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Direct Partial Oxidations Using Molecular Oxygen – Final report: DOE-UNM-15765

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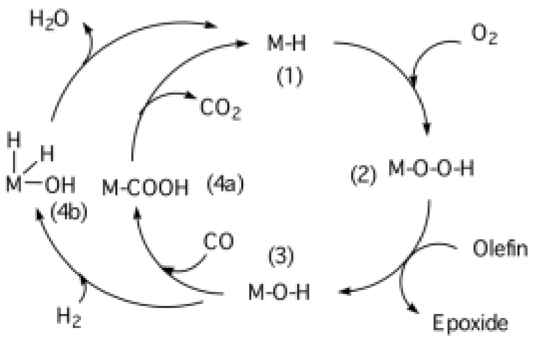
In 2006, Richard A. Kemp (University of New Mexico) and Karen I. Goldberg (University of Washington) formed a team to investigate new strategies to accomplish direct selective aerobic oxidations, with a particular emphasis on the epoxidation of propylene and higher olefins. This DOE-BES funded project was renewed twice and concluded after a no-cost extension earlier this year. Multiple novel strategies involving homogeneous catalyst systems were initiated and investigated during the award. Important fundamental understanding and insight concerning requirements for promotion of aerobic olefin epoxidation was generated. During the tenure of this project, new knowledge was generated concerning the synthesis, characterization and aerobic reactivity of metal hydrides and hydroxides. Key results describing synthetic strategies and optimization of the preparation of mononuclear late metal hydrides were published.[1,2,3,4,5,6,7,8,9] The team reported first example of O_2 insertion into a Pd-H bond,[10] a reaction which had been proposed in the literature but never previously observed. Our experimental investigation of the mechanism was later followed by computational work,[11] and a description of what is now referred to as the Hydrogen Atom Abstraction (HAA) pathway for this reaction has been widely accepted in the community. After investigation of many other late metal hydrides, both experimentally and computationally, the team put together a chapter that included a description of key contributing factors that allow reaction by the HAA mechanism.[12] A brief sampling of other classic papers from our project include hydrogenolysis reactions of late metal hydroxide and alkoxide complexes,[13,14] the synthesis of nickel-hydrides,[4] and the involvement of hemilabile ligands in promoting new reaction pathways.[1,15]

Figure 1. Proposed Catalytic Cycles for Making Epoxides

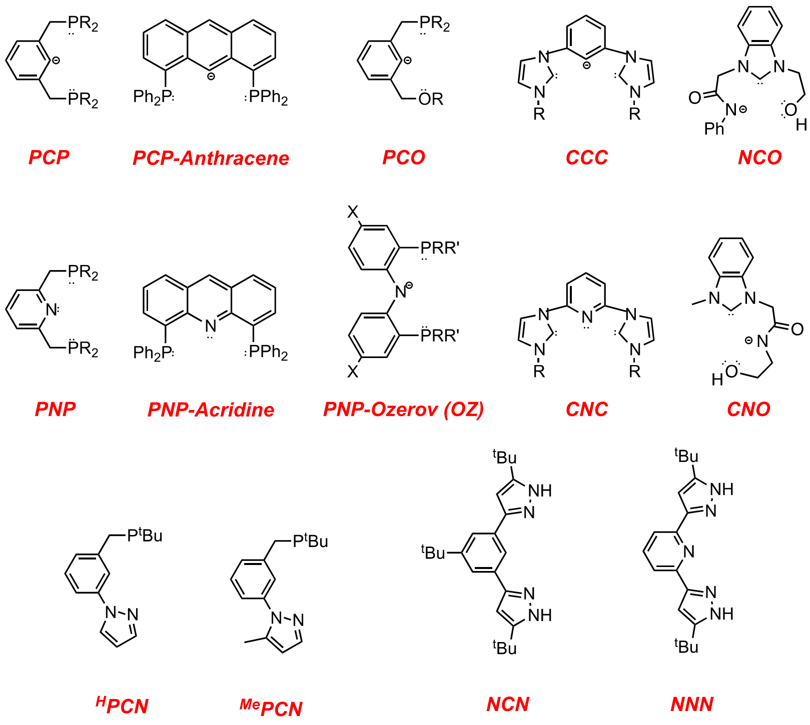


When this first project began, we anticipated catalytic cycles as shown in Figure 1 would be capable of accomplishing the goal of aerobic olefin epoxidation. The cycle involves O_2 insertion into a M-H (1) bond to form a M-OOH species (2), transfer of an oxygen atom from M-OOH (2) to an olefin to form M-OH (3), followed by reaction with either CO to form M-COOH (4a) and elimination of CO_2 regenerating M-H (1) or with H_2 to form $M(H)_2(OH)$ and elimination of H_2O to regenerate M-H (1). Early on, we abandoned the CO route as we determined that the reactions to generate 4a from M-OH complexes (3) and CO were not selective. Further, we found that hydrogenolysis reactions with M-OH (3) led directly to M-H (1) and based on computational evidence the intermediacy of a higher oxidation state species like 4b was deemed unlikely.

