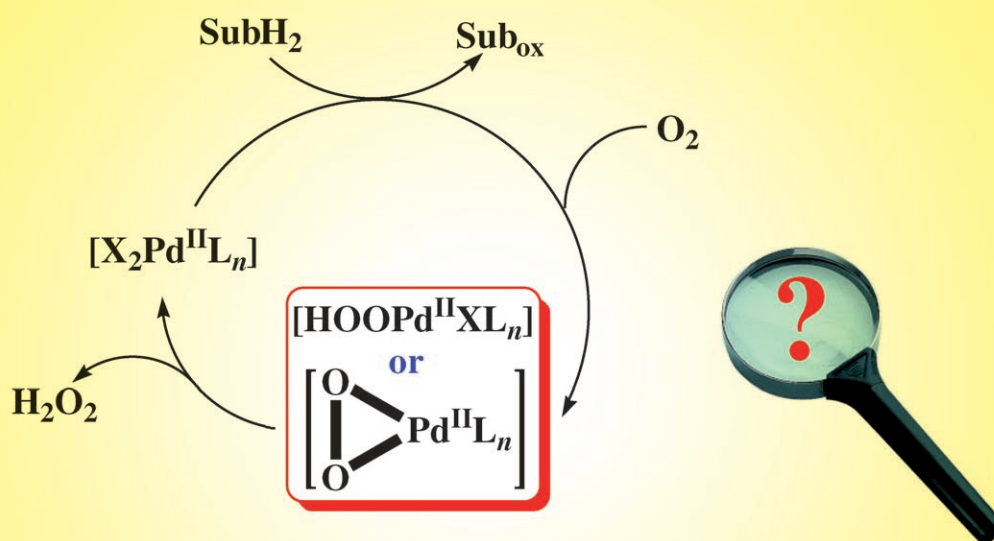


Molecular Oxygen To Regenerate Pd^{II} Active Species

Jacques Muzart*^[a]

Nature of the Oxygenated Palladium Intermediate?



Experimental and theoretical investigations



Could depend on the nature of L

Abstract: Palladium(II) catalysis allows various aerobic oxidation reactions, but the mechanism of the regeneration of the active catalytic species remains, in many cases, undetermined. In recent years, considerable effort has been directed toward the comprehension of the reaction of dioxygen with hydridopalladium(II) and palladium(0) complexes. This Focus Review highlights the results of

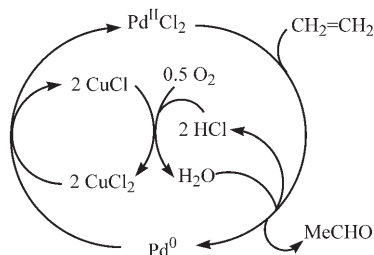
these experimental and theoretical studies that can contribute to the exploitation of the powerful nature of Pd^{II} catalysis.

Keywords: homogeneous catalysis · oxidation · oxygen · palladium · regeneration

1. Introduction

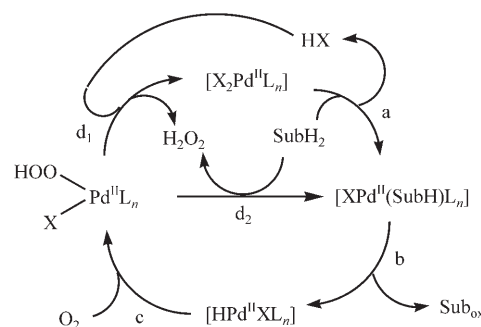
A number of Pd^{II}-mediated reactions require the addition of oxidants to be catalytic. For this purpose, oxidants such as copper salts and benzoquinone are often employed in stoichiometric quantities and even in excess. In some cases, substoichiometric amounts of redox mediators are used in conjunction with oxygen as, for an example, in the Wacker process, for which CuCl₂ is the oxidant of palladium and oxygen the oxidant of copper (Scheme 1);^[1] such conditions reduce the cost of the processes. Nevertheless, the use of mediators complicates product isolation, increases reaction waste, and limits large-scale applications.

Interestingly, various Pd^{II}-catalyzed reactions occur efficiently with only molecular oxygen to regenerate active Pd^{II} species.^[2] For some of them, such as the homocoupling of arylboronic acids in the presence of dioxygen,^[3] it has been established that the reaction causes the reduction of the catalyst, the regeneration of which occurs via the peroxopalladi-



Scheme 1. Oxidation of ethylene by the Wacker process.

