

Open-shell rhodium and iridium species in (catalytic) oxygenation reactions

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Abstract

Mechanisms for the rhodium-catalyzed oxidation of olefins have been a matter of debate for a long time. So far, mainly closed-shell intermediates such as metallo-oxetanes, metallo-peroxides and metallo-dioxolanes have been proposed as intermediates in these catalytic cycles. Nevertheless some reports were published in which was indicated that open-shell species, such as rhodium superoxides may well be involved in such reaction mechanisms.

In this paper an overview is given of catalytic and stoichiometric oxidation of substrates at open-shell rhodium and iridium complexes. Rhodium and iridium superoxide complexes have been observed at low temperatures or at room temperature, when enough steric bulk is provided. The chemistry and properties of these species are discussed. Furthermore, the involvement of open-shell species and especially rhodium and iridium superoxides, in oxygenation of coordinated olefins, non-innocent ligands and external substrates starting from both closed-shell as well as open-shell starting materials, is reviewed.

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1. Introduction

Dioxygen activation and substrate oxygenation in biology almost exclusively proceeds via metallo-radicals [1–6]. Some well-known examples are hemoglobin, cytochrome P450, methane monooxygenase, lipid oxygenase (all Fe) and catalase (Mn). In addition, a large number of oxidation pathways covering the whole periodic system, which were thought to proceed via closed-shell species, proved later on to involve open-shell intermediates [7].

For the second and third row platinum metals, open-shell species are rare and their chemistry has been nearly unexplored [8–10]. As a result, little is known about the reactivity of such species towards dioxygen, and these are hardly invoked in mechanistic proposals of second and third row platinum metal catalyzed oxidation pathways. Rather than open-shell species, intermediates such as metallo-peroxo, metallo-dioxolanes and metallo-oxetanes have been proposed as key-intermediates in these mechanisms [11–13].

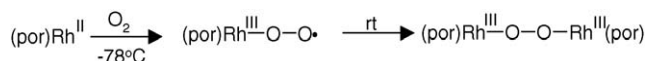
Recently, quite some stable and well characterized open-shell rhodium [14–17] and iridium [18–20] species have been reported. With this increasing number of well-defined complexes and new insights in their chemistry, one might consider their potential role in various reaction mechanisms. Especially reaction mechanisms involving other (bi)radicals, such as triplet dioxygen, may very well involve open-shell intermediates. In fact, paramagnetic ‘side-products’ are frequently observed during these oxidation reactions, but due to their NMR (and sometimes also EPR) silence, these species are not always recognized and hardly documented.

In this overview we want to stress out the possibility of such open-shell species being involved as intermediates in

Abbreviations: bpy, 2,2-bipyridine; Cat, catacholate in general; DMPO, 5,5-dimethyl-2-pyrrolidine-1-oxide; cod, Z,Z-1,5-cyclooctadiene; dpa, dipicolylamine=bis-(2-pyridylmethyl)amine; DTBCat, 3,5-di-tert-butylcatacholate; DTBSQ, 3,5-di-tert-butylsemiquinonate; en, ethylenediamine; Me-dbia, bis(benzimidazol-2-ylmethyl)methylamine; Me₃tpa, tri(6-methyl-2-pyridylmethyl)amine; OEP, octaethylphorphyrinate; por, porphyrinate in general; SQ, semiquinonate in general; tpa, tripicolylamine; TPP, tetraphenylphorphyrinate; triphos, MeC(CH₂PPH₂)₃; Q, quinone in general

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Scheme 1. Formation of porphyrinato rhodium superoxides and dinuclear peroxides.

dioxygenation pathways of various substrates. Furthermore we will review the reported open-shell rhodium and iridium oxidation catalysts in the light of this discussion. As in nature, metallo-superoxo complexes play a key role in these dioxygenation reactions. Section 2 describes the nature and the characterization of these species, whereas Sections 3–5 cover the oxidation of external substrates, non-innocent ligands and coordinating olefins.

