

Recyclable Homogeneous Catalysis Enabled by Dynamic Coordination on Rhodium(II) Axial Sites of Metal-Organic Polyhedra

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The activity of catalytic nanoparticles is strongly dependent on their surface chemistry, which controls colloidal stability and substrate diffusion toward catalytic sites. In this work, we studied how the outer surface chemistry of nanostructured Rh(II)-based metal-organic cages or polyhedra (Rh-MOPs) impacts their performance in homogeneous catalysis. Specifically, through post-synthetic coordination of aliphatic imidazole ligands onto the exohedral Rh(II) axial sites of Rh-MOPs, we solubilized a cuboctahedral Rh-MOP in dichloromethane, there-

by enabling its use as a homogeneous catalyst. We demonstrated that the presence of the coordinating ligand on the surface of the Rh-MOP does not hinder its catalytic activity in styrene aziridination and cyclopropanation reactions, thanks to the dynamic Rh-imidazole coordination bond. Finally, we used similar ligand exchange post-synthetic reactions to develop a ligand-mediated approach for precipitating the Rh-MOP catalyst, facilitating the recovery and reuse of Rh-MOPs as homogeneous catalysts.

Introduction

The structuration of catalysts in the form of small and ultrasmall nanoparticles is an efficient strategy to increase their performance due to the facile access of substrates to the catalytic nanoparticle surface.^[1] Furthermore, catalytic nanoparticles can be employed in a wide range of reaction media thanks to the possibility of tailoring their colloidal dispersibility through control of their surface chemistry.^[2] As an alternative type of material, metal-organic cages or polyhedra (MOPs)^[3–6] assembled from metal ions or clusters and organic ligands, also

fall within the size regime of ultrasmall nanoparticles (2–5 nm) and share several physicochemical characteristics with them. These include a high surface density of catalytic metal ions and functional organic groups, which can additionally be post-synthetically modified.^[7] However, unlike nanoparticles, MOPs are molecular entities that can be solubilized, characterized at the atomic level, and reacted stoichiometrically.^[8] Using all these characteristics, we have recently demonstrated that, thanks to the presence of 12 dirhodium paddle-wheel units connected through 24 *m*-*bdc* linkers, the outer surface of cuboctahedral rhodium-based MOPs (Rh-MOPs)^[9] can be post-synthetically functionalized via coordination and covalent chemistry,^[10] opening the way to tuning their solubility and using them as nanoscale scaffolds to transfer substances between immiscible phases^[11] or to capture and recover pollutants under different aqueous and solvent conditions.^[12]

Given the catalytic performance recently reported for structures based on dirhodium paddle-wheel clusters,^[13–15] we explored herein the use of solubilized archetypal cuboctahedron $[\text{Rh}_2(m\text{-bdc})_2]_{12}$ (where *m*-*bdc* = 1,3-benzenedicarboxylate) as a homogeneous catalyst (Figure 1). This strategy combines the leveraging of inherent nanostructuring and concentration of rhodium active sites within the MOP skeleton, along with the post-synthetic adjustability of Rh-MOPs' solubility in various solvents. Interestingly, a pioneer study has shown that the solubilization of low-nuclearity lantern-type Cu(II)-based MOPs through covalent post-synthetic modifications enables the synthesis of homogenous catalysts toward cyclopropanation reactions.^[16] In our study, we selected two reactions typically catalyzed by Rh(II): styrene aziridination and the cyclopropanation of styrene. These reactions usually take place in organic solvents such as dichloromethane. Accordingly, $[\text{Rh}_2(m\text{-bdc})_2]_{12}$ MOP has been modified through the post-synthetic coordination of the aliphatic imidazole ligand 1-dodecyl-1H-imidazole

