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Reactions of Late Transition Metal Complexes with Molecular Oxygen

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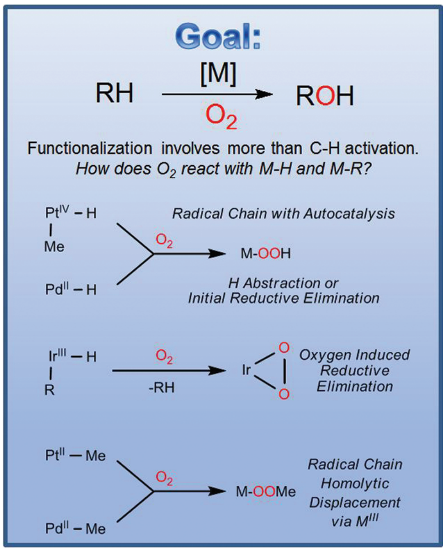
CONSPECTUS



Limited natural resources, high energy consumption, economic considerations, and environmental concerns demand that we develop new technologies for the sustainable production of chemicals and fuels. New methods that combine the selective activation of C–H bonds of hydrocarbons with oxidation by a green oxidant such as molecular oxygen would represent huge advances toward this goal. The spectacular selectivity of transition metals in cleaving C–H bonds offers the potential for the direct use of hydrocarbons in the production of value-added organics such as alcohols. However, the use of oxygen, which is abundant, environmentally benign, and inexpensive (particularly from air), has proven challenging, and more expensive and less green oxidants are often employed in transition-metal-catalyzed reactions. Advances in the use of oxygen as an oxidant in transition-metal-catalyzed transformations of hydrocarbons will require a better understanding of how oxygen reacts with transition metal alkyl and hydride complexes. For alkane oxidations, researchers will need to comprehend and predict how metals that have shown particularly high activity and selectivity in C–H bond activation (e.g. Pt, Pd, Rh, Ir) will react with oxygen.

In this Account, we present our studies of reactions of late metal alkyls and hydrides with molecular oxygen, emphasizing the mechanistic insights that have emerged from this work. Our studies have unraveled some of the general mechanistic features of how molecular oxygen inserts into late metal hydride and alkyl bonds along with a nascent understanding of the scope and limitations of these reactions. We present examples of the formation of metal hydroperoxide species M-OOH by insertion of dioxygen into Pt(IV)–H and Pd(II)–H bonds and show evidence that these reactions proceed by radical chain and hydrogen abstraction pathways, respectively. Comparisons with recent reports of insertion of oxygen into other Pd(II)–H complexes, and also into Ir(III)–H and Rh(III)–H complexes, point to potentially general mechanisms for this type of reaction.

Additionally, we observed oxygen-promoted C–H and H–H reductive elimination reactions from five-coordinate Ir(III) alkyl hydride and dihydride complexes, respectively. Further, when Pd(II)Me_2 and Pt(II)Me_2 complexes were exposed to oxygen, insertion processes generated M–OOMe complexes. Mechanistic studies for these reactions are consistent with radical chain homolytic substitution pathways involving five-coordinate M(III) intermediates. Due to the remarkable ability of Pt(II) and Pd(II) to activate the C–H bonds of hydrocarbons (RH) and form M–R species, this reactivity is especially exciting for the development of partial alkane-oxidation processes that utilize molecular oxygen.

Our understanding of how late transition metal alkyls and hydrides react with molecular oxygen is growing rapidly and will soon approach our knowledge of how other small molecules such as olefins and carbon monoxide react with these species. Just as advances in understanding olefin and CO insertion reactions have shaped important industrial processes, key insight into oxygen insertion should lead to significant gains in sustainable commercial selective oxidation catalysis.

I. Introduction

Molecular oxygen is, in many ways, an ideal oxidant. It is abundantly available, inexpensive (particularly if used directly from air), and environmentally benign. Not surprisingly, many of the most important industrial oxidation processes utilize O_2 as the oxidant.[1] Nevertheless, there are still significant

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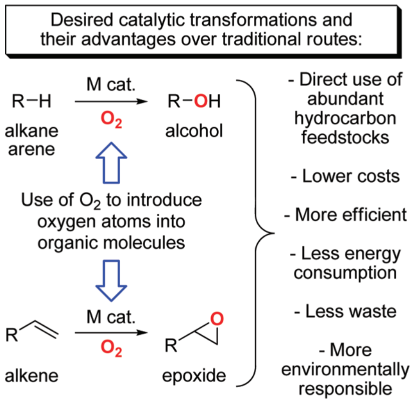
commercial processes that use more expensive and hazardous oxidants. One of the biggest challenges in industrial chemistry is the development of more economically and environmentally sustainable oxidation technologies.[2]

A major difficulty in using dioxygen as a source of oxygen atoms in chemical transformations is that its reactivity is not easily controlled, often leading to overoxidation or low selectivity.[3] In the last decades, organometallic compounds have emerged as powerful catalysts for a wide variety of valuable transformations used in the industrial preparation of chemicals.[2,4] However, combining the high selectivity of these organometallic catalysts with the use of oxygen to produce value-added oxidized organics has proven challenging.[5] A large barrier in the ability to design catalysts that utilize molecular oxygen is a relatively limited understanding of how O_2 reacts with transition metal complexes.

With the goal of developing organometallic catalyst systems that selectively oxidize hydrocarbons with molecular oxygen, our laboratory set out to investigate how metal alkyls and hydrides react with O_2. Surprisingly little was known about such reactions. Our discovery of several unprecedented reactions with oxygen prompted detailed mechanistic studies that have helped to build a framework for how oxygen interacts with organometallic species. Our investigations in this area are the subject of this Account.

SCHEME 1

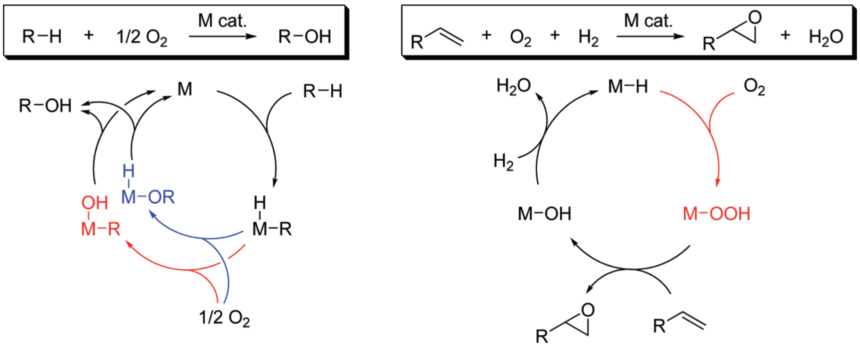


Two transformations in which the reaction of late metal alkyls or hydrides with dioxygen could be particularly useful are the oxyfunctionalization of alkanes and the epoxidation of alkenes (Scheme 1). The current industrial methods of forming organic oxygenates such as alcohols are multistep, energy-intensive processes, and no direct partial alkane oxidations are currently commercially practiced.[4] There are also no industrial processes that use oxygen or air for the epoxidation of alkenes higher than ethylene; current methods for the production of propylene oxide use chlorine, organic peroxides, and hydrogen peroxide as oxidants.[1−4]

