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Rhodium Complexes Promoting C–O Bond Formation in Reactions with Oxygen: The Role of Superoxo Species

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In memory of Prof. Dr. Rafael Usón, an outstanding leader of the renaissance of the chemical research in Spain.

Abstract: C–O bond formation in reactions of olefins with oxygen is a long standing challenge in chemistry for which the very complicated –sometimes controversial– mechanistic panorama slows down the design of catalysts for oxygenations. In this regard, the mechanistic details of the oxidation of the complex [Rh(cod)(Ph₂N₃)] (**1**) (cod = 1,5-cyclooctadiene) with oxygen to the unique 2-rhodoxetane compound [[Rh(OC₈H₁₂)(Ph₂N₃)]₂] (**2**) has been investigated by DFT calculations. The results of this study provide evidences for a novel bimetallic mechanism in which two rhodium atoms redistribute the four electrons involved in the cleavage of the O=O bond. Further, both oxygen atoms are used to create two new C–O bonds in a controlled fashion with 100% atom-economy. The key intermediates that we have found in this process are a mononuclear open-shell triplet superoxo compound, an open-shell singlet ‘μ-(peroxo)’ derivative, and a closed-shell singlet ‘bis(μ-oxo)’ complex. Some of the findings are used to predict the reactions of Rh(I) complexes with oxygen, exemplified by that of the complex [Rh(cod)(OnapyMe₂)] (**3**). Starting from **3**, [[Rh(OC₈H₁₂)(OnapyMe₂)]₂] (**4**) has been prepared and characterized, which represents the second example of a 2-rhodoxetane compound coming from a oxygenation reaction with oxygen.

Introduction

Catalytic oxygenation constitutes an important method of converting readily available alkenes into chemicals with high added value such as alcohols, ketones, epoxides, etc.^[1] This value will increase by making this method environmentally friendly with the use of oxygen as reagent.^[2] Nonetheless, this approach is challenged by the spin-forbidden nature of reactions between triplet O₂ and closed-shell organic molecules, which results in extremely slow kinetics. Therefore, dioxygen should be pre-activated, which is generally achieved by its interaction with a transition metal centre. At this level, the diversity of plausible intermediates considered in the current unified picture of the dioxygen activation mechanism (Scheme 1, left)^[3] along with the complexes characterized for Cr,^[4] Pd,^[5] Rh,^[6] and Ir^[7] (Scheme 1, right), show the complexity associated with the activation of O₂ by transition metals. Moreover, the key factors governing the C–O bond formation with these species are still poorly understood, hindering the design of new catalysts for oxygenations using molecular oxygen as primary oxidant.

Scheme 1. Proposed mechanisms for dioxygen activation (left) and related cores from reactions with O₂ (right).

The ability of rhodium and iridium complexes to catalyse reactions with dioxygen is well-known since the pioneering works of Mimoun,^[8] although three decades had to elapse to initiate the understanding of such systems. Pivotal role for this advance was the organometallic studies on functional models bearing N-based multidentate oxidation-resistant ligands.^[9] The reactions were found to yield a wide variety of oxidation products, as illustrated in Scheme 2 for the [M](cod) moiety (M = Rh, Ir; cod = 1,5-cyclooctadiene). Thus, Ir(cod)(peroxo) complexes were observed in the reactions of oxygen with complexes supported by guanidinato^[10] or acetamidato^[11] coligands, which yielded (1-oxo-2-irida)(hydroxo) complexes, presumably through

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3-irida-1,2-dioxolane intermediates (Scheme 2).^{[10]–[12]} In other instances, the products were found to be 1-hydroxy-2-rhoda/irida-5,6,7-allylcyclooctenyl complexes coming from intermediates having a 2-rhoda/iridaoxetane moiety.^[13] More recently a 1-hydroxy-2-irida fragment has been reported (Scheme 2).^[14]

Scheme 2. Intermediates and products in the oxygenation of $M(\text{cod})$ complexes ($M = \text{Rh}, \text{Ir}$) with O_2 .

For the less studied rhodium and iridium ethylene complexes bearing the tetrapodal tris-(2-pyridylmethyl)amine ligand, 3-metalla-1,2-dioxolanes were prepared from solid-gas reactions with dioxygen.^[15] They were found to be highly reactive species evolving to the corresponding (hydroxo)(formylmethyl) complexes upon exposure to light.^[16] In sharp contrast, related complexes with tris-(6-methyl-2-pyridylmethyl)amine produce remarkably stable (ethylene)(peroxo) compounds, where C–O bond formation does not occur.^[17]

From a mechanistic point of view, radical chain processes have been proposed in some instances,^[18] but Scheme 2 suggests two main routes that can be related with the number of oxygen atoms remaining in the products. In the upper part of the Scheme 2, after activation of dioxygen to render (alkene)(peroxo) species, the C–O bond formation seems to be a consequence of alkene insertion into the M–O bond while the cleavage of the O–O bond requires an active β -hydrogen.^{[10]–[12], [15a], [16]} Such type of reactivity is not exclusive of olefins and has been also observed in the oxygenation of bis(picoyl)imine.^[19] Furthermore, the formation of 2-rhoda/iridaoxetane complexes requires several elementary steps, including O_2 coordination, O–O bond cleavage and C–O bond formation.

Although 2-metalla-1,2-dioxolanes have been known for a long time,^{[20], [21], [22]} those coming from reactions with dioxygen are very scarce with only two isolated examples in rhodium and

iridium chemistry, namely the mononuclear complex^[13d] $[\text{Ir}(\text{OC}_8\text{H}_{12})(\text{P}_3\text{O}_9)]^{2-}$ and the dinuclear $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{Ph}_2\text{N}_3)\}_2]$.^[13b] Noticeably, O_2 uptake measurements for both reactions proved that these are 100% atom-economy processes. Although this suggests a bimolecular mechanism, which could be similar to that well-known in copper^[23] or nickel^[24] chemistry for the cleavage of the O–O bond (Scheme 1), very little is known about the reaction pathways yielding rhoda- or irida-oxetanes.