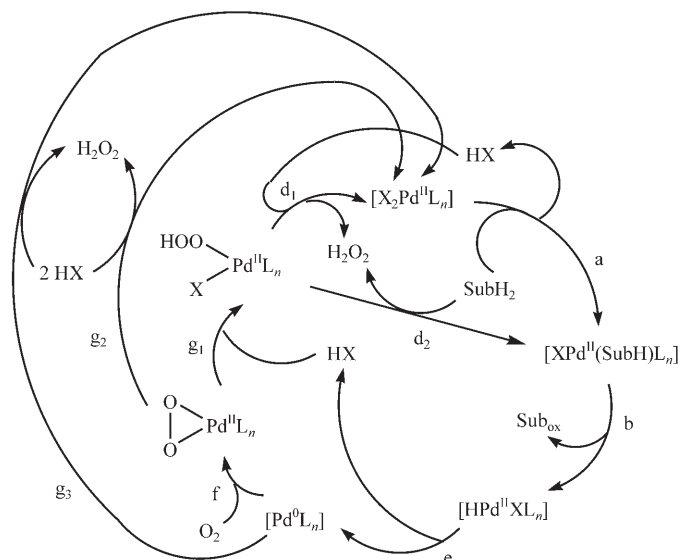
um complex $[(\eta^2\text{-O}_2)\text{Pd}^{\text{II}}\text{L}_2]$ ($\text{L} = \eta^2$ ligand). In contrast, the mechanism is much less obvious for oxidations that involve the loss of two hydrogen atoms, such as the oxidation of alcohols,^[2,4] the dehydrogenation of ketones,^[5] oxidative heterocyclization,^[6] and intermolecular oxidative C–H coupling reactions.^[2a,b,7] Indeed, the $[\text{X}_2\text{Pd}^{\text{II}}\text{L}_2]$ -catalyzed aerobic oxidation of SubH_2 to Sub_{ox} has been explained by the mechanisms depicted in Schemes 2 and 3 ($\text{X} = \eta^1$ ligand, mainly Cl and OAc, $\text{SubH}_2 =$ substrate, $\text{Sub}_{\text{ox}} =$ oxidized substrate). Both proposals involve $[\text{HPd}^{\text{II}}\text{XL}_n]$ as an intermediate (steps a and b) and lead to the regeneration of the active catalytic species with concomitant production of H_2O_2 .



Scheme 2. Pd-catalyzed aerobic oxidation of SubH_2 involving oxygen insertion into the H–Pd bond.

According to Scheme 2, oxygen inserts into the H–Pd bond to afford $[\text{HOOPd}^{\text{II}}\text{XL}_n]$ (step c),^[5,6a–c,8] and the formal +2 oxidation state of palladium is preserved all along the reaction pathway. The hydroperoxy complex leads to H_2O_2 and either $[\text{L}_n\text{Pd}^{\text{II}}\text{X}_2]$ (step d₁) or $[\text{L}_n\text{Pd}^{\text{II}}\text{X}(\text{SubH})]$ (step d₂) by reacting with HX ^[5] or SubH_2 ,^[6b,c,8b–e] respectively. The authors who proposed this mechanism for the oxidative cyclization of 2-allylphenols^[6b,c] and the oxidation of alcohols^[8b–e] suggested that step d₂ rather than d₁ occurs.^[6b,c,8b–e] Step d₂ is actually more suitable than d₁ for alcohol oxidations carried

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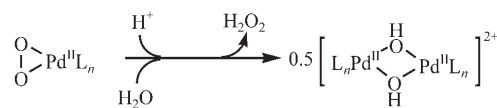


Scheme 3. Pd-catalyzed aerobic oxidation of SubH_2 involving the reduction of Pd^{II} .

out in the presence of a base.^[8] In contrast, for the $\text{Pd}(\text{OCOCF}_3)_2$ -catalyzed aerobic dehydrogenation of ketones explained with Scheme 2, the increase in the turnover with the addition of catalytic amounts of trifluoroacetic acid^[5] indicates the possible participation of step d_1 .

The other proposal (Scheme 3) is the reduction of $[\text{HPd}^{\text{II}}\text{XL}_n]$ to $[\text{Pd}^0\text{L}_n]$ (step e)^[6k,7,9] and the formation of a peroxopalladacycle (step f)^[6k,9b] from which the regeneration of the starting catalyst could occur via $[\text{HOOPd}^{\text{II}}\text{XL}_n]$ by protonolysis with HX (steps g_1 and d_1).^[6k] In fact, most of the published mechanistic schemes that suggest the formation of $[\text{Pd}^0\text{L}_n]$ intermediates do not mention the formation of $[\text{HOOPd}^{\text{II}}\text{XL}_n]$ from $[\text{O}_2\text{Pd}^{\text{II}}\text{L}_n]$, that is, path g_2 occurs in place of steps $g_1 + d_1$.^[9b,10,11] Moreover, simplified catalytic cycles that lead directly to $[\text{X}_2\text{Pd}^{\text{II}}\text{L}_2]$ from $[\text{Pd}^0\text{L}_n]$ (step g_3) have been published.^[7,9a,c,d,e] Consequently, step d_2 of Scheme 3 is usually not suggested. Scheme 3 with steps g_1 and d_1 has been proposed for the Pd^{II} -catalyzed aerobic intramolecular oxidative amination of olefinic substrates;^[6k] the low efficiency of this process in the absence of carboxyl-