Synthesis of Transition Metal Complexes

During the course of this project, the team investigated a wide range of different pincer ligands that vary in complexity and function, and these are shown in Figure 1 along with their common abbreviations. As much of our work was directed towards preparing new, stable metal hydride complexes that would be treated with oxygen, it was a requirement that the supporting ligand framework be both thermally- and chemically-stable to the conditions used in the system. As such, multidentate chelating ligands such as pincers emerged as the ligands of choice. These multidentate ligands afforded the ability to vary the rigidity and hence, stability, of the resulting complexes. Furthermore, the metal-ligand complexes we prepared from them also were resistant to reaction with water. In general, we used these to first prepare metal halide complexes (M-X), as we generally synthesized the M-H via the M-X precursor. We found and documented over the course of this project that the transformation of a late transition metal (Group 9 or 10) M-X bond

Figure 1. Examples of Ligand Backbones Used to Prepare Catalyst Precursors

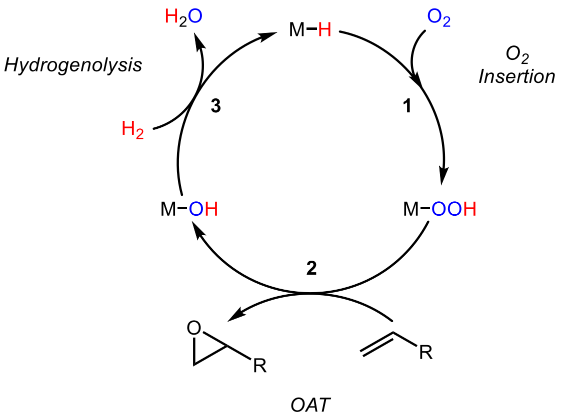


to a M-H bond is seldom trivial or straightforward, and our studies on transforming M-X to M-H bonds have been of significant interest to the organometallic chemistry community.

While there were several forays into other metals on this project, most of our work focused on the late transition metal complexes for one primary reason - to avoid systems where the metals might be too "oxophilic". This is required as the catalyst cycle shown in Scheme 1 requires a M-O bond to break during the addition of an "O" atom to the substrate (between **2** and **3**), and the resulting M-OH requires a M-O bond to be broken in the generation of water to regenerate the M-H catalyst (between **4b** and **1**).

Mechanistic Studies of Reactions

During this award, we carried out extensive studies of the individual steps in the proposed reaction sequence in order to identify the factors that encourage or limit each transformation within the cycle, the goal being to optimize the entire cycle under similar reaction conditions. Our detailed kinetics and mechanistic experimental studies were complemented by extensive computational analyses exploring the potential intermediates and transition state species. From these investigations, we learned a significant amount about the fundamental organometallic reactions that make up the anticipated cycle (reproduced in Scheme 2 with our improved understanding of the reactions developed over the course of this project). The steps as shown in Scheme 2 are: selective insertion of molecular oxygen into a metal-hydride bond (step 1), OAT to substrate from a metal hydroperoxide species (step 2), and hydrogenolysis of a metal-hydroxide (step 3). Critical in terms of the wider impact of our studies is that these fundamental reactions may be applicable to catalytic aerobic oxidations of a range of substrates (not just olefins) in systems under development by other catalysis researchers. Notably, fundamental steps pictured in **Scheme 2** have been proposed in reported catalytic reactions for other transformations.



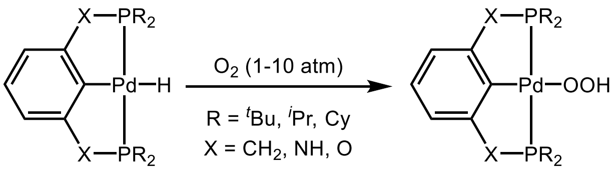
Scheme 2. Targeted catalytic epoxidation cycle.

In the course of this project, we successfully demonstrated all three steps of the targeted catalytic cycle in **Scheme 2** with a variety of late transition metal complexes.[12] However, OAT was observed to alternative substrates, rather than olefins. As noted above, we concentrated on late metal systems due to the anticipated low oxophilicity that will be needed to allow for catalytic turnover with regeneration of a M-H species. Below we describe the results of our investigations into the mechanistic details of the individual steps and, in particular, illustrate how we identified the requirements (what is needed at the metal center and the reaction conditions) to accomplish each of these transformations.

Step 1: Activation of O_2, forming a metal-hydroperoxide complex

The reactivity of organotransition-metal complexes with oxygen has historically been viewed as unfavorable with anticipation of uncontrolled and unselective decomposition. The ubiquitous use of gloveboxes and Schlenk and high vacuum lines in organometallic laboratories well illustrates how it has been the primary goal of organometallic chemists to keep oxygen *away* from their metal complexes. However, if organometallic complexes are to be used successfully in oxidation catalysis, we need to understand how they react with oxygen. Due to the efforts of this lab and others in the field of late transition metal oxidation catalysis, general trends in O_2 activation at homogeneous metal centers are only now beginning to emerge.