This mechanistic panorama, which is based on the closed-shell M^I and M^{III} states ($M = \text{Rh}, \text{Ir}$), becomes more complicated if open-shell intermediates are involved. Paramagnetic species have been seldom invoked in this context, but de Bruin *et al.* elegantly demonstrated that 'Ir(cod)' moieties leading to stable 'Ir(cod)(O_2)' complexes enhanced their reactivity towards C–O bond formation after one-electron oxidation to $[\text{Ir}^{\text{II}}(\text{cod})]^+$ radicals.^[25] Moreover, this group also characterized rare paramagnetic superoxo intermediates of the type $[\text{Ir}^{\text{III}}(\text{cod})(\text{O}_2)]^+$.^[26]

Some of us reported the oxygenation of cod in the mononuclear complex $[\text{Rh}(\text{cod})(\text{Ph}_2\text{N}_3)]$ (**1**) to the unique dinuclear 2-rhoda-oxetane compound $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{Ph}_2\text{N}_3)\}_2]$ (**2**, Scheme 3), which has remained since then as the single example in rhodium chemistry.^[13b]

Scheme 3. Oxygenation of $[\text{Rh}(\text{cod})(\text{Ph}_2\text{N}_3)]$ (**1**) to render the 2-rhoda-oxetane complex **2**.

The extraordinary behavior of complex **1** towards O_2 prompted us to find the key factors driving the reaction towards selective C–O bond formation. In this work, we showcase a joint experimental-computational study giving a fundamental understanding of how dioxygen activation by Rh can yield effective oxygen transference to olefins. This study provides evidences for a bimetallic mechanism in which two rhodium atoms assist the 4-electron reduction of dioxygen giving a di- μ -oxo intermediate. This species undergoes an intramolecular rearrangement via a concerted transfer of each oxygen atom to a co-ordinated olefin resulting in two new C–O bonds in a controlled fashion.

Results and Discussion

Oxygenation of the cod ligand in complex **1**.

Studies were initiated by optimizing with the MPWB1K functional (see Supporting Information) the ground-state structure of the mononuclear complex $[\text{Rh}(\text{cod})(\text{Ph}_2\text{N}_3)]$ (**1**) and the 2-

rhodaoxetane compound $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{Ph}_2\text{N}_3)\}_2]$ (**2**). Metric parameters of the optimized structure for **2** were found to be in a very good agreement to those found in the molecular structure of the complex^[13b] (see Supporting Information). For the mononuclear compound **1**, no molecular structure is available.^[27]

O₂-binding to 1. The binding of dioxygen to $[\text{Rh}(\text{cod})(\text{PhN}_3\text{Ph})]$ (**1**) to give $[\text{Rh}(\text{cod})(\text{O}_2)(\text{PhN}_3\text{Ph})]$ (**1-O₂**, **I2**) has been analyzed in the closed-shell singlet (CSS, green), open-shell triplet (OST, red), and open-shell singlet (OSS, blue) potential energy surfaces (Figure 1). The reaction starts in the triplet energy surface with the interaction of the filled d_{z^2} orbital of rhodium with the π^* -MO of O₂. After the formation of an initial van der Waals complex (OST-I1), the system evolves to OST-I2 through the easily accessible transition state OST-TS1.

Spin densities and natural atomic orbital occupancies in OST-I2 indicate that one unpaired electron lies primarily in the O₂- π^* orbital and is equally distributed over both oxygen atoms. The second unpaired electron is mostly localized in a rhodium-centered MO. Accordingly, the spin densities on Rh, O1, and O2 were found to be 0.52, 0.66 and 0.79, respectively (Figure 1, inset). No spin-density was found on the redox non-innocent triazenide ligand despite it is potentially suitable to accommodate the unpaired electron.^[28]

Figure 1. Gibbs energy profile in toluene, for dioxygen binding to $[\text{Rh}(\text{cod})(\text{PhN}_3\text{Ph})]$ (**1**) (MPW1K/SMD/BS2). Spin state of the stationary points are depicted in red (OST), blue (OSS) and green (CSS). Only the N atoms of the triazenide ligand and the double bonds of the cod ligands are shown by clarity. The inset shows the spin-density plot for OST-I2. O–O bond distances (Å) are given in red. Color code: Rh, yellow; O, red; N, blue; C, gray.

These data are thus consistent with a description of OST-I2 as a diradical in which an ‘end-on’ monohapto superoxo ligand $\{\text{O}_2\}^-$ is bonded to a $\{\text{Rh}^{\text{II}}(\text{cod})(\text{Ph}_2\text{N}_3)\}^+$ moiety. In addition, the O–O bond distance in OST-I2 (1.251 Å) is slightly longer than in free oxygen (1.21 Å) –as expected for a η^1 -superoxo ligand–

although somewhat shorter than those reported in previous DFT-calculated η^1 -superoxo ligands in complexes of cobalt,^[29] iridium^[29] or palladium.^[30]

From an inner-sphere mechanism (Figure 1), coordination of dioxygen to **1** triggers the transfer of one electron (from rhodium to dioxygen) eventually giving OST-I2. Nonetheless, this species could have also been the result of an outer-sphere mechanism^[31] leading to the ionic-radical pair $\{\text{Rh}^{\text{II}}(\text{cod})(\text{Ph}_2\text{N}_3)\}^+$ and $\{\text{O}_2\}^-$ in a first instance, but the collapse of this ionic pair to produce OST-I2 is expected, since the reaction takes place in a non-polar solvent.

The corresponding configurations of the open-shell singlet (OSS-I2) and closed-shell singlet (CSS-I2) have been also included in Figure 1, right. Metric parameters of OSS-I2 were found to be almost identical than those showed by OST-I2, while CSS-I2 fits in a description as $[\text{Rh}^{\text{III}}(\text{cod})(\text{O}_2)(\text{Ph}_2\text{N}_3)]$ with dioxygen reduced in two electrons (peroxo ligand) and η^2 -coordinated to rhodium. Accordingly, elongation of the O–O bond distance to 1.35 Å was observed in CSS-I2.

From an energetic point of view, OSS-I2 was found to be less stable than OST-I2 by 7.5 kcal mol^{−1} and, much to our surprise, this also applies to the closed-shell singlet peroxo-complex (CSS-I2), although the difference relative to OST-I2 was found to be smaller (5.9 kcal mol^{−1}) (Figure 1).

It is worth noting that the well-known redox ‘non-innocent’ nature of dioxygen can yield three extreme canonic forms when bound to a transition metal as a consequence of the internal-transfer of 0/1/2 electrons (A/B/C, respectively, for an ‘RhL₄’ fragment, Scheme 4). Among them, the peroxo species C having dioxygen reduced in two-electrons are the typical products in rhodium chemistry,^[32] with no known examples of the A and B forms to the best of our knowledge.

Scheme 4. Canonic forms of ‘RhL₄(O₂)’ and square-planar dioxygen Rh complexes.