ic acids agrees with the critical role of HX in this catalytic cycle. Besides, the formation of water-soluble cationic binuclear complexes from $[\text{O}_2\text{Pd}^{\text{II}}\text{L}_n]$ (L_n = phenanthroline derivatives) has been assumed for oxidations in aqueous solvents (Scheme 4).^[12]



Scheme 4. Formation of a cationic palladium dimer from a peroxopalladacycle.

Over the last few years, the reaction of oxygen with Pd^{II} hydrides and Pd^0 species has led to experimental and theoretical studies that can contribute to the exploitation of the powerful nature of Pd^{II} catalysis. Therefore, this literature makes for interesting discussion.

2. Peroxopalladacycles from Pd^0 Complexes—Synthesis and Reactivity

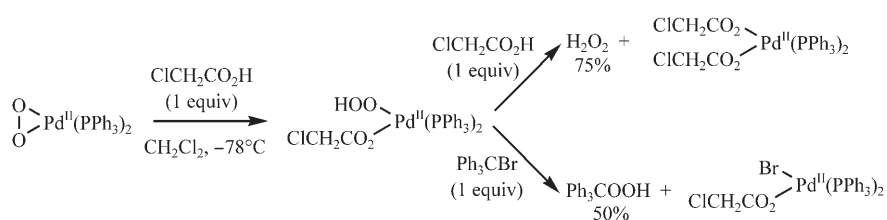
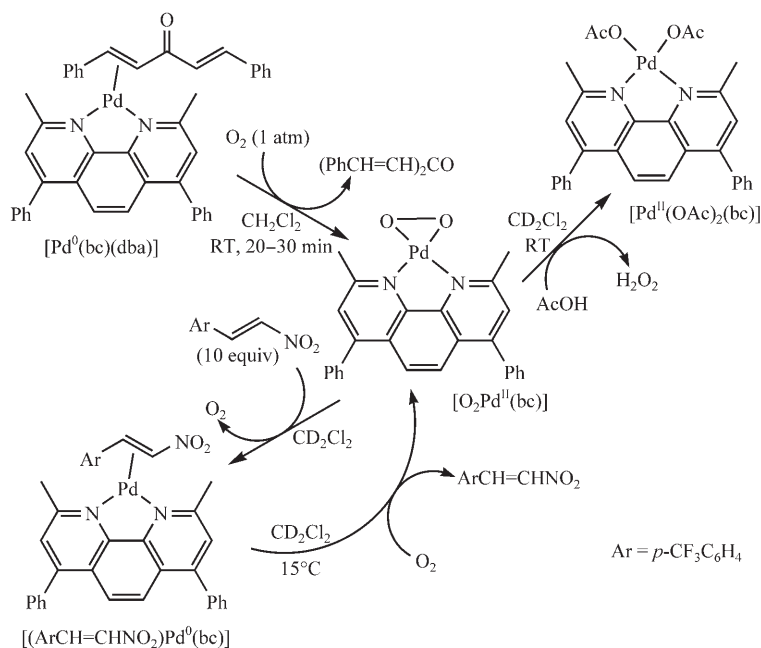
The formation of peroxopalladacycles from the oxygenation of Pd^0 complexes^[13] has been established since 1966 mainly from phosphine-coordinated complexes, but their reactivity towards acids was, until recently, not studied except by Muto and Kamiya.^[14] These authors demonstrated the formation of H_2O_2 and $[(\text{RCO}_2)_2\text{Pd}^{\text{II}}(\text{PPh}_3)_2]$ from the addition of RCO_2H ($\text{R} = \text{Me}$, ClCH_2) to $[\text{O}_2\text{Pd}^{\text{II}}(\text{PPh}_3)_2]$.^[13b,c] The study of this reaction, with the successive addition of $\text{ClCH}_2\text{CO}_2\text{H}$ and Ph_3CBr to the peroxo complex and its monitoring by IR spectroscopy with $\text{ClCH}_2\text{CO}_2\text{H}$ and AcOD as reagents, led them to suggest a stepwise mechanism (Scheme 5).^[14]