In 2006, we reported the first unambiguous O_2 insertion into a Pd^{II}-H bond using (^{tBu}PCP)Pd-H to form the hydroperoxo (^{tBu}PCP)Pd-OOH.[10] Notably, O_2 insertion into a Pd^{II}-H bond has been postulated as a key step for oxygen activation in numerous Pd catalyzed aerobic oxidations. We further demonstrated this reaction to be general with respect to other modified ^{R}PCP systems, with different R-groups on the phosphine (^{t}Bu, ^{i}Pr, Cy) as well as with different bridging groups on the pincer arm (X = CH_2, NH, O) (**Scheme**).[5,6,7,8,12,] Mechanistic and computational studies of the reaction of (^{tBu}PCP)Pd-H with O_2 were consistent with a pathway involving abstraction of the H-atom by O_2, and rapid radical recombination to yield the final Pd^{II}-OOH product.[11] This is referred to as a hydrogen atom abstraction (HAA) pathway. As homolytic cleavage of the Pd^{II}-H bond is implicated here, it was proposed that stronger *trans* donors should allow more facile abstraction by O_2. This theory was supported by computational work in which the transition state energy of the oxygen-insertion reaction was calculated as the ligand *trans* to the hydride was varied.[16] The Pd^{II}-H bond lengths increased with stronger *trans* donor ligands and a direct relationship was found between increased Pd^{II}-H bond length and favorable H-atom abstraction (**Figure 1**): *the longer the Pd^{II}-H bond, the easier the H-atom was abstracted by O_2.*



Scheme 3. Insertion of O_2 into the Pd^{II}-H bond of (^{R}PCP)Pd-H derivatives by HAA.

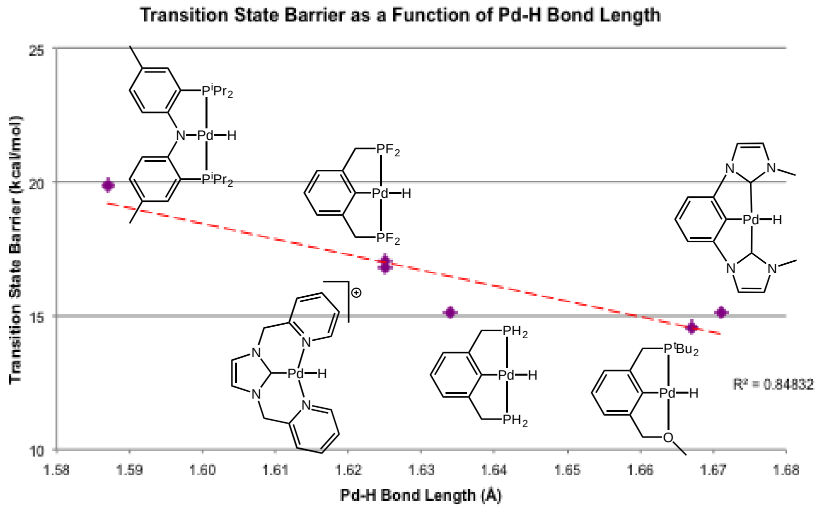
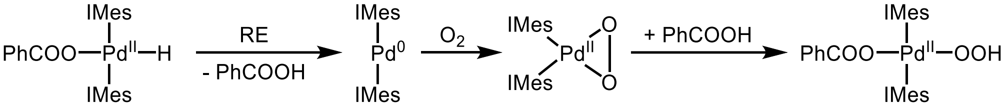


Figure 1. Comparison of calculated Pd-H bond length and transition state energy for O_2 insertion at 6 pincer complexes.

Surprisingly, no reaction was observed with the platinum analog (^{tBu}PCP)Pt-H and O_2 even at high pressure and elevated temperatures.[6] Similarly, we found that the pyridine based cationic species [(^{tBu}PNP)M-H]$^{+}$ (M=Pd, Pt) did not react with O_2, even at elevated temperatures.[2] Examining the M-H stretching frequencies of both the Pd^{II} and Pt^{II} cations by IR spectroscopy led us to propose that the pyridine backbone was not a strong enough *trans* donor to the hydride ligand, and therefore the hydride was not sufficiently activated towards cleavage and O_2 insertion ($\nu_{Pd\text{-}H+}$: 1977 cm^{-1}; $\nu_{Pt\text{-}H+}$: 2163 cm^{-1}). For comparison, the M-H stretch for (^{tBu}PCP)Pd-H is at 1730 cm^{-1}. This interpretation is also consistent with the lack of reactivity of O_2 with the (^{tBu}PCP)Pt-H complex ($\nu_{Pt\text{-}H}$= 1917 cm^{-1}). The M-H complexes with the higher stretching frequencies appear to indicate that the M-H bonds are too strong for cleavage by reaction with O_2. Thus, even with a very strong aryl *trans* donor, the Pt^{II}-H bond is evidently too strong for H-atom abstraction. We also investigated the Ni analogs (^{R}PCP)Ni-H (R = ^{t}Bu, ^{i}Pr, Cy). Unfortunately, these reactions of the Ni-H complexes with O_2 were not clean and extensive complex degradation, likely due to the expected weaker M-P bonds, was observed.[5]

