and H_2O, 15% of $[VO_2H_2]^+$ and $[C_4H_8]$, 40% of $[VC_2H_6O_2]^+$ and C_2H_4, 10% of $[VC_3H_6O_2]^+$ and CH_4, and 4% of $[VC_3H_4O_2]^+$, CH_4, and H_2.

5. C−H Bond Activations by Group VI Metal Oxo Compounds

Scott et al. studied the kinetics of the reactions of CrO_{aq}^{2+} (i.e., $(H_2O)_5CrO^{2+}$) with various alcohols, aldehydes, and carboxylates and proposed a hydride-transfer mechanism for these oxidation reactions.[22] The CrO_{aq}^{2+} was obtained upon reacting Cr_{aq}^{2+} with one equivalent of O_2 in an aqueous acidic environment. Large excesses (~20-fold) of O_2 caused formation of $Cr(O_2)_{aq}^{2+}$.

An example of the oxidation of alcohol by CrO_{aq}^{2+} is shown below:

$$CrO_{aq}^{2+} + CH_3OH \rightarrow Cr_{aq}^{2+} + HCHO + H_2O \quad (2)$$

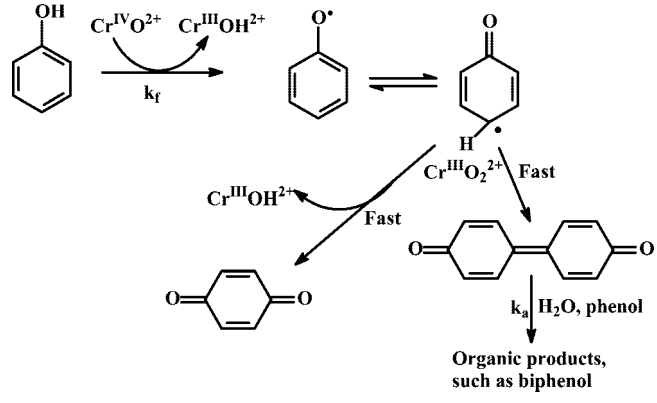
$$Cr_{aq}^{2+} + O_2 \rightarrow Cr(O_2)_{aq}^{2+}$$

The rate constant was reported as $k = 52.2 \pm 1.4\ M^{-1}\ s^{-1}$ with an isotope effect of $k_H/k_D = 3.46$ when CD_3OH was reacted with CrO_{aq}^{2+}.

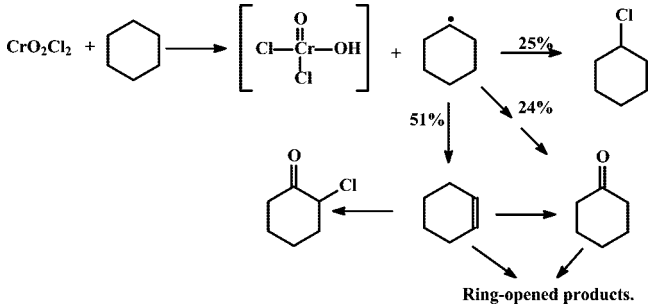
The same chromium oxo ion, CrO_{aq}^{2+} ($(H_2O)_5CrO^{2+}$), was utilized in the oxidation of phenols to *p*-benzoquinone (Scheme 2).[23]

According to the proposed mechanism, phenols are first oxidized by one electron to the corresponding phenoxyl

Scheme 2. Oxidation of Phenols to *p*-Benzoquinone by Aqueous Chromium Oxo Ion



Scheme 3. Oxidation of Cyclohexane by Chromyl Chloride



radicals via hydrogen atom abstraction. Then, superoxochromium(III) ($(H_2O)_5CrO_2^{2+}$ or $Cr^{III}O_2^{2+}$), which is also present in the solution, oxidizes the phenoxyl radicals to benzoquinone.

An extensive study of C−H bond activations of cyclohexane,[24] cyclooctane, isobutane, and toluene with chromyl chloride (CrO_2Cl_2) under mild conditions was reported by Cook and Mayer.[25] The reaction of CrO_2Cl_2 and cyclohexane at 75 °C produced a dark precipitate, chlorocyclohexane (10%), and cyclohexene (0.3%). Hydrolysis of the precipitate yielded cyclohexanone (8.0%) and chlorocyclohexanone (2.5%), where the yields are based on chromium. The observed organic products corresponded to only 26% of chromium's oxidizing equivalents. The remainder was assumed to form ring-opening products such as adipic acid. The rate of the reaction of cyclohexane with CrO_2Cl_2 was determined to be $k = 1.07 \times 10^{-5}$ M^{-1} s^{-1} at 75 °C with activation parameters of $\Delta H^{\ddagger} = 26.6$ (8) kcal/mol and $\Delta S^{\ddagger} = -5$ (2) eu. According to the data, initial hydrogen atom transfer from cyclohexane to CrO_2Cl_2 takes place. Then, the cyclohexyl radical is rapidly trapped by oxidizing chromium species via either chlorine atom abstraction or formation of a C−O bond or transfer of a second hydrogen atom as shown in Scheme 3.

It was noted that the reaction takes place not because of any radical character at the oxygen in diamagnetic CrO_2Cl_2 but because of the strength of the O−H bond formed in $Cr(O)(OH)Cl_2$.

An analogous mechanism and similar reactivity were observed in the reactions of CrO_2Cl_2 with cyclooctane, isobutane, and toluene.[25] Parallel to the oxidation of cyclohexane, these reactions proceeded by an initial hydrogen atom transfer from substrate to CrO_2Cl_2. The rates of the hydrogen atom abstraction were directly correlated with the C−H bond strength of the substrate being activated and decreased in the order toluene > cyclooctane ≈ isobutane > cyclohexane. Once again it was deduced that the bond strength but not any radical character is the primary cause for the hydrogen atom abstraction. Although CrO_2Cl_2 has no unpaired spins, it abstracts hydrogen atoms just like oxygen radicals.

Oxidation of organic substrates (alkanes, alkenes and alcohols) were catalyzed by chromium(III) heteropolytungstate complexes or their corresponding oxygenated forms, the Cr(V) oxo complexes $[X^{n+}W_{11}O_{39}Cr^{V}O]^{(9-n)-}$ ($X^{n+} = P^{5+}$ and Si^{4+}), with various oxidants such as OCl^-, H_2O_2, and iodosylbenzene.[26] Oxo chromium(V) complex $[R_4N]_{9-n}[X^{n+}W_{11}O_{39}Cr^{V}O]$ ($X^{n+} = P^{5+}$, Si^{4+}; R = *n*-C_4H_9, *n*-C_6H_{13}, *n*-C_7H_{15}) was prepared by reacting hydrophobic tetra-*n*-alkylamonium salts of the Cr(III) complexes $[X^{n+}W_{11}O_{39}Cr^{III}(OH_2)]^{(9-n)-}$ ($X = P^{5+}$, Si^{4+}) with an aqueous oxidant (3.7% H_2O_2 or 1.7% NaOCl) in aprotic organic media.

Overall, the reaction was described as proceeding in the two following reaction steps (eq 3):

$$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-} + DO \rightarrow [PW_{11}O_{39}Cr^{V}O]^{4-} + D + H_2O$$

DO: (Oxygen donor oxidant) OCl^-, H_2O_2, or PhIO.

$$Cr^{V}{=}O + X \rightarrow XO + Cr^{III}$$

X: (Organic substrate) alkene, alcohol, alkane, or Ph_3P. (3)

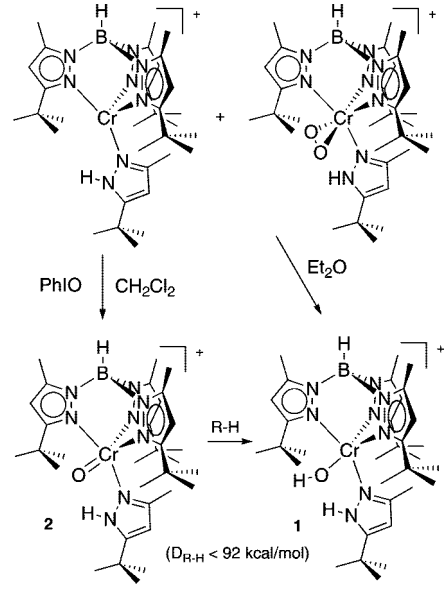
The second step was the rate limiting reaction for all organic substrates examined. The oxidation products of alkenes by the oxo Cr(V) complexes at 50 °C were epoxides, allylic alcohols and ketones.

Radical addition to the double bond by the oxo chromium(V) moiety was the most probable mechanism according to data obtained in the oxidation of alkenes.

Brown hydroxide complex $[Tp^{tBu,Me}Cr(OH)(pz'H)]BARF$ (**1**), $Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)-borate, pz′H = 3-*tert*-butyl-methylpyrazole, BARF = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate), was synthesized in excellent yield by reacting superoxo complex $[Tp^{tBu,Me}Cr(\kappa^2\text{-}O_2)(pz'H)]BARF$ with $[Tp^{tBu,Me}Cr(pz'H)]BARF$ in Et_2O at room temperature (Scheme 4).[27] **1** was also prepared by reacting $[Tp^{tBu,Me}Cr(pz'H)]BARF$ with oxygen atom donors such as iodosylbenzene and trimethylamine-*N*-oxide in Et_2O. Therefore, a chromium oxo intermediate, $[Tp^{tBu,Me}Cr(O)(pz'H)]BARF$ (**2**), was proposed and independently synthesized. **2** abstracts hydrogen atoms from substrates of modest R-H bond strength (<92 kcal/mol). For example, the reaction of stoichiometric amounts of 1,4-cyclohexadiene or 9,10-dihydroanthracene in CD_2Cl_2 solution of **2** rapidly produced **1** and benzene or anthracene, respectively. **2** also abstracts hydrogen atoms from NEt_3, toluene, Et_2O, and THF. A kinetic isotope effect of 10 (1) at 75 °C was observed for the reaction of **2** with THF.

Cr(V) oxo complex $Cp^*Cr(O)Cl_2$ was synthesized by exposing a CH_2Cl_2 solution of $[Cp^*Cr(\mu\text{-}Cl)Cl]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) to O_2 gas at ambient pressure and temperature. This

Scheme 4. Synthesis of $[Tp^{tBu,Me}Cr(OH)(pz'H)]BARF$ (1) by Reacting Superoxo Complex $[Tp^{tBu,Me}Cr(\kappa^2\text{-}O_2)(pz'H)]BARF$ with $[Tp^{tBu,Me}Cr(pz'H)]BARF$ in Et_2O at Room Temperature



Cr(V) oxo complex catalyzes the dehydrogenation of 1,4-cyclohexadiene to benzene and water. In addition, chromium oxo species generated by direct activation of O_2 are capable of epoxidizing olefins.[28]

6. C−H Bond Activations by Group VII Metal Oxo Compounds

Arylalkanes (toluene, ethylbenzene, diphenylmethane, triphenylmethane, 9,10-dihydroanthracene, xanthene, and fluorene) were oxidized by $^nBu_4NMnO_4$ in toluene solvent.[29] Oxidation products of toluene were benzoic acid and a small amount of benzaldehyde. All reactions showed first-order behavior in both $^nBu_4NMnO_4$ and organic substrates. The oxidation of toluene and dihydroanthracene showed primary isotope effects of $k_{C_7H_8}/k_{C_7D_8} = 6$ (±1) at 45 °C and $k_{C_{14}H_{12}}/k_{C_{14}D_{12}} = 3.0$ (±0.6) at 25 °C. The first and the rate-limiting step was the H• transfer from substrate to a permanganate oxo group (Scheme 5).

The reason for the H• atom abstraction mechanism was the high thermodynamic affinity of permanganate for H• as the enthalpy for addition of H• to MnO_4^- was calculated to be −80 ± 3 kcal/mol. The mechanism for this reaction is very similar to that of the oxidation of alkanes by chromyl chloride, described above.

The first example of C−H bond oxidation by a dinuclear mixed-valent (μ-oxo)manganese(III,IV) complex, $[(phen)_2Mn(\mu\text{-}O)_2Mn(phen)_2](PF_6)_3$ (phen = 1,10-phenanthroline), was reported by Mayer and Wang.[30] Reaction of $[(phen)_2Mn(\mu\text{-}O)_2Mn(phen)_2](PF_6)_3$ with 9,10-dihydroanthracene (DHA) in acetonitrile over 11 h at 65 °C resulted in the formation of 97% anthracene, 2% anthraquinone and 1% anthrone. The organic products accounted for 93% of manganese's oxidizing equivalents. The dinuclear manganese(μ-oxo) compound was converted into a dinuclear manganese(μ-hydroxo) compound (Scheme 6).

When a 1:1 mixture of DHA-h_{12} and DHA-d_{12} was oxidized, a kinetic isotope effect of 4.2 (3) was found. The kinetic and thermodynamic data supported the proposal that the reaction takes place via H• atom transfer from DHA to $[L_2Mn(\mu\text{-}O)_2MnL_2]^{3+}$ forming first $[L_2Mn(\mu\text{-}O)(\mu\text{-}OH)MnL_2]^{3+}$ (−79 kcal/mol) and then a second H• atom transfer from hydroanthracenyl radical to $[L_2Mn(\mu\text{-}O)(\mu\text{-}OH)MnL_2]^{3+}$ forming $[L_2Mn(\mu\text{-}OH)_2(MnL_2]^{3+}$ (−75 kcal/mol).

The first example of C−H bond oxidation via initial hydride abstraction in the reaction of toluene with manganese(IV) dimer $[(phen)_2Mn(\mu\text{-}O)_2Mn(phen)_2](ClO_4)_4$ (phen = 1,10-phenanthroline), was reported by Mayer and coworkers.[31] Kinetics of oxidation of various other alkylaromatic compounds indicated a highly electron deficient substrate in the transition state. In addition, products obtained in the oxidation of toluene implied the intermediacy of benzyl cations. Therefore, a mechanism involving hydride transfer for the oxidation of toluene by $[L_2Mn(\mu\text{-}O)_2MnL_2]^{4+}$ was proposed as shown in Scheme 7.

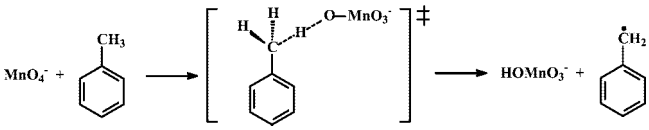
This mechanism was supported by the thermodynamic affinity of $[L_2Mn(\mu\text{-}O)_2MnL_2]^{4+}$ for H^-, which was reported as −122 kcal/mol. Removal of H^- from toluene requires 118 kcal/mol.[32,33] Oxidation of a mixture of toluene and $C_6H_5CD_3$ showed a kinetic isotope effect of 4.3 ± 0.8, which is in agreement with C−H bond activation in the rate-determining step.[34]

Oxidation of *p*-methoxytoluene with $[L_2Mn^{IV}(\mu\text{-}O)_2Mn^{IV}L_2]^{4+}$, however, proceeded by initial electron transfer and subsequent rate-limiting deprotonation.[31] Kinetic and mechanistic analyses showed preequilibrium electron transfer in the oxidation of *p*-methoxytoluene and naphthalene because addition of $[L_2Mn^{IV}(\mu\text{-}O)_2Mn^{III}L_2]^{3+}$ (the reduced form of $[L_2Mn^{IV}(\mu\text{-}O)_2Mn^{IV}L_2]^{4+}$) inhibited the reaction, and biaryls were the major products of the oxidation of *p*-methoxytoluene (Scheme 8).[34]

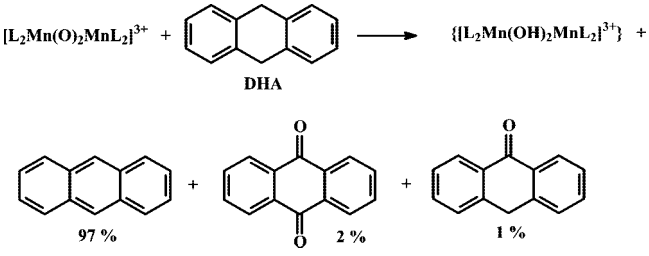
In summary, three different mechanisms were reported for the oxidation reactions by dinuclear manganese(μ-oxo) compounds: hydrogen atom transfer, hydride transfer, and electron transfer. Both thermochemistry and intrinsic barriers are the factors influencing the choice of mechanism for a particular oxidant and a particular substrate.