2. Rhodium and iridium superoxides: key intermediates?

Group VIII M^{III} superoxide species ($\text{M} = \text{Rh}$ and Ir) can be formed by treatment of a M^{II} species with dioxygen. Frequently, these reactions have to be carried out at low temperature to prevent decomposition or formation of dimeric peroxide bridged species [21–23]. Both the groups of Wayland and Collman reported the low temperature synthesis of $(\text{por})\text{Rh}^{\text{III}}\text{-O}_2^\bullet$ species and formation of $(\text{por})\text{Rh}^{\text{III}}\text{-O}_2\text{-(por)Rh}^{\text{III}}$ dinuclear complexes at elevated temperatures (Scheme 1). Formation of the peroxo bridged species can be prevented by introduction of steric bulk. Treatment of the more hindered complexes $[(\text{Me}_3\text{tpa})\text{Ir}^{\text{II}}(\text{ethene})]^{2+}$ and $[(\text{dpa})\text{Rh}^{\text{II}}(\text{cod})]^{2+}$ with dioxygen yields superoxide complexes, which are stable for several seconds at room temperature [18,24,25]. Formation of peroxide bridged species has in these cases not been observed.

Due to the scarceness of the M^{II} precursors [8–10,14–20], M^{III} superoxide species are also rare. X-ray structures of iridium-superoxide species are unknown and so far only a single X-ray structure of a rhodium superoxide species has been reported (Fig. 1) [26]. This (*meso*- $\text{Me}_6\text{-[14]aneN}_4$)(MeCN) $\text{Rh}^{\text{III}}\text{-O}_2^\bullet$ species has the macrocyclic ligand coordinated in the equatorial plane and an acetonitrile moiety coordinated *trans* to the superoxide fragment. The superoxide moiety is stabilized by hydrogen-bonding interactions with three ligand amine hydrogens. Remarkably, the authors did not report any EPR data for this exact species. It can therefore not be

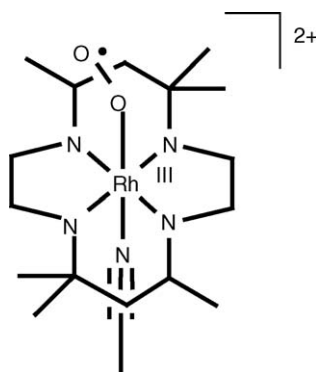


Fig. 1. Structure of $[(\text{meso-Me}_6\text{-[14]aneN}_4)(\text{MeCN})\text{Rh}^{\text{III}}(\text{O}_2^\bullet)]^{2+}$.