Shortly after our work on (^{tBu}PCP)Pd-H, a bis-N-heterocyclic carbene (NHC) Pd^{II} hydride was reported to react with O_2, forming the analogous hydroperoxide complex (**Scheme 4**). Through detailed mechanistic studies, Stahl and coworkers proposed a pathway for the activation of O_2 in which the benzoate and hydride ligand first undergo reductive elimination, forming a Pd^0 intermediate that is oxidized by O_2.[17] The formed η^2-peroxo complex is then protonated by the free benzoic acid, resulting in the final Pd^{II}-OOH complex (**Scheme 4**). This mechanism is referred to as the HX reductive elimination path (HXRE). Furthermore, Stahl and coworkers found that a mechanistic crossover from HXRE to the HAA mechanism occurred when the electron donating capability of the benzoate ligand was increased (modification of the *para* substituent in the aryl ring).[18] Thus, the HXRE mechanism complements the HAA mechanism for hydroperoxide formation, as strong *trans* donors promote HAA, while more withdrawing *trans* groups promote HXRE. The two mechanisms implicated thus far allow for a variety of ligand archetypes to be utilized for the activation of O_2.



Scheme 4. Insertion of O_2 into the Pd^{II}-H bond of $(IMes)_2(PhCOO)Pd$-H by HXRE.

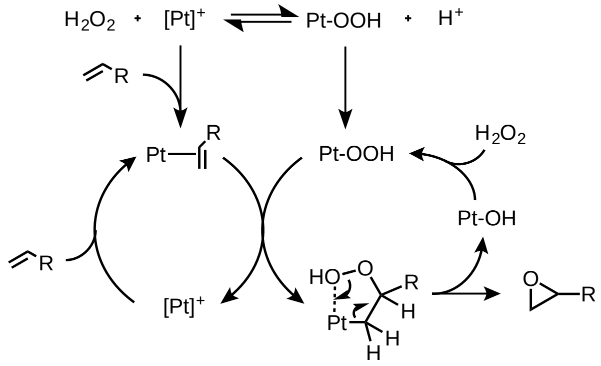
Below is a summary of what we learned about the requirements for O_2 insertion into M-H bonds to form M-OOH complexes:

- HAA mechanism
    - *A strong trans donor is needed to weaken the metal-hydride bond for homolytic cleavage by O_2.*
    - *IR analysis of the M-H stretch provides insight into the relative hydride bond strength and the propensity for reaction via HAA.*
    - *Pt^{II}-H complexes appear inert towards HAA.*
- HXRE mechanism
    - *An appropriate X group that can undergo reductive elimination with the hydride ligand is needed.*
    - *The low-valent metal intermediate must coordinate O_2 to form a peroxo species.*
    - *Supporting ligands must stabilize both the low valent M^n and high valent M^{n+2} geometries, for example, linear/tetrahedral Pd^0 and square planar Pd^{II}.*

Step 2: O-Atom Transfer (OAT) from a Late-Metal Hydroperoxide Complex

The most difficult step in the catalytic cycle shown in **Scheme** has been the transfer of an oxygen atom from the late metal hydroperoxide species to the substrate. The hydroperoxide complexes described above have all been evaluated for O-atom transfer (OAT). As found for other late metal hydroperoxides, (^{tBu}PCP)Pd-OOH decomposes over time to generate (^{tBu}PCP)Pd-OH which confirms that OAT can occur from late transition metal hydroperoxide species.[10] Furthermore, we found that the (^{tBu}PCP)Pd-OOH complex will oxidize substrates such as PPh_3 and ^{t}BuN≡C by OAT producing $O{=}PPh_3$ and ^{t}BuN=C=O, respectively.[5,6] In contrast, no reaction was observed with both electron-rich and electron-poor olefins and a range of (^{R}PCP)Pd-OOH complexes.

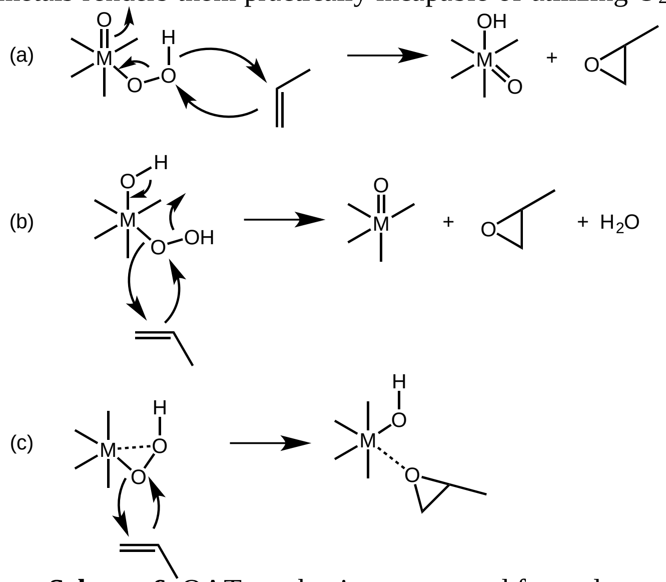
Historically, catalysts for epoxidation have primarily been homo/heterogeneous early transition metals or heterogeneous Ag/Au surfaces. Only a few late metal homogenous hydroperoxide complexes have been observed to transfer oxygen to olefins to form epoxides. For example, in 1984, Strukul and Michelin published the first group 10 homogeneous epoxidation catalyst; it used hydrogen peroxide as the oxidant.[19] They found that Pt^{II} hydroxide or hydride species of the type $(PP)Pt(CF_3)X$ (PP = 1,2-



Scheme 5. Proposed bifunctional catalytic cycle for olefin epoxidation by $[(diphoe)Pt(CF_3)(CH_2Cl_2)]BF_4$.