Nonetheless, complexes with dioxygen coordinated to rhodium(I) without neat electron transfer have been also reported, but they are species of the type $\text{RhL}_3(\text{O}_2)$ with dioxygen being the fourth ligand in a square-planar geometry (D, Scheme 4).^[33]

The consistence of this unexpected result was checked by computing the relative stabilities of the superoxo (OST-I2) and peroxo (CSS-I2) intermediates with different functionals. Regardless the percentage of exact exchange in the functional (see Supporting Information), the open-shell triplet $\text{Rh}(\text{II})\{\text{O}_2\}^+$ intermediate was found to be more stable than the closed-shell singlet $\text{Rh}(\text{III})\{\text{O}_2^{2-}\}$ with all functionals (PBE-D3: 1.8 kcal mol^{−1}; TPSSH: 1.8 kcal mol^{−1}; M06: 7.1 kcal mol^{−1}; MPWB1K: 5.9 kcal mol^{−1}; MPWB1K-D3: 4.7 kcal mol^{−1}).

O–O-bond cleavage. Once the mononuclear complex **1-O2** (**I2**) is formed, it could start a bimolecular process toward species of the type $\text{Rh}_2(\mu\text{-peroxo})$ and then $\text{Rh}_2(\mu\text{-oxo})_2$, allowing the cooperative cleavage of the oxygen–oxygen bond. This possibility has been studied in the three potential energy surfaces, CSS (green), OST (red), and OSS (blue) (Figure 2). Selected structural parameters of intermediates **I3**, **I4**, and **I5** have been included in Table 1 and in the Supporting Information, as well as for the transition states.

The interaction of complex **1** with OST-**I2** leads to an end-on $\{\text{Rh}(\mu\text{-}\kappa^1\text{-O}_2)\text{Rh}\}$ adduct (OST-**I3**) with a low barrier (1.1 kcal mol⁻¹). Major change in the structure of OST-**I3** relative to **1** and OST-**I2** is the de-coordination of one of the nitrogen atoms from Rh' in such a way that one oxygen atom in OST-**I2** has literally replaced one of the nitrogen ends of the triazenide ligand in the incoming molecule (Figure 2). Therefore, an almost perfect square-planar geometry for Rh' was observed in OST-**I3**.

Figure 2. Gibbs energy profile (in kcal mol⁻¹) in toluene, for the cleavage of the molecule of dioxygen (MPW1K/SMD/BS2). The spin states of the stationary points are depicted in red (OST), blue (OSS) and green (CSS). Only the N atoms of the triazenide ligand and the double bonds of the cod ligands are shown by clarity. O–O bond distances (Å) are given in red. Color code: Rh, yellow; O, red; N, blue; C, gray.

The corresponding Gibbs energy profiles of the open-shell singlet and closed-shell singlet surfaces (in blue and green, respectively, Figure 2), give both OSS-**I3** and CSS-**I3** higher in energy than OST-**I3** by 5.1 and 5.3 kcal mol⁻¹, respectively. The structure of OSS-**I3** was found to be very similar to that described above for OST-**I3**. However, the diamagnetic intermediate CSS-**I3** is better described as an $\{\text{Rh}(\mu\text{-}\kappa^1\text{-}\eta^2\text{-O}_2)\text{Rh}\}$ complex (Table 1 and Supporting Information).

Spin-density plots of intermediates OST-**I3** and OSS-**I3** (Figure 3, top) indicate that one of the two electrons is mainly located on one of the rhodium atoms (Rh) and the other is almost equally distributed between the two oxygen atoms in both species. Moreover, since the electron distributions of OST-**I3** was found to be similar to that of the corresponding mononuclear intermediate OST-**I2**, we can conclude that this step takes place

without further transference of electrons from dioxygen to rhodium.

Table 1. Selected bond distances (Å) for complex **1**, MECP, and intermediates **I2–I5**.

	Rh,Rh'	Rh–O	Rh–N	Rh'–O	Rh'–N'
1	---	---	2.10, 2.10	---	---
I2	---	2.08, 2.38	2.06, 2.36	---	---
I2	---	2.02, 2.42	2.06, 2.33	---	---
I2	---	1.97, 1.99	2.01, 2.16	---	---
I3	4.51	2.07, 2.41	2.05, 2.31	2.13, 3.00	2.11, 2.79
I3	4.51	2.06, 2.44	2.05, 2.29	2.11, 2.99	2.11, 2.81
I3	4.16	1.97, 2.00	2.01, 2.11	2.17, 3.04	2.10, 2.92
MECP	4.28	2.03, 2.14	2.02, 2.20	2.18, 3.00	2.11, 2.72
I4	4.13	2.00, 2.43	2.08, 2.34	2.02, 2.36	2.07, 2.34
I4	4.08	2.03, 2.29	2.06, 2.34	2.03, 2.83	2.06, 2.34
I5	3.03	1.97, 1.99	2.09, 2.13	1.97, 1.99	2.09, 2.13

Figure 3. Spin-density plots of intermediates OST-**I3**, OSS-**I3**, OST-**I4**, and OSS-**I4**.

The next step in the reaction gives intermediates **I4** in the open-shell singlet and open-shell triplet surfaces, while CSS-**I3** directly evolves to CSS-**TS4** (Figure 2). From a structural point of view, the dioxygen binding to rhodium in OST-**I4** and OSS-**I4** was found to be quite different, being $\mu\text{-}\kappa^1\text{-}\kappa^1\text{-peroxo}$ in the former, but $\mu\text{-}\eta^2\text{-}\eta^2\text{-peroxo}$ in the later (Figures 2, 3, Table 1, and Supporting Information).

The open-shell singlet OSS-**I4** was found to be more stable than the corresponding open-shell triplet OST-**I4** by 2.7 kcal mol⁻¹. Consequently, a spin-crossover from the open-shell triplet to the open-shell singlet potential energy surface takes place through **MECP**, which was found to be located 8.5 kcal mol⁻¹ above OST-**I3**.

Spin-density plots of the intermediates **OST-I4** and **OSS-I4** (Figure 3, bottom) revealed that the spin density is mainly located on the rhodium atoms, with the two electrons antiferromagnetically coupled in the later. In full agreement with the peroxo nature of the O–O unit in the intermediates **I4**, they show a stretched O–O bond distance of 1.42 Å.

The significance of this step is notable, since it accounts for a second reduction of dioxygen in one electron. Moreover, it is now clear why the closed-shell singlet **CSS-I3** directly evolves to **CSS-TS4**, since two electrons were already transferred in the formation of the peroxo derivative **CSS-I2**. At this point, and knowing the tendency of dinuclear Rh^{II}/Rh^{III} complexes to form metal-metal bonds,^[34] which also applies to mixed-valent Rh^I/Rh^{II} derivatives,^[35] the hypothetical dinuclear complexes with a rhodium–rhodium bond and {Rh^{II}(μ-κ¹:κ¹-peroxo)Rh^{II}} and {Rh^{II}(μ-η²:η²-peroxo)Rh^{II}} cores have also been studied. In both cases a minimum of energy was located in the closed-shell potential energy surface (Figure 4), but more than 40 kcal mol⁻¹ above **OSS-I4**.