The catalytic cycles in Scheme 2 show possible pathways to achieve alkane functionalization and olefin epoxidation using dioxygen. In the alkanes-to-alcohols sequence (Scheme 2, left), oxidative addition of an alkane yields a metal alkyl hydride complex. Insertion of oxygen into the M−H or M−C bond followed by C−O or O−H reductive elimination then leads to the desired product. An epoxidation catalytic cycle involving the insertion of O_2 into a M−H bond can also be envisioned (Scheme 2, right). In this cycle, the metal hydroperoxide formed by O_2-insertion into a M−H bond epoxidizes the olefin. The catalytic cycle is completed by hydrogenolysis of the metal hydroxide.

Our group has contributed detailed mechanistic insight for many of the steps proposed in Scheme 2, including oxidative addition of C−H bonds,[6,7] reductive elimination of C−O bonds,[8,9] and hydrogenolysis reactions.[10,11] Our focus has been on late transition metal complexes as they are especially adept at activating C−H bonds to form metal alkyls and hydrides.[12] In addition, their low oxophilicity is promising for the proposed reactions. Prior to the studies described below, there were very few well-characterized examples of reactions of late transition metal alkyl and

SCHEME 2



hydride complexes with O_2. We set out to document such reactions and determine their mechanisms. The goal of our studies is to develop the mechanistic understanding that will allow the use of oxygen in late transition-metal-catalyzed transformations of organic compounds.

II. A Brief Look at Organic Autoxidations

The insertion of O_2 into M–H and M–R bonds shown in Scheme 2 is similar to the autoxidation of organic compounds which, in its most basic form, involves the insertion of O_2 into the C–H bonds of organic compounds (R–H) to form alkylhydroperoxides (ROOH).[3] It is thus relevant to consider the metal-centered reactions in the context of this well-understood chemistry. To illustrate the similarities and differences between the autoxidation of organics and the new reactions involving metal complexes, the main aspects of the autoxidation of organics are briefly reviewed.

The generally accepted mechanism for autoxidations is a radical chain process consisting of initiation, propagation, and termination steps (Scheme 3). Under sufficient oxygen pressure, the reaction rate is independent of $p(O_2)$ and a simple rate law such as that shown in eq 1 or 2 is observed. Under these conditions, there is a steady-state concentration of ROO• with the rate of initiation R_i equal to that of termination R_t.[3] Notably, mechanistic studies of organic oxidations are typically conducted with rapid stirring to ensure efficient diffusion of O_2 into the solution and in the presence of radical initiators such as 2,2′-azobis(2-methylpropionitrile) (AIBN) to eliminate induction periods and provide reproducible rates.

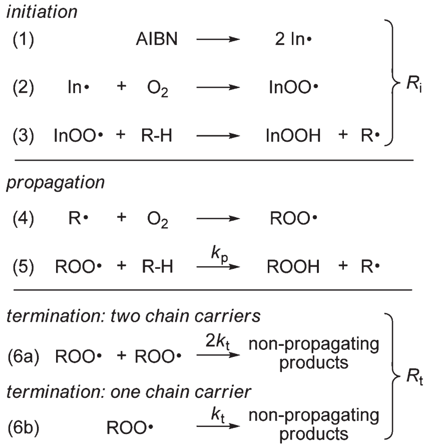
As illustrated in eq 1, the reaction rate is influenced by all three steps (initiation, propagation, and termination). A change in any one of the steps can lead to a change in the rate law. For example, in most studies, the main termination step is the coupling of two peroxyl radicals (step 6a). In this scenario, the reaction exhibits a first-order dependence on [RH] and a half-order dependence on [initiator] (eq 1).[3] In contrast, if the termination involves only one chain carrier (e.g., unimolecular reaction of the chain carrier or its reaction with vessel walls or solvent, step 6b), the rate has a first-order dependence on [initiator] (eq 2).

$$\text{rate} = -\frac{d[O_2]}{dt} = k_p[\text{RH}]\left(\frac{R_i}{2k_t}\right)^{1/2} \tag{1}$$

$$\text{rate} = -\frac{d[O_2]}{dt} = k_p[\text{RH}]\left(\frac{R_i}{k_t}\right) \tag{2}$$

Features of these radical chain mechanisms will be revisited below in our discussion of the reactions of organometallic complexes with oxygen.

SCHEME 3



III. Reaction Between Transition Metal Hydrides and O_2

A. Insertion of O_2 into Pt–H Bonds. One of the first complexes that we examined for reactivity with oxygen was $Tp^*PtMe_2(H)$ (**1**) (Tp* = hydridotris(3,5-dimethylpyrazolyl)-borate). We were very excited to observe a selective insertion of O_2 into the Pt–H bond of **1** to form the crystallographically characterized complex $Tp^*PtMe_2(OOH)$ (**2**) (Scheme 4).[13]

The discovery of this O_2-insertion reaction was particularly exciting because complex **1** is analogous to Pt(IV) dialkyl hydrides formed by oxidative addition of alkanes to Pt(II). The first observation of alkane C–H oxidative addition at a Pt(II) center to generate stable Pt(IV) alkyl hydride complexes was reported with this Tp* ligand set as shown in Scheme 5.[6] Notably, the activation of pentane yielded the *n*-pentyl derivative, which corresponds to the desired selectivity for an alkane-to-linear alcohol process. Thus, the same metal–ligand system can support both the selective oxidative addition of an alkane C–H bond and the incorporation of molecular oxygen.

Preliminary studies of the reaction of **1** with oxygen indicated that oxygen insertion into the platinum–hydride bond probably involved radical intermediates: the reaction was accelerated by light and radical initiators, and inhibited by radical inhibitors.[13,14] The progress of the reaction was easily followed by ^1H NMR spectroscopy, and it was observed that the hydroxide complex $Tp^*PtMe_2(OH)$ (**3**) formed in minor amounts. While high yields of **2** could be obtained when no initiator was present, reaction rates were reproducible only when AIBN was added. In addition, it was determined that, under sufficient pressures of oxygen [$p(O_2) = 5-10$ atm], the reaction rates were independent of $p(O_2)$ (Figure 1a).