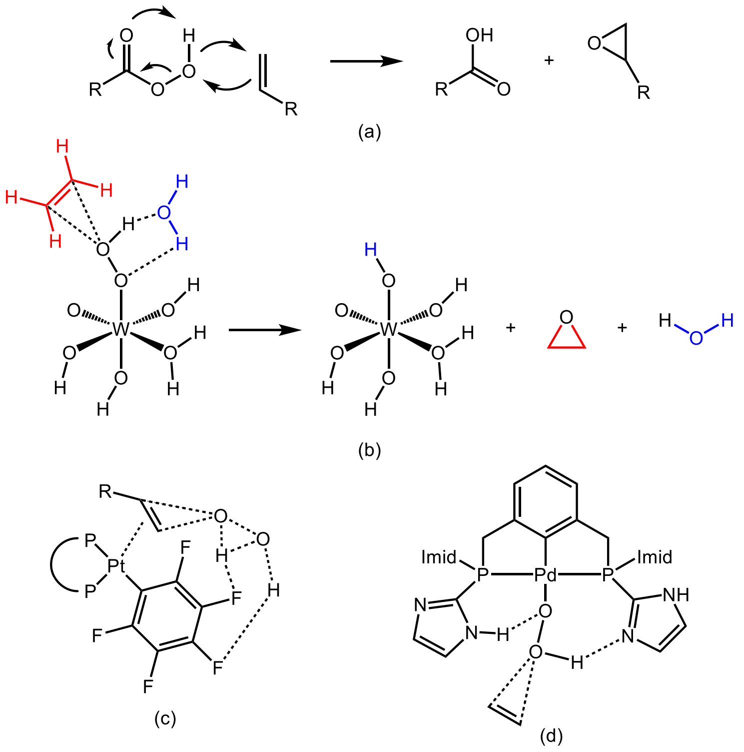
bis(diphenylphosphino)ethane (dppe), *cis*-1,2-bis(diphenylphosphino)ethylene (diphoe), 2 PPh_2Me; X = OH, H) reacted with hydrogen peroxide solutions to form the hydroperoxide $(PP)Pt(CF_3)OOH$, and that this species was capable of epoxidizing propylene and higher terminal olefins. In mechanistic work on this Pt^{II} system, a bifunctional and bimolecular role for Pt was implicated; one Pt^{II} center activates hydrogen peroxide to form a Pt-OOH species, but a second Pt center binds the olefin and activates it toward nucleophilic attack (**Scheme 5**).[20] They found that protic media was a requirement for epoxidation, as solutions like water or alcohols allowed for the dissociation of the nucleophilic HOO^- ion from the Pt^{II} center. This scenario implies that oxygen transfer to an olefin could be accomplished by two metal centers designed individually for the tasks of activating O_2 to form a nucleophilic hydroperoxide species, and of activating an olefin substrate towards nucleophilic attack through coordination. Inspired by these results, we examined the reactions of our MOOH complexes with cationic metal coordinated olefin species but did not observe similar reactivity.

Beyond looking to the isolated examples of late metals that can carry out this reaction for inspiration, we also considered that partial oxidation of olefins to epoxides is currently performed at the industrial scale by early transition metal hydroperoxide complexes. The primary catalyst of choice is a titanium center supported on silicate (catalyst TS-1). A variety of mechanisms by which the epoxidation takes place have been proposed. The most prevalent mechanisms are outlined in **Scheme 6**. Ancillary ligand cooperation has been proposed in assisting OAT of either β or α oxygen to a nucleophilic olefin (**Scheme** , a and b, respectively). The oxophilic nature of the early metal also allows for η^2 coordination of the hydroperoxide moiety, and transfer of the α oxygen to a nucleophilic olefin (**Scheme** , c). In all cases, it should be noted that the olefin acts as a nucleophile, and the oxophilic early metal imparts a high degree of electrophilicity to the hydroperoxide ligand, allowing OAT. However, the same oxophilicity of the early metals renders them practically incapable of utilizing O_2 as the oxidant; the M-O bond is far too inert for catalyst turnover. As such, hydrogen peroxide or alkyl hydroperoxides are utilized to regenerate the active species. As our goal is to use the less expensive, more available, and less hazardous O_2 as an oxidant, late, less oxophilic metals are more attractive. However, as it is the early/middle transition metal centers that show the most proclivity for this OAT step, we can gain inspiration from the mechanisms by which these metals carry out this reaction and use that in the design of our late metal systems. For example, as shown in **Scheme** , additional basic sites and proton movement are often intimately involved in these transfers.