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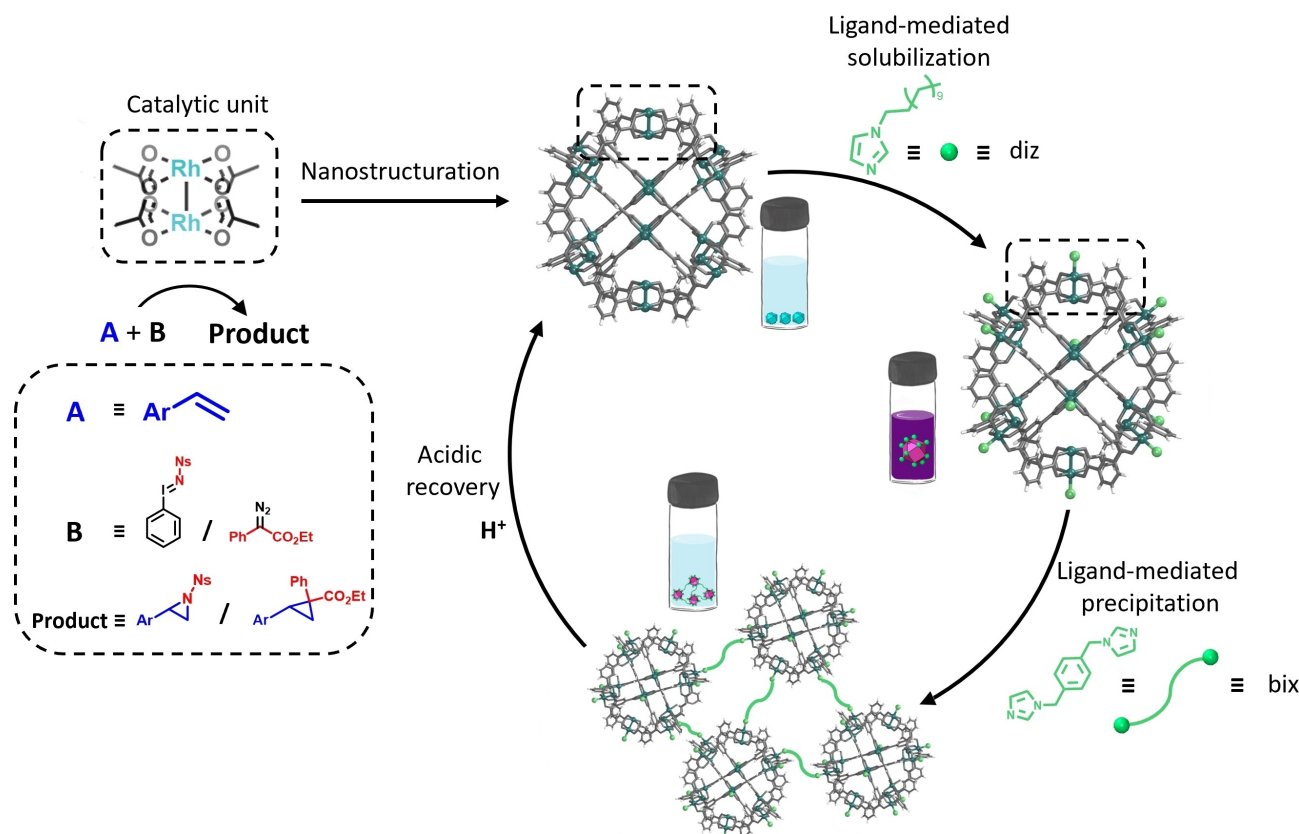


Figure 1. Schematic representation of the different supramolecular strategies implemented aiming to structure, solubilize and recover dirhodium paddlewheel-clusters with catalytic activity towards styrene aziridination and cyclopropanation.

(hereafter referred to as diz) on the outer Rh(II) axial sites, resulting in a soluble MOP with the formula $[Rh_2(m\text{-}bdc)_2]_{12}(diz)_{12}$ (hereafter named as H-RhMOP(diz)).^[17] Thanks to this solubilization in dichloromethane, H-RhMOP(diz) can be utilized as a homogeneous catalyst for both aziridination and cyclopropanation of styrene. In addition, we took advantage of the reversible nature of the coordination of diz to the catalytic surface of H-RhMOP to *in situ* replace it by the ditopic linker 1,4-bis(imidazol-1-ylmethyl)benzene (bix) that triggers the polymerization of $[Rh_2(m\text{-}bdc)_2]_{12}$ clusters into an insoluble product, which can be easily recovered through centrifugation. The subsequent acid-triggered detachment of bix and further addition of diz resulted in the regeneration of H-RhMOP(diz), thus enabling the recovery of the homogeneous catalyst (Figure 1). Overall, we demonstrated that the catalytic properties of the axial Rh(II) sites on the surface of Rh-MOP are preserved in the presence of coordinating imidazole ligands. Thus, it enables their concomitant use as catalytic centres and binding sites to control the solubility and recovery of the Rh-MOP, allowing their use as recyclable homogeneous catalysts for styrene aziridination and cyclopropanation reactions.