Table 1
EPR data for various rhodium and iridium superoxides

Species	g_{11}	g_{22}	g_{33}	Reference
<i>trans</i> - $[\text{Rh}(\text{en})_2\text{Cl}(\text{O}_2)]^+$	2.0768	2.0229	1.9996	[27]
<i>cis</i> - $[\text{Rh}(\text{en})_2\text{Cl}(\text{O}_2)]^+$	2.0861	2.0229	1.9919	[27]
$\{[\text{Rh}(\text{en})_2\text{Cl}]_2(\mu\text{-O}_2)\}^{3+}$	2.0972	2.0301	1.9889	[27]
$\{[\text{Rh}(\text{4Me-py})_4\text{Cl}](\mu\text{-O}_2)\}^{3+}$	2.0917	2.0268	1.9898	[27]
$[(\text{Me-dbia})(\text{PPh}_3)_2\text{Rh}^{\text{III}}(\text{O}_2)]$	2.099	2.028	2.007	[28]
$[(\text{dpa})\text{Rh}(\text{cod})]^{2+}$	2.0891	2.0090	2.0090	[25]
<i>trans</i> - $(\text{H}_2\text{O})([\text{14]aneN}_4)\text{Rh}(\text{O}_2)]^{2+}$	2.099	2.014	1.998	[29]
$[(\text{OEP})\text{Rh}(\text{O}_2)]$	2.100	2.010	1.988	[21,22]
$[(\text{TPP})\text{Rh}(\text{O}_2)]$	2.084	2.025	1.993	[21,22]
$[(\text{OEP})\text{Rh}(\text{O}_2)(\text{pip})]$	2.094	2.010	1.996	[21,22]
$[(\text{OEP})\text{Rh}(\text{O}_2)(\text{P}(\text{OBu})_3)]$	2.084	2.004	2.000	[21,22]
$[(\text{TPP})\text{Rh}(\text{O}_2)(\text{P}(\text{OEt})_3)]$	2.086	2.009	2.004	[22]
$\{[\text{Rh}(\text{bpy})_2\text{Cl}_2]_2(\text{O}_2)\}^{3+}$	2.088	2.020	1.992	[30]
$[(\text{OEP})\text{Rh}(\text{O}_2)(\text{PEt}_3)]$	2.002	1.964	1.964	[23]
$[(\text{Me}_3\text{tpa})\text{Ir}(\text{CH}_2\text{CH}_2)(\text{O}_2)]^{2+}$	2.191	2.030	1.987	[25]
$\text{O}_2^{\bullet-}$	2.10	2.01	2.01	[31–34]
$\text{CH}_3\text{OO}^\bullet$	2.033	2.003	2.003	[35]

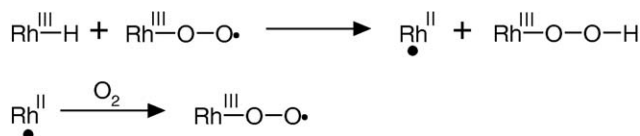
ruled out, that the X-ray structure could actually be a diamagnetic rhodium(III)-hydroperoxo instead of a paramagnetic rhodium(III)-superoxo complex. After all, it is difficult to locate protons with X-ray diffraction.

Upon formation of a superoxide complex by treatment of the corresponding metallo-radical, electron density of the unpaired electrons shifts from the metal to the dioxygen fragment. As a result g -values of such metallo-superoxides are observed very close to those reported for $\text{O}_2^{\bullet-}$ and ROO^\bullet and to those in numerous related superoxo-cobalt complexes [27]. The g -values of the reported rhodium and iridium superoxides are summarized in Table 1.

3. Oxidation of external substrates

Oxidation of additional substrates by M^{III} superoxides is nearly limited to the work of Bakac and coworkers. They found that rhodium(III) superoxides similar to (*meso*- $\text{Me}_6\text{-[14]aneN}_4$)(MeCN) $\text{Rh}^{\text{III}}\text{-O}_2^\bullet$ are capable of oxidizing nitrogen monoxide (via rhodium(III) nitrate intermediates) [36,37] and iodide [38]. Furthermore they reported that $\text{Rh}^{\text{III}}(\text{O}_2^\bullet)$ species can abstract a hydrogen atom from $\text{Rh}^{\text{III}}(\text{H})$ species, yielding a $\text{Rh}^{\text{III}}(\text{OOH})$ and a Rh^{II} species (Scheme 2). The latter quickly picks up a dioxygen molecule, thereby regenerating $\text{Rh}^{\text{III}}(\text{O}_2^\bullet)$, allowing rhodium superoxide species to participate in the auto-oxidation of $\text{Rh}^{\text{III}}(\text{H})$ to $\text{Rh}^{\text{III}}(\text{OOH})$ [39].

In addition, Moszner and coworkers proposed that $[(\text{Me-dbia})(\text{PPh}_3)_2\text{Rh}^{\text{III}}(\text{O}_2^\bullet)]$ is involved in the rhodium mediated



Scheme 2. Auto-oxidation of rhodium(III) hydrides via open-shell $\text{Rh}^{\text{III}}\text{OO}^\bullet$ intermediates.