Scheme 6. OAT mechanisms proposed for early M-OOH species.

Proton transfer and/or hydrogen bonding have also been proposed to be important in OAT transformations involving transition metal systems and also organic peracids. **Scheme** reactions a and b illustrate examples of proposed OAT mechanism for early metals where an oxo/hydroxo ligand participates by accepting a proton in the concerted transformation, forming a bound hydroxide or free water molecule, respectively. Epoxidation mechanisms by organic peracids (**Scheme** , a), for example *m*-chloroperbenzoic acid (mCPBA), mimic that shown in **Scheme** , a. Related interactions are proposed in OAT reactions involving middle and late transition metal centers as well. For example, Musaev and coworkers proposed that an adventitious water molecule assisted OAT from a tungsten-hydroperoxide complex by an H-bonding network (**Scheme 7**, b). [21] In their second generation catalyst, Strukul and coworkers propose H-bonding of H_2O_2 with a perfluorophenyl ligand assists in activating the oxidant (**Scheme** , c). Similarly, we have shown via computations that that incorporating H-bonding substituents onto a PCP framework of (^{R}PCP)Pd-OOH significantly reduced the barrier for OAT to olefins. DFT analysis predicted that a PCP variant with imidazole substituents on the phosphine arms could interact with the hydroperoxide ligand on Pd^{II} and assist through hydrogen-bonding to deliver the β-O to a free olefin substrate (**Scheme** , d).[22] The reaction barrier with this imidazole substitute ^{Imid}PCP ligand was calculated to be 8-9 kcal lower than when ^{tBu}PCP was used. We have prepared this ligand but have not as yet attached it to a metal.



Scheme 7. Examples of H-bonding/proton transfer in proposed OAT mechanisms.

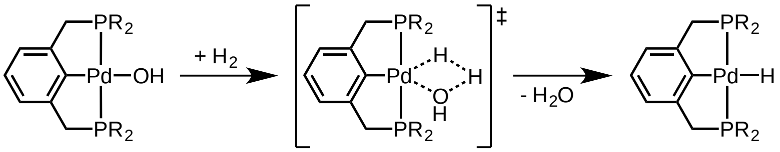
Below is a summary of the requirements for OAT to olefinic substrates from M-OOH or MO(H) species:

- *Umpolung reactivity to activate olefins to nucleophilic attack by HOO$^-$ is possible.*
  - *Protic media assists in solvating HOO$^-$ ions.*
  - *Olefin is activated toward nucleophilic HOO$^-$ attack through coordination to a metal center.*
- *Ligand assisted OAT.*
  - *Supporting ligands can assist in shuttling protons in concerted OAT from M-OOH species.*

Step 3: Hydrogenolysis of a metal-hydroxide to form a metal-hydride and water

After the transfer of an oxygen atom from the metal-hydroperoxide, the metal-hydroxide must be reduced in order to turn the catalyst over. Hydrogenolysis of a metal-hydroxide would yield a metal-hydride and an equivalent of water. In this cycle, water would be the only byproduct. When we began our studies, the hydrogenolysis of a M-O bond lacked significant precedent in the literature. The scarcity of isolable and well characterized mononuclear terminal late metal hydroxides and alkoxides likely limited studies of this reaction. We found that pincer ligands were excellent supporting ligands to allow for the isolation of a variety of Pd-OR species (R = H, alkyl, aryl). Using these complexes, we were able to carry out detailed studies of M-O hydrogenolysis reactions.[13,14] The sterics and tridentate binding of the pincer ligands around the metal inhibited dimerization of the hydroxide species and restricted access to the traditional β-hydride elimination decomposition path for metal alkoxides.

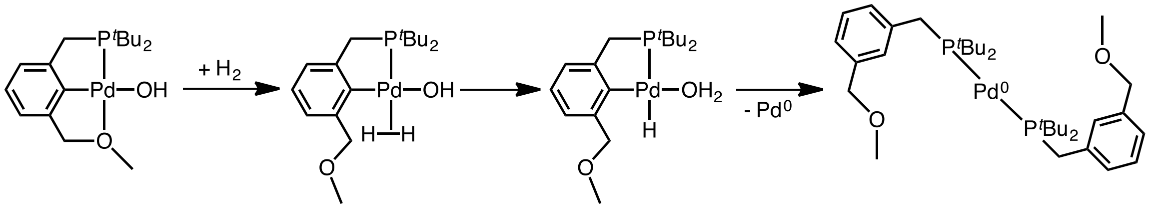
In our early work, we demonstrated that the hydroxide complex (^{tBu}PCP)Pd-OH underwent clean hydrogenolysis under a H_2 atmosphere to produce the hydride (^{tBu}PCP)Pd-H (**Scheme**).[13] Kinetic and mechanistic studies were consistent with a direct reaction of H_2 with the mononuclear (^{tBu}PCP)Pd-OH. Further studies found similar hydrogenolysis reactions with (^{tBu}PCP)Pd-OR (R = alkyl and aryl) with the direction of the reaction (thermodynamics) largely controlled by the acidity of the ROH product.[14] DFT computations suggested that the transition state for hydrogenolysis was a 4-centered interaction, where H_2 deposits across the Pd-O bond (internal electrophilic substitution, IES). This finding emphasizes the importance of an available lone pair on oxygen, as the H-H bond formally breaks heterolytically, delivering H^+ to the hydroxide ligand, and H^- to palladium.