With O_2 pressures greater than 5 atm and with AIBN present, reproducible sigmoidal reaction profiles were obtained when the concentrations of **1** and of **2** were plotted with respect to time (Figure 1a). Increasing the amounts of AIBN led to faster reactions, but the retention of the sigmoidal curves indicated that the lower initial rates were not due to induction periods. Such sigmoidal reaction profiles are characteristic of autoaccelerated processes in which species formed during the reactions (intermediates, products, and/or side products) increase the reaction rate.[15]

Addition of the product Tp*$PtMe_2(OOH)$ (**2**) resulted in a considerable increase in the reaction rate, confirming the proposed autoacceleration (Figure 1b). In contrast, the addition of the side-product Tp*$PtMe_2(OH)$ (**3**) resulted in a slightly slower reaction. Thus, the rate law for this process should have the general form rate $\propto k'[\mathbf{1}] + k''[\mathbf{1}][\mathbf{2}]$. The $k'[\mathbf{1}]$ contribution is needed because there has to be some way for the reaction to progress before the autoaccelerating product is generated.

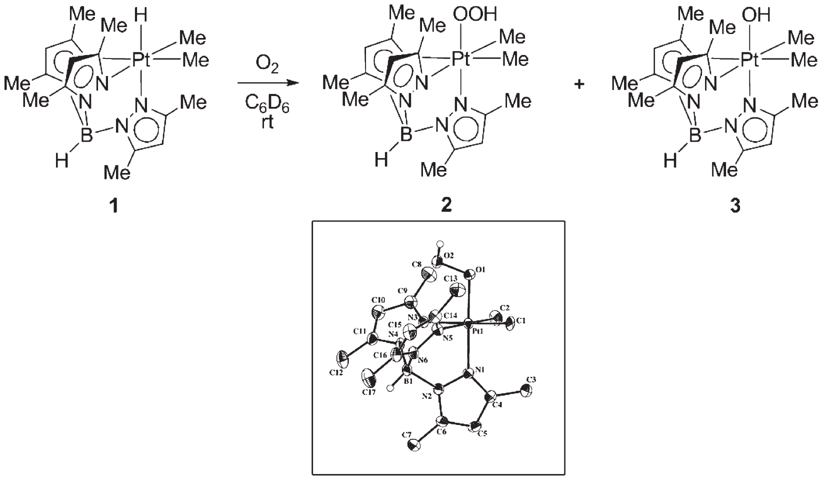
Surprisingly, initial rate studies showed an apparent first-order dependence on [**1**]; doubling the concentration of **1** doubled the instantaneous rate of the reaction. This result was unexpected as an autocatalytic reaction cannot actually be first-order in substrate. To understand this point, consider the case where the reaction would be first-order in the starting material. If the concentration of the starting material were doubled, then halfway through the reaction the concentration of the autoaccelerating product would also double. So for an autocatalytic reaction where the concentration of the starting material was doubled, at 50% conversion the rate should actually quadruple instead of doubling as would be expected for a first-order process.[14]

We were able to determine an empirical rate law that fits all of the available data. This rate law explains the apparent discrepancy of being autocatalytic and displaying an apparent first-order dependence on the starting material concentration as well as the zero- and first-order dependencies observed for O_2 and AIBN, respectively. This empirical rate expression shown in eq 3 was the only one found that numerically fit every kinetic experiment.

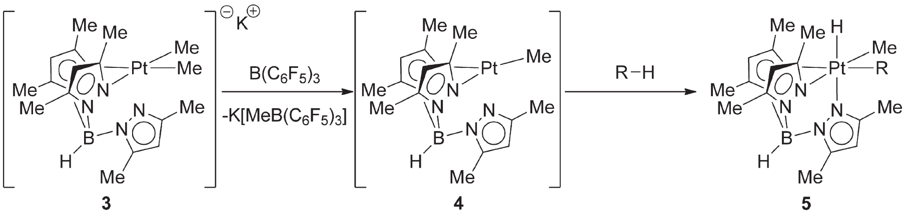
$$\text{rate} = k_1[\mathbf{1}][\text{AIBN}] + k_2\frac{[\mathbf{1}][\mathbf{2}][\text{AIBN}]}{[\mathbf{1}]+[\mathbf{2}]+[\mathbf{3}]} \tag{3}$$

$$\text{rate} = k_p[\mathbf{1}]\left(\frac{R_i}{k_t[\text{Pt}]_{\text{tot}}}\right) \tag{4}$$

SCHEME 4



SCHEME 5



$R = C_6H_5, C_5H_{11}, C_6H_{11}$

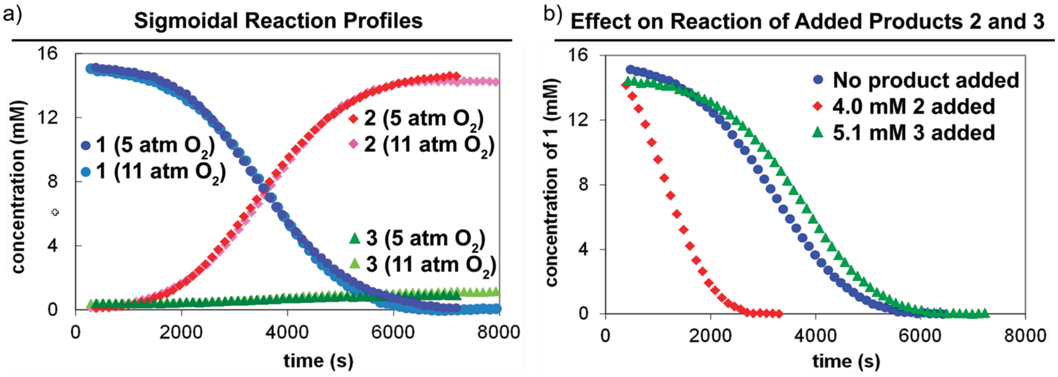


FIGURE 1. Reaction profiles. (a) The autoxidation of **1** ($[\mathbf{1}]_0 = 16$ mM) is independent of the O_2 pressure. 5 atm O_2: **1** (dark blue circles), **2** (red diamonds), **3** (dark green triangles); 11 atm O_2: **1** (light blue circles), **2** (pink diamonds), **3** (light green triangles). (b) The autoxidation of **1** ($[\mathbf{1}]_0 = 15-16$ mM, $p(O_2) = 11$ atm) with no added **2** (blue circles) is slower than that with 4 mM **2** added (red diamonds), while 5 mM of added **3** (green triangles) has little effect. All reactions: [AIBN] = 0.1 mM, C_6D_6, 323 K.