Scheme 3. Rhodium induced dehydrogenation and decarbonylation of ethanol.

dehydrogenation and decarbonylation of ethanol (Scheme 3) [28].

4. Oxygenation at non-innocent ligands

The catalytic mechanism of intra and extra catechol cleaving dioxygenases is still a matter of debate, since the intermediate transient oxygen adduct has never been isolated in these enzymes. In 1990, the synthesis and characterization of a rhodium analog of the active site of these enzymes has been reported by Bianchini et al. [40]. This species, [(triphos)Rh(3,5-DTBcat)]⁺, reacts with dioxygen to give a dioxygen adduct, [(triphos)Rh(OO)-(DTBSQ)]⁺, which was initially assigned as the open-shell diradical A, but later reassigned as closed-shell structure B (Fig. 2). Later on several similar rhodium and iridium analogs were reported, which were analyzed by X-ray diffraction. Each of these complexes was assigned having the electronic structure B (Fig. 2) [41–43]. These species are homogenous catalysts for either the oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butyl-*o*-benzoquinone or the oxygenation of 3,5-di-tert-butylcatechol to muconic acid anhydride (intradiol C–C cleavage) and 2H-pyran-2-one (extradiol cleavage). The mechanism of dioxygen activation is not entirely clear.

Reactions of quinone/catechol type rhodium and iridium complexes can be ruled by redox reactions at both the metal and the redox non-innocent ligands. The complication of the redox non-innocent character [44–47] of these type of ligands is clear from the resonance structures depicted in Fig. 3.

For triplet O₂ to react with a closed-shell metal complex, a singlet-triplet crossing has to take place at some point of the reaction. Direct binding of ³O₂ to diamagnetic complexes has long been believed to be spin forbidden [48,49]. Therefore, a

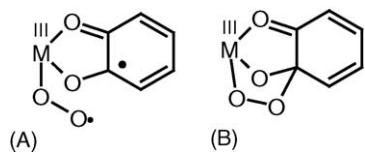
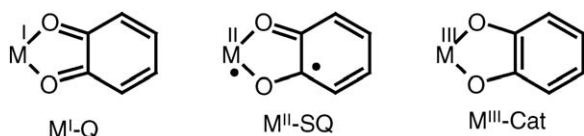
Fig. 2. Possible structures of [(P-donor)Rh(OO)-(DTBSQ)]⁺ relevant in Rh catalyzed oxidation and oxygenation of substituted catechols.

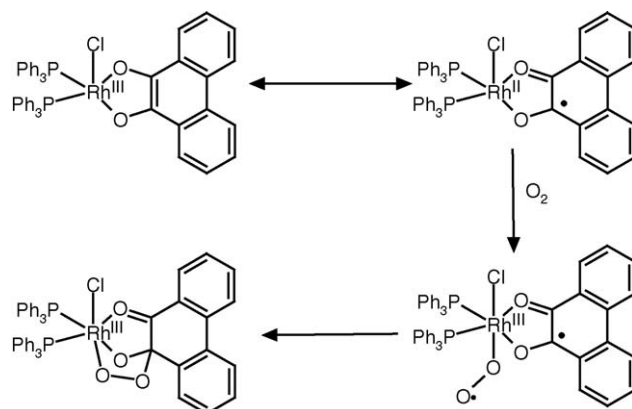
Fig. 3. Resonance structures of quinone/catechol type metal complexes.