Results and Discussion

Catalytic Properties Toward Styrene Aziridination

We initially investigated the catalytic properties of the homogeneous H-RhMOP(diz) catalyst for styrene aziridination in dichloromethane at 25 °C (Figure 2). This reaction relies on the

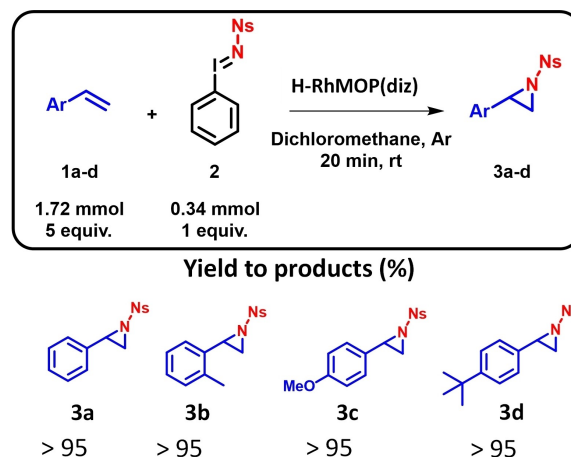


Figure 2. Catalytic results of the styrene aziridination reactions. For all reactions, TONs are higher than 65. TONs were calculated considering only the 12 external rhodium centers.

ability of rhodium(II) centres to form nitrene active intermediates, which further react with olefins to yield the three-membered ring in the aziridine product. All reactions were carried out by adding dropwise the aryl sulfonyl iminoiodane compound (**2**) (0.34 mmols) to a dichloromethane solution containing the styrene substrate (1.72 mmol) and the H-RhMOP(diz) catalyst (0.4 μ mol) at room temperature. Under these conditions, H-RhMOP(diz) catalyst achieved full conversion for the different styrene substrates, including styrene (**1a**), 2-methylstyrene (**1b**), 4-methoxystyrene (**1c**), and 4-*tert*-butylstyrene (**1d**) (Figures 2 and S7–S10).

These results are significant as they suggest that the presence of coordinated diz on the outer surface of H-RhMOP(diz) does not inhibit its catalytic performance. In fact, similar observations were made with axial ligands such as carbenes, pyridines, or thioethers, which do not always impede the catalytic reactivity of dirhodium molecular clusters.^[18,19] In these cases, the preservation of the reactivity of the dirhodium molecular clusters in the presence of coordinating axial ligands is typically explained by either the reversible nature of the coordinative interaction between the ligand and the axial Rh(II) site or the activity of the second Rh(II) axial site in the paddlewheel unit,^[20] which has a much lower association constant with coordinating ligands.^[21] In the case of H-RhMOP(diz), the two catalytically active axial sites are not equivalent, as there is an endohedral and exohedral site. Considering that diz only coordinates to the exohedral axial site,^[17] one could hypothesize that the catalytic activity of H-RhMOP(diz) proceeds through its inner axial site, implying confined catalysis. To investigate the possibility of confined catalysis in H-RhMOP(diz), we performed *in situ* ¹H-NMR studies in dichloromethane-*d*₂. In these experiments, we combined styrene with H-RhMOP(diz) in dichloromethane-*d*₂ and recorded the ¹H-NMR spectrum. We found that the chemical shift and the amplitude of the styrene peaks were not affected by the presence of the MOP (Figure S1). Furthermore, DOSY analysis revealed that the diffusion coefficient of styrene is maintained after the addition of MOP (Figure S2). The results of this ¹H-NMR study rule out any possible host-guest interaction between H-RhMOP(diz) and styrene, indicating that styrene is not confined within the MOP cavity and consequently, the activity of H-RhMOP(diz) proceeds through its outer surface. In line with this hypothesis, we did not observe any significant effect of the degree of steric hindrance of the styrene substrate on the catalytic activity, as shown in Figure 2. Therefore, the catalytic mechanism of H-RhMOP(diz) differs from that of the majority of homogeneous MOP catalysts, in which the catalytic reaction proceeds within their inner cavity.^[22–24]