To investigate the transfer of hydrogen atoms in synthetic model systems, nonheme manganese complexes with terminal hydroxo or oxo ligands, that is, $[Mn^{III/II}H_3\mathbf{1}(OH)]^{-/2-}$ and $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ ($H_3\mathbf{1}$ is the tripodal ligand tris[(*N*′-*tert*-butylurealylato)-*N*-ethyl]aminato) were prepared because they are proposed to mediate the transfer of hydrogen atoms in metalloproteins.[35] $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ reacted with organic substrates with C−H bonds weaker than 80 kcal/mol, such as 9,10-dihydroanthracene and 1,4-cyclohexadiene, to pro-

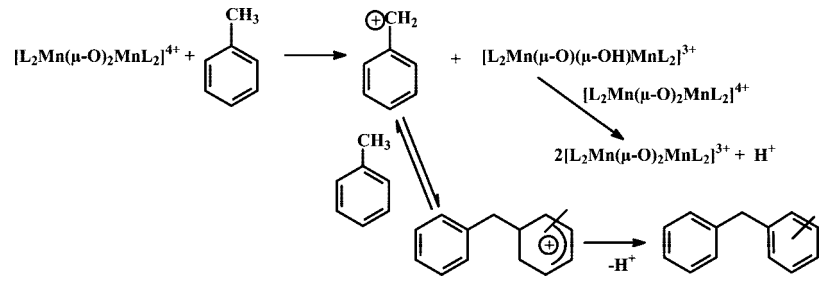
Scheme 5. Hydrogen Atom Transfer from Toluene to Permanganate Oxo Ligand



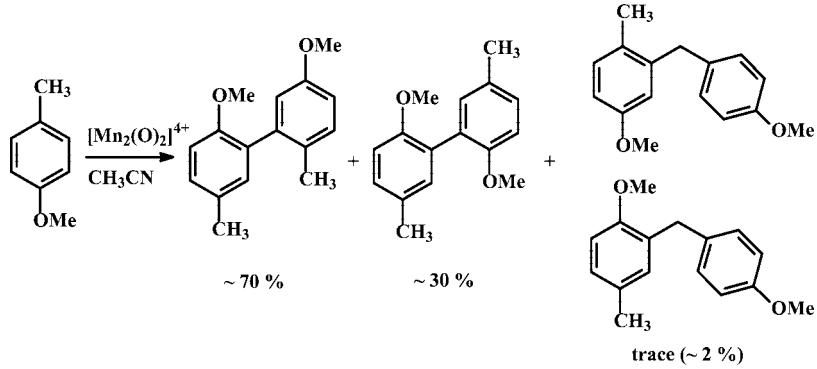
Scheme 6. C−H Bond Oxidation of Dihydroanthracene by a Dinuclear (μ-Oxo)Manganese Complex (L = 1,10-phenanthroline)



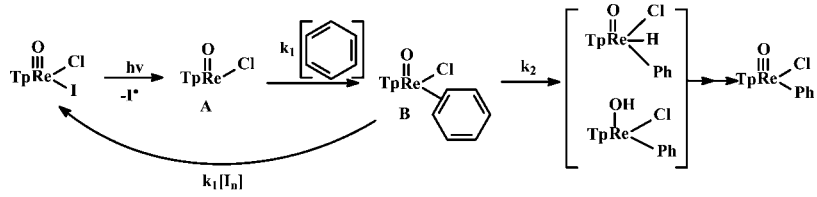
Scheme 7. C−H Bond Oxidation of Toluene via Initial Hydride Abstraction by Manganese(IV) Dimer $[(phen)_2Mn(\mu\text{-}O)_2Mn(phen)_2](ClO_4)_4$ (L = 1,10-Phenanthroline)



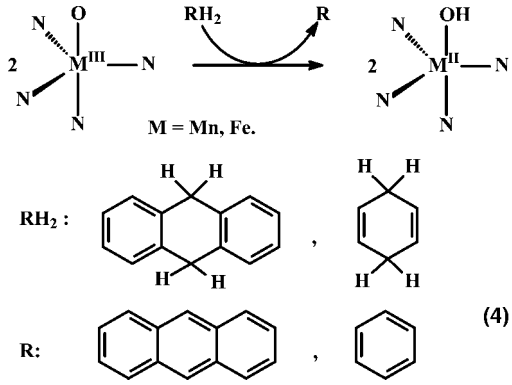
Scheme 8. Oxidation of *p*-Methoxytoluene with $[L_2Mn^{IV}(\mu\text{-}O)_2Mn^{IV}L_2]^{4+}$ (L = 1,10-Phenanthroline)



Scheme 9. Aromatic C−H Bond Activation and Formation of Rhenium Oxo Aryl Compounds via Photolysis of a Re(V) Oxo−Iodide Compound in Arene Solvents



duce $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ and deyhdrogenated products in more than 80% yield (eq 4). This reactivity was explained by the bond dissociation energy of O−H in $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ comparing favorably to the C−H bond strength in substrates.



The reaction of an isolated $(TBP_8Cz)Mn^{V}{\equiv}O$ (TBP_8Cz = octakis(*para-tert*-butylphenyl)corrolazinato^{3-}) complex with cyclohexadiene (CHD) and dihydroanthracene (DHA) has been studied to gain an understanding of the effect of high-valent metal-oxo complexes in the enzymatic and synthetic processes.[36] The reaction was first-order in these substrates and second-order rate constants (normalized per reactive C−H bonds) were determined as $k''(CHD) = 3.32 \pm 0.12 \times 10^{-5}$ M^{-1} s^{-1} and $k''(DHA) = 1.76 \pm 0.48 \times 10^{-5}$ M^{-1} s^{-1}. These findings are consistent with previous observations of H-atom abstractions by metal compounds.[37]

Aromatic C−H bond activation and formation of rhenium oxo aryl compounds were reported upon photolysis of Re(V) oxo-iodide compound in arene solvents.[38,39] When substituted arenes were reacted, an exclusive electrophilic selectivity to aromatic C−H bonds was observed, and various functional groups were tolerated. The proposed mechanism for the general reaction is shown in Scheme 9:

The arene was activated in two steps. First intermediate **A** coordinates to arene without C−H bond cleavage (k_1) forming **B**. This step determines the intermolecular selectivity. Then **B** irreversibly cleaves the C−H bond (k_2) which introduces the intramolecular selectivity.

The C−H bond activation step (k_2) was proposed to be a $[2_\sigma + 2_\pi]$ addition to the Re═O bond because of its electrophilic regiochemistry.

Selective oxidation of the alkyl ligand in rhenium(V) oxo compounds was shown by DuMez and Mayer.[40] Rhenium(V) oxo alkyl triflate compounds $(HBpz_3)ReO(R)OTf$ (R= Me, Et, *n*-Bu) were prepared by sequential reaction of $(HBpz_3)ReOCl_2$ with dialkyl zinc reagents and AgOTf.

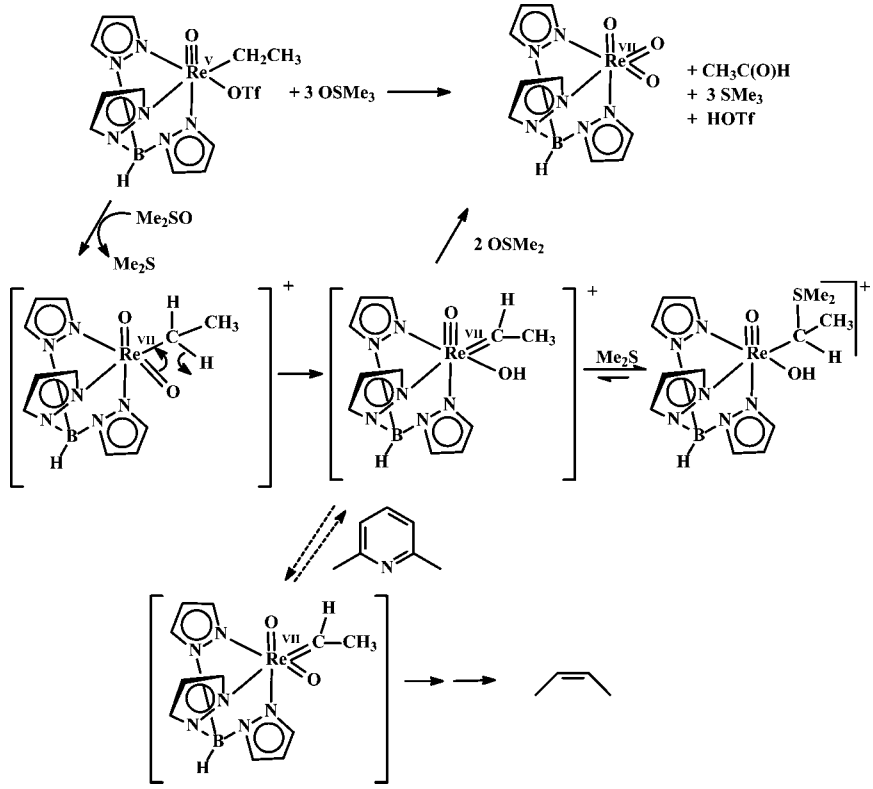
According to the proposed mechanism (Scheme 10), first oxygen atom donor (Me_2SO) displaces the triflate ligand producing Re(VII) dioxo alkyl cation. A carbene complex forms upon transfer of an α-hydrogen from the alkyl group to an oxo ligand. The carbene complex was trapped by pyridine or SMe_2 to form $[(HBpz_3)ReO(OH)\{CH(py)CH_3\}$-OTF or $[(HBpz_3)ReO(OH)\{CH(SMe_2)CH_3\}]OTF$, which were observed by NMR at low temperatures. Either by carbene-oxo coupling on the rhenium center or by attack of the oxygen atom donor on the carbene, $(HBpz_3)ReO_3$, and acetaldehyde formed.

7. C−H Bond Activations by Group VIII Metal Oxo Compounds

Under anaerobic conditions, photoreduction of heme/nonheme diiron μ-oxo complex $[(^6L)Fe^{III}-O-Fe^{III}-Cl]^+$ (**3**) in THF and toluene (C−H BDE ~ 90 kcal/mol) produced the corresponding diferrous compound $[(^6L)Fe^{II}\cdots Fe^{II}-Cl]B(C_6F_5)_4$ (**4**) (Figure 2).[41]

In contrast, the same photoreduction was not observed in benzene (C−H BDE > 100 kcal/mol). On the basis of transient absorption laser photolysis studies, homolytic C−H bond cleavage in solvents with weak C−H bonds (THF and toluene) via a photochemically generated Fe-oxo intermediate was suggested. When the reaction was carried out in the presence of O_2, multiple product turnovers from THF to γ-butyrolactone and from toluene to benzaldehyde were

Scheme 10. Proposed Mechanism of Selective Oxidation of the Alkyl Ligand in a Rhenium(V) Oxo Compound



achieved, implying the involvement of dioxygen as an oxidant in a photocatalytic mechanism (Scheme 11).

To clarify whether the reaction mechanism involves a metal-based oxidation or a radical chain autoxidation, Que et al. have investigated catalytic alkane functionalization by Fe(TPA)/^{t}BuOOH systems as catalysts ($[Fe(TPA)Cl_2]^+$ (**5**), $[Fe(TPA)Br_2]^+$ (**6**), and $[Fe_2O(TPA)_2(H_2O)_2]^{4+}$ (**7**), TPA = tris(2-pyridylmethyl)amine).[42] The nature of the products formed, their dependence on O_2, and the kinetic isotope effects associated with the products can distinguish the two mechanisms. The metal-based oxidation mechanism is expected to produce mostly alcohol with a large KIE because it is analogous to heme-catalyzed hydroxylations. The radical chain autoxidation requires alcohol and ketone products in a ratio of 1:1 or smaller which is observed upon reacting catalysts **5**, **6**, and **7** with alkane and 150 equiv of ^{t}BuOOH. When run under argon purge, these product yields decreased, suggesting the participation of O_2 in the reaction.

However, alcohol was observed as sole product with $k_H/k_D = 10$ when **7**-catalyzed oxidation was carried out in the presence of a limited amount (<20 equiv) of ^{t}BuOOH, implying a metal-based oxidation. A unifying scheme was formulated that can explain the many observations associated with Fe(TPA)-catalyzed alkane hydroxylations.[43−47] A metal-based, two-electron oxidant alkylperoxoiron(III) species was proposed to be at the center of this scheme. At low ROOH

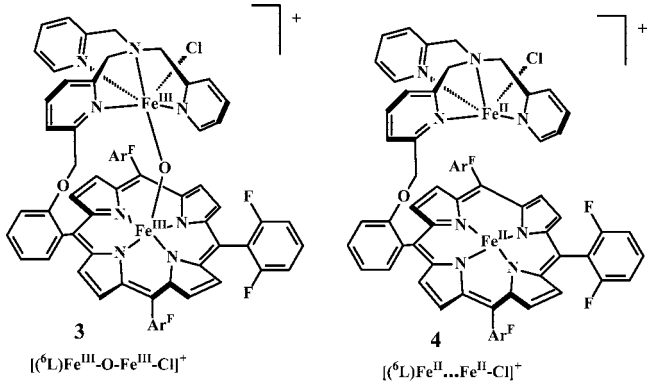
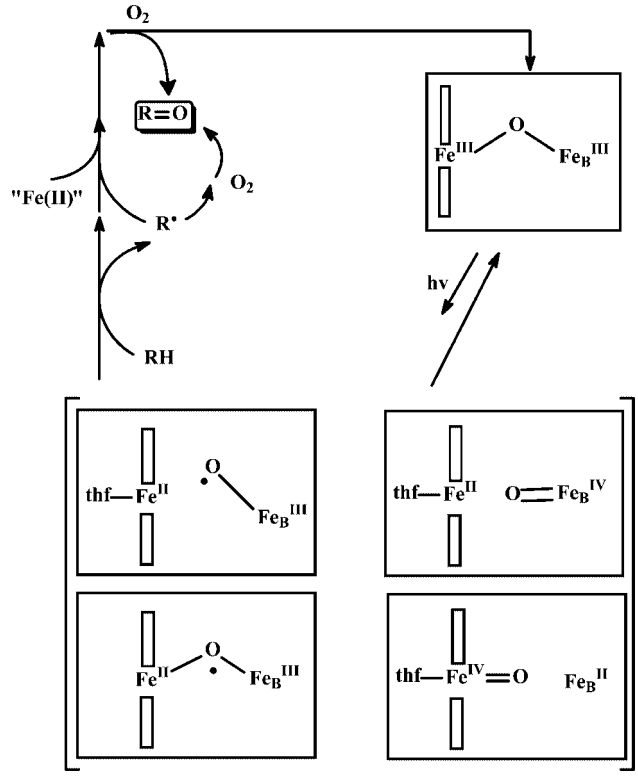
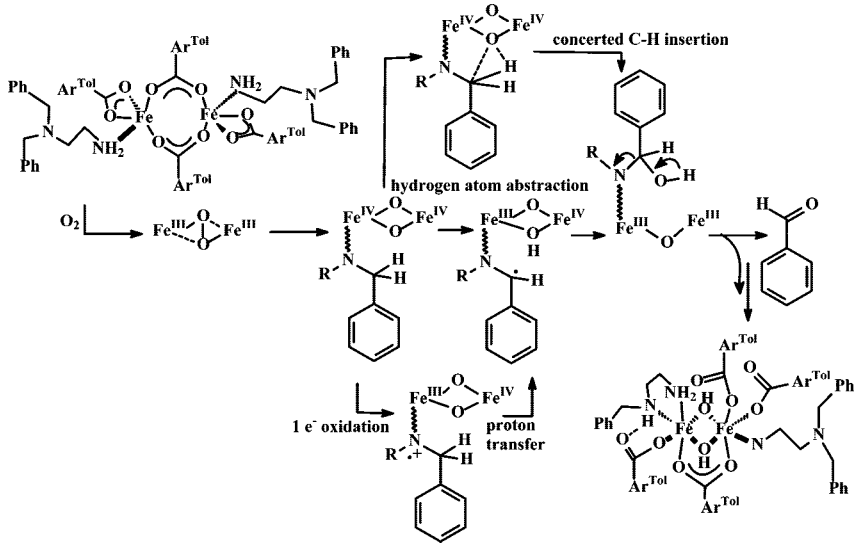


Figure 2. $[(^6L)Fe^{III}-O-Fe^{III}-Cl]^+$ (**3**) and $[(^6L)Fe^{II}\cdots Fe^{II}-Cl]$ (**4**).