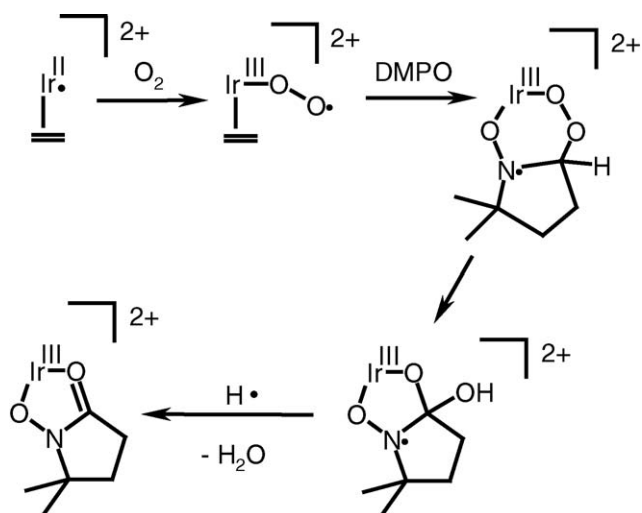
widely accepted model for the attack of a dioxygen molecule to metal centre is the spin-pairing model [50,51], in which triplet O₂ must spin-pair with unpaired electron density of a paramagnetic metal centre, either in the ground state (e.g. Co^{II} d⁷) or via excited states (if the complex has a diamagnetic ground state). According to this model, reactions of quinone/catechol rhodium and iridium complexes are usually thought to proceed via the M^{II}-SQ biradical form.

However, no signs of paramagnetism are observed in the oxygenation reactions of rhodium, iridium or iron models [5] of the intra- and extradiol dioxygenases. This does not rule out the possibility of the complexes to have a small contribution of the M^{II}-SQ form. But on the other hand, recent insights from DFT calculations of diamagnetic Pd⁰ with ³O₂, made clear that the reaction could well proceed largely at the triplet surface via electron transfer from d¹⁰ Pd⁰ to ³O₂. This results in a triplet diradical Pd^I-O₂^{•-}, which considerably facilitates the eventual spin-crossover, leading to fast “spin-forbidden” reactions between Pd⁰ and ³O₂ [52]. Although rhodium and iridium generally participate in two-electron redox steps, similar one-electron steps to the above Pd system might facilitate the spin-restrictions of these metals as well. In good agreement with this hypothesis, DFT calculations indicate that triplet O₂ initially binds to the metal center of [(triphos)Ir(Cat)]⁺ rather than directly to the semiquinone fragment [54].

Results of Bhattacharya and coworkers are however more in favor of the spin-pairing model. They showed that quinones with weak oxidation strength and the resulting complex in a M^{II}-SQ form are sensitive towards dioxygenation, whereas strong oxidizing quinones with complexes in the M^{III}-Cat form are air-stable (Scheme 4) [53].

Recently, we obtained a related structure to the peroxide bridged oxygenated semiquinones after treatment of paramagnetic [(Me₃tpa)Ir^{III}(ethene)(O₂^{•-})]²⁺ with DMPO [25]. The unpaired electron, mainly located at the superoxo fragment, transfers to the amine nitrogen of DMPO upon coupling with the superoxide moiety. The obtained peroxy bridge rearranges to an acetal moiety with the nitroso oxygen coordinating to iridium. Upon standing at room temperature this acetal [(Me₃tpa)Ir^{III}(O-DMPO-OH)]²⁺ converts to ketone adduct [(Me₃tpa)Ir^{III}(O-

Scheme 4. Oxidation mechanism of rhodium catechol species via the M^{II}-SQ state.



Scheme 5. Oxygenation of DMPO at an open-shell iridium site.

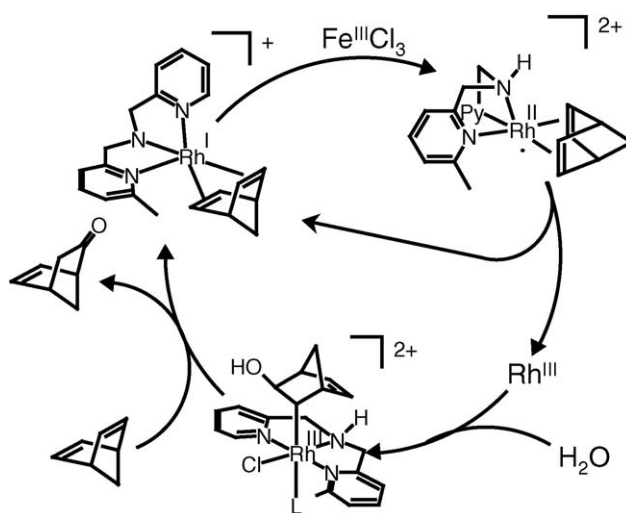
DMPO)]²⁺, upon extraction of a hydrogen atom from the solvent and elimination of water (Scheme 5).