Figure 4. Optimized structures of Rh^{II}/Rh^{III} metal-metal bonded peroxo complexes. Only the N atoms of the triazenide ligand are shown by clarity. Color code: Rh, yellow; O, red; N, blue; C, gray.

In addition, complexes derived from changes in the geometry of the rhodium atoms in the intermediate **OSS-I4** were also investigated, in particular, those having rhodium in a pseudo-tetrahedral geometry.^[36] All the attempts ended up in **OSS-I4**, which appears to be the key intermediate in which the O–O bond cleavage starts. Noteworthy, the diamond core μ-η²:η²-peroxo was only obtained in the open-shell singlet potential surface (**OSS-I4**), which in turn shows the lowest activation barrier (**OSS-TS4**) to the intermediate **I5** (Figure 2). Optimization toward the products starting from **OSS-TS4**, following the transition vector, leads to the closed-shell singlet intermediate **CSS-I5**. Structural parameters for this closed-shell singlet intermediate (Table 1 and Supporting Information) agree with a complex having a 'Rh^{III}(μ-O)₂Rh^{III}' core, as a consequence of the transference of two electrons from oxygen to both rhodium atoms (one electron per rhodium). **CSS-I5** thus represents the last step in the cleavage of the molecule of dioxygen, d(O,O) = 2.55 Å. Interconversion between the μ-η²:η²-peroxo and the di-μ-oxo cores have been extensively studied in copper chemistry,^[23] but it has not precedent in rhodium chemistry. It is important to remark that the spin density of the transition state in which the O–O bond cleavage occurs (**OSS-TS4**) is equally distributed between both rhodium and both oxygen atoms; more specifically, the rhodium atoms are coupled

antiferromagnetically in the same way that oxygen atoms are (Figure 5, right).

Figure 5. Spin-density plots of **OST-TS4** (left) and **OSS-TS4** (right).

The transition states describing the O–O bond cleavage in **OST-TS4** and **CSS-TS4** were found to be at higher energies (36.3 and 47.1 kcal mol⁻¹, respectively) than **OSS-TS4** (29.7 kcal mol⁻¹). To check the consistence of the results, the relative Gibbs energies of the transition states **TS4** were recalculated with two more functionals (TPSSH and M06). Whatever the functional is, we found that the open-shell structure of **OSS-TS4** is the lowest in energy (with relative Gibbs energies of 18.4 and 24.6 kcal mol⁻¹ from TPSSH and M06, respectively). Moreover, **CSS-TS4** was found at 22.5 and 30.7 kcal mol⁻¹, and **OST-TS4** at 29.4 and 34.3 kcal mol⁻¹ (TPSSH and M06 values, respectively).

Next, it should be indicated that the value of 29.7 kcal mol⁻¹ for **OSS-TS4** (Figure 2) seems to be too high for a reaction that proceeds to completion at room temperature in two hours. Consequently, the open-shell singlet and triplet structures of **TS4** have been reoptimized including Grimme's dispersion corrections (MPWB1K-D3 calculations).^[37] Despite the influence of dispersion interactions in the geometries of the transition states is very small, dispersion has a huge effect in the stabilities of these dinuclear transition states. Both are stabilized by more than 15 kcal mol⁻¹ with respect the mononuclear **1** + O₂. The relative Gibbs energies of **OSS-TS4** and **OST-TS4** were found to be 13.9 and 21.2 kcal mol⁻¹, respectively (MPWB1K-D3), in better agreement with the experimental data. In the same line, reoptimization of **OST-I2** and **CSS-I2** including Grimme's dispersion corrections (MPWB1K-D3 calculations) stabilize both species, placing their relative Gibbs energies 6.7 (**OST-I2**) and 11.4 (**CSS-I2**) kcal mol⁻¹ above **1** + O₂, without significant change in their geometries.

C–O-bond formation. Finally, the oxygenation of the two cod ligands from the di-μ-oxo complex **CSS-I5** takes place in two sequential steps with low energy barriers, which involve the insertion of the oxide ligands into the Rh–olefin bonds to yield the very stable dirhodadioxetane product **2** (Figure 6). This noticeable reaction arises from the enhanced electrophilicity of the oxo ligand when bonded to two rhodium(III) atoms. Overall, according to the Gibbs energy profile shown in Figures 1, 2, and 6, the oxygenation of two cod units in [Rh(cod)(PhN₃Ph)] (**1**) is an exoergic process by –63.2 kcal mol⁻¹.

Figure 6. Gibbs energy profile (in kcal mol⁻¹) in toluene for the oxygenation of the cod ligands (MPW1K/SMD/BS2) in the closed-shell potential surface (green). Hydrogens have been omitted and only the N atoms of the triazenide ligand are shown for clarity. Color code: Rh, yellow; O, red; N, blue; C, gray.

Comments on the mechanism for the oxygenation of cod in complex 1.

The mechanism we have characterized for dioxygen incorporation into cod promoted by the rhodium complex **1** and via a superoxo intermediate is schematized in Scheme 5, showing the evolution of the spin density along the reaction. Noticeably, O₂ activation and coordination of the second rhodium reactions take place at the open-shell triplet PES, the cleavage of the O–O bond occurs at the open-shell singlet PES, while C–O bond formation takes place at the closed-shell PES.

Scheme 5. Mechanism for the dioxygen activation in **1**, showing the evolution of the spin state and density along the reaction.

Although the most energy-demanding step in this energy diagram corresponds to the O–O bond cleavage (OSS-TS4), which takes place in the open-shell singlet PES, a key intermediate is the triplet superoxo OST-I2 complex. This species can be considered as a ‘carrier of activated-dioxygen’, since a new molecule of complex **1** prefers to react with OST-I2 rather than with free O₂, initiating thus the bimolecular path for the O–O bond cleavage. Moreover, from a general perspective, we propose that a superoxo complex [Rh(cod)(L₂)(O₂)] more stable than the corresponding peroxo redoxomer, but less stable than the starting materials [Rh^I(cod)(L₂)] + O₂ is the suitable candidate for olefin oxygenation. Consequently, the relative stability of the superoxo/peroxo redoxomers in a series of

complexes of the type [Rh(cod)(L₂)(O₂)] (L₂ = N,N-binucleating ligand) is currently being analysed by DFT calculations.^[38] Interestingly, during the course of this analysis we found that the mononuclear complex [Rh(cod)(OnapyMe₂)] (**3**, HOnapyMe₂ = 5,7-dimethyl-1,8-naphthyridine-2-one) also fits in the above described requirements. As shown in Figure 7, the Gibbs energy of the open-shell triplet OST-3-O₂ was found to be in between those of **3** + O₂ and CSS-3-O₂ at the same level of theory than above (see Figure 1).