Scheme 11. C−H Bond Cleavage in Solvents with Weak C−H Bonds (THF and Toluene) via Photochemically Generated Fe-Oxo Intermediate



Scheme 12. Benzylic C−H Bond Activation on a Carboxylate-Bridged Diiron(II) Compound



concentrations, this metal-based oxidant is responsible for alkane hydroxylation. At high ROOH concentrations, ROOH initiates a radical chain process producing alkoxy radical and O_2. Substrate alkyl radicals generated by either the alkoxy radical or the metal-based oxidant are trapped by O_2 to produce the alcohol and ketone observed at high ROOH concentrations.

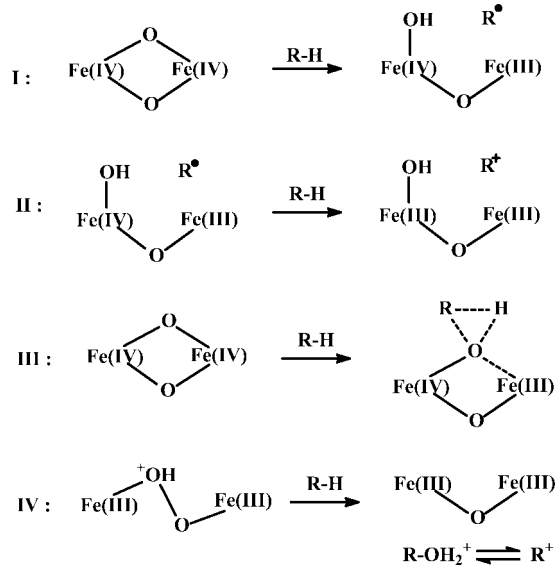
To investigate the transfer of hydrogen atoms in synthetic systems, nonheme iron complexes with terminal hydroxo or oxo ligands, $[Fe^{III/II}H_3\mathbf{1}(OH)]^{-/2-}$ and $[Fe^{III}H_3\mathbf{1}(O)]^{2-}$ ($H_3\mathbf{1}$ is the tripodal ligand, tris [(*N*′-*tert*-butylurealylato)-*N*-ethyl]-aminato) were prepared because they are proposed to mediate the transfer of hydrogen atoms in metalloproteins.[35] $[Fe^{III}H_3\mathbf{1}(O)]^{2-}$ reacts with organic substrates with C−H bonds less than 80 kcal/mol such as 9,10-dihydroanthracene and 1,4-cyclohexadiene to produce $[Fe^{II}H_3\mathbf{1}(OH)]^{2-}$ and deyhdrogenated products in more than 80% yield (eq 4). This reactivity was explained by the bond dissociation energy of O−H in $[Fe^{II}H_3\mathbf{1}(OH)]^{2-}$ compared to the C−H bond strength in substrates.

A benzylic C−H bond activation takes place on a carboxylate-bridged diiron(II) compound, a synthetic analogue of bacterial multicomponent monooxygenases, in the presence of O_2 during the oxidative *N*-dealkylation reaction.[48] On the basis of the positive slope of ρ and a small KIE_{intra}, one-elecron transfer from nitrogen of the ligand to a transient electrophilic diiron intermediate was postulated, followed by proton transfer (Scheme 12).

Scheme 13 summarizes four different mechanisms that have been proposed so far for the substrate oxidation by soluble methane monooxygenase (sMMO):[49,50] (I) hydrogen atom abstraction from the substrate followed by radical recombination;[51] (II) cation formation by electron abstraction from the substrate radical intermediate generated in I followed by reaction with metal bound hydroxide;[52] (III) direct insertion of the oxygen atom from a high-valent bis-μ-oxo $Fe(IV)_2$ cluster-containing species into the C−H bond;[53−56] and (IV) cation formation on the substrate by transfer of a protonated oxygen from a hydroperoxy intermediate (derived from O_2) followed by loss of water.[53]

Catalytic oxidation of norcarane by soluble methane monooxygenase (sMMO) afforded 3-hydroxymethylcyclohexene (characteristic of radical intermediate), 3-cycloheptenol (characteristic of cationic intermediate) and 2- and

Scheme 13. Four Different Mechanisms for the Substrate Oxidation by Soluble Methane Monooxygenase (sMMO)



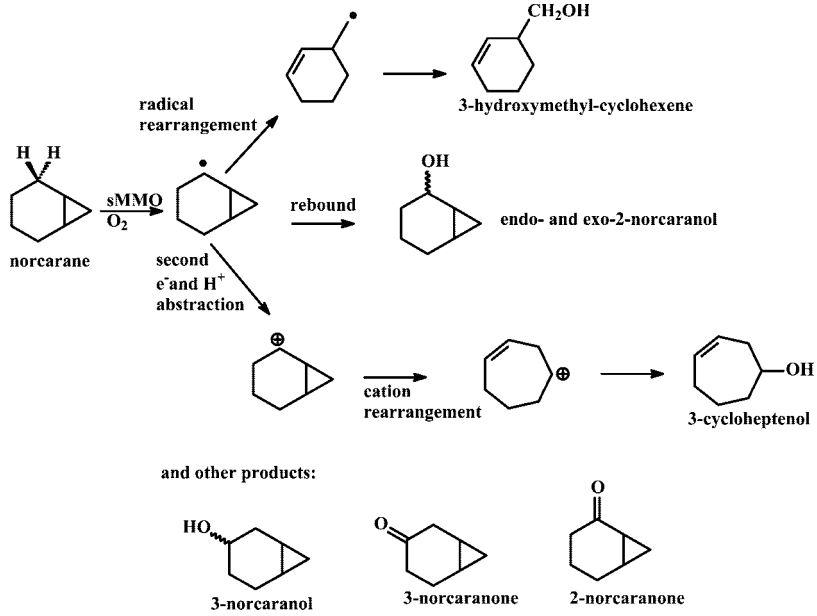
3-norcaranols.[57] The high-valent bis-μ-oxo $Fe(IV)_2$ cluster-containing species was reported to do the majority of the oxidation because the presence of norcarane increases the rate of decay of only it. On the basis of the products obtained in the oxidation of norcarane catalyzed by sMMO, a mechanism in which an initial substrate radical intermediate forms by hydrogen atom abstraction is proposed. Then, this intermediate could follow three pathways: (I) oxygen rebound, (II) intramolecular rearrangement followed by oxygen rebound, and (III) loss of a second electron to yield a cationic intermediate (Scheme 14).

A new 3-fold symmetric, nonheme iron pyrrole system that activates C−H bonds both inter- and intramolecularly was reported by Chang and Harman[58] (Scheme 15).

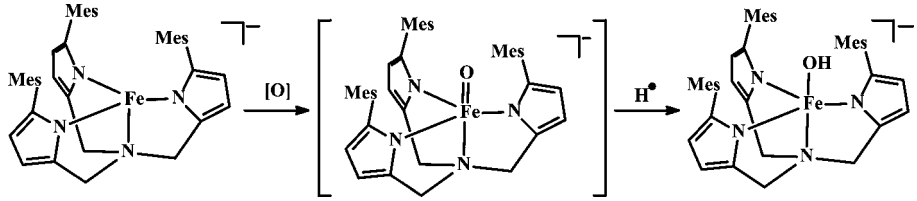
They showed a rare example of oxygen transfer from N_2O to iron. An intramolecular C−H activation or aryl hydroxylation was observed when **8** was reacted with Me_3NO in THF (Scheme 16).

It has not been isolated and characterized but intermediacy of iron-oxo compound is suggested based on the kinetic barriers to arene C−H hydroxylation and literature precedent.[59] The reaction of **9** with N_2O produced azobenzene in

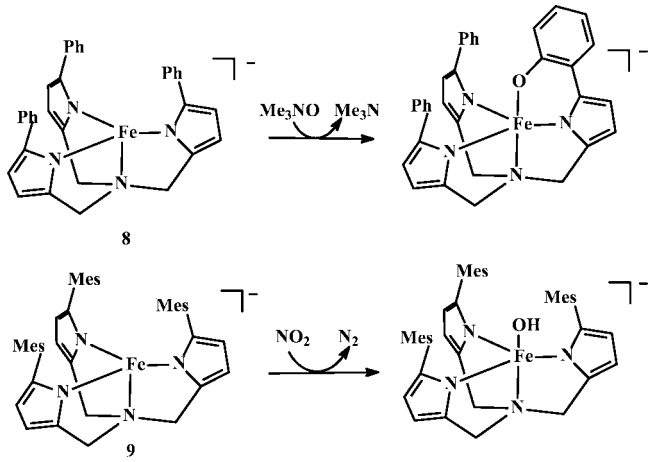
Scheme 14. Three Pathways and the Products in the Oxidation of Norcarane by sMMO



Scheme 15. 3-Fold Symmetric, Non-heme Iron Pyrrole System That Activates C−H Bonds Both Inter- and Intramolecularly



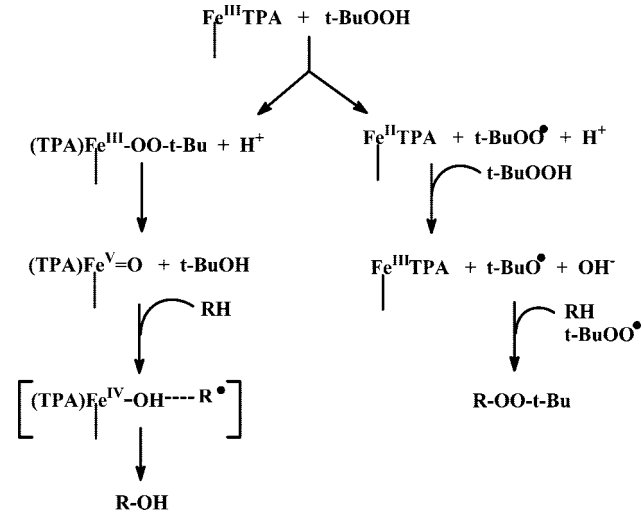
Scheme 16. (a) Intramolecular C−H Activation or Aryl Hydroxylation Observed when 8 Was Reacted with Me_3NO in THF and (b) Oxygen Transfer from NO_2 to 9



92% yield in the presence of diphenylhydrazine, and benzene in the presence of cyclohexadiene.

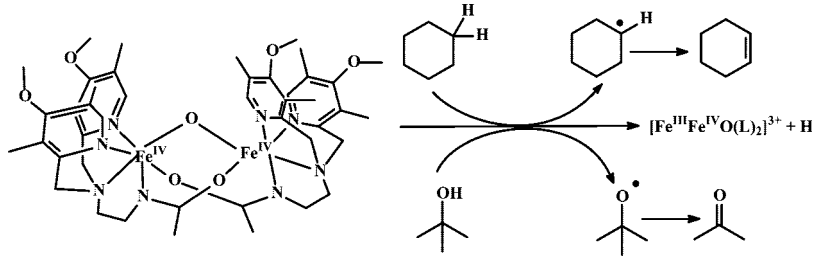
In order to model dinuclear sites in nonheme iron enzymes, the reactivity of $[Fe_2(TPA)_2O(OAc)](ClO_4)_3$ (TPA = tris(2-pyridylmethyl)amine, OAc = acetate) with ^{t}BuOOH in CH_3CN for the functionalization of cyclohexane has been investigated.[43] The μ-oxo diferric compound ($[Fe_2(TPA)_2O(OAc)](ClO_4)_3$) oxidizes cyclohexane catalytically and affords 9 equiv of cyclohexanol, 11 equiv of cyclohexanone, and 16 equiv of (*tert*-butylperoxy)cyclohexane in 15 min at ambient temperature and pressure. Varying the electron donating/withdrawing features of the tripodal ligand and various solvents resulted in various ratios of cyclohexanol + cyclohexanone to (*tert*-butylperoxy)cyclohexane. Therefore, two competing pathways have been proposed for the decomposition of ^{t}BuOOH with catalyst: (I) a heterolytic mechanism generating a high-valent iron-oxo species, which causes the formation of cyclohexanol and cyclohexanone analogous to cytochrome P450 and synthetic heme hydroxylation chemistry,[60] and (II) a homolytic mechanism generating ^{t}BuO$^\cdot$ and ^{t}BuOO$^\cdot$ radicals which are responsible for the formation of (*tert*-butylperoxy)cyclohexane (Scheme 17).[61−63]

Scheme 17. Reactivity of $[Fe_2(TPA)_2O(OAc)](ClO_4)_3$ (TPA = tris(2-pyridylmethyl)amine, OAc = acetate) with ^{t}BuOOH in CH_3CN for the Functionalization of Cyclohexane



$[Fe_2O(TPA)_2(H_2O)_2](CF_3SO_3)_4$ has been synthesized and characterized as a (μ-O)diiron(III) complex with terminal aquo ligands.[64] Together with ^{t}BuOOH, $[Fe_2O(TPA)_2(H_2O)_2]$-

Scheme 18. Activations of C−H and O−H Bonds by a New Diiron(IV) Complex



$(CF_3SO_3)_4$ catalyzes the C−H bond activation reaction and converts cyclohexane to cyclohexanol (7 turnovers) and cyclohexanol to cyclohexanone (18 turnovers). On the basis of the resonance Raman spectroscopy, electrospray ionization mass spectrometry, EPR, and NMR data, the intermediacy of a mononuclear iron alkylperoxide species is proposed when $[Fe_2O(TPA)_2(H_2O)_2](CF_3SO_3)_4$ is reacted with cyclohexanol in excess ^{t}BuOOH.