5. Oxygenation of coordinated olefins

As stated before, mechanisms for the rhodium catalyzed Wacker oxidation of olefins, has been a matter of debate since the early 1980s [11–13]. So far paramagnetic species have not been incorporated in the cycles proposed for these transformations. Recently, we reported that a rhodium(II) intermediate plays a crucial role in the Wacker mono-oxygenation of norbornadiene [16]. One could stress out that FeCl₃ directly oxidizes the rhodium(I) species to the rhodium(III) complex. However, using mild one-electron oxidants, such as silver(I), incapable of oxidizing the rhodium species directly to the +III state, similar results were obtained. In absence of chloride, the rhodium(II) intermediate could be isolated. Chloride is therefore believed to be the trigger for disproportionation of the rhodium(II) intermediate to form the rhodium(III) species, which in turn undergo external attack of water (Scheme 6).

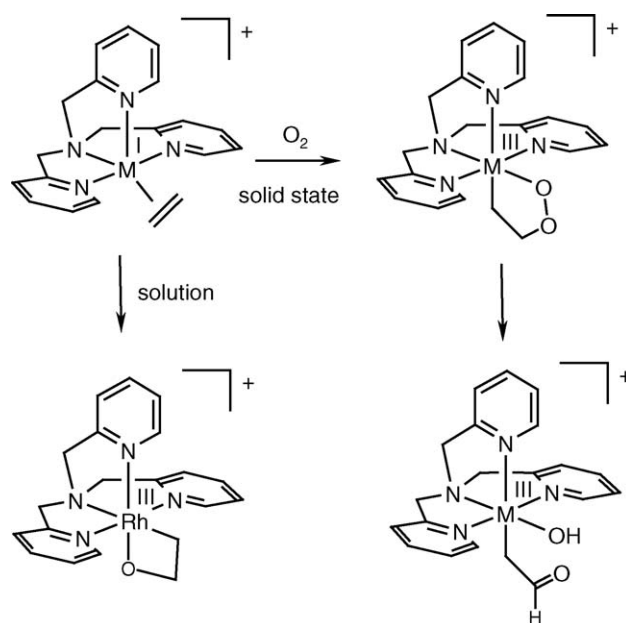
In the cycles of rhodium catalyzed olefin oxidation of Mimoun et al. [11] and Drago et al. [12], rhodium-dioxolane species play a key role. Until recently, such a species was never isolated from a dioxygenation reaction in solution. Krom et al., on the other hand, obtained a metallo-dioxolane species [(tpa)M^{III}(CH₂CH₂OO)]²⁺ by treatment of solid [(tpa)M^I(ethene)]⁺ with dioxygen (M = Rh and Ir) [55,56]. In solution a completely different reaction was observed. Instead of formation of a dioxolane, oxetane species [(N-ligand)M^{III}(CH₂CH₂O)]²⁺ were observed [57,58]. The resulting dioxolane from the solid phase–gas reaction rearranged to formylmethylhydroxo species [(tpa)Rh^{III}(OH)(CH₂CHO)]²⁺ under influence of light or heat (Scheme 7) [59].

We recently followed the reaction of solid [(tpa)Rh^I(ethene)]⁺ with dioxygen using EPR spectroscopy. As the reaction proceeds, a clear EPR spectrum appears with rising intensity (Fig. 4). The spectrum is very similar to that of the reaction product of [(Me₃tpa)Ir^{II}(ethene)]²⁺ with dioxygen (vide infra)

Scheme 6. Wacker-type oxidation of norbornadiene via a Rh^{II} intermediate.