SCHEME 6

initiation

$$\left.\begin{array}{lll} (1) & \text{AIBN} \longrightarrow 2\,\text{In}\bullet \\ (2) & \text{In}\bullet + O_2 \longrightarrow \text{InOO}\bullet \\ (3) & \text{InOO}\bullet + \text{Pt-H} \longrightarrow \text{InOOH} + \text{Pt}\bullet \end{array}\right\} R_i$$

propagation

$$(4)\quad \text{Pt}\bullet + O_2 \longrightarrow \text{PtOO}\bullet$$

$$(5)\quad \text{PtOO}\bullet + \text{Pt-H} \xrightarrow{k_p} \text{PtOOH} + \text{Pt}\bullet$$

autocatalysis

$$(6)\quad \text{PtOOH} + \text{In}\bullet \longrightarrow \text{PtOO}\bullet + \text{In-H}$$

termination

$$(7)\quad \text{PtOO}\bullet + \begin{pmatrix} \text{Pt} \\ \text{PtOH} \\ \text{PtOOH} \end{pmatrix} \xrightarrow{k_t} \begin{array}{c} \text{non-propagating} \\ \text{products} \end{array}$$

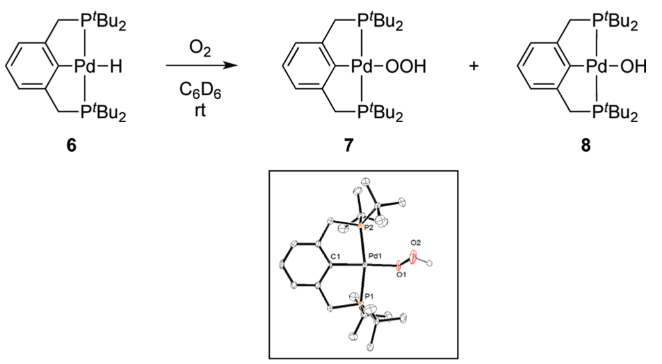
How can this empirical rate law be interpreted? As discussed in section II, the rate is determined by all three steps of the radical chain (initiation, propagation, and termination). A radical chain mechanism for the autoxidation of **1** is shown in Scheme 6 where Pt = Tp*$PtMe_2$. If the termination step involves the reaction between one PtOO• radical and one indiscriminant Pt(IV) species (Tp*$PtMe_2$(H), Tp*$PtMe_2$(OOH) or Tp*$PtMe_2$(OH)), then a rate law as shown in eq 4 is obtained ($[\text{Pt}]_{tot} = [\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}]$) . Comparison of eqs 3 and 4 indicates that the rate of initiation R_i is proportional to [AIBN][**2**]. This is accounted for by a radical-induced decomposition of the product by AIBN to generate the radical chain carrier (Scheme 6).

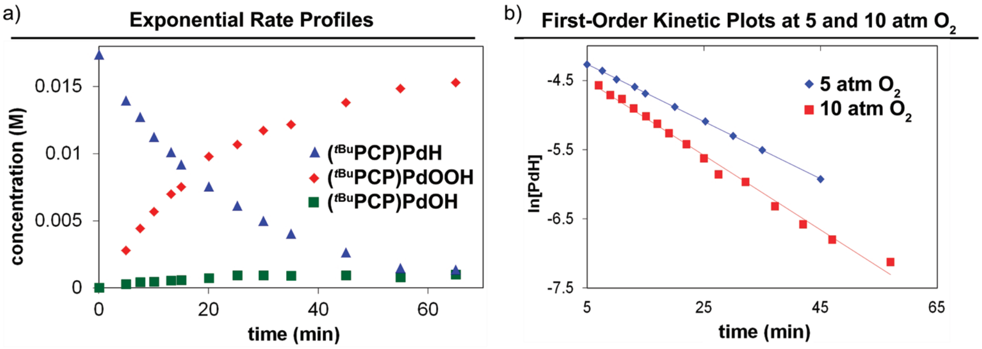
The diphenyl analogue, Tp*$PtPh_2$(H), was also found to undergo insertion of O_2 to form the related hydroperoxide complex Tp*$PtPh_2$(OOH).[14] While the specifics of the mechanisms differ slightly for the autoxidation of Tp*$PtMe_2$(H) and Tp*$PtPh_2$(H), the general features of a radical chain process proceeding by H atom abstraction and involving autoacceleration are the same.

B. Insertion of O_2 into Pd–H Bonds. Our investigations of Pd complexes led to another high yield O_2-insertion reaction involving a late transition metal hydride. The Pd(II) complex (^{tBu}PCP)PdH (**6**) (^{tBu}PCP = $[1{,}3\text{-}(CH_2P^tBu_2)_2C_6H_3]^-$) reacts cleanly at room temperature with O_2 (0.8–10 atm) to afford the Pd(II) hydroperoxide (^{tBu}PCP)PdOOH (**7**) (Scheme 7), another rare example of a crystallographically characterized terminal late transition metal hydroperoxide.[16] Analogous to our observations with the platinum(II) hydride **1**, small amounts of the hydroxide complex (^{tBu}PCP)PdOH (**8**) also formed in this reaction.

The O_2-insertion chemistry of the palladium(II) complex **6** initially seemed similar to that observed for the platinum(IV) complexes described in the previous section. However, significant differences emerged as soon as we started studying the mechanism of the reaction. For example, the concentration profiles were exponential curves (Figure 2a), not sigmoidal curves as had been observed in the platinum system. The reaction rate exhibited a clear first-order

SCHEME 7



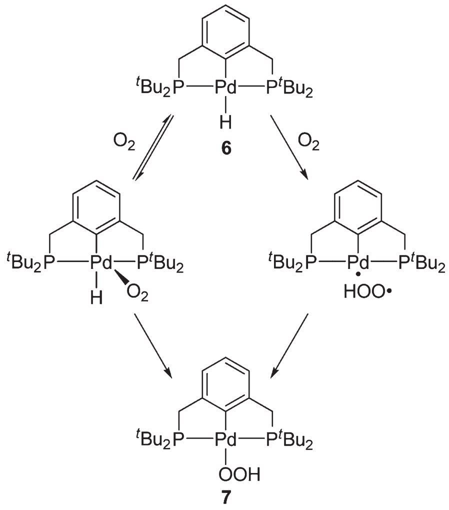


$[\mathbf{6}]_0 = 0.017$ M, $p(O_2) = 5$ atm

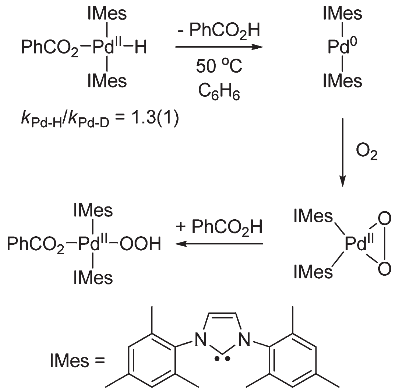
$[\mathbf{6}]_0 = 0.017$ M

FIGURE 2. In C_6D_6 at 298 K: (a) Reaction profile for the autoxidation of **6** with 5 atm O_2. (b) First-order linear fits of concentration of **6** with respect to time for reactions at 5 and 10 atm O_2.