Synthesis and characterization of a nonheme Fe^{IV}═O complexes with pentadentate N5 ligands N4Py (*N*,*N*-bis(2-pyridylmethyl)-bis(2-pyridyl)methylamine) and Bn-tpen (*N*-benzyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)-1,2-diaminoethane) have been reported.[65] High-resolution electrospray mass spectrometry revealed mass values fully consistent with their formulations as $\{[Fe^{IV}(O)(N4Py)](ClO_4)\}^+$ and $\{[Fe^{IV}(O)(Bn\text{-}tpen)](O_3SCF_3)\}^+$ ions. In addition, Mössbauer spectra confirms the presence of iron(IV) in both compounds. These pentadentate Fe^{IV}═O complexes are thermally more stable than tridentate iron-oxo compounds, and they can hydroxylate C−H bonds as strong as 99.3 kcal/mol with large KIE.

By electrochemical oxidation, an oxo-bridged diiron(IV) complex is generated to model the chemistry of MMO's species Q.[66] MMO is a biological catalyst that oxidizes methane to methanol. Q is a diiron(IV) intermediate in this oxidation reaction. Two diiron(IV) complexes were previously reported,[67,68] but their reactions with C−H bonds were much slower than the actual enzyme. The new diiron(IV) compound is capable of activating C−H bonds as strong as 100 kcal/mol and it reacts with cyclohexane 100- to 1000-fold faster than mononuclear Fe^{IV}═O complexes of similar ligands. Unexpectedly, this new diiron(IV) compound also shows the first example of O−H bond cleavage by an iron compound because it activates the O−H bonds of methanol and *t*-butanol rather than their weaker C−H bonds (Scheme 18). A proton-coupled electron transfer mechanism is proposed for the oxidation of alcohol. That is, proton transfer from the O−H group is coupled with the electron abstraction from the O atom. The strong oxidizing power of the new diiron(IV) complex is exemplified by its high redox potential (+1.50 V versus $Fc^{+/0}$) which is the highest of three types of (μ-O)diiron(IV) complexes reported to date.

High-yield synthesis of a high spin ($S = 2$) oxoiron(IV) complex, $[Fe^{IV}(O)(TMG_3tren)]^{2+}$, was achieved by equimolar reaction of TMG_3tren (Figure 3) and $[Fe^{II}(OTf)_2(CH_3CN)_2]$ in THF followed by addition of one equivalent of 2-(*tert*-butylsulfonyl)-iodosylbenzene in CH_3CN.[69] This trigonal bipyramidal oxoiron(IV) was fully characterized by spectroscopy. The high-spin oxoiron(IV) compound oxidizes dihydroanthracene and cyclohexadiene in CH_3CN at −30 °C with second-order rate constants of 0.090 and 1.2 M^{-1} s^{-1}, respectively. However, when these rate constants are compared to those of well-studied $S = 1$ oxoiron(IV) complexes, $[Fe^{IV}(O)(TMC)(CH_3CN)]^{2+}$[70−72] and $[Fe^{IV}(O)(N4Py)]^{2+}$,[73,65] they are not appreciably higher, as might have been expected from an $S = 2$ oxoiron(IV) compound. This unexpected result and the fact that DHA is oxidized 13 times more slowly than CHD are attributed to the steric hindrance caused by the bulky TMG_3tren ligand. Finally, a kinetic isotope effect of 18 was measured when high-spin oxoiron(IV) was reacted with DHA/DHA-d_4. Therefore, there is a significant contribution from hydrogen tunneling in the activation of C−H bond by $S = 2$ oxoiron(IV) compound, as well as $S = 1$ complexes.

As iron(IV)-oxo porphyrin compounds are relatively weak oxidants, they are rarely used as oxidants in nature.[74,75] Nam et al. have reported the first examples of C−H bond cleavage of alkyl aromatics and hydride transfer of dihydronicotinamide adenine dinucleotide (NADH) analogues by iron(IV)-oxo porphyrin compounds (Figure 4).[76]

Reactions of xanthenes, DHA, CHD, and fluorene with $[Fe^{IV}(O)(tpfpp)]$ afforded xanthone (40 ± 8%), anthracene (42 ± 7%), benzene (41 ± 7%), and 9-fluorene (26 ± 5%), respectively. Second-order rate constants of $k_2 = 14 \pm 2$ M^{-1} s^{-1} (for the reaction of xanthene), $k_2 = 13 \pm 2$ M^{-1} s^{-1} (for the reaction of DHA), $k_2 = 9 \pm 0.8$ M^{-1} s^{-1} (for the reaction of CHD), and $k_2 = 2.3 \pm 0.2$ M^{-1} s^{-1} (for the reaction of fluorene), which decrease as the BDE of the C−H of the substrates increases, were reported. On the basis of these results and the large KIEs (~ 20) of the oxidations of DHA and xanthene, H-atom abstraction is stated as the rate-

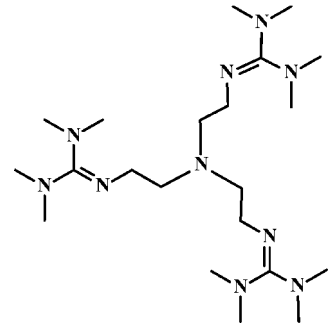


Figure 3. TMG_3tren.

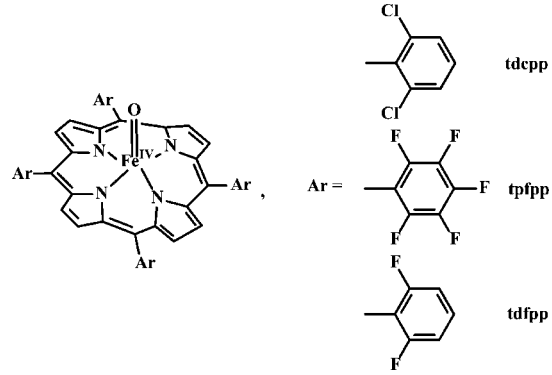
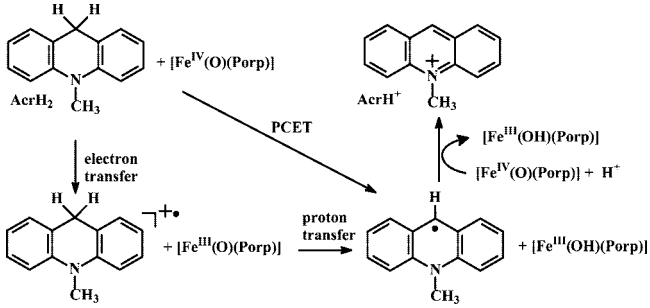


Figure 4. Iron(IV)-oxo porphyrin compounds.

Scheme 19. Hydride Transfer Reaction from NADH Analogues 10-Methyl-9,10-dihydroacridine ($AcrH_2$) to Iron(IV)-oxo Porphyrin



determining step for the C−H bond oxidation of alkyl aromatics by iron(IV)-oxo porphyrins.

The hydride transfer reactions from NADH analogues 10-methyl-9,10-dihydroacridine ($AcrH_2$) and 1-benzyl-1,4-dihydronicotinamide (BNAH) to iron(IV)-oxo porphyrins have been studied, and second-order rate constants of 75 ± 3 M^{-1} s^{-1} (for the reaction of $AcrH_2$) and $7.0 \times 10^2 \pm 30$ M^{-1} s^{-1} (for the reaction of BNAH) were reported. In addition, large KIE values of 17 and 8.6 were obtained for the reactions of $AcrH_2$ and BNAH, respectively. These data revealed that C−H bond activation of NADH analogues is involved as a rate-determining step in these reactions. Further studies showed that the hydride transfer from NADH analogues to $[Fe^{IV}(O)(Porp)]$ takes place by PCET from $AcrH_2$ to $[Fe^{IV}(O)(Porp)]$[77−79] followed by fast electron transfer from $AcrH^{\cdot}$ to $[Fe^{IV}(O)(Porp)]$ molecule resulting in $AcrH^+$ as shown in Scheme 19. (The proton source for the proton-transfer step in Scheme 19 is H_2O added into the reaction solution to generate $[Fe^{IV}(O)(Porp)]$).

Kinetics and mechanistic analyses were conducted on the oxidation of 2-propanol to acetone in water by $Ru^{IV}(trpy)(bpy)O^{2+}$ (trpy = 2,2′,2″-terpyridine, bpy: 2,2′-bipyridine).[80] First, 2-propanol was oxidized by Ru(IV) and then slower oxidation by Ru(III), namely $Ru^{III}(trpy)(bpy)OH^{2+}$ occurred. Kinetic data and activation parameters for this reaction are $k_{IV}(25\ °C) = 6.7 \times 10^{-2}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 9 \pm 1$ kcal/mol, $\Delta S^{\ddagger} = -34 \pm 4$ eu, $k_H/k_D = 18 \pm 3$; $k_{III}(25\ °C) = 6 \times 10^{-5}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 19 \pm 2$ kcal/mol, $\Delta S^{\ddagger} = -12 \pm 4$ eu, $k_H/k_D = 2.7 \pm 1.4$. According to the isotope labeling and spectral experiments, oxygen atom does not transfer from oxidant to the substrate. It was proposed that the mechanism of this reaction involves a concerted hydride (H^-) transfer from the α-C−H bond to Ru^{IV}=O (Scheme 20). The Ru(III) reaction, however, occurs by an initial one-electron, outer-sphere electron transfer.

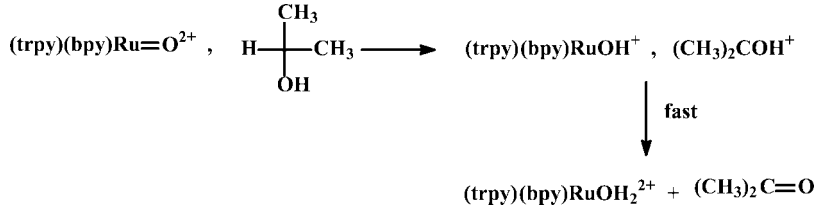
The same substrate (2-propanol) was also oxidized in acetonitrile by $Ru^{IV}(bpy)_2(py)O^{2+}$ (py is pyridine). In this case, Ru(III) reacts differently; H-atom transfer involving the α−C−H group was proposed as the mechanism. Kinetic data and the activation parameters for this reaction are $k(25\ °C) = (8 \pm 2) \times 10^{-4}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 10 \pm 2$ kcal/mol, $\Delta S^{\ddagger} = -38 \pm 7$ eu, $k_H/k_D \geq 8$.

Kinetics of oxidation of aromatic hydrocarbons (p-$^-O_2CC_6H_4CH(CH_3)_2$, p-$^-O_2CC_6H_4CH_2CH_3$, and p-$^-O_2CC_6H_4CH_3$ in water by $Ru^{IV}(trpy)(bpy)O^{2+}$, $C_6H_5CH(CH_3)_2$, and $C_6H_5CH_3$ in acetonitrile by $Ru^{IV}(bpy)_2(py)O^{2+}$) were studied.[81] A similar mechanism was proposed with the oxidation of 2-propanol by Ru(IV)-oxo compounds. A hydride ion transfer was involved in the redox step for these reactions (Scheme 21). The oxygen atom of the oxidant does not transfer to the substrate.

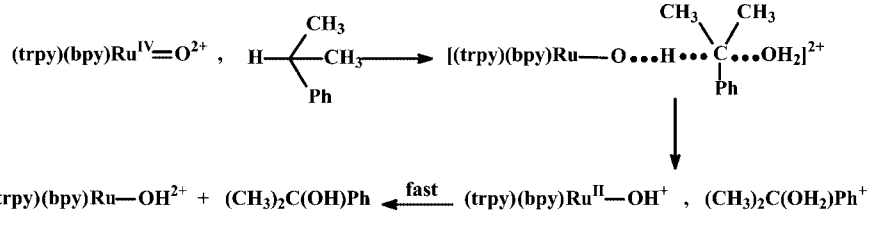
According to the spectrophotometrically obtained kinetic data, for the carboxylates in water, rate constants increase as the alkyl substitution increases. In water, added O_2 or changes in ionic strength do not affect the rate constants. In acetonitrile, however, added nucleophiles (water, *tert*-butyl alcohol or bromide) affect the rate law as first order in added nucleophile. Compared to the oxidation reactions in water, rate constants decrease significantly for the reactions in acetonitrile.

The kinetics of oxidation of a series of alcohols by $[Ru^{IV}(bpy)_2(py)O]^{2+}$ in aqueous solution and in acetonitrile showed that the reactions are first order in both alcohol and Ru^{IV}=O^{2+} and slightly slower in acetonitrile than in water.[82] Tertiary alcohols were unreactive and rate constants increased with substituent in the order of methyl < primary < secondary < allylic ≤ benzylic. A wide range of rate constants were reported, for example, in aqueous solution for the oxidation of methanol the rate constant is $(3.5 \pm 0.1) \times 10^{-4}$ M^{-1} s^{-1}, while it is $2{,}43 \pm 0.03$ M^{-1} s^{-1} for the oxidation of benzyl alcohol. Large kinetic isotope effects were observed; at 25 °C, for CH_3OH/CD_3OH, $k_H/k_D = 9$ and for $C_6H_5CH_2OH/C_6H_5CD_2OH$, $k_H/k_D = 50 \pm 3$. Oxidation of alcohols by $[Ru^{IV}(bpy)_2(py)O]^{2+}$ was suggested to occur via hydride transfer based on the spectral evidence and the kinetic isotope effects (eq 5).