Recent research has been focused on Pd complexes that bear heterocyclic ligands. In 2001, Stahl et al. used a Pd^0 complex with a bidentate nitrogen ligand, $[\text{Pd}^0(\text{bc})(\text{dba})]$ ($\text{bc} = \text{bathocuproine}$, $\text{dba} = \text{dibenzylideneacetone}$), to obtain the peroxopalladium^{II} complex $[\text{O}_2\text{Pd}^{\text{II}}(\text{bc})]$ (Scheme 6).^[15] Addition of AcOH to $[\text{O}_2\text{Pd}^{\text{II}}(\text{bc})]$ led to H_2O_2 (73% yield) and $[\text{Pd}^{\text{II}}(\text{OAc})_2(\text{bc})]$ (quantitative). The oxygenation of $[\text{Pd}^0(\text{bc})(\text{dba})]$ is irreversible,^[15] but electron-deficient alkenes displace dioxygen from $[\text{O}_2\text{Pd}^{\text{II}}(\text{bc})]$ reversibly to form the corresponding alkene complexes (Scheme 6).^[16,17] It is of interest to point out the role of the ligands on the reversibility and stability of the peroxopalladium complexes. Indeed, $[\text{O}_2\text{Pd}^{\text{II}}\{\text{PPh}(t\text{Bu})_2\}_2]$ binds dioxygen reversibly;^[13f,g] $[\text{O}_2\text{Pd}^{\text{II}}(\text{PPh}_3)_2]$ in benzene decomposes slowly at 20 °C to the free metal and OPPh_3 ;^[13b] $[\text{O}_2\text{Pd}^{\text{II}}(t\text{BuNC})_2]$ in the crystalline state is fairly stable at ambient temperature, whereas the decomposition of its solution in CHCl_3 occurs rapidly at 0 °C.^[13d]

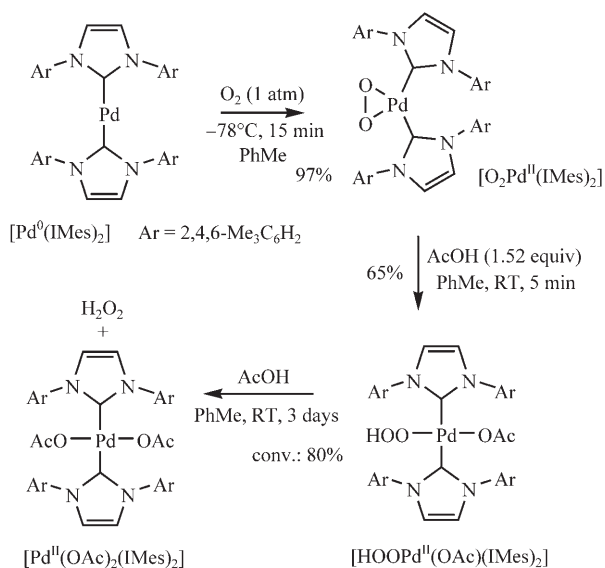
Stahl et al. also reported the synthesis, even without solvent, of the N-heterocyclic carbene (NHC)-coordinated peroxopalladium complex $[\text{O}_2\text{Pd}^{\text{II}}(\text{IMes})_2]$ ($\text{IMes} = 1,3\text{-di}(2,4,6\text{-trimethylphenyl})\text{imidazolin-2-ylidene}$) from $[\text{Pd}^0(\text{IMes})_2]$



Jacques Muzart was born in 1946 in Vienne la Ville, France. He obtained his PhD at the Université de Champagne-Ardenne with J.-P. Pête. He was appointed at the CNRS in 1971 and spent 15 months (1977–1978) as a postdoctoral fellow of the NSF working with E. J. Corey at Harvard Univ. His research interests focus on transition-metal catalysis with particular emphasis on oxidations, asymmetric reactions, and mechanisms. For a few years now, he has also been involved in the valorization of agricultural by-products and the use of water and molten salts as solvents for organic synthesis.

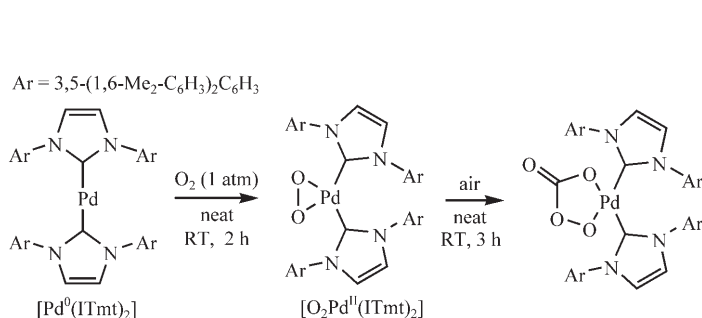
Scheme 5. Reaction of $[(\eta^2\text{-O}_2)\text{Pd}(\text{PPh}_3)_2]$ in acidic medium.Scheme 6. Synthesis and reactions of an $[(\eta^2\text{-O}_2)\text{Pd}(\text{NN})]$ complex.

and its fast transformation into the Pd^{II} hydroperoxide $[\text{HOOPd}^{\text{II}}(\text{OAc})(\text{IMes})_2]$ by protonolysis with acetic acid (Scheme 7).^[18] Further reaction of $[\text{HOOPd}^{\text{II}}(\text{OAc})(\text{IMes})_2]$

Scheme 7. Synthesis and protonolysis of an $[(\eta^2\text{-O}_2)\text{Pd}(\text{NHC})]$ complex.