SCHEME 8



SCHEME 9



dependence on [**6**] (Figure 2b). The doubling of the observed rate constant when $p(O_2)$ was doubled from 5 to 10 atm indicated a first-order dependence on $p(O_2)$. Reactions conducted in ambient light and in the dark showed comparable rates, and radical inhibitors had no significant effect. A kinetic isotope effect (KIE) of $k_H/k_D = 5.8(5)$ was observed for insertion of O_2 into the Pd–H/Pd-D bond, suggesting significant bond-breaking of the Pd–H bond in the rate-determining step.

The results presented above strongly argue against a radical chain pathway for the insertion of O_2 into the Pd(II)-H bond of (^{tBu}PCP)PdH. Two mechanisms consistent with the experimental data were then considered. In the first mechanism, O_2 reversibly coordinates to the 16e palladium center followed by rate-determining insertion into the Pd–H bond (Scheme 8, left). An alternative mechanism involves direct attack of oxygen at the Pd–H bond (Scheme 8, right). These two mechanisms are indistinguishable based on the experimental data so we turned to computational methods. Calculations on this system revealed that coordination of oxygen to the palladium center was unlikely. Instead, a pathway that proceeds by hydrogen atom abstraction by O_2 followed by rapid radical recombination was identified.[17]

Shortly after our publication on (^{tBu}PCP)PdH, another example of O_2-insertion into a Pd(II)-H bond was reported by Stahl and co-workers (Scheme 9).[18] Mechanistic studies of this system point to a different pathway for the insertion of oxygen into the Pd(II)–H bond. Rate-determining reductive elimination to Pd(0) is followed by formation of a Pd(II) peroxo complex and subsequent protonation. Important for the understanding and further development of this chemistry, Stahl and co-workers have shown that these two different mechanisms may be energetically similar and that subtle changes within the complex can lead to either path being dominant.[19] Through experimental and computational studies on *trans*-$(IMes)_2Pd(H)(O_2CC_6H_4X)$, it was determined that the reductive elimination, peroxo formation, and protonation pathway was favored by benzoate ligands with electron-withdrawing substituents while hydrogen atom abstraction was favored by benzoate ligands with electron-donating substituents. Thus, the electronics of the *trans* ligand play a significant role in determining which pathway is followed.

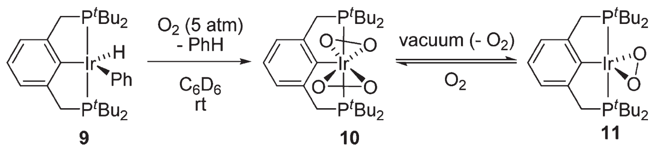
In the examination of three different metal−hydride systems (one Pt and two Pd), three distinct mechanisms were uncovered for the seemingly simple reaction of insertion of O_2 into a M−H bond. While there may indeed be other as yet undiscovered mechanisms, recent reports indicate that the mechanisms discussed above have some generality with respect to other late metal hydrides. For example, Rauchfuss and Heiden reported the hydrogenation of molecular oxygen by a Ir complex[20] and calculations support a mechanism proceeding by insertion of O_2 into a Ir(III)−H bond by a pathway analogous to that proposed for (^{tBu}PCP)PdH.[21] Meanwhile, Bakac's base-assisted O_2-insertion into a Rh(III)−H bond[22] was proposed to proceed by a mechanism that is reminiscent of that put forth by Stahl and co-workers for O_2 insertion into the Pd(II)−H bond of $(IMes)_2Pd(O_2CPh)(H)$. As investigations of O_2 reactions with transition metal complexes continue, our understanding of the mechanisms of O_2-insertion should soon approach levels comparable to those of the more ubiquitous CO and alkene insertion reactions.

C. O_2-Promoted Reductive Elimination of R−H. Neither of the mechanisms for O_2-insertion into a Pd−H bond described above involve coordination of oxygen to the open site of the d^8 metal center. Intrigued by this result, we decided to investigate if this would still be the case with an unsaturated d^6 metal center and we turned our attention to five-coordinate Ir(III) hydrides.

The (^{tBu}PCP)Ir(III) phenyl hydride complex **9**[23] was found to react with O_2 (5 atm) to form the bis-dioxygen complex (^{tBu}PCP)Ir(η^2-O_2) (**10**) (Scheme 10).[24] No evidence of insertion into the Ir(III)−H bond was found. Lowering the pressure showed that **10** was in equilibrium with the Ir(III) peroxide complex **11**.

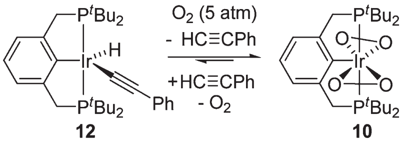
Two mechanisms were considered for the reaction of (^{tBu}PCP)Ir(Ph)(H) with O_2: (1) direct reaction of oxygen with the five-coordinate species followed by reductive elimination of benzene and (2) reductive elimination of benzene followed by oxygen coordination to the (PCP)Ir(I) center. The latter was initially considered an attractive option as C−H reductive elimination of benzene from **9** had previously been shown to be rapid and reversible in benzene solution at room temperature.[23] In addition, a mechanism involving reductive elimination followed by reaction of a lower-valent Ir center with oxygen would mimic the preliminary steps in the mechanisms proposed for oxygen insertion in Stahl's Pd(II)−H[18] and Bakac's Rh(III)−H systems.[22]

SCHEME 10



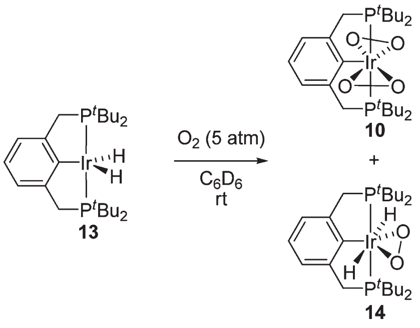
To provide mechanistic insight into the reaction of (^{tBu}PCP)Ir(Ph)(H) with oxygen, we investigated the reactions of the closely related (^{tBu}PCP)Ir(C≡CPh)(H) (**12**)[25] and (^{tBu}PCP)Ir$(H)_2$ (**13**)[26] complexes with O_2. Both of these complexes are reported to be thermally robust and do not undergo reductive elimination at room temperature.[25,26]

We found that the bis-dioxygen complex **10** was rapidly formed along with phenylacetylene when **12** was exposed to O_2 (5 atm) at room temperature (eq 5). Degassing the solution containing **10** resulted in the formation of the peroxo species **11** along with the regeneration of **12**. Thus, the bound O_2 in the Ir peroxo species can be displaced by phenylacetylene.