Scheme 20. Oxidation of 2-Propanol to Acetone in Water by $Ru^{IV}(trpy)(bpy)O^{2+}$

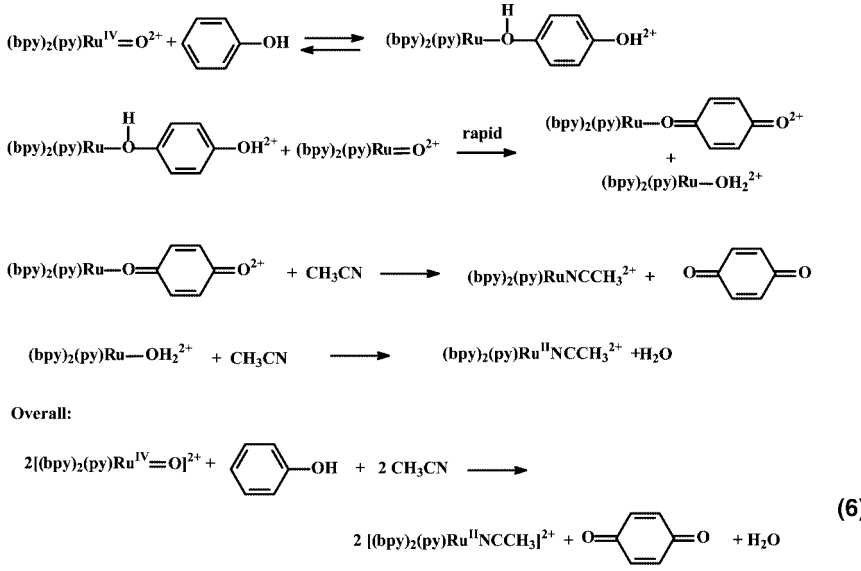


Scheme 21. Oxidation of Aromatic Hydrocarbons by $Ru^{IV}(trpy)(bpy)O^{2+}$



$$\begin{aligned}
&Ru^{IV}{=}O^{2+} + R_1R_2CHOH \rightarrow \\
&\qquad Ru^{II} - OH_2^{2+} + R_1R_2C{=}O \qquad k_{IV}\\
&Ru^{IV}{=}O^{2+} + Ru^{II} - OH_2^{2+} \rightarrow \\
&\qquad 2Ru^{III} - OH^{2+} \qquad k_{com}\\
&2Ru^{III}{-}OH^{2+} + R_1R_2CHOH \rightarrow \\
&\qquad 2Ru^{III} - OH_2^{2+} + R_1R_2C{=}O \qquad k_{III}\\
&\text{Overall: } 2Ru^{IV}{=}O^{2+} + 2R_1R_2CHOH \rightarrow \\
&\qquad 2Ru^{II} - OH_2^{2+} + 2R_1R_2C{=}O
\end{aligned} \tag{5}$$

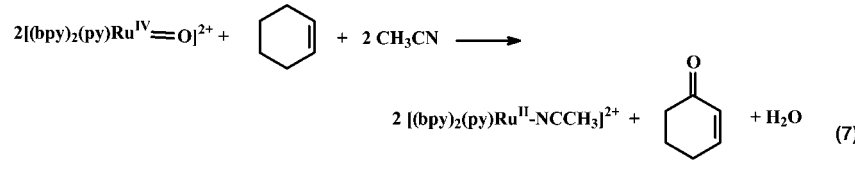
Oxidation reactions of phenol and alkylated phenol derivatives by $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ and $[(bpy)_2(py)Ru^{III}(OH)]^{2+}$ producing the corresponding quinines have been studied in acetonitrile and water.[83,84] The reactions are first order in both phenol and $Ru^{IV}{=}O^{2+}$ or $Ru^{III}{-}OH^{2+}$. An intermediate Ru(II) complex was detected. Quantitative transfer of oxygen atom from oxidant to substrate was observed. On the basis of the kinetic studies, an electrophilic attack by $Ru^{IV}{=}O^{2+}$ on the aromatic ring was suggested for the oxidation of phenol (eq 6).



(6)

Similarly, oxidation of cyclohexene by $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ was shown to take place via electrophilic attack by $Ru^{IV}{=}O^{2+}$.[84] A stepwise reaction with the initial formation of Ru^{III} followed by slower formation of Ru^{II} as the solvento complex was observed. The overall reaction is shown in eq 7.

Oxidation of 9,10-dihydroanthracene (DHA), xanthenes, and fluorene by $[(bpy)_2(py)Ru^{IV}O]^{2+}$ in acetonitrile produces oxygenated, dehydrogenated, or radical-coupled products (eq 9).[87] Oxidation of DHA/DHA-d_4 showed a kinetic isotope effect of $k_H/k_D \geq 35 \pm 1$, implying that initial hydrogen-atom abstraction to form radicals takes place in the mechanism.



(7)

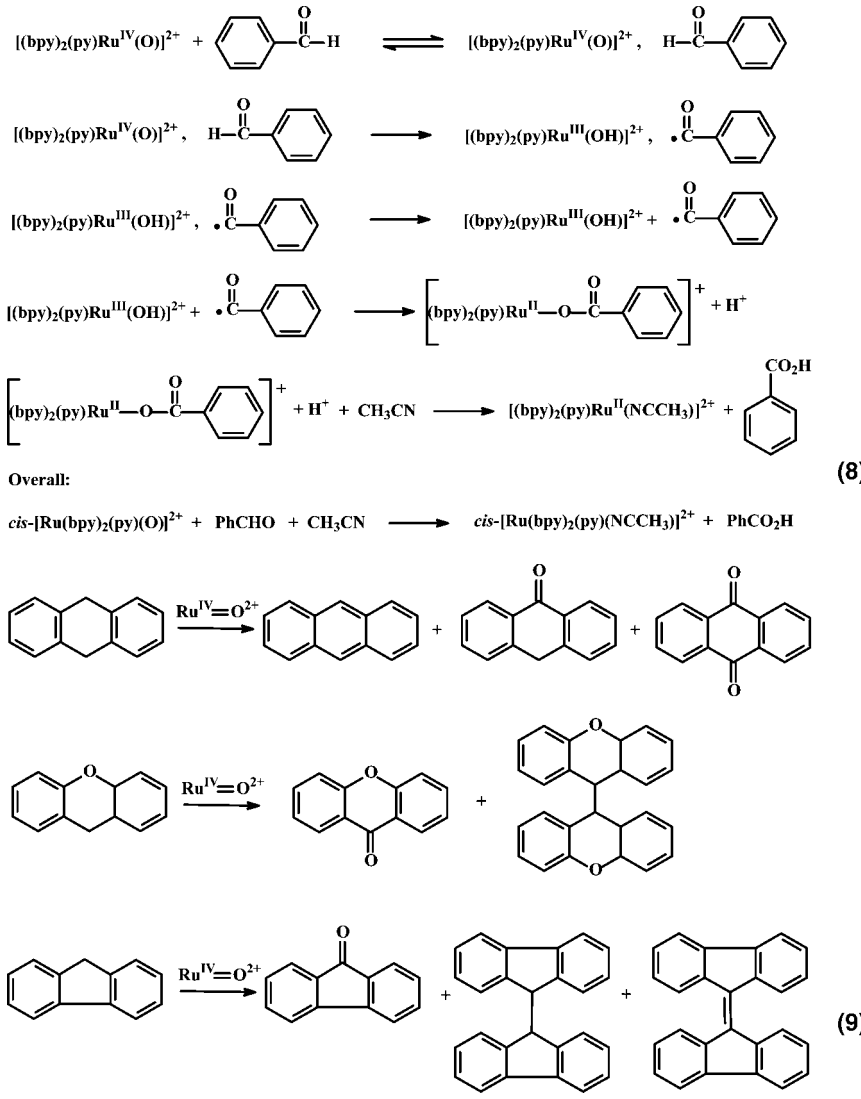
Benzaldehyde was obtained as the sole product upon oxidation of benzyl alcohol by *trans*-$[Ru^{VI}(trpy)(O)_2(L)]^{2+}$ (L is H_2O or CH_3CN) in acetonitrile and water.[85] The rate law is first order in both alcohol and Ru complex in both solvents. In acetonitrile, sequential $Ru^{VI} \rightarrow Ru^{IV}$ and $Ru^{IV} \rightarrow Ru^{II'}$ steps occur. ^{18}O labeling experiments showed that the oxygen atom of the oxo group transfers to benzyl alcohol. A mechanism involving coordination of the alcohol followed by O atom insertion into a benzylic C−H bond is proposed.

The mechanism of oxidation of benzaldehyde and several of its derivatives by polypyridyl oxo complexes, that is, *cis*-$[Ru^{VI}(bpy)_2(py)(O)]^{2+}$, *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ and $[Ru^{VI}(tpy)(bpy)(O)]^{2+}$, has been studied.[86] For the key redox step, in the oxidation of benzaldehyde hydrogen atom (H•) transfer was proposed and supported by several lines of evidence. Kinetic isotope effects, $k_{C-H}/k_{C-D} = 8.1 \pm 0.3$ in CH_3CN, 9.4 ± 0.4 in H_2O, and 7.2 ± 0.8 in D_2O, were moderate; compared to *cis*-$[Ru^{VI}(bpy)_2(py)(O)]^{2+}$ in the oxidation of benzaldehyde by *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ the rate constant decreased only by a factor of ~5 in acetonitrile and ~8 in water; rather than *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$, *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ appeared as the initial product; and in the oxidation of a series of aldehydes the ρ value (-0.65 ± 0.03) was small.

According to the proposed mechanism, in the absence of O_2, first reactants preassociate, then H-atom transfers to $Ru^{IV}{=}O^{2+}$ to make $Ru^{III}{-}OH^{2+}$ and PhC−O, and $Ru^{III}{-}OH^{2+}$ captures PhC−O to make $Ru^{II}{-}OC(O)Ph^+$ and H^+, and finally solvolysis produces *cis*-$[Ru^{II}(bpy)_2(py)(NCCH_3)]^{2+}$ or the aqua complex and the carboxylic acid (eq 8).

On the basis of the formed products; radicals dimerize, disproportionate, and are trapped by the oxidant. There is a good correlation between the rate constants for the initial hydrogen atom transfer and the strength of the C−H bond being activated.

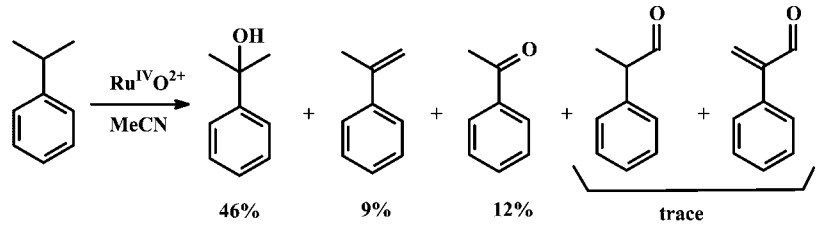
The same mechanism applies to the oxidations of cyclohexene, indene, cumene, ethylbenzene, and toluene.



(8)

(9)

Although the oxidation of cumene by $[(bpy)_2(py)Ru^{IV}O]^{2+}$ was proposed to occur via nucleophile-assisted hydride transfer,[81] reexamination of the kinetics showed that the rate of oxidation is not accelerated by nucleophiles.[86,88] Instead, the data suggested that initial hydrogen atom transfer from the weak benzylic C−H bond in cumene to $[(bpy)_2(py)Ru^{IV}O]^{2+}$ takes place as shown in Scheme 22. Trapping of the cumyl radical by ruthenium complexes and epoxidation of the α-methylstyrene intermediate explain the various observed products (eq 10).



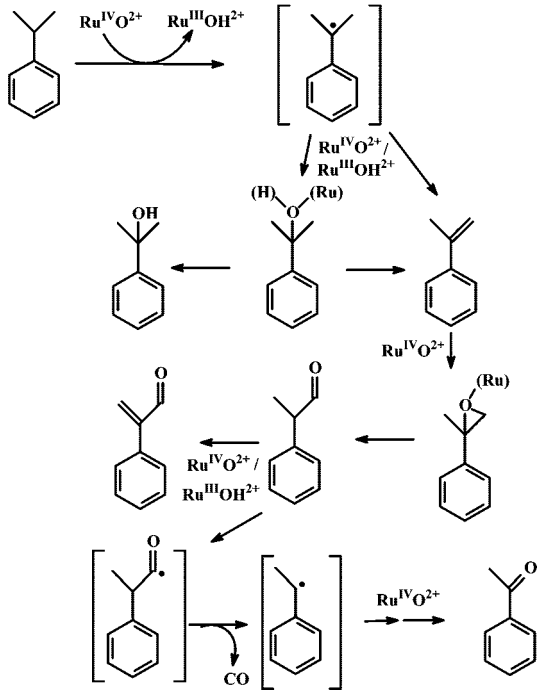
(10)

Kinetics of oxidation of NADH analogues 10-methyl-9,10-dihydroacridine ($AcrH_2$) and *N*-benzyl 1,4-dihydronicotinamide (BNAH) by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ also showed that the mechanism involves hydrogen atom transfer rather than hydride transfer.[78] The rate law is first order in both $AcrH_2$ and *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ with $k = (5.7 \pm 0.3) \times 10^3\ M^{-1}\ s^{-1}$ at 25 °C, and a large kinetic isotope effect, $k_{AcrH_2}/k_{AcrD_2} = 12 \pm 1$, is observed. In addition, under an atmosphere of O_2 the oxidation of $AcrH_2$ occurs significantly faster, suggesting the intermediacy of the acridinyl radical AcrH˙. According to the proposed mechanism (Scheme 23), after initial hydrogen atom abstraction, by electron transfer the acridinyl radical rapidly reacts and gives $AcrH^+$ or by C−O bond formation it leads to AcrO.

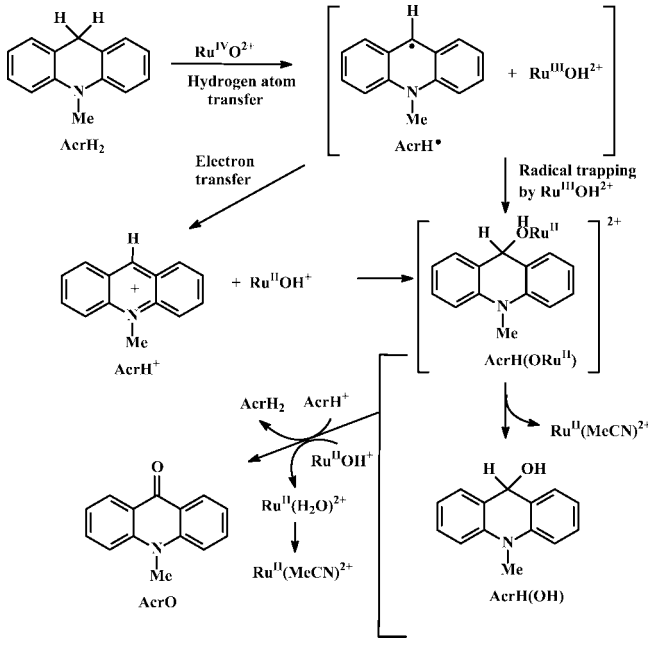
8. C−H Bond Activations by Group IX Metal Oxo Compounds

The first side-on superoxo complex was synthesized by magnesium reduction of the cobalt halides $Tp^{tBu,Me}Co^{II}X$

Scheme 22. Proposed Mechanism for Oxidation of Cumene by $[(bpy)_2(py)Ru^{IV}O]^{2+}$



Scheme 23. Proposed Mechanism of $AcrH_2$ Oxidation of $Ru^{IV}O^{2+}$ under Anaerobic Conditions



($Tp^{tBu,Me}$ = hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borate, X = Cl, I) under nitrogen atmosphere, followed by exposure of a pentane solution of $Tp^{tBu,Me}Co(N_2)$ to an excess of dioxygen as shown in Scheme 24.[89] The crystal structure of this dioxygen complex, $Tp^{tBu,Me}Co(O_2)$, was reported.

Although rigorously dried solvent (THF) was used, both reactions of $Tp^{tBu,Me}Co(N_2)$ with O_2 and $Tp^{tBu,Me}Co(N_2)$ with $Tp^{tBu,Me}Co(O_2)$ resulted in significant amounts of $Tp^{tBu,Me}$-CoOH. When the latter reaction was performed in toluene-d_8, no incorporation of the deuterium into the hydroxyl group was detected by IR spectroscopy. However, by mass spectroscopy some incorporation of the deuterium into the *tert*-butyl groups of the $Tp^{tBu,Me}$ ligand in the $Tp^{tBu,Me}$CoOH was observed. Therefore, a mechanism involving hydrogen atom abstraction from *tert*-butyl groups of the Tp ligand by a metal-oxo group (presumably a cobalt bis(μ-oxo))[90] was proposed.