Figure 7. DFT-calculated structures (MPWB1K/SMD/BS2) for complexes **3** (left) and **3**-O₂ as open-shell triplet (middle) and closed-shell singlet (right). Code color: Rh, yellow; O, red; N, blue; C, gray. Relative Gibbs energies in acetone given in kcal mol⁻¹.

Moreover, the Gibbs energy difference between OST-3-O₂ and CSS-3-O₂ was found to be even larger (by 9.3 kcal mol⁻¹) than that found for the pair OST-I2/CSS-I2 (5.9 kcal mol⁻¹, Figure 1). As for the pair OST-I2/CSS-I2, the open-shell triplet OST-3-O₂ was found to be more stable than the two-electron reduced closed-shell singlet CSS-3-O₂ with all the functionals employed (PBE-D3: 5.5 kcal mol⁻¹; TPSSH: 5.0 kcal mol⁻¹; M06: 9.6 kcal mol⁻¹; MPWB1K: 9.3 kcal mol⁻¹).

Oxygenation of the cod ligand in complex 3.

According to the above calculations and forecast, complex [Rh(cod)(OnapyMe₂)] (**3**) was found to react with oxygen to give the 2-rhodaioxetane complex [[Rh(OC₈H₁₂)(OnapyMe₂)]₂] (**4**), which was isolated as yellow microcrystals. Complex **4** represents the second example of a 2-rhodaioxetane compound coming from an oxygenation reaction with dioxygen. However, complex **3** was found to be more reluctant to react with dioxygen in toluene than **1**, since the reaction progressed only a 10 % after one day under atmospheric pressure. This poor reactivity can be attributed to the main occurrence of the dinuclear complex [[Rh(cod)(OnapyMe₂)]₂] in non-polar solvents.^[39] Nonetheless, in acetone, where the mononuclear isomer is the major species,^[39] a 100 % of conversion was achieved in 24 h. This reaction time could be reduced to 8 h working under 3.5 bar of dioxygen.

In the molecular structure of **4** (Figure 8) two crystallographically equivalent rhodium atoms are held by two bridging oxygen atoms, which is remarkable considering the ability of the anionic [OnapyMe₂]⁻ ligand to act as bridge in di- and trinuclear complexes.^[39] Nonetheless, this feature by itself is very suggestive of a dimetallic activation of dioxygen.

Figure 8. Molecular structure (ORTEP at 50 % level) of $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{OnapyMe}_2)\}_2]$ (**4**). Hydrogen atoms and solvent molecules have been removed for clarity. Selected bond lengths [Å] and angles [°]: Rh1–O2, 2.075(2); Rh1–O2', 2.075(2); Rh1–N1, 2.053(3); Rh1–N2, 2.517(3); Rh1–C12, 2.036(3); Rh1–Ct1, 2.100(3); O2–C11, 1.463(4); C15–C16, 1.372(5); C11–C12, 1.523(5); O2–Rh1–N1, 169.5(1); O2'–Rh1–Ct1, 176.3(1); C12–Rh1–N2, 168.6(1). Ct1 corresponds to the middle point of the C15–C16 bond. Primed atoms are related to the unprimed ones by the symmetry operation 1-x, -y, 1-z.

The coordination of both rhodium atoms is completed by an oxygenated cod moiety acting as a tridentate ligand (through the σ -Rh–C12 bond, the C15=C16 double bond and the oxygen, O2, of the 2-rhodaioxetane entity) and the nitrogen atoms from the $[\text{Me}_2\text{Onapy}]^-$ ligand. The strong *trans*-influence of the alkyl group produces a considerable enhancement of the Rh–N2 distance up to 2.517(3) Å. Excluding this bond, the geometry around rhodium can be described as square pyramidal.

Complex **4** remained unaltered in CD_2Cl_2 at temperatures below -30°C according to the spectroscopic data (see Supporting Information). The carbon atom bound to rhodium (C1, Scheme 6) resonates at a relatively high field ($\delta = 36.6$ ppm) as a doublet ($J_{\text{C,Rh}} = 16$ Hz) while that bonded to oxygen (C2) gives a singlet shifted to low field ($\delta = 93.4$ ppm). Carbons corresponding to the intact olefin (C5, C6) give the expected two doublets at $\delta = 93.2$ ppm ($J_{\text{C,Rh}} = 6$ Hz) and 104.4 ($J_{\text{C,Rh}} = 7$ Hz), respectively. Broad-line effects were observed in the ^1H NMR spectra on raising temperature to 25°C and simultaneously an orange solid (**5**) precipitates. On a preparative scale, this fully insoluble material could be obtained as single monocrystals by keeping undisturbed a diluted solution of **4** in acetone. Its molecular structure revealed it to be a tetranuclear complex, $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{OnapyMe}_2)\}_2\{\text{Rh}(\text{HO}-\text{C}_8\text{H}_{11})(\text{OnapyMe}_2)\}_2]$ (**5**), in which an almost intact complex **4** (Rh1 and Rh1') binds two mononuclear 1-hydroxy-2-rhoda-5,6,7-allylcyclooctenyl isomers $[\text{Rh}(\text{HO}-\text{C}_8\text{H}_{11})(\text{OnapyMe}_2)]$ (Rh2 and Rh2') through the oxygen atoms of the $[\text{OnapyMe}_2]^-$ ligand (Figure 9).

Figure 9. Molecular structure (ORTEP at 50 % level) of **5**. Hydrogen atoms – except those of the OH groups – and solvent molecules have been removed for clarity. Selected bond lengths [Å] and angles [°]: Rh2–O1, 2.220(3); Rh2–N3, 2.165(4); Rh2–N4, 2.147(4); Rh2–C30, 2.035(5); Rh2–C33, 2.152(5); Rh2–C34, 2.069(4); Rh2–C35, 2.142(5); Rh2–Ct2, 1.838(5); O4–C29, 1.395(6); O1–Rh2–C30, 175.4(2); N3–Rh2–Ct2, 146.9(2); N4–Rh2–Ct2, 151.0(2); hydrogen bond: O4–H, 0.840; O3–H, 2.245; O3–O4, 3.028(8); O3–H–O4, 155.1. Ct1 and Ct2 correspond to the middle point of the C15–C16 bond and the allyl moiety (C33, C34, C35), respectively. Primed atoms are related to the unprimed ones by the symmetry operation 1-x, 1-y, -z.