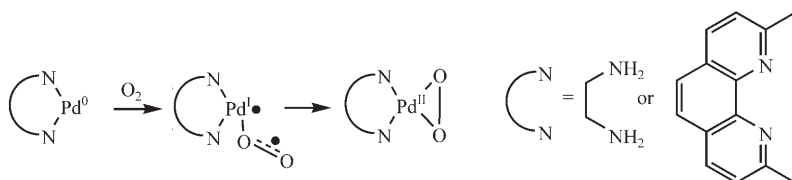
with AcOH occurred at a slow rate to afford hydrogen peroxide and $[\text{Pd}^{\text{II}}(\text{OAc})_2(\text{IMes})_2]$. The nature of the ligand plays a role in the isolation of $[\text{HOOPdXL}_2]$ from $[\text{O}_2\text{PdL}_2]$, as the addition of less than 2 equivalents of AcOH to $[\text{O}_2\text{Pd}^{\text{II}}(\text{bc})]$ led only to unconverted starting complex, H_2O_2 , and $[\text{Pd}^{\text{II}}(\text{OAc})_2(\text{bc})]$.^[18] Hydroperoxopalladium complexes were isolated^[19] before this report by Stahl et al., and the formation of $[\text{HOOPd}^{\text{II}}(\text{OCOCF}_3)(\text{PPh}_3)_2]$ from the treatment of $[\text{O}_2\text{Pd}^{\text{II}}(\text{PPh}_3)_2]$ with $\text{CF}_3\text{CO}_2\text{H}$ was suspected by Igersheim and Mimoun,^[20] but the transformation $\text{PdO}_2 \rightarrow [\text{XPdOOH}]$ was demonstrated for the first time by Stahl. At this level, we have to remember that most of the published mechanistic schemes depicting the regeneration of PdX_2 from PdO_2 ^[9b,10,11,21] do not include $[\text{XPdOOH}]$ as an intermediate (path g_2 in Scheme 3).

Another peroxopalladium complex with an NHC ligand, $[\text{O}_2\text{Pd}^{\text{II}}(\text{Itmt})_2]$, was prepared by Kawashima and co-workers from $[\text{Pd}^{\text{II}}(\text{Itmt})_2]$ and dioxygen (Itmt = 1,3-bis(2,2',6,6'-tetramethyl-*m*-terphenyl-5'-yl)-imidazol-2-ylidene).^[22] This reaction was immediate and quantitative when C_6D_6 was used as solvent; however, $[\text{O}_2\text{Pd}^{\text{II}}(\text{Itmt})_2]$ is very sensitive to CO_2 from air, thus producing the corresponding peroxocarbonate (Scheme 8). As with $[\text{Pd}^{\text{II}}(\text{IMes})_2]$,^[18] the oxidation of $[\text{Pd}^{\text{II}}(\text{Itmt})_2]$ also occurred in the solid state; this contrasts with the phosphine complexes $[\text{Pd}(\text{PCy}_3)_2]$, $[\text{Pd}(\text{P}t\text{Bu}_3)_2]$, and the NHC-coordinated complex $[\text{Pd}(\text{Ipr})_2]$ (Cy = cyclohexyl, Ipr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), which did not react with O_2 under such conditions.^[22]

Scheme 8. Synthesis of an $[(\eta^2\text{-O}_2)\text{Pd}(\text{NHC})]$ complex and its reaction with CO_2 .

FOCUS REVIEWS

With $[\text{Pd}^0(\widehat{\text{NN}})]$ complexes as model substrates, Stahl et al. used spin-unrestricted density functional theory to investigate the spin-forbidden reaction between $[\text{Pd}^0\text{L}_2]$ and molecular oxygen.^[23] According to the authors, initial delocalization of spin density from $^3\text{O}_2$ onto the Pd center decreases the exchange interaction between the unpaired spins and facilitates cross-over from the triplet to the singlet surface; the formation of the $[(\eta^2\text{-O}_2)\text{Pd}^{\text{II}}]$ complex occurs via the $[(\eta^1\text{-O}_2)\text{Pd}^{\text{I}}]$ diradical (Scheme 9).