We reasoned that the surface catalytic activity of H-RhMOP(diz) should be attributed to the dynamic nature of the Rh-imidazole coordination bond. To gather evidence of this dynamic coordination behaviour, we conducted variable temperature UV-Vis experiments on a chloroform solution of H-RhMOP(diz). These experiments revealed clear thermochromic behaviour over a temperature range from 60 °C to –30 °C (Figure 3). Specifically, the band with a maximum at 580 nm observed at high temperatures gradually disappeared, leading

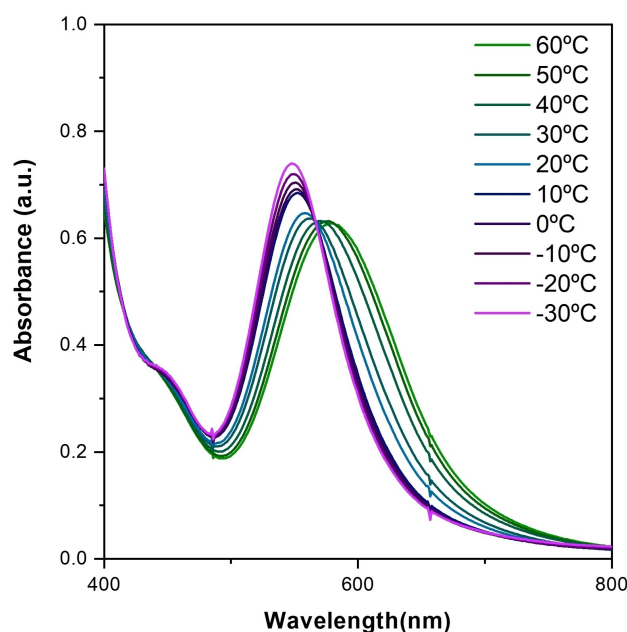


Figure 3. Variable-temperature UV-Vis spectra measured in a chloroform solution of H-RhMOP(diz) (10 mg/mL, in a 0.2 cm quartz cuvette).

to the formation of a new band with a maximum at 550 nm at low temperatures. These changes in spectroscopic features depending on temperature were reversible in series of heating-cooling-heating cycles. The absorption in the range of 550–580 nm corresponds to Band I of the Rh(II) paddlewheel and is very sensitive to the presence of coordinated molecules on its axial site, which, in the case of N-based ligands, induces a blue shift upon coordination, as observed at low temperatures in the variable temperature UV-Vis experiment.^[10] Thus, changes in this region are directly related to changes in the coordination sphere of rhodium centres. Such reversible temperature-dependent changes could be attributed to coordination-discoordination on the external side of H-RhMOP(diz). However, the partial discoordination of diz from the MOP surface at high temperatures did not cause the precipitation of the insoluble H-RhMOP core. This result suggests that despite the shifting of the Rh-imidazole coordination reaction toward dissociation at elevated temperatures, the surface of the H-RhMOP is still influenced by diz. To prove this hypothesis, we conducted ¹H-NMR and DOSY spectroscopy of H-RhMOP(diz) at 25 °C and at 50 °C. We found that neither the chemical shift nor the diffusion coefficient of diz was significantly changed upon heating, indicating that the equilibrium coordination of Rh-imidazole is only partially shifted toward discoordination at elevated temperatures (Figures S3 and S4).

Therefore, the reversible Rh(II)-imidazole coordination equilibrium is capable of maintaining the MOP soluble without blocking its surface catalytic reactivity by transiently leaving the outer Rh(II) axial site available without changing the surface chemistry of the MOP that governs its solubility.

Catalytic Properties Toward Cyclopropanation of Styrene

Once we confirmed that H-RhMOP(diz) is catalytically active, we aimed to study its performance toward a second catalytic process: the cyclopropanation of styrene by reaction with a diazo compound ($\text{N}_2\text{C}(\text{Ph})\text{CO}_2\text{Et}$) in dichloromethane at 39°C (Figure 4). Analogously to the previous reaction, cyclopropanation is based on the formation of a rhodium-carbene active species, which further evolves in the presence of olefines to form the three membered ring in the cyclopropane product. The initial reaction was performed by adding dropwise the diazo compound (1 mmol) in a dichloromethane solution containing the H-RhMOP(diz) catalyst (0.4 μmol s) and styrene (1a) (1.5 mmols) under stirring at 39°C . In this instance, the reaction proceeded with a 38% yield and the most favourable trans isomer was uniquely observed (Figure S11).