(5)

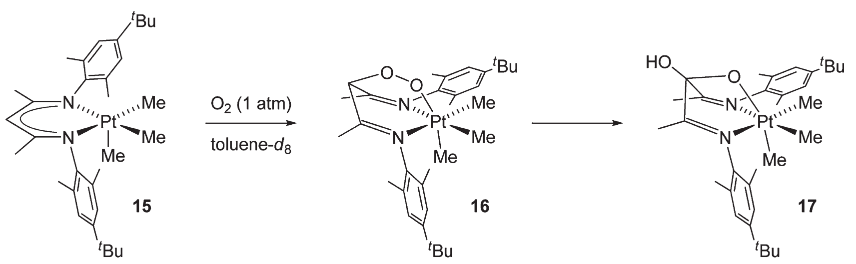
Exposure of the related five-coordinate complex (^{tBu}PCP)Ir$(H)_2$ (**13**) to oxygen also yielded **10** and another species, tentatively assigned by NMR spectroscopy as trans-(^{tBu}PCP)Ir$(H)_2(O_2)$ (**14**) (eq 6).[24]



(6)

Since **12** and **13** do not undergo reductive elimination in the absence of O_2 at room temperature, these reactions cannot proceed via reaction of low-valent Ir(I) species with dioxygen. The formation of complex **14** from complex **13** points to the involvement of O_2 coordination to the open site of the

SCHEME 11



Ir(III) center in these reductive elimination reactions. The coordination of dioxygen to the Ir(III) center then promotes the C−H or H−H reductive elimination.

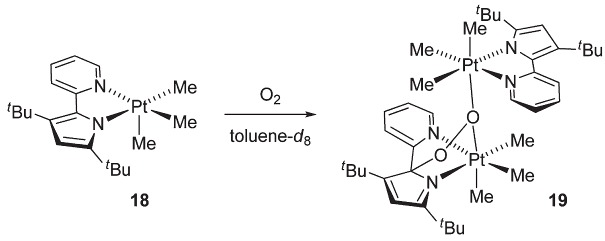
IV. Reaction Between Transition Metal Alkyls and O$_2$

In section III, the reaction between metal hydrides and metal hydrocarbyl hydrides with dioxygen either resulted in insertion of O$_2$ into M−H bonds or in O$_2$-promoted reductive elimination of R−H. Strikingly, no reaction of oxygen with metal−hydrocarbyl bonds was observed. To investigate the possibility of insertion into M−hydrocarbyl bonds, we turned to studies of organometallic complexes lacking M−H bonds.

A. Metal−Ligand Cooperativity in O$_2$ Activation. Five-coordinate Pt(IV) complexes have long been proposed as intermediates in the oxidative addition/reductive elimination of C−C, C−H, and C−X bonds at Pt(II)/Pt(IV) centers.[27] Only recently have five-coordinate Pt(IV) alkyl complexes been isolated and characterized.[27,28]

The five-coordinate complex (nacnac)PtMe$_3$ (**15**) (Scheme 11) is stable at ambient temperature and promotion of C−C reductive elimination of ethane requires elevated temperatures.[29] Exposure of **15** to oxygen did not result in reductive elimination of the hydrocarbon at room temperature as had been observed for the five-coordinate Ir(III) hydrocarbyl hydrides (section IIIC). Instead, oxygen oxidized the central carbon of the nacnac ligand to form the crystallographically characterized complex **17**.[30] Notably, the intermediate peroxo complex **16** was observed and characterized by NMR spectroscopy at low temperature. In this complex, one oxygen atom is bound to the platinum center and the other to the ligand backbone. Other unsaturated small molecules such as ethylene and *tert*-butylacetylene were observed to react similarly with **15** to form bicyclic structures analogous to the peroxo complex **16**. This type of cycloaddition reactivity to form bicyclic structures has been reported for other coordinatively unsaturated nacnac−metal complexes.[30]

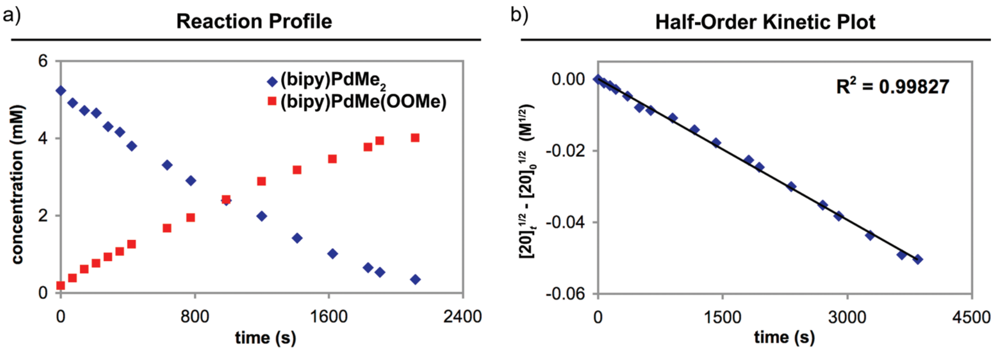
We also observed a formal cycloaddition of dioxygen to form a peroxo species with (^{tBu}pypyr)PtMe$_3$ (**18**) (eq 7).[27] The product of this reaction, characterized by X-ray crystallography, was the bimetallic peroxo species **19**, in which the peroxo moiety binds to both metal centers and to a carbon in the ligand backbone of one of the metals. The spectroscopic data support a monomeric structure in solution under one atmosphere of O$_2$.



(7)

The presence of a site where a negative charge can be localized on the ligand appears to play a significant role in promoting the observed reactions of oxygen with the five-coordinate complexes **15** and **18**. Further investigations are needed to fully understand the importance of such metal−ligand cooperativity in oxygen activation by unsaturated late-metal complexes.

B. Insertion of O$_2$ into a Pd−Me Bond. Given the large number of important catalytic transformations involving O$_2$ and Pd, we were surprised to discover the unprecedented reaction of O$_2$-insertion into a Pd−Me bond of the common d^8 Pd(II) complex (bipy)PdMe$_2$ (**20**, bipy = 2,2′-bipyridine) to form the methylperoxide complex (bipy)PdMe(OOMe) (**21**) (eq 8).[31] The insertion of O$_2$ into M−R bonds is well documented for main group and early transition metal complexes,[32] but few examples have been reported involving late transition metals.[33] As shown in Scheme 2, with the strong precedence for C−H activation by late transition metal complexes, insertions of O$_2$ into late transition metal M−R bonds to form alkylperoxide (MOOR) or alkoxide (MOR) complexes could potentially

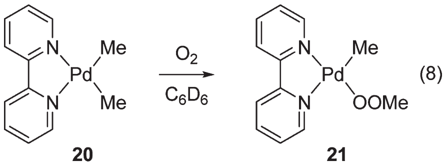


$[\mathbf{20}]_0$ = 5.2 mM, [AIBN] = 5.8 mM, $p(O_2)$ = 10 atm

$[\mathbf{20}]_0$ = 5.3 mM, [AIBN] = 2.2 mM, $p(O_2)$ = 10 atm

FIGURE 3. In C_6D_6, at 323 K: (a) Exponential reaction profile for the autoxidation of **20**. (b) Linear kinetic plot showing a half-order dependence of the reaction rate on the concentration of **20**.

be a very powerful means of functionalization of hydrocarbons.