[18,24] and those of other reported rhodium-superoxo species (see Table 1). In addition Morvillo and Bressan, reported that paramagnetic species are observed in small quantities upon treatment of rhodium(I) norbornadiene complexes equipped with bidentate phosphine ligands with dioxygen [60,61]. The authors assigned the paramagnetism to a Rh^{II}(O₂•) diradical species. This, however, was not adequately investigated. It seems unlikely that the two unpaired electrons are uncoupled in such a system, and one would expect (EPR silent) *S* = 1 or 0 spin states for such species. It nevertheless indicates that paramagnetic species are formed in oxygenation reactions at rhodium sites.

In case of dioxolane formation one could imagine that the metal is oxidized in the solid phase to give oxidation state

Scheme 7. Solid phase dioxygenation of M^I(ethene) species to metallo-dioxolanes (M = Rh and Ir).

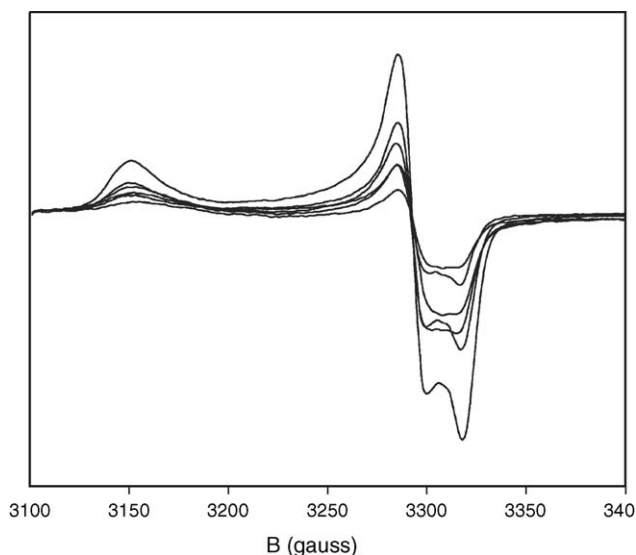
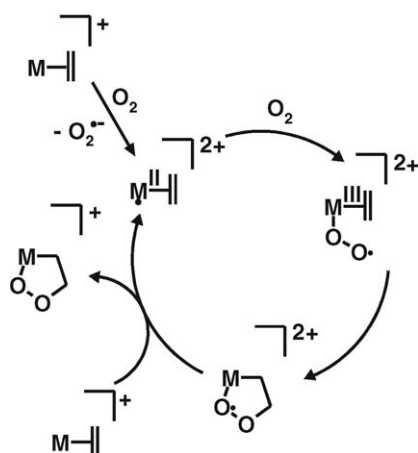


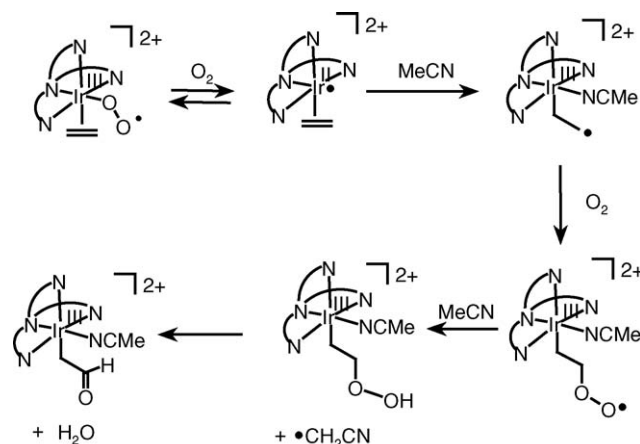
Fig. 4. EPR spectrum of solid $[(\text{tpa})\text{Rh}^{\text{I}}(\text{ethene})]^+$ upon treatment with dioxygen. Conditions—frequency: 9.3083 GHz; T : 20 K; mod.amp.: 4 G. Corresponding g -values obtained from simulation— g_{11} : 2.112; g_{22} : 2.020; g_{33} : 2.004.