By employing the less hindered $Tp^{iPr,Me}$ ligand (i.e., hydridotris(3-isopropyl-5-methylpyrazolyl)borate) on cobalt, formation of $Tp^{iPr,Me}Co(O_2)$ and C−H bond activation of the ligand have been observed directly.[91] First, $Tp^{iPr,Me}Co^{II}I$ was reduced by Mg in THF under N_2 to yield $[(Tp^{iPr,Me}Co^{I})_2(\mu\text{-}N_2)]$. Then, by reacting $[(Tp^{iPr,Me}Co^{I})_2(\mu\text{-}N_2)]$ with CO, $Tp^{iPr,Me}Co^{I}(CO)$ was obtained. The reaction of $Tp^{iPr,Me}$-$Co^{I}(CO)$ with O_2 afforded carbonate complex $[(Tp^{iPr,Me}$-$Co^{II})_2(\mu\text{-}\eta^2, \eta^2\text{-}CO_3)]$ when carried out in solution, but pure $Tp^{iPr,Me}Co^{II}(O_2)$ when carried out in the solid state. In solution, $Tp^{iPr,Me}Co^{II}(O_2)$ decomposed with concomitant release of O_2 and formed $[(Tp^{iPr,Me}Co^{II})_2(\mu{-}OH)_2]$ along with uncharacterized paramagnetic species. Acid hydrolysis of this mixture followed by addition of excess NH_3 (aq) and extraction with ether yielded 3-isopropyl-5-methylpyrazole and dehydrogenated pyrazole in 9:1 ratio (Scheme 25). In the thermal decomposition of $Tp^{iPr,Me}Co^{II}(O_2)$, a transient intermediate of $[(Tp^{iPr,Me}Co^{II})_2(\mu\text{-}O_2)]$ is observed by ^{1}H NMR spectroscopy. Because of the importance of this intermediate in O_2 activation and ligand functionalization, it was independently synthesized (Scheme 26). Later, in a separate report, $[\{Tp^{iPr,Me}Co(O_2)\}_2]$ was proposed as another intermediate which was observed by ^{1}H NMR at low temperature and characterized by X-ray crystallography.[92]

Kinetic studies of the decomposition of $[(Tp^{iPr,Me}Co^{II})_2(\mu$-$O_2)]$ revealed a first-order rate law with $k_1(281\ K) = 2.27(3) \times 10^{-3}\ s^{-1}$, and a k_H/k_D of 22(1) was measured when $Tp^{iPr,Me}$-d_3 was utilized. Therefore, it was concluded that C−H bond activation was involved in the rate-determining step and that the KIE and the activation pareameters provided evidence for hydrogen atom tunneling. On the basis of the results and observations, a mechanism is proposed where alkyl radicals are generated by hydrogen atom abstraction from the isopropyl groups of the $Tp^{iPr,Me}$ ligands. These radicals disproportionate to isopropyl and isopropenyl substituents in the hydroxide complex (Scheme 25).

Dinuclear bis(μ-oxo) iridium(III) complex $(CpIr(\mu\text{-}O))_2$, was synthesized by treatment of air-stable (trishydroxy)diiridium cation with lithium diisopropylamide in toluene at 25 °C.[93] Addition of 2 equiv of phosphine (PPh_3 or P(*p*-tol)$_3$) to this bis-μ-oxo compound produced the unsymmetrically bridged dinuclear iridum oxo compounds (**10**) (Scheme 27).

The transfer of the H atom from a C−H bond to an oxygen atom receptor was observed upon heating compounds **10a,b** in benzene or toluene solution without added reagents.

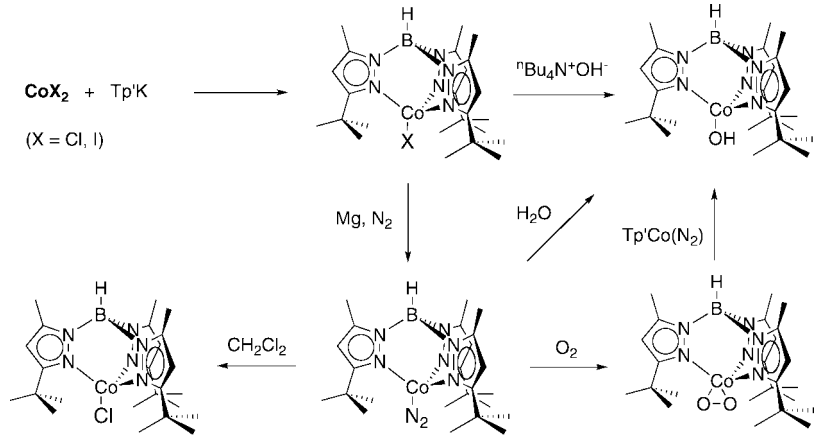
9. C−H Bond Activations by Group X Metal Oxo Compounds

The first aliphatic ligand hydroxylation by a $[Ni_2(\mu\text{-}O)_2]$ complex has been reported by Itoh et al.[94] The formation and decay of $[\mathbf{L}^x{}_2Ni_2(\mu\text{-}O)_2]$ were monitored by spectroscopy. Tridentate ligands $\mathbf{L}^X$ (X = OMe, Me, H, Cl) (see Figure 5) were employed.

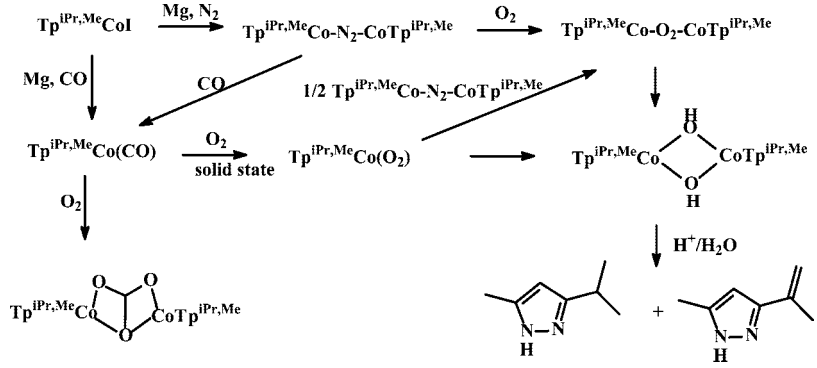
The rate-determining hydrogen abstraction (k_d) followed by hydroxyl rebound was suggested as the mechanism of ligand hydroxylation in $[(\mathbf{L}^XNi^{III})_2(\mu\text{-}O)_2]^{2+}$ complex (Scheme 28).

Dinuclear $Ni^{III}(\mu\text{-}O)_2$ compound $[\{Tp^{Me2,X}Ni^{III}\}_2(\mu\text{-}O)_2]$ ($Tp^{Me2,X}$ = hydrotris(3,5-dimethyl-4-X-1-pyrazolyl)-

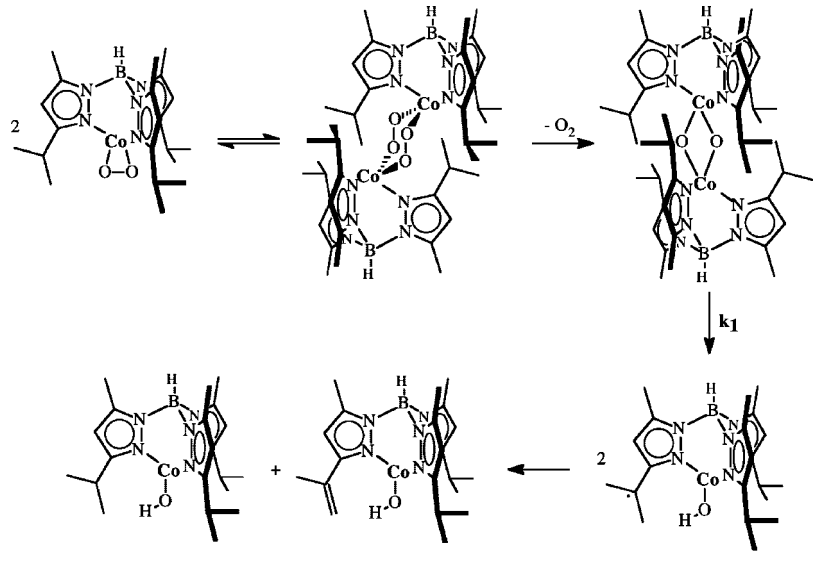
Scheme 24. Synthesis and Reactivity of the First Side-on Superoxo Complex, $Tp^{tBu,Me}Co(O_2)$



Scheme 25. Formation of $Tp^{iPr,Me}Co(O_2)$ and C−H Bond Activation of the Ligand



Scheme 26. Mechanism of the decomposition of $Tp^{iPr,Me}Co^{II}(O_2)$, involving C−H activation by a Co(III) bis(μ-oxo) complex



borate; X = Me, H, Br), was synthesized by 1:1 reaction of $[\{Tp^{Me2,X}Ni^{III}\}_2(\mu\text{-}OH)_2]$ with H_2O_2.[95] A series of $Tp^{Me2,X}$ ligands renders the isolation and structural characterization possible by stabilizing this thermally unstable Ni^{III} complex. Upon thermal decomposition of $[\{Tp^{Me2,X}Ni^{III}\}_2(\mu\text{-}O)_2]$, oxidation of the saturated hydrocarbyl substituents of the Tp ligand occurs. Hydrogen atom abstraction from the primary C−H bond of the methyl substituents mediated by $[\{Ni^{III}(Tp^{R})\}_2(\mu\text{-}O)_2]$ was reported as the rate-determining step because large k_H/k_D values were obtained from the first-order decomposition rates of the Tp^{Me3} and $Tp^{(CD_3)_2,Me}$ derivatives of $[\{Tp^{Me2,X}Ni^{III}\}_2(\mu\text{-}O)_2]$. By following the exact same synthetic procedure, cobalt analogues of these dinuclear $Ni^{III}(\mu\text{-}O)_2$ compounds were prepared. Toward the oxidation reaction, $Ni^{III}(\mu\text{-}O)_2$ compound is 10^3 time more reactive than the Co analogue.

Reactions of bis(μ-oxo) dinickel(III) compounds with external substrates such as 2,4-di-*tert*-butylphenol, 2,6-di-*tert*-butylphenol and 1,4-cyclohexadiene proceeded with oxidation of the substrates and concomitant formation of the corresponding diphenol derivatives and benzene, respectively.[96] In these oxidation reactions, second-order rate constants of 1.08 (for the reaction of 2,4-di-*tert*-butylphenol), 1.66×10^{-2} (for the reaction of 2,6-di-*tert*-butylphenol), and

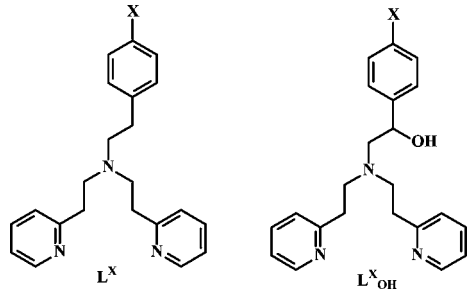


Figure 5. Tridentate ligands $\mathbf{L}^{X}$ (X = OMe, Me, H, Cl) and $\mathbf{L}^{X}_{OH}$.

$1.19 \times 10^{-1}\ M^{-1}\ s^{-1}$ (for the reaction of 1,4-cyclohexadiene) were measured. The reactions were performed in a temperature range from −50 to −70 °C, where ligand hydroxylation was negligible. On the other hand, triphenylphosphine and thioanisole were not oxidized under these conditions.

When a *m*-xylyl ligand system (Figure 6) was employed, aromatic ligand hydroxylation did not occur. Adopting a dinucleating ligand with a longer alkyl strap (Figure 6) enhanced the thermal stability of the $[Ni_2(\mu\text{-}O)_2]$ complex significantly.

When $[Ni_2(OH)_2(Me_2\text{-}tpa)_2]^{2+}$ (Me_2-tpa = bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine) (Figure 7) was reacted with H_2O_2, oxidation of a methylene group of the Me_2-tpa ligand to give an N-dealkylated ligand and oxidation of a methyl group to give a ligand-based carboxylate and an alkoxide were reported.[97] From this oxidation reaction various intermediates including the bis(μ-oxo) dinickel(III)

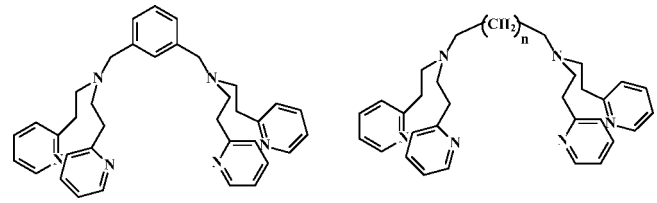
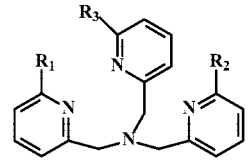


Figure 6. *m*-Xylyl ligand system and a dinucleating ligand with a longer alkyl strap.



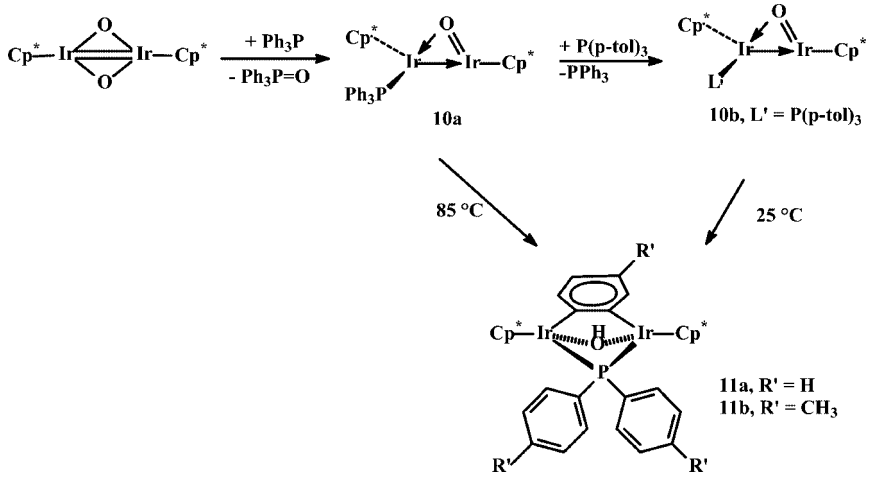
	R_1	R_2	R_3
Me_3-tpa:	CH_3	CH_3	CH_3
Me_2-tpa:	CH_3	CH_3	H

Figure 7. Me_2-tpa: bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine.

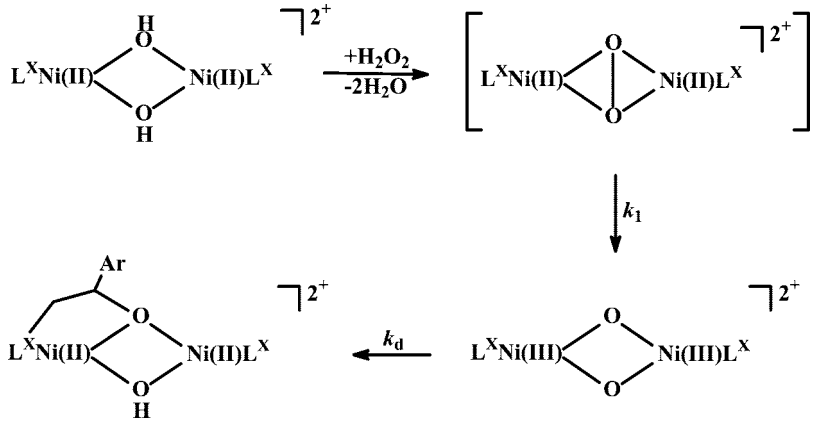
species ($[Ni_2(O)_2(Me_2\text{-}tpa)_2]^{2+}$) have been isolated and characterized.