20 **21** (8)

The identity of **21** was confirmed through independent synthesis, and the mechanism of the reaction was carefully investigated.[31] The O_2-insertion was found to be faster in light than in the dark and accelerated by the radical initiator AIBN. These results strongly imply a mechanism involving radical intermediates. Kinetic studies monitoring the reactions by ^{1}H NMR spectroscopy were then undertaken (benzene-d_6, 50 °C, $p(O_2) = 5-10$ atm, [AIBN] $= 2-32$ mM). Typical reaction profiles are shown in Figure 3a. The sigmoidal curves that were found for the radical chain autoxidation of Tp*PtMe$_2$(H) (Figure 1a) are not evident, indicating that autoacceleration does not occur in the autoxidation of (bipy)PdMe$_2$. Reaction rates were fully reproducible in the presence of AIBN and showed a half-order dependence on [AIBN]. A half-order dependence on the concentration of the substrate was also found, as can be seen from the linear fit in Figure 3b. The reaction is zero-order with respect to the pressure of O_2; very similar slopes were found (9.8(3) and 9.1(3) $\times 10^{-4}$ s^{-1}) for plots of k_{obs} versus [AIBN]$^{1/2}$ for reactions at 5 and 10 atm of O_2, respectively. Overall, the empirical rate law for this reaction was determined as

$$\text{rate} = k[\mathbf{20}]^{1/2}[\text{AIBN}]^{1/2} \qquad (9)$$

A zero-order dependence on $p(O_2)$ and a half-order dependence on [AIBN] are often encountered in radical chain autoxidations of organics (sections II and IIIA).[3] Together with the accelerative effect of light and AIBN, these results point to a radical chain mechanism for the formation of (bipy)PdMe(OOMe) (**21**). Since (bipy)PdMe$_2$ (**20**) is a Pd(II) complex, this hypothesis suggests the possible involvement of Pd(I) or Pd(III) species, which have been proposed or observed as intermediates in a variety of transformations.[34,35]

A reasonable radical chain mechanism for this autoxidation would involve the reaction between (bipy)PdMe$_2$ (**20**) and a ROO• radical. Two possible pathways were considered: ROO• reacts with **20** by attack at either the Pd center or at the carbon of the Pd-Me bond. A mechanism involving substitution at the carbon of Pd−Me would be analogous to the mechanism shown in Scheme 3 for the autoxidation of alkanes (replacing R−H with (bipy)PdMe−Me). Accordingly, the derived rate law (see eqs 1 and 2, replace RH with (bipy)PdMe$_2$) would not agree with the empirical rate law found experimentally (eq 9). Therefore, a mechanism for the insertion of O_2 into a Pd−Me bond of (bipy)PdMe$_2$ (**20**) that proceeds by homolytic substitution at carbon is not viable.

The alternative mechanism involving attack of the ROO• radical at the Pd center was then considered. This hypothesis would be similar to that proposed for the reported autoxidation of main group and early transition metal M−R compounds.[32] Notably, there is also precedent for radical substitution mechanisms in Pt(II) chemistry.[36,37] These substitutions proceed via a radical attack at the metal center and dissociation of another radical in an analogous manner to the well-known nucleophilic ligand substitution at square planar d^8 metal centers. The literature precedents concerning Pt(II) complexes led us to propose that the reaction between (bipy)PdMe$_2$ and a ROO• radical resulting in a homolytic displacement of a methyl group is a stepwise process with

SCHEME 12

initiation							
(1)			AIBN	$\longrightarrow$	2 In•		
(2)	In•	+	O_2	$\longrightarrow$	InOO•		
(3)	InOO•	+	$(\mathrm{bipy})\mathrm{Pd^{II}Me_2}$ **20**	$\longrightarrow$	$(\mathrm{bipy})\mathrm{Pd^{II}Me(OOIn)}$	+	Me•
propagation							
(4)	Me•	+	O_2	$\longrightarrow$	MeOO•		
(5a)	MeOO•	+	$(\mathrm{bipy})\mathrm{Pd^{II}Me_2}$ **20**	$\rightleftharpoons$	$(\mathrm{bipy})\overset{\mathrm{OOMe}}{\underset{\bullet}{\mathrm{Pd}}}{}^{\mathrm{III}}\mathrm{Me_2}$ **22**		
(5b)			$(\mathrm{bipy})\overset{\mathrm{OOMe}}{\underset{\bullet}{\mathrm{Pd}}}{}^{\mathrm{III}}\mathrm{Me_2}$ **22**	$\longrightarrow$	$(\mathrm{bipy})\mathrm{Pd^{II}Me(OOMe)}$ **21**	+	Me•
termination							
(6)	$(\mathrm{bipy})\overset{\mathrm{OOMe}}{\underset{\bullet}{\mathrm{Pd}}}{}^{\mathrm{III}}\mathrm{Me_2}$ **22**	+	MeOO•	$\longrightarrow$	non-propagating products		

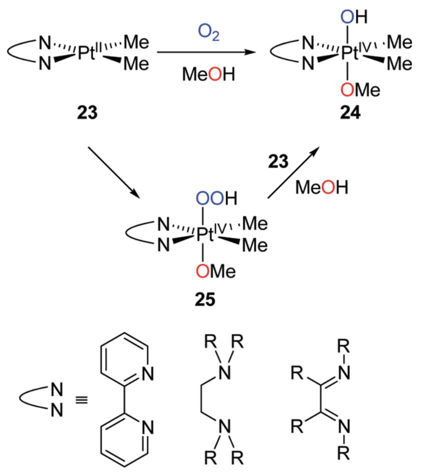
initial formation of a pentacoordinate Pd(III) intermediate $(\mathrm{bipy})\mathrm{Pd^{III}(Me)_2(OOMe)}$• (**22**).[31]

A complete mechanism incorporating the five-coordinate Pd(III) intermediate would include the steps in Scheme 12, where steps 5a and 5b correspond to the stepwise substitution at Pd. Notably, the five-coordinate Pd(III) species **22** is expected to be highly fluxional and either MeOO• or Me• could dissociate. The former is simply the equilibrium shown in step 5a. In the latter case, the subsequent rapid reaction of free Me• with O_2 would result in an irreversible step 5b. Termination by homocoupling of two MeOO• radicals would lead to a first-order dependence on [**20**] and thus would not be consistent with the observed kinetics (eq 9). Involvement of species **22** in the termination step is key in explaining the experimentally determined rate expression and a likely mechanism for termination involves the reaction of MeOO• with **22** (Step 6). In this case, the expected rate law is consistent with that determined empirically for the autoxidation of $(\mathrm{bipy})\mathrm{PdMe_2}$ (**20**).