Scheme 8. Hydrogenolysis of (^{tBu}PCP)Pd-OH proceeds through a 4-centered transition state.

This work was followed up with further computational studies on a variety of neutral donor arm aryl-based pincer complexes (NCN, SCS, CCC and OCO).[15] All but the ether based OCO complex followed the same 4-centered transition state. In the (OCO)Pd-OH system, H_2 was found to approach the metal-ether arm first, rather than the hydroxide ligand. No 4-centered transition state similar to the reaction of the other complexes was found. Displacement of the ether arm by H_2 was calculated to occur with minimal energy cost, and after hydrogenolysis, a *cis* hydride aquo complex was computed to be lowest in energy.

We initially sought to introduce a hemilabile pincer arm to allow for olefin coordination and assist in OAT from the M-OOH moiety (**Scheme 2**, step 2). The terminal hydroxide complex (^{tBu}PCO)Pd-OH (**Scheme**) was investigated for hydrogenolysis.[1] However, we found that the ether arm, as described in the computational studies above, opened up *in the hydrogenolysis step*. When the hydroxide complex (^{tBu}PCO)Pd-OH was exposed to an H_2 atmosphere, no hydride species was observed. Instead, the metal was reduced to Pd^0 and a bis-phosphine Pd^0 complex was formed (**Scheme**). Deuterium labeling studies suggested that H_2 displaces the hemilabile ether arm and IES with the hydroxide ligand occurs, forming water and a hydride ligand *cis* to the aryl group (as foreshadowed in the computations[15]). The reaction then continues with C-H reductive elimination of the hydride and the aryl group followed by coordination of a second phosphine ligand to yield the Pd^0 bis-phosphine complex. Similar results were observed in a (PCN^R)Pd-OH system.**Error! Bookmark not defined.** While displacement of an amine arm in (NCN)Pd-OH was computed to be much higher in energy than displacement of an ether arm in (OCO)Pd-OH,[15] the asymmetric nature of the PCN^R ligand still resulted in hemilability.[3] The strong *trans* phosphine moiety weakens the Pd-N bond. When (PCN^{Me})Pd-OH was subjected to H_2, again no hydride was observed and similar to the PCO system, full reduction of the metal was observed, yielding the bis-phosphine complex $(PCN^{Me})_2Pd^0$.



Scheme 9. Reduction of (^{tBu}PCO)Pd-OH under a H_2 atmosphere

Below is a summary of the requirements for hydrogenolysis of M-OR species:

- *Strongly binding pincer ligands that can stabilize both M-OR and M-H species.*
    - *Hemilabile arms should be avoided if a M-H product is desired.*
- *An available lone pair on the -OR ligand is required for H_2 heterolysis.*
    - *A proton is delivered to the -OR ligand while a hydride is delivered to the metal in a concerted activation of H_2.*
- *Other functionality with available lone pairs (-NR_2, -OR) or X-type pincer "arms" on the ligand should be avoided.*

These results and insights into the requirements for the three key reaction steps are currently being applied by the Goldberg group in a new DOE-BES grant in which research on novel strategies for aerobic epoxidation with late transition metals are underway. Kemp continues to interact with the Goldberg team as a valued consultant.

Training of the next generation of scientists

Catalysis will be a key part of all solutions to the significant problems facing our society concerning energy and the environment. This training of the next generation of catalysis scientists will assure an educated and trained workforce ready as we move forward in addressing these important issues. 13 graduate students, 6 postdoctoral associates, 5 undergraduates and a visiting researcher all received training and research mentorship under this award.

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[1] Fulmer, G. R.; Kaminsky, W.; Kemp, R. A.; Goldberg, K. I. "Syntheses and Characterization of Palladium Complexes with a Hemilabile "PCO" Pincer Ligand" *Organometallics* **2011**, *30*, 1627-1636.

[2] Bailey, W. D.; Kaminsky, W.; Kemp, R. A.; Goldberg, K. I. "Synthesis and Characterization of Anionic, Neutral, and Cationic PNP Pincer Pd^{II} and Pt^{II} Hydrides" *Organometallics* **2014**, *33*, 2503-2509

[3] Bailey, W. D.; Luconi, L.; Rossin, A.; Yakhvarov, D.; Flowers, S. E.; Kaminsky, W.; Kemp, R. A.; Giambastiani, G.; Goldberg, K. I. "Pyrazole-Based PCN Pincer Complexes of Palladium(II): Mono- and Dinuclear Hydroxide Complexes and Ligand Rollover C-H Activation" *Organometallics* **2015**, *34*, 3998-4010

[4] Suh, H.-W.; Schmeier, T. J.; Hazari, N.; Kemp, R. A. 'Experimental and Computational Studies of the Reaction of Carbon Dioxide with Pincer Supported Nickel and Palladium Hydrides.' *Organometallics* **2012**, *31*, 8225-8236.