An N-dealkylated ligand Me-dpa ((6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine) and a coupled ligand dimer (Me-tpa-CH_2)$_2$ were obtained upon thermal decomposition of $[Ni_2(O)_2(Me_2\text{-}tpa)_2]^{2+}$ under N_2. The formation of (Me-tpa-CH_2)$_2$ implies the intermediacy of Me-tpa-$CH_2^{\bullet}$ radical, which is probably generated via H-atom abstraction by the oxo group (Scheme 29). An isotope-labeling experiment showed that (Me-tpa-CH_2)$_2$ forms via intramolecular coupling, which implies that the oxygen rebound is slower than

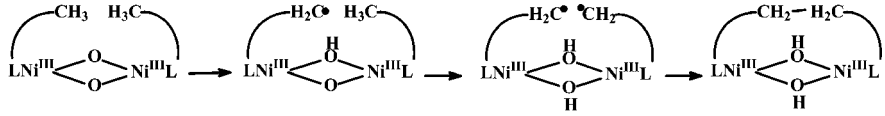
Scheme 27. Transfer of H Atom from a C−H Bond to an Oxygen Atom Receptor



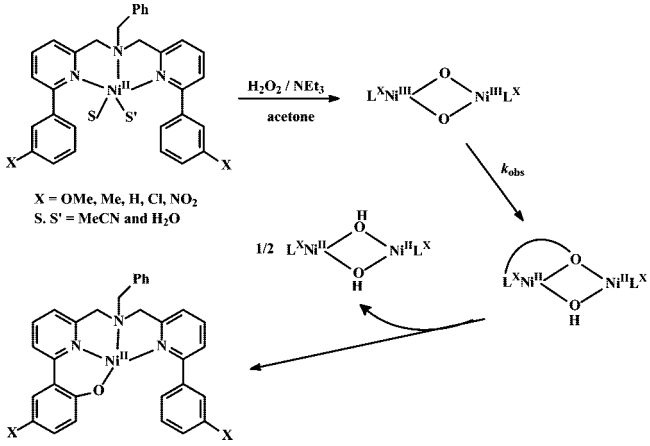
Scheme 28. Mechanism of Ligand Hydroxylation of $[(L^{X}Ni^{III})_2(\mu\text{-}O)_2]^{2+}$ Complex



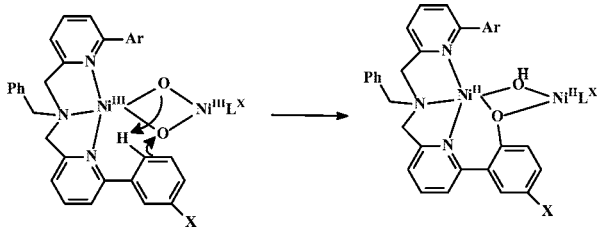
Scheme 29. Thermal Decomposition of $[Ni_2(O)_2(Me_2\text{-tpa})_2]^{2+}$ under N_2



Scheme 30. Bis(μ-oxo)dinickel(III) Intermediates Result in Mononuclear Nickel(II)-phenolate Compounds



Scheme 31. Reaction of $[Ni_2^{III}(\mu\text{-}O)_2(L^X)_2]$ to (μ-Phenoxo)(μ-hydroxo)dinickel(II), an Electrophilic Aromatic Substitution



that observed for various high-valent bis(μ-oxo)dimetal compounds.

The reaction of $[Ni^{II}(L^X)(CH_3CN)(H_2O)](ClO_4)_2$, where L = *N,N*-bis[(6-*m*-substituted-phenylpyridin-2-yl)methyl]benzylamine and X = OMe, Me, H, Cl, NO_2, with H_2O_2 in acetone produced bis(μ-oxo) dinickel(III) complexes, $[Ni_2^{III}(\mu\text{-}O)_2(L^X)_2]$, formation of which was confirmed by UV−vis and resonance Raman spectroscopy.[98] The $Ni^{III}_2(\mu\text{-}O)_2$ intermediates result in mononuclear nickel(II)-phenolate compounds via aromatic ligand hydroxylation. The intermediate (μ-phenoxo)(μ-hydroxo)dinickel(II) was observed in the last step (Scheme 30).

In the reaction of $[Ni_2^{III}(\mu\text{-}O)_2(L^X)_2]$ to (μ-phenoxo)(μ-hydroxo)dinickel(II), based on the kinetic studies, an electrophilic aromatic substitution mechanism was proposed, where C−O bond formation and C−H bond activation occur at the same time (Scheme 31).

An arene hydroxylation of the ligand (H-L-H = 1,3-bis[bis(6-methyl-2-pyridylmethyl)aminomethyl]benzene) coordinated to a bis(μ-oxo)dinickel(III) core has recently been reported by Suzuki et al.[99] Reaction of a green acetonitrile solution of the bis(μ-hydroxo)dinickel(II) complex, $[Ni_2(OH)_2(H\text{-}L\text{-}H)]^{2+}$, with one equivalent of H_2O_2 at −40 °C produced a brown species which was assigned to be bis(μ-oxo) dinickel(III) complex $[Ni_2(O)_2(H\text{-}L\text{-}H)]^{2+}$, by spectroscopy. Thermal decomposition of $[Ni_2(O)_2(H\text{-}L\text{-}H)]^{2+}$ in acetonitrile afforded $[Ni_2(O)_2(H\text{-}L\text{-}OH)]^{2+}$, that is, the xylyl linker of the ligand was hydroxylated (Scheme 32).

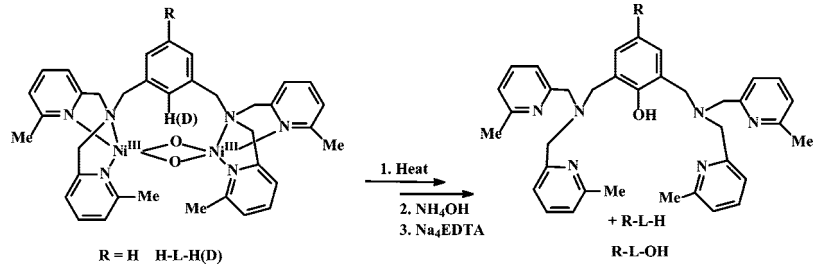
Almost identical rate constants (i.e., KIE ≈ 1) were obtained in the reactions of $Ni_2(O)_2(H\text{-}L\text{-}H)]^{2+}$ and $Ni_2(O)_2(H\text{-}L\text{-}D)]^{2+}$, suggesting that H-atom abstraction from the xylyl linker is not the rate-determining step. Electrophilic aromatic substitution is suggested as the mechanism of this oxidation.

10. C−H Bond Activations by Group XI Metal Oxo Compounds

The first example of the intermolecular C−H bond activation of external substrates such as $AcrH_2$ and CHD by a bis(μ-oxo) dicopper(III) complex has been reported.[100] The reaction of acetone solutions of $[Cu^I(\mathbf{L}^{Py1Bz})(CH_3CN)]PF_6$ ($\mathbf{L}^{Py1Bz}$ = *N*-ethyl-*N*-[2-(2-pyridyl)ethyl]-α,α-dideuterio-benzylamine (Figure 8)) with O_2 at −94 °C produced bis(μ-oxo) dicopper(III) complex **12**.

When external substrates $AcrH_2$ and CHD were reacted with an acetone solution of **12** at −94 °C, quantitative formation of oxidation products $AcrH^+$ and benzene, respectively, was observed. Two important results were found in the kinetic studies of these oxidation reactions: (I) in the reaction of **12** with $AcrH_2/AcrD_2$, a large KIE of 22.7 was found, suggesting the involvement of a tunneling hydrogen-atom transfer process in the rate-determining step of the C−H bond activation, and (II) second-order dependence on **12** was found in these oxidation reactions, suggesting the disproportionation of two molecules of **12** to form one molecule of (μ-oxo)(μ-oxylradical)dicopper(III) (**13**) and one molecule of bis(μ-oxo)Cu(II)Cu(III) (**14**) (Scheme 33). Since **13** is a rather active species for the H-atom abstraction from the substrates, second-order dependence on **12** can be explained. Formation of a tetranuclear copper-oxo complex from two molecules of **12** would also be consistent with the kinetic data.

Scheme 32. Arene Hydroxylation of the Ligand (H-L-H = 1,3-bis[bis(6-methyl-2-pyridylmethyl)aminomethyl]benzene) of a Bis(μ-oxo)dinickel(III) Compound



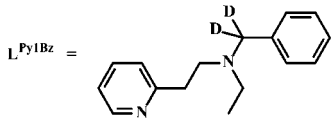
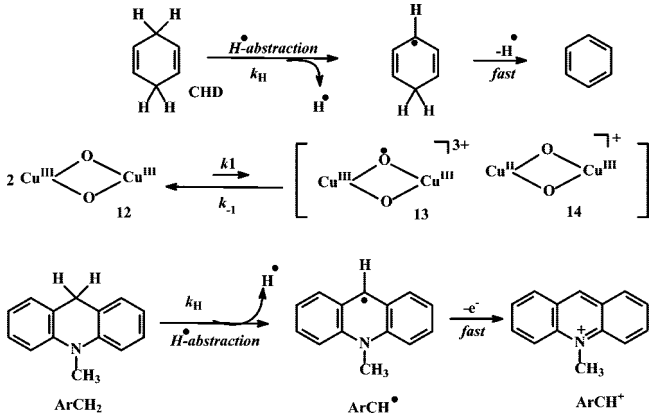
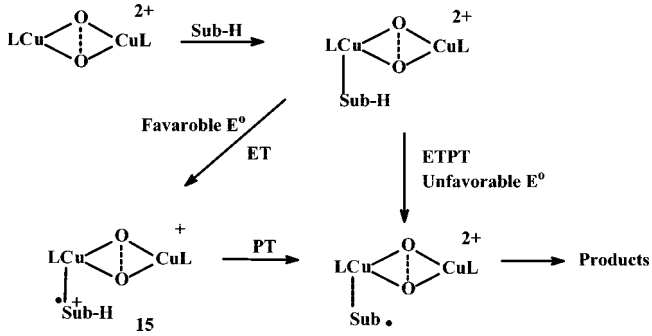


Figure 8. L^{Py1Bz} = *N*-ethyl-*N*-[2-(2-pyridyl)ethyl]-α,α-dideuteriobenzylamine.

Scheme 33. Oxidation of External Substrates $AcrH_2$ and CHD by Bis(μ-O)dicopper(III) (12) Complex



Scheme 34. Oxidations of Various Substrates by a Series of Copper−Dioxygen Adducts



Oxidations of various substrates by a series of copper-dioxygen adducts $[\{Cu^{II}(MePY2)^R\}_2(O_2)][B(C_6F_5)_4]_2$ (R= H, MeO, and Me_2N) have been studied.[101] It was found that thermodynamics do not always determine the reactivity because while THF (C−H BDE ∼ 92 kcal/mol)[102] undergoes C−H bond activation, toluene (C−H BDE ∼ 89 kca /mol)[103] or 9,10-dihydroanthracene (C−H BDE ∼ 78 kcal/mol)[104] does not show any reactivity with $[\{Cu^{II}(MePY2)^R\}_2(O_2)](B(C_6F_5)_4)_2$. The authors have corrected their previous report, which initially described the oxidation of 9,10-dihydroanthracene by this copper-oxo compound.[105,106]

Clear evidence for substrate coordination to one of the two copper centers was provided (Scheme 34). It was found that a stepwise ET/PT process is dominant when thermodynamic driving forces for electron transfer from substrate to **15** are only moderately unfavorable. When thermodynamic forces are very unfavorable, the concerted ETPT process is significant.

A hydroperoxo-copper(II) complex with a dibenzylamino substrate (R-$N(CH_2Ph)_2$) showed oxidative N-debenzylation along with formation of PhCH=O.[107] The reaction pathway and the substrate are shown in Scheme 35. According to the proposed mechanism, $[(L^{N(CH_2R')_2})Cu^{II}(OOH)]^+$ (L is shown in Scheme 35) undergoes HAT from the substrate giving alkoxide and an iminium radical cation via a possible formation of a high-valent $Cu^{II}-O^{\cdot}$ (or $Cu^{III}=O$). Via a facile nucleophilic attack of a second equivalent of the hydroperoxide anion, an further oxidized amide is formed. Since a $Cu^{II}(OR)$ complex forms also in the reaction of Cu^{I}/PhIO, formation of a high-valent copper-oxo (a cupryl) reactive intermediate was suggested and the existence of this intermediate was supported by ESI-MS data.

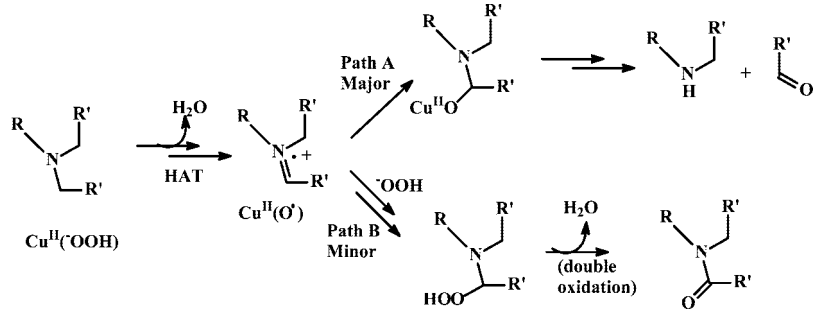
N-dealkylation reactions of bis(μ-oxo) dicopper complexes $[(LCu)_2(\mu\text{-}O)_2](ClO_4)_2$ (L = 1,4,7-tribenzyl-(L^{Bn_3}), 1,4,7-triisopropyl-(L^{iPr_3}), and 1,4-diisopropyl-7-benzyl-1,4,7-triazacyclononane (L^{iPr_2Bn})) were reported.[108] N-dealkylated ligands and aldehydes or ketones, which derive their oxygen atom from the bis(μ-oxo) dicopper center, were produced in these reactions as shown in Scheme 36, where all the possible pathways are outlined. Hydroxyl rebound or a concerted mechanism were proposed.

The N-dealkylation reaction shown here is analogous to monooxygenase reactions carried out by various metalloenzymes such as cytochrome P450, dopamine β-monooxygenase, and peptidyl glycine α-amidating monooxygenase. The observed first-order kinetics, the results of H/D- and $^{16}O/^{18}O$-isotope labeling experiments, large KIEs, and activation parameters supported direct, intramolecular attack of the bis(μ-oxo) dicopper center at the ligand C−H bond during the rate-determining step. Magnitude and temperature dependence of the KIEs implied tunneling in the C−H bond cleavage step.