+II species upon treatment with dioxygen. These M^{II} species are susceptible towards dioxygen binding as stated before for other M^{II} species in solution (Section 2). C–O binding results in a paramagnetic dioxolane type species, which is able to oxidize another nearby M^{I} species. In solution, these intermediates are too reactive and would immediately decompose. In the solid phase however, they are shielded from themselves and their environment, resulting in selective oxygenation reactions. The precise mechanism of dioxygenation of ethene in the solid phase is still under investigation in our group (Scheme 8).

Inspired by the paramagnetism observed in the stoichiometric dioxygenation of ethene in the solid phase, we recently investigated one-electron oxidation of $[(\text{Me}_3\text{tpa})\text{Ir}^{\text{I}}(\text{ethene})]^+$ in solution [18,19,62]. For stability, methyl groups were introduced at the six-position of the ligand-pyridine rings. In non-coordinating solvents $[(\text{Me}_3\text{tpa})\text{Ir}^{\text{II}}(\text{ethene})]^{2+}$ is attacked



Scheme 8. Mechanism of dioxolane formation from $\text{M}^{\text{I}}(\text{ethene})$ species in the solid state.



Scheme 9. Direct attack of dioxygen to a carbon atom of iridium(II) bound ethene.

by dioxygen at the metal site resulting in the formation of $[(\text{Me}_3\text{tpa})\text{Ir}^{\text{III}}(\text{O}_2^\bullet)(\text{ethene})]^{2+}$ (Scheme 9). The resulting superoxide species is stable for several minutes at low temperature, but at room temperature it rapidly converts to a mixture of diamagnetic products.

In acetonitrile, however, a completely different chemistry is observed. Upon coordination of acetonitrile to the metal center a species that holds the middle between a 19 VE metallo-radical iridium(II) with a “slipped” ethene ligand and an 18 VE Ir^{III} -ethyl radical species is obtained. The olefin ligand non-innocent behavior of this $[(\text{Me}_3\text{tpa})\text{Ir}^{\text{III}}(\text{NCMe})(\text{CH}_2\text{CH}_2^\bullet)]^{2+}$ species allows direct radical coupling of external $^3\text{O}_2$ to the olefinic substrate and subsequent formation of $[(\text{Me}_3\text{tpa})\text{Ir}^{\text{III}}(\text{CH}_2\text{CHO})(\text{NCMe})]^{2+}$ [24]. So far, however, we can not completely rule out an alternative oxygenation pathway via the metal involving superoxo $[(\text{Me}_3\text{tpa})\text{Ir}^{\text{III}}(\text{O}_2^\bullet)(\text{ethene})]^{2+}$ species. DFT calculations however reveal that the direct oxygenation of ethene as depicted in Scheme 8 is a reasonable alternative to more traditional pathways via the metal.

6. Conclusions

Understanding dioxygen activation is not easy. In addition to traditional closed-shell mechanisms involving two electron oxidation processes, oxygenation at rhodium and iridium centers may very well involve open-shell species. Despite difficulties to characterize these intermediates, various clues have been presented which indicate that assuming only closed-shell species in oxygenation at rhodium and iridium sites is at least rather ignorant.

The possibility of open-shell species involved in these oxidation pathways is fascinating and may be expanded to a whole range of catalytic transformations. Understanding and exploring the chemistry of the species involved in these pathways may lead towards a whole new fascinating area, which brings together the chemistry of ligand- and metallo-radicals such as observed in nature and the (organometallic) chemistry of platinum metals. We anticipate that this generates many new possibilities in explorative metal-organic chemistry.

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