Next, we aimed to broaden the applicability of this reaction to 2-methylstyrene (1b), 4-methoxystyrene (1c), and 4-*tert*-butylstyrene (1d), obtaining moderate to good yields in all cases (Figures 4, S13, S15 and S17). Interestingly, we did not observe a decline in catalytic efficiency when larger substrates were utilized. For example, the yield increased from 38% to 60% when the styrene substrate was changed to the bulkier 4-

tert-butylstyrene. These findings demonstrate that the cyclopropanation of styrene is also facilitated by the outer surface of the Rh-MOPs, thus suggesting that non-confined catalysis is taking place.

The incomplete conversion observed in the cyclopropanation reaction catalyzed by H-RhMOP(diz) could be ascribed to the presence of diz on the axial site of the catalytic Rh(II). To evaluate the impact of diz on the catalytic reaction, we conducted the cyclopropanation reaction using a hydrophobic Rh-MOP that is soluble in dichloromethane but lacks axial imidazole ligands on its Rh(II) sites. To this end, we employed a Rh-MOP with formula $[\text{Rh}_2(\text{C}_{12}\text{O-bdc})_2]_{12}$ (hereafter named as C_{12} -RhMOP; where $\text{C}_{12}\text{O-bdc}$ is 5-dodecoxybenzene-1,3-benzene dicarboxylate), as catalyst.^[25] C_{12} -RhMOP is covalently functionalized with aliphatic chains on its surface. Catalytic tests performed with C_{12} -RhMOP revealed a performance very similar to that of H-RhMOP(diz) (Figures 4, S12, S14, S16 and S18), providing further support for our hypothesis that the presence of diz does not hinder the catalytic activity of Rh-MOPs.

To assess the similarity in catalytic activities between C_{12} -RhMOP and RhMOP(diz), we performed a competition experiment using an equimolar mixture of styrene and 4-*tert*-butylstyrene in the presence of either MOP. This test should allow us to identify eventual kinetic discriminations of these catalysts toward the substrates due to the presence of coordinating diz. In this experiment, we used 1.5 mmols of each styrene reagent in 11 mL of dichloromethane in the presence of 0.4 μmol s of either C_{12} -RhMOP or H-RhMOP(diz). Under these reaction conditions, the observed product ratio styrene to 4-*tert*-butylstyrene was 11:89 for C_{12} -RhMOP and 33:67 for H-RhMOP(diz) (Figure S19). These data indicate that the kinetic discrimination observed in both C_{12} -RhMOP and H-RhMOP(diz) is very similar, with the 4-*tert*-butylstyrene being favoured over the bare styrene derivative in both cases (Figure S20). This preference for the bulkier reagents appears to be driven more by electronic effects than steric factors. Interestingly, this preference persists regardless of the presence of imidazole ligands coordinating the external rhodium centers. These results further confirm that the catalytic activity of the Rh-MOPs studied proceed predominantly through their exohedral surface rather than within the MOP cavities. In addition, these results suggest that the diffusion requirements of both catalysts are comparable, and therefore, the presence of diz does not introduce an additional steric hindrance penalty on the outer Rh(II) sites. Therefore, the presence of diz attached to the surface of H-RhMOP does not modify or hinder the catalytic activity of the exohedral Rh(II) axial sites. Conversely, Furukawa and co-workers observed that the presence of imidazole ligands in the Rh(II) axial sites of MOP-based heterogeneous catalysts leads to an increase in the electron density on the metallic site, resulting in changes in their catalytic activity.^[14] We do not observe this effect due to the dynamic nature of the imidazole-Rh(II) coordination bond in solution, which, at the reaction temperature (39°C), is partially shifted toward dissociation (Figure 3).