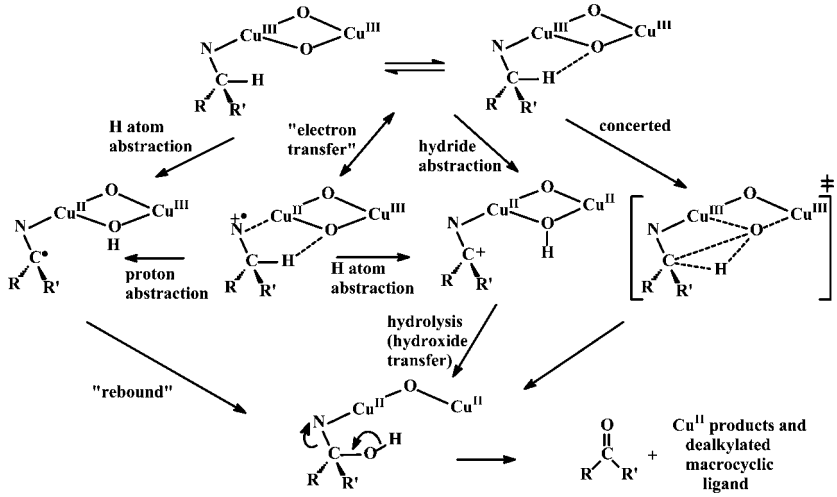
The reactivity of dicopper(I) complexes of α−α′-bis(4,7-diisopropyl-1,4,7-triazacyclononan-1-yl)-*p* and *m*-xylene (*p*- and *m*-XYL^{iPr_4}) ligands (Figure 9) with O_2 has been examined by spectroscopy and rapid stopped-flow kinetics.[109]

When *p*-XYL^{iPr_4} is utilized with Cu(I), upon oxygenation only bis(μ-oxo)dicopper(III) was observed, which subsequently underwent oxidative N-dealkylation of its isopropyl groups. However, when *m*-XYL^{iPr_4} is bound to the dicopper(I) complex, both bis(μ-oxo)dicopper(III) and ($\mu-\eta^2:\eta^2$-peroxo)-dicopper(II) were observed upon oxygenation, the latter of which afforded a product resulting from hydroxylation of the bridging arene.

Scheme 35. Reaction Pathway of Oxidative N-Debenzylation on a Hydroperoxo-copper(II) Complex with a Dibenzylamino Substrate (R-$N(CH_2Ph)_2$)



Scheme 36. N-Dealkylation Reactions of Bis(μ-oxo) Dicopper Complexes



Heterobimetallic CuPt and CuPd bis(μ-oxo) complexes have been prepared as shown in Scheme 37.[110] These complexes were characterized by spectroscopic data and DFT calculations. The oxo ligands in the $[Cu(\mu\text{-}O)_2Pt]^+$ core behave as bases and nucleophiles as opposed to the electrophilic oxo groups in a more typical $[Cu_2(\mu\text{-}O)_2]^{2+}$ core. The mixed-metal core, $L^{Me2}Cu(\mu\text{-}O)_2Pt(PPh_3)_2$ is a competent one-electron oxidant; it oxidatively couples 2,4-di-*tert*-butylphenol or 2,4-di-*tert*-butylphenolate. It also shows significantly higher reactivity than the homometallic dicopper analogue $(L^{Me2}Cu)_2(\mu\text{-}O)_2$.

The oxidative decarboxylation pathway for substrate oxidations by iron(II)-α-ketocarboxylate species in enzymes and model complexes[59,111−114] is extended to copper analogues.[115] By treatment of $[Cu(Mes)]_4$ with benzoyl or mesitoyl formic acid, followed by addition of the N-donor ligand, copper(I)-α-ketocarboxylate complexes (**16**−**19**) were synthesized as shown in Scheme 38.

Reaction of these copper(I)-α-ketocarboxylate complexes with O_2 resulted in decarboxylation and arene-substituent hydroxylation. The mechanism of this reaction was probed by calculations and novel copper-oxo species ($[Cu^I-OOC(O)R]$ and $[Cu^{II}-O^{-\bullet} \leftrightarrow Cu^{III}=O^{2-}]^+$) were claimed to appear as highly reactive intermediates (see Scheme 39).

The reaction of copper(I) complexes of sterically hindered the tetradentate tripodal ligands bis(6-methyl-2-pyridylmethyl)(2-pyridylethyl)amine (Me_2-etpy, see Figure 10) and its methylene-deuterated version (d_4-Me_2-etpy) with O_2 at −80 °C in acetone generated bis(μ-oxo)dicopper(III) complexes $[Cu_2(\mu\text{-}O)_2(Me_2\text{-}etpy)_2]^{2+}$ and $[Cu_2(\mu\text{-}O)_2(d_4\text{-}Me_2\text{-}etpy)_2]^{2+}$, respectively.[116]

Thermal decomposition of $[Cu_2(\mu\text{-}O)_2(Me_2\text{-}etpy)_2]^{2+}$ proceeded via N-dealkylation, where the C−H bond activation was suggested to be the rate-determining step because the deuterated ligand d_4-Me_2-etpy greatly stabilizes the bis(μ-O)dicopper(III) complex $[Cu_2(\mu\text{-}O)_2(d_4\text{-}Me_2\text{-}etpy)_2]^{2+}$.

The reaction of copper(II) supported by a β-diketiminate ligand (Figure 11) without substituent on the α-carbon (R_2), with H_2O_2 generated the bis(μ-O)dicopper(III) intermedi-

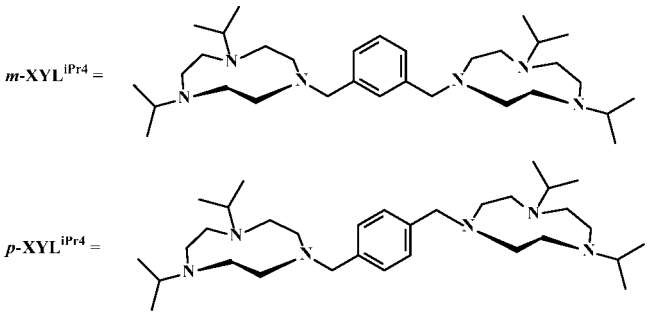
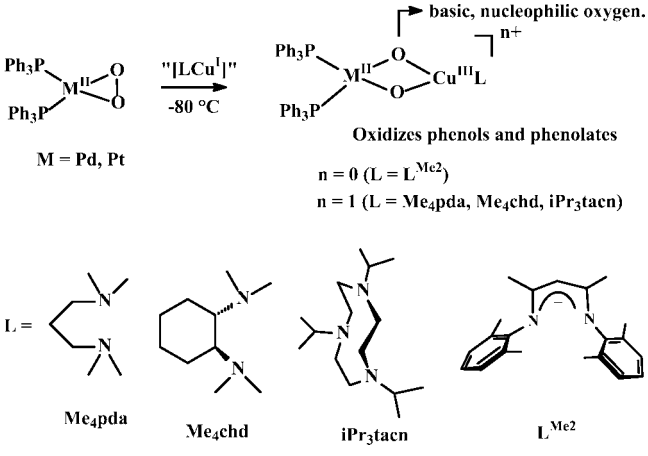
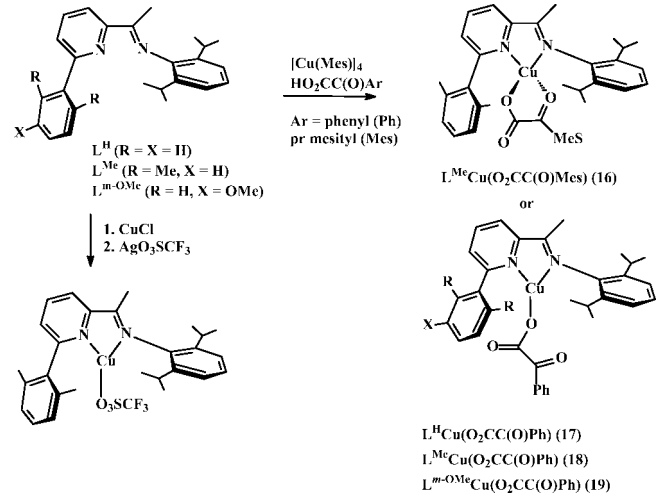


Figure 9. *p*- and *m*-XYL^{iPr_4} ligands: α−α′-bis(4,7-diisopropyl-1,4,7-triazacyclononan-1-yl)-*p* and *m*-xylene.

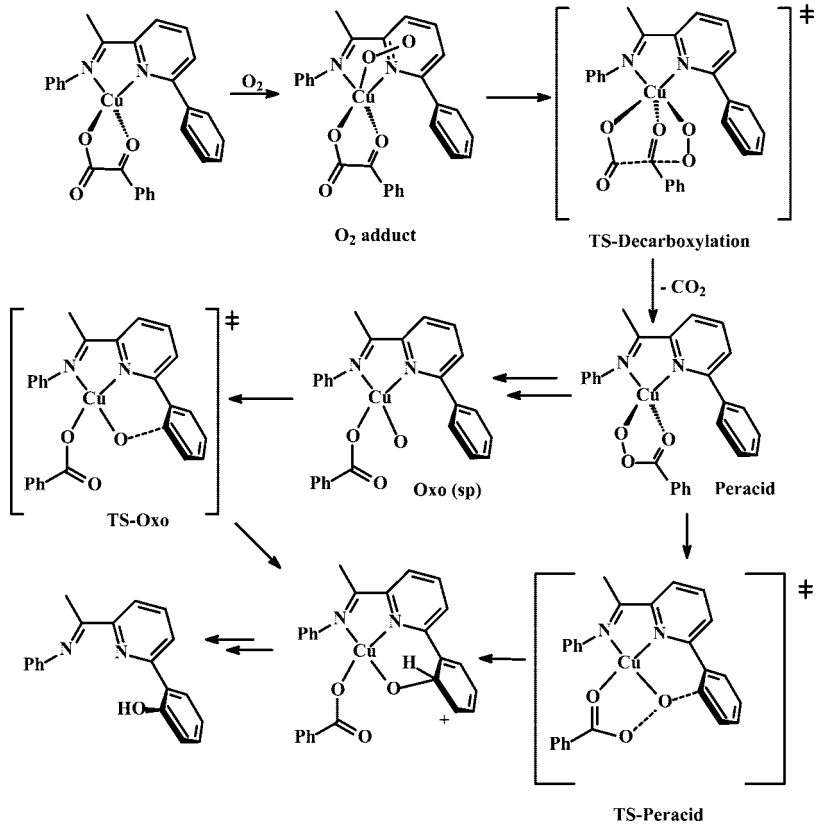
Scheme 37. Preparation of Heterobimetallic CuPt and CuPd Bis(μ-oxo) Complexes



Scheme 38. Synthesis of Copper(I)-α-ketocarboxylate Complexes (11−14)



Scheme 39. Computationally Supported Mechanisms of O_2-Induced Decarboxylation



ate.[117] However, when R2 was methyl, bis(μ-oxo)dicopper(III) intermediate was not produced but a mononuclear copper(III) side-on peroxo compound was observed. Such a reactivity difference was attributed to the steric effect of the alkyl substituents of the ligand backbone.

High catalytic activity of the oxygenation of alkanes with H_2O_2 was observed when the β-carbon was substituted by electron withdrawing groups (R_1 = NO_2 or CN) and R_2 = H. Therefore both steric and electronic effects of the ligand substituents were critical for the catalytic activity of the β-diketiminatocopper(II) complexes.

A series of Cu(I) compounds, [Cu(MeCN)(Et_3CY)]SbF_6, [Cu(MeCN)(iBu_3CY)]SbF_6 and [Cu(MeCN)(Bn_3CY)]SbF_6, supported by *cis,cis*-1,3,5-triaminocyclohexane derivatives (R_3CY, R = Et, iBu, and Bn) (Figure 12), has been synthesized.[118] Their reactions with O_2 at −105 to −80 °C in CH_2Cl_2 or THF produced the corresponding bis(μ-oxo)dicopper(III) intermediates, $[Cu_2(\mu\text{-}O)_2(Et_3CY)_2]^{2+}$, $[Cu_2(\mu\text{-}O)_2(iBu_3CY)_2]^{2+}$ and $[Cu_2(\mu\text{-}O)_2(Bn_3CY)_2]^{2+}$, respectively.

While thermal decompositions of $[Cu_2(\mu\text{-}O)_2(iBu_3CY)_2]^{2+}$ and $[Cu_2(\mu\text{-}O)_2(Bn_3CY)_2]^{2+}$ in THF proceeded via an intramolecular mechanism resulting in N-dealkylation and formation of aldehyde, respectively, heating of $[Cu_2(\mu\text{-}O)_2(Et_3CY)_2]^{2+}$ oxidized THF to generate 2-hydroxy tetrahydrofuran and γ-butyrolactone. This reactivity difference is explained by the steric repulsion, which is lowest in $[Cu_2(\mu\text{-}O)_2(Et_3CY)_2]^{2+}$, thereby facilitating the interaction between the $Cu_2(\mu\text{-}O)_2$ core and exogenous substrate THF.

The reaction of copper(I) precursor $^{O}LCu^{I}$, supported by the anisole containing polypyridylamine ligand ^{O}L (see Figure 13), with O_2 at −80 °C in noncoordinating solvents generated the dicopper(II)-μ-peroxo complex $[\{^{O}LCu^{II}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2)]^{2+}$.[119]

An unusual C−H bond activation was observed in the oxidation reactions of toluene and ethylbenzene with

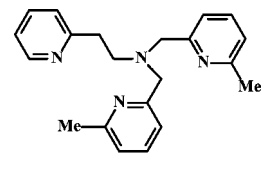


Figure 10. Sterically hindered tetradentate tripodal ligand bis(6-methyl-2-pyridylmethyl)(2-pyridylethyl)amine (Me_2-etpy).

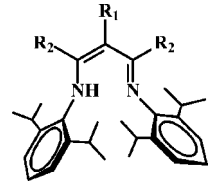


Figure 11. β-Diketiminate ligand.

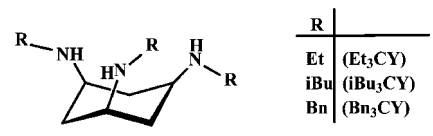


Figure 12. *cis,cis*-1,3,5-Triaminocyclohexane derivatives (R_3CY, R = Et, iBu, and Bn).

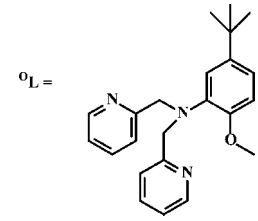


Figure 13. Anisole-containing polypyridylamine ligand, ^{O}L.

$[\{^{O}LCu^{II}\}_2(O_2)]^{2+}$, resulting in benzaldehyde and an acetophenone/1-phenylethanol mixture, respectively. For the oxidation of toluene, a KIE of 7.5 ± 1 was found, indicating that the rate-determining step is the α-H-atom abstraction from the alkylbenzene.

11. C−H Bond Activations by Group XII Metal Oxo Compounds

Zn, Cd, or Hg oxo compounds cleaving C−H bonds have not been encountered to date.

12. Conclusions

As might have been expected, significant reactivity with C−H bonds is observed for those oxo species that are significantly destabilized by occupied d-orbitals (i.e., possessing d^n configurations with $n = 4$ or higher). Only then is the metal oxo multiple bond sufficiently weakened to render alternatives, such as the formation of hydroxo groups, energetically competitive. Strongly oxidizing metal oxo groups, whose reduced forms are strongly basic, make strong O−H bonds. It is apparent that these attributes are to be expected from late transition metals; their highest oxidation states are increasingly unstable and population of π-antibonding MOs will polarize the metal oxygen bond.

To a first approximation, the rates of reaction of M═O fragments with C−H bonds seem to increase with decreasing C−H bond strength. Such selectivity parallels radical reactivity, and thus it bodes ill for selective hydrocarbon functionalization because initial functionalization typically weakens the remaining C−H bonds. However, the field is still young, and much remains to be discovered and explained. To wit, nature has developed highly selective C−H bond functionalizations driven by the hydrogen affinity of suitable metal oxo active sites. It is to be hoped that this status report will motivate further studies toward the rational synthesis of equally effective man-made catalysts.

13. Acknowledgments

Our work on the activation of O_2 and the study of C−H activations by multiply bonded ligands (oxo and imido species) has been supported by DOE (DE-FG02-92ER14273).

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