On the whole, complex **5** is the result of the isomerization of the 2-rhodaioxetane complex **4** into the 16 VE 1-hydroxy-2-rhoda-5,6,7-allylcyclooctenyl complex (**6**, Scheme 6) up to a 50 %, followed by the trapping of two molecules of **6** by the free oxygen atoms (O1 and O1') of the unreacted complex **4**. Accordingly, leaving complex **5** in CD_2Cl_2 or CDCl_3 for 24 h caused the complete transformation into $[\text{Rh}(\text{HO}-\text{C}_8\text{H}_{11})(\text{OnapyMe}_2)]$ (**6**), which was isolated in high yield after working-up (See Supporting Information).

Scheme 6. Transformation of **4** into the 1-hydroxy-2-rhoda-5,6,7-allylcyclooctenyl complex **6**.

Isomerization of **4** into **6** can be easily understood in terms of a shift of the allylic proton H^4 toward the closest oxygen with formation of the allyl moiety and the cleavage of the Rh–O bond. A similar isomerization was observed for complex $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{Ph}_2\text{N}_3)\}_2]$ (**2**),^[13b] so that in both cases, the 2-rhodaioxetane complexes **2** and **4** were found to be the kinetic isomers of the oxygenation reaction, while the 1-hydroxy-2-rhoda-5,6,7-allylcyclooctenyl complexes are the thermodynamic ones.

Conclusions

DFT calculations have been performed to shed light on the outstanding reactivity of the mononuclear complex $[\text{Rh}(\text{cod})(\text{Ph}_2\text{N}_3)]$ (**1**) with dioxygen, which gives the unique 2-rhodaioxetane complex $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{Ph}_2\text{N}_3)_2\}]$ (**2**) with a 100% atom-economy. Calculations revealed that a superoxo open-shell triplet complex is a key intermediate in this oxygenation, which opens the pathway for the bimetallic cooperative cleavage of the O–O bond. Noticeably, the single-electron oxidation of each one of the rhodium atoms in the open-shell singlet intermediate 'Rh(II)(μ -O₂)Rh(II)' to give the closed-shell singlet species 'Rh(III)(μ -O₂)Rh(III)' was found to be the most energetically demanding step. From the di- μ -oxo complex 'Rh(III)(μ -O₂)Rh(III)' the formation of two new C–O bonds takes place in two sequential steps with low energy barriers in the closed-shell singlet PES.

It is worth noting that the mechanism for the oxygenation of olefins with oxygen we have found confirms for the first time the suitability of the electrophilic oxide ligand bonded to rhodium to form C–O bonds by insertion of the oxide into the Rh–olefin bond. This peculiarity is quite remarkable, since related Cu₂O₂ motifs are, on the contrary, particularly important in aromatic ring oxygenation (tyrosinase-activity).^[23,40]

The bimolecular mechanism reported here for O=O cleavage and C–O bond formation is expected to be operative for complexes that give the closed-shell singlet peroxo complex Rh(III){O₂}²⁻ higher in energy than the superoxo counterpart Rh(II){O₂}^{•-}. In this regard, we have found a second example of a rhodium(I) complex, $[\text{Rh}(\text{cod})(\text{OnapyMe}_2)]$ (**3**), which produces a superoxo complex more stable than the related peroxo one and that, according to our predictions, it undergoes a similar oxygenation reaction to the 2-rhodaioxetane compound $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{OnapyMe}_2)_2\}]$ (**4**). Both complexes **2** and **4** are the kinetic products from the reactions of **1** and **3** with dioxygen that evolve to the thermodynamic 1-hydroxy-2-rhoda-5,6,7-allylcyclooctenyl isomers.

The characterization of a Rh(II)-superoxide is still a synthetic challenge. However, this work gives computational evidences that, with the appropriate set of ligands, these species are accessible and can be incorporated in oxidation cycles, as it had been suggested.^[41] Finally, we believe that the important new mechanistic insights shown here will greatly aid the development of Rh-mediated oxygenation reactions with the inexpensive and environmentally friendly dioxygen.

Experimental Section

General methods. Solvents were dried and distilled under argon before use by standard methods.^[42] Carbon, hydrogen, and nitrogen analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer. High-resolution electrospray mass spectra were acquired on a Bruker Microtof-Q (ESI⁺). NMR spectra were recorded on Bruker AV 300, AV 400 and AV 500 spectrometers operating at 300.13, 400.13 MHz and 500.13 MHz, respectively, for ¹H. Chemical shifts are reported in ppm and referenced to SiMe₄, using the internal signal of the deuterated solvent (¹H and ¹³C). The numbering of the OnapyMe₂, OC₈H₁₂ and HO–C₈H₁₁ ligands is

shown in Figure 10. HR-MS High-resolution electrospray mass spectra were acquired on a Bruker Microtof-Q (ESI⁺). Complex $[\text{Rh}(\text{cod})(\text{OnapyMe}_2)]$ (**3**) was prepared according to the literature description.^[39] All other chemicals are commercially available and were used without further purification.

Figure 10. Labels used for the NMR data.

