

Revisiting the Mukaiyama-type epoxidation for paving the way to the direct conversion of styrene into styrene carbonate in the presence of O₂

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Supplementary materials

The mechanism of the Mukaiyama epoxydation has long been investigated, and it is generally accepted that there is no single mechanism. It is strongly dependent on both the nature of the catalyst and the reaction conditions. Thus, according to Nam, Valentine and co-workers,¹ an acylperoxy radical (**a**) is most likely formed in the first step by the autoxidation of the aldehyde as seen in **Figure S1**. From this point, two different general mechanisms may be envisaged depending on the metallic active center involved. In the first pathway (namely metal-oxo mechanism in red), (**a**) would be later involved in a radical chain, where the Mⁿ⁺ metal center first acts as an initiator, affording the corresponding percarboxylic acid (**b**) that needs further activation through its coordination to Mⁿ⁺ (**c**). Subsequent heterolytic cleavage of the O-O bond in the resulting acylperoxy complex (**c**) afford a metal-oxo species (M⁽ⁿ⁺²⁾⁺=O), that would be the active reagent for oxygen transfer onto the alkene substrate. In the second pathway (namely Lewis acid mechanism, in blue), the radical (**a**) species would directly interact with Mⁿ⁺ affording an acylperoxy complex (**d**) with a higher metal oxidation state than (**c**). Intermediate (**d**) was then proposed to be responsible for the transfer of the oxygen atom to the alkene substrate. It should be noted, however, that the authors do not exclude *a priori* a non-metal assisted mechanism (on the left, in blue).

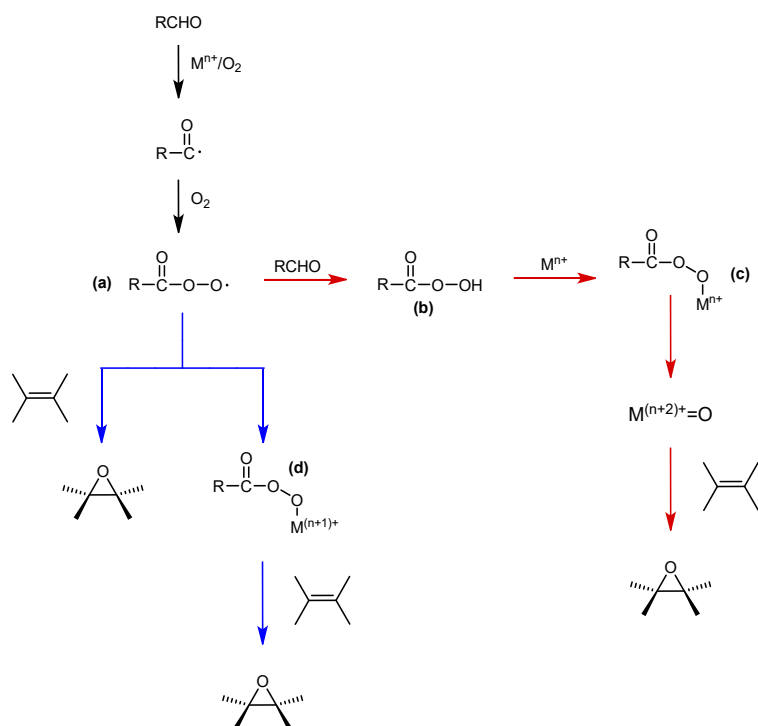


Figure S1. Proposed mechanisms for the Mukaiyama-type epoxidation of olefins with O_2

Preparation of *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1-carboxy-3,4-phenylene-diamine-chloro-Manganese(III) (Mn(III)-Salophen-CO₂H). H₂Salophen ligand² (0.347 g, 0.60 mmol) was dissolved in 20 mL of dry THF under argon in a two-neck round-bottom flask connected to a condenser. [MnCl₂(THF)₂] (0.160 g, 0.60 mmol) was then added to the solution and the mixture was stirred at room temperature for 1 h, then refluxed for 20 min. After cooling at room temperature, triethylamine (0.12 g, 1.20 mmol, 0.17 mL) was then added and the mixture stirred for another 45 min. The volume of the solution was then reduced up to 10 mL under vacuum and allowed to stand at room temperature overnight. After this period, a white powder (triethylammonium chloride) was filtered and discarded. The brown solution was evaporated, leading to a brown solid (Mn(III)-Salophen-CO₂H) that can be recrystallized in THF (yield: 0.350 g, 0.50 mmol, 88 %). IR (KBr, cm⁻¹): 3416 (m), 2958 (m), 1680 (sh), 1610 (s), 1573 (s), 1466 (s), 1392 (s), 1361 (s), 1325 (s), 1249 (s), 1198 (s), 1178 (s), 1097 (s), 1026 (s), 807 (s), 781 (s), 548 (m). HRMS [$\{Mn(III)\text{-Salophen-CO}_2\text{H}\}\text{-Cl}\}^+$ (ESI) : $m/z = 637.28$.