[5] Boro, B. J. Investigations of Pincer-Ligated Transition Metal Complexes for the Activation of Molecular Oxygen. Ph. D. Dissertation, University of New Mexico, 2009

[6] Fulmer, G. R. "Investigations of Palladium Pincer Complexes Towards a Catalytic Olefin Epoxidation Process." Ph. D. Dissertation, University of Washington, 2010

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[7] Mrutu, A. “Studies on Group 10 Pincer Carbene Metal Complexes” University of New Mexico, 2010.

[8] Lansing, R. B. Jr. “Investigations into Late Transition Metal Pincer Complexes as Possible Direct Partial Oxidation Catalysts” University of New Mexico, 2010.

[9] Bailey, W. D. “Late Transition-Metal Complexes Supported by Pincer Ligands: Applications in Partial Oxidation Catalysis” Ph. D. Dissertation, University of Washington, 2016

[10] Denney, M. C.; Smythe, N. A.; Cetto, K. L.; Kemp, R. A.; Goldberg, K. I. “Insertion of Molecular Oxygen into a Palladium(II) Hydride Bond” *J. Am. Chem. Soc.* **2006**, *128*, 2508-2509

[11] Keith, J. M.; Muller, R. P.; Kemp, R. A.; Goldberg, K. I.; Goddard, W. A., III; Oxgaard, J. “Mechanism of Direct Molecular Oxygen Insertion in a Palladium(II) Hydride Bond” *Inorg. Chem.* **2006**, 45, 9631-9633.

[12] Bailey, W. D.; Parkes, M. V.; Kemp, R. A.; Goldberg, K. I. *Reactions of Square Planar* d^8 *Pincer Complexes with Oxygen and Hydrogen.* Pincer and Pincer-Type Complexes: Application in Organic Synthesis and Catalysis*;* Szabo, K. J., Ed.; Wendt, O. F., Ed; Wiley-VCH: Weinheim, Germany, 2014; pp 281-298.

[13] Fulmer, G. R.; Muller, R. P.; Kemp, R. A.; Goldberg, K. I. “Hydrogenolysis of Palladium(II) Hydroxide and Methoxide Pincer Complexes” *J. Am. Chem. Soc.* **2009**, *131*, 1346-1347

[14] Fulmer, G. R.; Herndon, A. N.; Kaminsky, W.; Kemp, R. A.; Goldberg, K. I. “Hydrogenolysis of Palladium(II) Hydroxide, Phenoxide, and Alkoxide Complexes” *J. Am. Chem. Soc.* **2011**, *133*, 17713-17726

[15] Parkes, M. V.; Bailey, W. D.; Goldberg, K. I.; Kemp, R. A. “The Effect of the *cis*-Donor in Pincer Ligands on Hydrogenolysis of Pd-OH: A DFT Study” *J. Organomet. Chem.* **2017***, 845,* 165-170.

[16]. Parkes, M. V. A Proposed Palladium-Catalyzed Cycle for the Epoxidation of Alkenes. Ph.D. Dissertation, University of New Mexico, 2012.

[17]. Konnick, M. M.; Stahl, S. S. “Reaction of Molecular Oxygen with a Pd^{II} Hydride to Produce a Pd^{II} Hydroperoxide: Experimental Evidence for an HX-Reductive-Elimination Pathway” *J. Am. Chem. Soc.* **2008**, *130*, 5753-5762.

[18]. Konnick, M. M.; Decharin, N.; Popp, B. V.; Stahl, S. S. “O_2 Insertion into a Palladium(II)-Hydride Bond: Observation of Mechanistic Crossover Between HX-Reductive-Elimination and Hydrogen-Atom-Abstraction Pathways” Chem. Sci. **2011**, 2, 326-330.

[19]. Strukul, G.; Michelin, R. A. Selective Epoxidation of Terminal Alkenes with Diluted Hydrogen Peroxide Catalyzed by Pt-OH Species” *J. Chem. Soc., Chem. Commun.* **1984**, 1538-1539.

[20]. Strukul, G.; Michelin, R. A. “Catalytic Epoxidation of 1-octene with diluted hydrogen peroxide. On the Basic Role of Hydroxo Complexes of Platinum(II) and Related Species” *J. Am. Chem. Soc.* **1985**, *107*, 7563-7569.

[21]. Prabhakar, R.; Morokuma, K.; Hill, C. L.; Musaev, D. G. “Insights into the Mechanism of Selective Olefin Epoxidation Catalyzed by $[\gamma\text{-}(SiO_4)W_{10}O_{32}H_4]^{4-}$. A Computational Study.” *Inorg. Chem.* **2006**, *45*, 5703-5709.

[22]. Muller, R.; Goldberg, K. I.; Kemp, R. *Unpublished Results*.