Synthesis of the complexes: $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{OnapyMe}_2)_2\}]$ (4**).** A suspension of $[\{\text{Rh}(\text{cod})(\text{OnapyMe}_2)_2\}]$ (250.0 mg, 0.651 mmol) in acetone (15 mL) was exposed to an atmosphere of dioxygen (3.5 bar) for 8 h. The resulting yellow suspension was concentrated to ca. 2 mL and then it was decanted. The remaining yellow solid was washed with cold acetone (3 x 1 mL) and dried under vacuum. Yield: 140.0 mg (54 %). ¹H NMR (400.13 MHz, CD₂Cl₂, –60 °C) δ = 7.54 (d, *J* = 9.3 Hz, 1H, H³), 6.72 (s, 1H, H⁶), 6.37 (d, *J* = 9.3 Hz, 1H, H²), 2.82 (s, 3H, Me¹) and 2.36 (s, 3H, Me²) (OnapyMe₂), 6.02 (t, *J* = 8.0 Hz, 1H, H⁵), 5.36 (t, *J* = 5.5 Hz, 1H, H¹), 4.71 (q, *J* = 7.8 Hz, 1H, H⁶), 4.37 (t, *J* = 6.6 Hz, 1H, H²), 3.64 (m, 1H, H^{8a}), 2.26 (m, 2H, H^{4a}+H^{7a}), 1.93 (m, 1H, H^{4b}), 1.87 (m, 1H, H^{7b}), 1.67 (dq, *J* = 11.9, 5.9, 4.3 Hz, 1H, H^{3a}), 1.51 (dd, *J* = 16.9, 7.5 Hz, 1H, H^{3b}) y 0.88 (dd, *J* = 14.0, 8.1 Hz, 1H, H^{8b}) (OC₈H₁₂). ¹³C{¹H}-apt NMR (100.6 MHz, CD₂Cl₂, –60 °C) δ = 170.1 (C¹), 159.6 (C⁸), 157.7 (C⁷), 145.5 (C⁵), 131.8 (C³), 122.3 (C²), 118.6 (C⁶), 112.2 (C⁴), 23.6 (Me¹) and 18.1 (Me²) (OnapyMe₂), 104.4 (d, *J*_{C,Rh} = 7 Hz, C⁶), 93.4 (C²), 93.2 (d, *J*_{C,Rh} = 6 Hz, C⁵), 36.6 (d, *J*_{C,Rh} = 16 Hz, C¹), 35.1 (C⁸), 27.7 (C³), 25.4 (C⁷), 20.2 (C⁴) (OC₈H₁₂). HRMS (ESI⁺, *m/z*, %): 823.1234 (100) [*M*+Na]⁺ (calc. for [*M*+Na]⁺: 823.1208) (error[mDa] = –2.6). Anal. calc. (%) for C₃₆H₄₂O₈N₄Rh₂ (800.55): C 54.01, H 5.29, N 7.00; found: C 54.08, H 4.94, N 7.01.

$[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{OnapyMe}_2)_2\}(\text{Rh}(\text{HO}-\text{C}_8\text{H}_{11})(\text{OnapyMe}_2)_2)]$ (5**).** A solution of $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{Me}_2\text{Onapy})_2\}]$ (**4**) (50.0 mg, 0.060 mmol) in dry chloroform (4 mL) was maintained undisturbed for two days leading. The deposited crystals were decanted, washed with diethyl ether (2 x 3 mL) and dried under vacuum. Yield: 22.3 mg (46 %). Anal. Calc. (%) for C₇₂H₈₂O₈N₈Rh₄·4(CHCl₃) (2076.55): C 43.96, H 4.17, N 5.39; found: C 44.08, H 4.29, N 5.27.

$[\text{Rh}(\text{HO}-\text{C}_8\text{H}_{11})(\text{OnapyMe}_2)]$ (6**).** A solution of $[\{\text{Rh}(\text{OC}_8\text{H}_{12})(\text{OnapyMe}_2)_2\}]$ (**4**) (85.0 mg, 0.106 mmol) in dry chloroform (10 mL) was stirred for two days. The precipitation and further redissolution of complex **5** was observed. The resulting solution was concentrated to ca. 1 mL and layered with diethyl ether (5 mL). After two days the deposited solid was decanted, washed with diethyl ether (3 x 3 mL) and dried under vacuum. Yield: 73.2 mg (86 %). ¹H NMR (400.13 MHz, CDCl₃, 0 °C) δ = 7.04 (br s, 1H, H³), 6.72 (s, 1H, H⁶), 5.81 (br s, 1H, H²), 2.73 (s, 3H, Me¹) and 2.28 (s, 3H, Me²) (OnapyMe₂), 5.50 (br s, 2H, H⁴+H⁶), 4.56 (br s, 1H, OH), 4.35 (br s, 1H, H⁵), 2.73 (s, 4H, Me¹+H²), 2.68 (sh, 1H, H¹), 2.03 (m, 2H, H^{3a}+H^{7a}), 1.87 (br s, 1H, H^{8a}), 1.24 (br m, 2H, H^{3b}+H^{7b}), 0.81 (m, 1H, H^{8b}) (HO-C₈H₁₁). ¹³C{¹H}-apt NMR (100.6 MHz, CDCl₃, 0 °C) δ = 172.8 (C¹), 161.6 (C⁸), 157.9 (C⁷), 144.9 (C⁵), 130.4 (C³), 121.5 (C²), 118.6 (C⁶), 112.3 (C⁴), 23.7 (Me¹) and 17.8 (Me²) (OnapyMe₂), 92.7 (d, *J*_{C,Rh} = 8 Hz, C⁵), 85.3 (C²), 71.03 (d, *J*_{C,Rh} = 11 Hz) and 65.9 (d,

$J_{C,Rh} = 13$ Hz) (C^4 and C^6), 53.6 (d, $J_{C,Rh} = 23$ Hz, C^1), 38.3 (C^8), 35.4 (C^3), 24.7 (C^7). HR-MS (ESI⁺, m/z , %): 401.0731 (100) $[M+H]^+$ (calc. para $[M+H]^+$: 401.0731) (error[mDa] = 0). Anal. calc. (%) for $C_{18}H_{21}O_2N_2Rh$ (400.28): C 54.01, H 5.29, N 7.00; found: C 53.26, H 4.83, N 6.90.

X-ray diffraction studies on complexes 4-4CHCl₃ and 5-4C₃H₆O.

Intensity measurements were collected with a Smart Apex diffractometer, with graphite-monochromated Mo K α radiation. A semiempirical absorption correction was applied to each data set, with the multiscan^[43] method. All nonhydrogen atoms were refined with anisotropic displacement parameters, except a disordered chloroform molecule in 4-4CHCl₃ that was modelled with a four-fold disorder, with geometrical restraints, and with two isotropic displacement parameters. The hydrogen atoms were placed at calculated positions except those of the carbon atoms bonded to the metal centres and to the μ -O ligands that were located in difference-Fourier maps. All hydrogen atoms were refined isotropically in riding mode. The structures were solved by the direct methods (SHELX97)^[44] and refined by full-matrix least squares (SHELX2013)^[44] in the WINGX^[45] package. CCDC 1521199 and 1521200 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Selected crystallographic data for 4-4CHCl₃: $C_{40}H_{46}Cl_{12}N_4O_4Rh_2$, $M_r = 1278.03$, triclinic, space group P-1, $a = 10.4734(5)$, $b = 11.9502(6)$, $c = 12.1471(10)$ Å, $\alpha = 114.601(1)^\circ$, $\beta = 95.183(1)^\circ$, $\gamma = 110.300(1)^\circ$, $V = 1246.36(13)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.703$ g cm⁻³, $F(000) = 640$, $T = 150(2)$ K, MoK α radiation ($\lambda = 0.71073$ Å, $\mu = 1.349$ mm⁻¹). Data collected with a prismatic block ($0.14 \times 0.07 \times 0.07$ mm). Of 11803 measured reflections (2θ 3.8–55.7°), 5750 were unique ($R_{\text{int}} = 0.0210$). Final agreement factors were $R_1 = 0.0392$ (5059 observed reflections) and $wR_2 = 0.0939$. Data/restraints/parameters 5750/133/300; GOF = 1.027. Largest peak and hole in the final difference map 1.280 and -0.928 e Å⁻³.