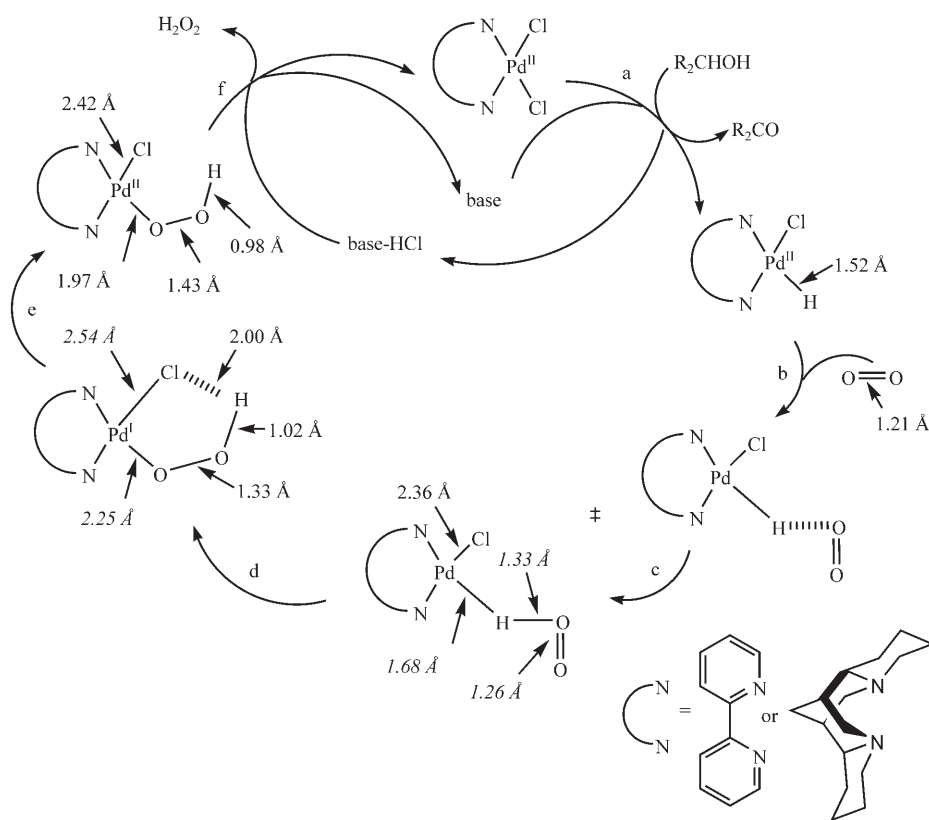
Scheme 9. Theoretical intermediate leading to a peroxy complex from $[\text{Pd}(\widehat{\text{NN}})]$.

3. Hydroperoxopalladium Complexes from Hydridopalladium Complexes—Computational Studies and Synthesis

Although the insertion of dioxygen into an H–Pd bond had been suspected since at least 1973^[24] and often proposed as a reactive intermediate,^[5,6a–c,8,25] its first observation, by Kemp, Goldberg, and co-workers,^[26] was only disclosed in 2005 after theoretical studies reported simultaneously and independently by Goddard and co-workers^[27] and Privalov et al.^[28] in 2004.

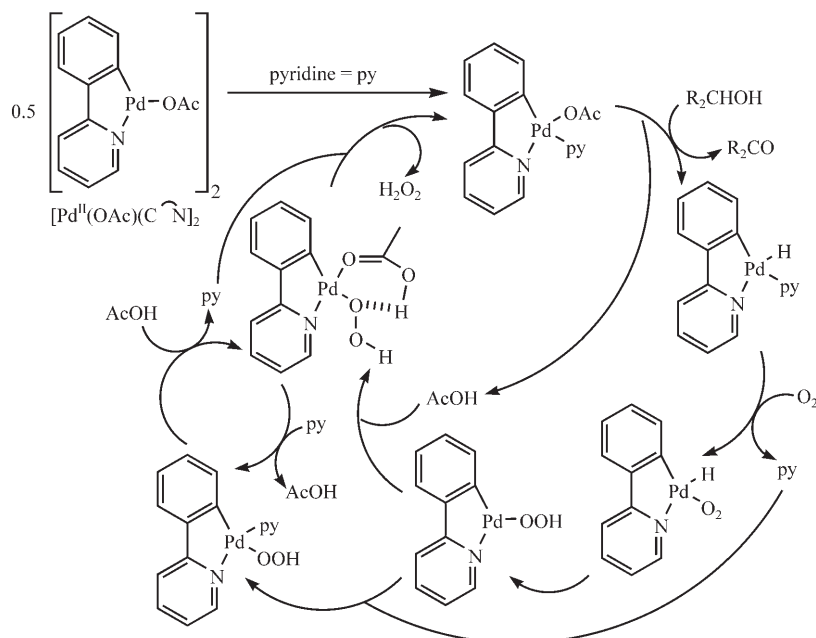
Goddard and co-workers carried out a computational study of the insertion of dioxygen into the toluene-solvated Pd–H bond of $[\text{HPd}^{\text{II}}\text{Cl}(\text{-sparteine})]$ and the model compound $[\text{HPd}^{\text{II}}\text{Cl}(\text{bipyridine})]$.^[27] In fact, the $\text{PdX}_2/(\text{-sparteine})$ system was independently disclosed by Ferreira and Stoltz^[29] and Sigman and co-workers^[30] for the efficient catalyzed oxidative kinetic resolution of secondary alcohols with oxygen, whereas Uemura and co-workers showed experimentally that $[\text{Pd}(\text{OAc})_2(\text{bipyridine})]$ is not a competent catalyst for the aerobic oxidation of alcohols.^[8a] The main results of the quantum mechanics for $[\text{HPd}^{\text{II}}\text{Cl}(\text{-sparteine})]$ and $[\text{HPd}^{\text{II}}\text{Cl}(\text{bipyridine})]$ are illustrated in