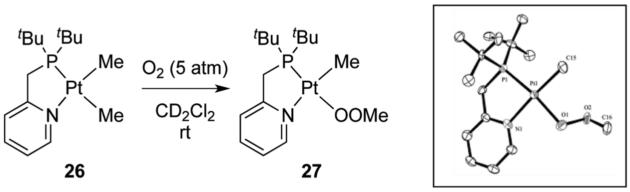
The mechanism proposed above for the insertion of oxygen into the metal–alkyl bond of $(\mathrm{bipy})\mathrm{PdMe_2}$ (**20**) implies that an open site may be required on a metal center to allow for expansion of valency on reaction with a radical chain carrier. That a coordinately unsaturated metal center is needed provides insight into potentially viable systems to consider for alkane activation and functionalization with O_2. This knowledge is particularly significant because of the well-documented ability of d^8 Pt(II) complexes to activate alkanes and form Pt(II) alkyls.[12] We then considered that if similar reactivity with oxygen and Pt(II) alkyls could be shown to be viable, a new paradigm for C–H functionalization could be envisioned.

C. Reaction of O_2 with Pt(II)–Alkyl Complexes. Several years ago, we studied the reaction of $(\mathrm{bipy})\mathrm{PtMe_2}$ with oxygen. In a joint publication with the Bercaw group, we reported that bipy-, diamine-, and diimine-ligated Pt(II) dimethyl complexes **23** react with O_2 in methanol to form platinum(IV) hydroxides (**24**) (Scheme 13).[38]

SCHEME 13



SCHEME 14



Later studies by Bercaw and co-workers demonstrated that these reactions proceed through the formation of hydroperoxide complexes (**25**).[39]

Notably, insertion of O_2 into the Pt(II)−Me bonds of these complexes was not observed during these reactions. Therefore, we decided to incorporate phosphine ligands, with the hope that the higher trans effect of phosphorus would lead to labilization of the Pt−Me bonds. Much to our delight, when a solution of 2-((di-*tert*-butylphosphino)methyl) pyridine dimethylplatinum (**26**) in CD_2Cl_2 was pressurized with O_2 (5 atm), the platinum methylperoxide complex **27** was formed in high yield (Scheme 14).[40] Complex **27** was crystallographically characterized, confirming that the insertion occurred trans to the phosphine.

Reaction rates were found to be variable (with notable induction periods) and significantly higher in light than in the dark. Addition of AIBN led to faster reactions while slower reactions were observed when the radical inhibitor 4-methyl-2,6-di-*tert*-butylphenol was present. These preliminary results are strongly suggestive of the involvement of a radical chain mechanism. A mechanism analogous to that found for (bipy)$PdMe_2$ (**20**) is proposed. Only one other example of oxygen insertion into a Pt−Me bond has been reported, and the authors conclude that singlet oxygen was involved in that case.[41]

V. Summary and Future Direction

As society searches for more sustainable methods for the production of fuels and chemicals, the use of environmentally benign and inexpensive oxidants such as O_2 will feature prominently in system design. Late transition metal complexes exhibit rich reactivity in the selective activation of hydrocarbons and their low oxophilicity is promising for the use of molecular oxygen in oxidation processes. In seeking to combine the high selectivity of organometallic reactions with the desirable activity of autoxidation, it is clear that a better understanding of how O_2 interacts with late transition metal alkyl and hydride complexes is needed. Our work has uncovered multiple examples of the insertion of oxygen into late metal hydride and alkyl bonds. Most important is that, through detailed studies on these systems, we have begun to develop and provide key insight into the mechanisms and the scope of these reactions.

Reactions of late transition metal alkyl and hydride complexes with O_2 exhibit surprisingly diverse mechanisms. In our work on the insertion of oxygen into Pt(IV)−H bonds, we found support for radical chain processes with autoacceleration.[13,14] In contrast, our studies of the insertion of oxygen into Pd(II)−H bonds led to the proposal of hydrogen atom abstraction from the metal by oxygen followed by rapid recombination to form the PdOOH product.[16,17] Work by others found a mechanism for O_2 insertion into a Pd(II)−H bond involving reductive elimination followed by reaction of the Pd(0) species with molecular oxygen to form a peroxo intermediate.[18,19] Protonation then forms the PdOOH product. Other examples with Ir(III)−H[20,21] and Rh(III)−H[22] seem to follow these mechanisms observed with Pd(II)−H and contribute to the development of general mechanistic understanding in this field. We also observed oxygen induced reductive elimination from unsaturated Ir(III) alkyl hydride complexes[24] and finally the insertion of oxygen into Pd(II)[31] and Pt(II)[40] alkyl bonds. The latter reactions apparently proceed via radical chain mechanisms involving M(III) five-coordinate intermediates.

With this nascent mechanistic understanding of oxygen insertion reactions into M−H and M−C bonds, the framework is developing that will be needed to design selective oxidations of hydrocarbons with dioxygen. With more examples and better understanding of the mechanisms involved, we can look forward to the greater use of this powerful, inexpensive, and benign oxidant in selective transformations.

We are profoundly grateful to our co-workers who have contributed to this research either directly performing the work or participating in our many discussions of this topic. Their experiments and their insight have been invaluable. We also thank the NSF, the DOE, and FQRNT, along with the NSF Center for Enabling New Technologies through Catalysis (CENTC) for support of this work. K.I.G. thanks the Weizmann Institute of Science for a Joseph Meyerhoff Visiting Professorship.

BIOGRAPHICAL INFORMATION

Luc Boisvert received his Ph.D. from Université de Sherbooke (Canada) in 2006 as an NSERC and FQRNT scholar with Prof. Claude Spino. He then moved to University of Washington working as a FQRNT postdoctoral fellow with Karen Goldberg. He is currently a visiting professor at Reed College.

Karen I. Goldberg received her A.B. from Barnard College and her Ph.D. from University of California, Berkeley where she worked with Bob Bergman. After postdoctoral study at the Ohio State University with Bruce Bursten, she spent six years on the faculty at Illinois State University. She then moved to the University of Washington where she is currently the Nicole A. Boand Endowed Professor in Chemistry and Director of the NSF Phase II Center for Chemical Innovation, the Center for Enabling New Technologies through Catalysis.

FOOTNOTES

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