Synthesis of *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1-carboxy-3,4-phenylene-diamine-chromium(III)chloride (Cr(III)-Salophen-CO₂H)³

H₂Salophen ligand (0.290 g, 1 eq, 0.50 mmol) was dissolved in 25 mL of dry THF under argon in a two-neck round-bottom flask connected to a condenser. Then, a solution of [CrCl₃(THF)₃]

(0.190 g, 1 eq, 0.50 mmol) in 25 mL of dry THF was prepared and transferred into a dropping funnel under argon. This solution was added dropwise and the resulting mixture was stirred under reflux for 15 min. After cooling at room temperature, the solution was evaporated under vacuum leading to a dark red solid (Cr(III)-Salophen-CO₂H) (yield: 0.179 g, 53%). IR (KBr, cm⁻¹): 3716 (s), 2958 (s), 2906 (m), 2869 (m), 1699 (m), 1645 (m), 1615 (m), 1585 (s), 1528 (s), 1461 (m), 1417 (m), 1386 (m), 1361 (m), 1324 (w), 1271 (m), 1252 (m), 1200 (m), 1170 (s), 1132 (w), 1027 (w), 963 (w), 915 (w), 879 (w), 830 (w), 771 (m), 748 (w), 638 (w), 549 (w) cm⁻¹. HRMS [$\{\text{Cr(III)-Salophen-CO}_2\text{H}\}-\text{Cl}+\text{H}_2\text{O}\}^+$] (ESI): $m/z = 652.30$.

Names (IUPAC) of the complexes in figure 1

Complex I: Manganese, chloro[[2,2'-[(1*S*,2*S*)-1,2-diphenyl-1,2-ethanediyl]bis[(nitrilo-κ*N*)methylidyne]]bis[6-(1,1-dimethylethyl)-4-methylphenolato-κ*O*]](2-)-

Complex II: Manganese, chloro[[2,2'-[(1*S*,2*S*)-1,2-cyclohexanediyl]bis[(nitrilo-κ*N*)methylidyne]]bis[6-(1,1-dimethylethyl)-4-methylphenolato-κ*O*]](2-)-

Complex IIIa: Manganese, chloro[[2,2'-[(1*S*,2*S*)-1,2-cyclohexanediyl]bis[(nitrilo-κ*N*)methylidyne]]bis[4,6-bis(1,1-dimethylethyl)phenolato-κ*O*]](2-)-

Complex IIIb: Manganese, chloro[[2,2'-[(1*R*,2*R*)-1,2-cyclohexanediyl]bis[(nitrilo-κ*N*)methylidyne]]bis[4,6-bis(1,1-dimethylethyl)phenolato-κ*O*]](2-)-

Complex IVa: Manganese, chloro[[2,2'-[(1*R*,2*R*)-1,2-cyclohexanediyl]bis[(nitrilo-κ*N*)methylidyne]]bis[4,6-bis(heptadecafluorooctyl)phenolato-κ*O*]](2-)-

Complex IVb: Manganese, chloro[[2,2'-[(1*R*,2*R*)-1,2-diphenyl-1,2-ethanediyl]bis[(nitrilo-κ*N*)methylidyne]]bis[4,6-bis(heptadecafluorooctyl)phenolato-κ*O*]](2-)-

Complex Va: Manganese, [[bis[5-methyl-2-(1-methylethyl)cyclohexyl]-2,2'-[(1,2-diphenyl-1,2-ethanediyl)bis(nitrilomethylidyne)]bis[3-oxobutanoato]](2-)-*N*²,*N*^{2'},*O*³,*O*^{3'}]chloro-, [*SP*-5-13-[1*R*-[1α[1*S*^{*},2*S*^{*}(1*R*^{*},2*S*^{*},5*R*^{*}),2β,5α]]]]-

Complex Vb: Manganese, [[bis(mesityl)]-2,2'-[(1,2-diphenyl-1,2-ethanediyl)bis(nitrilomethylidyne)]bis[3-oxobutanoato]](2-)-*N*²,*N*^{2'},*O*³,*O*^{3'}]chloro-, [*SP*-5-13-[1*R*-[1α[1*S*^{*},2*S*^{*}(1*R*^{*},2*S*^{*},5*R*^{*}),2β,5α]]]]-

Complex VI: Manganese(1+), [[2,2'-[1,2-cyclohexanediyl]bis(nitrilomethylidyne)]bis[5-methyl-6-(1-phenylpropyl)phenolato]](2-)-*N*,*N'*,*O*,*O'*-, [*SP*-4-2-[1*R*-[1α(*R*^{*}),2β(*R*^{*})]]]-, hexafluorophosphate(1-)

¹ W. Nam, H. J. Kim, S. H. Kim, R. Y. N. Ho, J. S. Valentine, *Inorg. Chem.* (1996), 35, 1045-1049.

² M. Balas, S. Beaudoin, A. Proust, F. Launay, R. Villanneau, *Eur. J. Inorg. Chem.*, (2021), 1581-1591.

³ M. Balas, L. K/Bidi, F. Launay, R. Villanneau, *Front. Chem.*, (2021), 9, 765108.