Selected crystallographic data for 5-4C₃H₆O: $C_{84}H_{108}N_6O_{12}Rh_4$, $M_r = 1833.42$, triclinic, space group P-1, $a = 10.570(4)$, $b = 13.590(5)$, $c = 15.233(5)$ Å, $\alpha = 85.754(6)^\circ$, $\beta = 70.637(6)^\circ$, $\gamma = 72.740(6)^\circ$, $V = 1970.8(12)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.545$ g cm⁻³, $F(000) = 944$, $T = 100(2)$ K, MoK α radiation ($\lambda = 0.71073$ Å, $\mu = 0.890$ mm⁻¹). Data collected with an irregular block ($0.16 \times 0.11 \times 0.06$ mm). Of 23251 measured reflections (2θ 4.2–54.0°), 8554 were unique ($R_{\text{int}} = 0.0552$). Final agreement factors were $R_1 = 0.0524$ (6708 observed reflections) and $wR_2 = 0.1107$. Data/restraints/parameters 8554/0/492; GOF = 1.069. Largest peak and hole in the final difference map 0.761 and -1.406 e Å⁻³.

Computational Details. All the calculations presented in this work were carried out using the Gaussian09 program^[46] by means of the Density Functional Theory (DFT). The study of oxygenation reactions with O₂ is challenging for DFT methods, for two main reasons. On one side, the system can adopt more than one spin state: the reactions start with a singlet transition metal complex and triplet O₂ and end up with singlet products. Accurate calculation of energy splitting between the low-spin and high-spin states is difficult due to the strong functional dependence it displays.^[47] On the other side, bimetallic μ -peroxo and (μ -oxo)₂ species should be computed, and theoretical studies on compounds with a Cu₂O₂ core have shown that there is also a strong functional dependence on the relative stabilities of both isomers.^[48] The strategy adopted to surmount these problems have been performing the exploration of the potential energy surfaces with the MPWB1K hybrid functional,^[49] that has proved to be suitable for describing open-shell hydrogen-transfer reactions,^[50] and then recalculating with a larger basis set the energy of selected MPWB1K optimized structures using different functionals. The influence of dispersion effects have been assessed by reoptimization of selected structures including Grimme's dispersion corrections^[51] (MPWB1K-D3

calculations). Given the sensitivity of the spin-state splitting with the amount of Hartree-Fock (HF) exchange in DFT functionals, we selected functionals spanning a large range of percentage of HF exchange. To do that, for key structures this splitting was computed, in addition to the MPWB1K (44% HF exchange) with M06^[52] (27% HF exchange), TPSSH^[53] (10% HF exchange) and PBE-D3^[54] (0% HF exchange) functionals. Geometry optimizations were performed in the gas phase with the triple- ζ 6-311G(d,p) basis set for the H, C, N and O atoms and the effective core potential LANL2TZ(f)^[55] basis set for the Rh atoms (BS1). The nature of all the stationary points was further verified through frequency calculations. Furthermore, for transition states, intrinsic reaction coordinate (IRC) calculations were carried out to assess that they connect the corresponding reaction minima. Solvent effects were introduced using the experimental solvents employed through single point calculations on the above gas-phase optimized geometries using the SMD solvation model^[56] and an extended triple- ζ 6-311++G(d,p) basis set for the H, C, N and O atoms (BS2). In this way absolute energies in solution (E_{sol}) were computed in toluene ($\epsilon = 2.374$) for complex 1 and acetone ($\epsilon = 20.493$) for complex 3. These E_{sol} were transformed into G_{sol} (Gibbs energies in solution) by means of:

$$G_{\text{sol}} = E_{\text{sol}} + \text{ZPE} + H_{\text{vib}} + 6k_B T - TS_{\text{mod}}$$

where H_{vib} is the vibrational enthalpy, ZPE is the zero point energy, and S_{mod} is the entropy calculated as proposed by Ziegler et al.^[57] by using the Wertz's approximation for the entropy to fit the experimental solvation entropy of small molecules.^[58] The latter term S_{mod} is defined as:

$$S_{\text{mod}} = S_{\text{elec}} + S_{\text{vib}} + 0.54(S_{\text{trans}} + S_{\text{rot}}) + 0.24$$

with S_{elec} , S_{vib} , S_{trans} , and S_{rot} being the electronic, vibrational, translational, and rotational contributions to the entropy, respectively. This approach has already been used in theoretical studies of O₂ activation with transition metal complexes.^[59] In order to change the standard state from the gas phase (1atm) to solution (1M) a correction of 1.9 kcal mol⁻¹ was applied to all G values.^[60] Unless stated, all the energies reported throughout this work are Gibbs energies in solution (G_{sol}) at the temperature of 298.15 K and 1 M, calculated at the MPW1K/SMD/BS2/MPW1K/BS1 level. As the reactions start with a singlet transition metal complex and triplet O₂ and end up with singlet products, the triplet (T) and singlet (S) potential energy surfaces, as well as the open-shell singlet (OS) have been explored. It is important to note that in open-singlet biradicals, the unrestricted wavefunction is often contaminated by higher spin states, especially by the triplet state. In order to take into account this spin contamination the energy of all stationary points with an open-shell singlet spin state was further corrected with the Yamaguchi approach.^[61] To locate the minimum energy crossing points (MECPs) between potential energy surfaces of different spin, the program developed by the group of Harvey was employed.^[62] To confirm that the MECPs relate the two potential energy surfaces, the MECP structures were optimized in the different spin states involved in the crossing. The Gibbs energies in solution of the MECPs were estimated by adding the contributions to the Gibbs and solvation energies of the previous intermediate to the calculated potential energies of the MECPs.

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Keywords: rhodium • C-O bond formation • rhodaoxetanes • DFT • dioxygen cleavage

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Layout 2:

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Crossing the open-shell triplet potential energy surface (PES) of a rhodium-superoxo complex into the open-shell singlet PES of a dinuclear μ -(peroxo) compound and then to the highly reactive bis(μ -oxo) species in the close-shell singlet PES allows rhodium the effective coupling of oxygen with a C=C bond to form single C–O bonds.

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Rhodium Complexes Promoting C–O Bond Formation in Reactions with Oxygen: The Role of Superoxo Species