Scheme 10. According to Goddard and co-workers, 1) the reaction of molecular oxygen with Pd^{II} hydride starts by a weak bonding between oxygen and hydrogen (step b), and 2) the formation of the $[\text{ClPd}^{\text{II}}\text{OOH}]$ complex requires assistance by Cl through hydrogen bonding between H and Cl (step d). $[\text{ClPd}^{\text{II}}\text{H-O}_2]$ obtained in step b would lead to $[\text{CPd}^{\text{II}}\text{OOH}]$ via 1) a transition state with elongated Pd–H, H–O, and O=O bonds (step c), and 2) the abstraction of the hydrogen atom by O_2 , leading to a hydrogen bond with Cl to afford an intermediate with stretched Pd–Cl and Pd–OOH bonds, the latter in particular (step d); this intermediate would be the result of an association between a Pd^{I} radical and the peroxy radical $\text{HO}_2\cdot$. The catalytic cycle is completed with protonation of $[\text{HOOPd}^{\text{II}}\text{Cl}(\widehat{\text{NN}})]$ by base-HCl (step f). From a complementary theoretical study with $[\text{HPd}^{\text{II}}\text{Me}(\text{bipyridine})]$ as a model, Goddard and co-workers assumed that, in the absence of a H-bond acceptor *cis* to the hydride and/or electron-withdrawing ligands that can stabilize Pd^{I} , the reaction, in a non-polar environment, will not proceed through the palladium hydride insertion of O_2 .



Scheme 10. Theoretical analysis of the reaction of O_2 with $[\text{HPd}^{\text{II}}\text{Cl}(\widehat{\text{NN}})]$. Bond lengths (elongated bonds in italics) were calculated with (–)-sparteine as the ligand.

Privalov et al. applied density functional theory to the mechanistic study of the interaction of O₂ with the Pd hydride [HPd^{II}(CN)(py)] (py = pyridine, CN = 2-(pyridin-2-yl)phenyl),^[28] which is suspected to be an intermediate in the aerobic alcohol oxidations mediated by the [Pd^{II}(OAc)(CN)]₂/pyridine system used by Moberg and co-workers and pyridine.^[31] Scheme 11 illustrates these computational



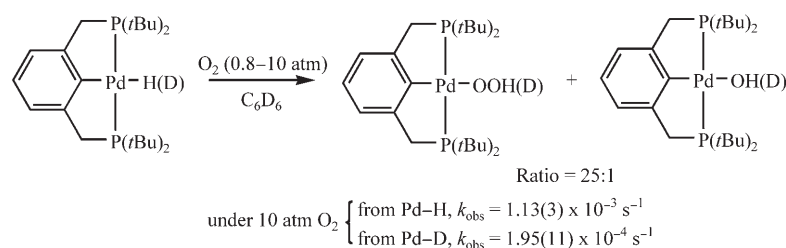
Scheme 11. Theoretical analysis of the regeneration of [AcOPd^{II}(CN)(py)] with O₂.

studies. The insertion of dioxygen into the Pd–H bond is preceded by the formation of an [HPd^{II}(η¹-O₂)] complex for which an interaction between the hydrogen and terminal oxygen atoms was identified. The release of H₂O₂ from the hydroperoxypalladium complex is promoted by AcOH, but the addition of AcOH to the catalytic system inhibits the rate of oxidation of alcohols by effective back-protonation of the alkoxide.^[28] This observation on the effect of AcOH on the formation of H₂O₂ is in agreement with the study of Muto and Kamiya^[14] (Scheme 5), whereas the insertion of O₂ into the Pd–H bond without a H-bond acceptor *cis* to the hydride contrasts with the above analysis of Goddard and co-workers.^[27]

As exemplified in Schemes 10 and 11, the above theoretical studies^[27,28] do not propose the same intermediates but, nevertheless, indicate that the insertion of dioxygen into a Pd^{II} hydride is, at least for a select subset of Pd complexes,^[27] a possible reaction pathway. Less than one year later, this theoretical conclusion agreed with the experimental studies of Kemp, Goldberg, and co-workers,^[26] who re-

ported that the oxygenation of an isolable hydridopalladium pincer complex, previously disclosed by Moulton and Shaw,^[32] provided the corresponding hydroperoxo and hydroxy complexes (Scheme 12). The main product was the hydroperoxo adduct; it evolved toward the hydroxy complex with time, especially upon exposure to light. According to Kemp and Goldberg, the decrease in the rate of oxygenation of the deuteropalladium analogue implicates the involvement of Pd–H(D) cleavage in the rate-determining step.

With a Pd–C bond, the above hydridopalladium complex is a suitable model of the catalyst of Moberg and co-workers but not of the diacetoxy- and dichloropalladium catalysts. This gap was very recently closed by Stahl and co-workers with [Pd⁰(IMes)₂] as the substrate.^[33] Addition of one equivalent of RCO₂H to [Pd⁰(IMes)₂] afforded [HPd^{II}(OCOR)(IMes)₂] quantitatively. Upon exposure to dioxygen, the hydrido complex led cleanly to [HOOPd^{II}(OCOR)(IMes)₂] (Scheme 13). The authors envisaged that the formation of this

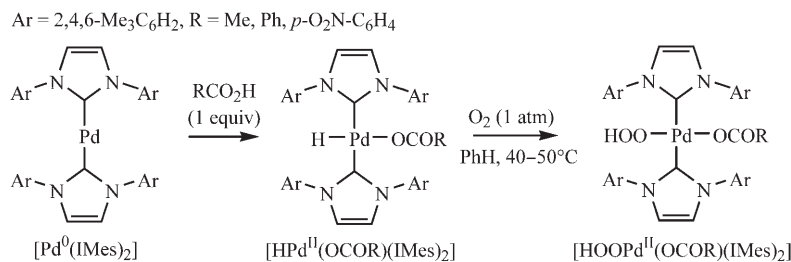


Scheme 12. Insertion of O₂ into the H–Pd bond of a pincer complex.

hydroperoxopalladium complex could occur by a retroreaction of [HPd^{II}(OCOR)(IMes)₂], leading to RCO₂H and [Pd⁰(IMes)₂] followed by oxidation (Scheme 7). However, the discovery that exogenous benzoic acid catalyzed the oxygenation of [HPd^{II}(OCOPh)(IMes)₂]^[33] is rather in agreement with the insertion of oxygen into the H–Pd bond, as the addition of acid should inhibit the retroreaction.

4. Conclusion

The experimental and theoretical investigations highlighted here contribute to a better understanding of the Pd^{II}-catalyzed oxidative intra- and intermolecular reactions that use

Scheme 13. Synthesis of an [HOOPd^{II}X] complex from an NHC-coordinated Pd⁰ complex.

dioxygen to regenerate active palladium species.^[34] Even though the above reactions of NHC-coordinated Pd⁰ and Pd^{II} complexes were analyzed with complexes not really used as catalysts, these studies have important applications in the mechanism of aerobic alcohol oxidation with other Pd–NHC catalysts reported by Sigman and co-workers.^[2d,10] It is, nevertheless, necessary to point out that even if peroxopalladacycles and hydroperoxopalladium complexes that bear the ligands used for the catalytic processes were isolated, they could be different from the real key intermediates involved in high-turnover catalytic reactions. A common mechanistic scheme that explains all Pd^{II}-catalyzed reactions for which the active Pd^{II} species are regenerated aerobically seems to be unrealistic as it appears that the pathway leading to the regeneration depends highly on the nature of the ligands. Furthermore, some reactions are carried out in the presence of a base that is able to capture the acid generated in step a of Schemes 2 and 3; this could also have an influence on the behavior of the H–Pd intermediates. In fact, the factors that lead to one of the two transformations, [HPd^{II}XL_n] + O₂ → [HOOPd^{II}XL_n] or [HPd^{II}XL_n] → [Pd⁰L_n] + HX, over the other remain to be determined.

Addendum (September 9, 2006)

Recently, the use of [(Ipr)Pd(OAc)₂(H₂O)] as the catalyst led Nielsen and Goddard III to question the traditional β-hydride elimination leading to [HPdOAc] and R₂CO from [R₂CHOPdOAc].^[35] According to correlations between experimental and calculated data, the β-hydrogen atom is rather directly transferred to the free oxygen atom of the acetate group.

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Received: June 29, 2006