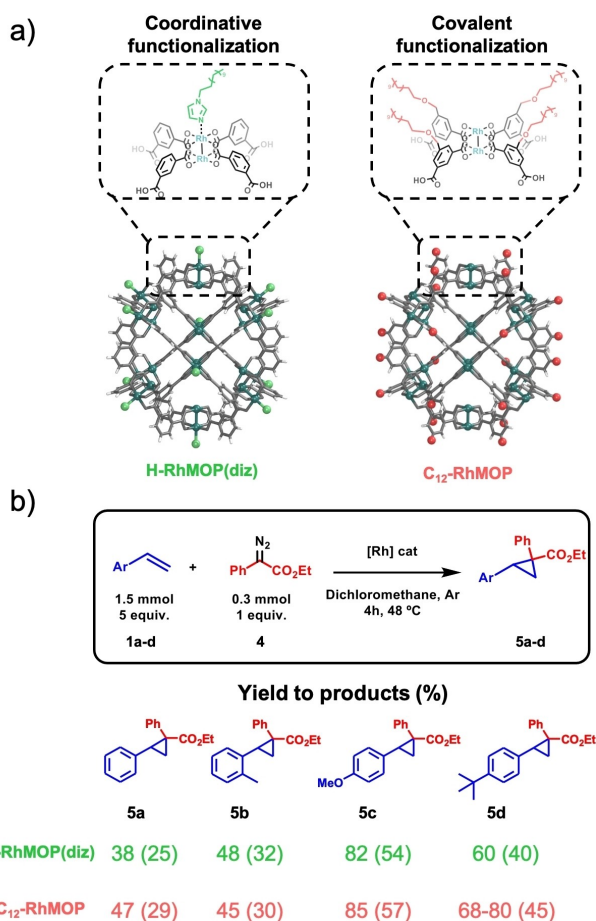


Figure 4. Catalytic results of the cyclopropanation of styrene reactions. Yields indicated in green and red correspond to reactions catalysed by H-RhMOP(diz) and C_{12} -RhMOP, respectively. TONs are indicated in parenthesis. TONs were calculated considering only the 12 external rhodium centers.

Ligand Mediated Precipitation and Re-Solubilisation of RhMOP for Homogeneous Catalysis

The reversible Rh-imidazole coordination is responsible for the solubility and catalytic properties of H-RhMOP(diz). We envisaged that such reversible interactions on the surface of H-RhMOP(diz) could also be used to *in situ* change the surface ligand to trigger its precipitation from the reaction medium, facilitating its recovery. Specifically, we aimed to *in situ* polymerize the H-RhMOP(diz) catalyst into an insoluble product by exchanging the monodentate diz ligand by the bidentate 4-bis(imidazol-1-ylmethyl)benzene (bix) linker.^[17,26] Thus, we added 24 molar equivalents of bix per MOP catalyst to the reaction mixture after the styrene cyclopropanation reaction. The addition of bix caused the quantitative precipitation of the H-RhMOP catalyst (Figure S5), which can be recovered through centrifugation. The ¹H-NMR analysis of the recovered solid after its digestion in acidic conditions confirmed the ligand exchange reaction between diz and bix (Figure S6). Once the catalyst was recovered, we aimed at its regeneration. To this end, we treated the purple solid with a 10 ml mixture containing methanol and HCl aqueous solution (0.03 M) at a volume fraction of 10:1. The acidic mixture induced the protonation of the imidazole groups of bix causing its detachment from the H-RhMOP surface (Figure 5a). Once H-RhMOP was recovered, it was reacted with 12 molar equivalents of diz to yield the dichloromethane soluble H-RhMOP(diz) (Figure 5b) that was used in a subsequent catalytic cycle without loss of activity (Figures S21 and S22).

Conclusions

In conclusion, we have developed an homogeneous Rh(II)-based catalyst from H-RhMOP through the coordination of an aliphatic imidazole ligand on its surface. Our results show that the catalytic activity of the outer surface of Rh-MOP is maintained despite the presence of coordinating ligands due to the dynamic, reversible nature of the imidazole-Rh coordination bond. This dynamic behaviour enabled us to trigger the polymerization of Rh-MOPs *in situ* through a ligand exchange reaction that caused the precipitation of the Rh-MOP catalyst, enabling its easy recovery. This recovered catalyst could then be converted back to the homogeneous form through further coordination chemistry. Therefore, our ligand mediated approach for the solubilization-precipitation for Rh-MOPs enables to combine the merits of homogeneous (i.e., ease of mass transfer) and heterogeneous (i.e., easy recovery) systems in a single nanostructured catalyst.

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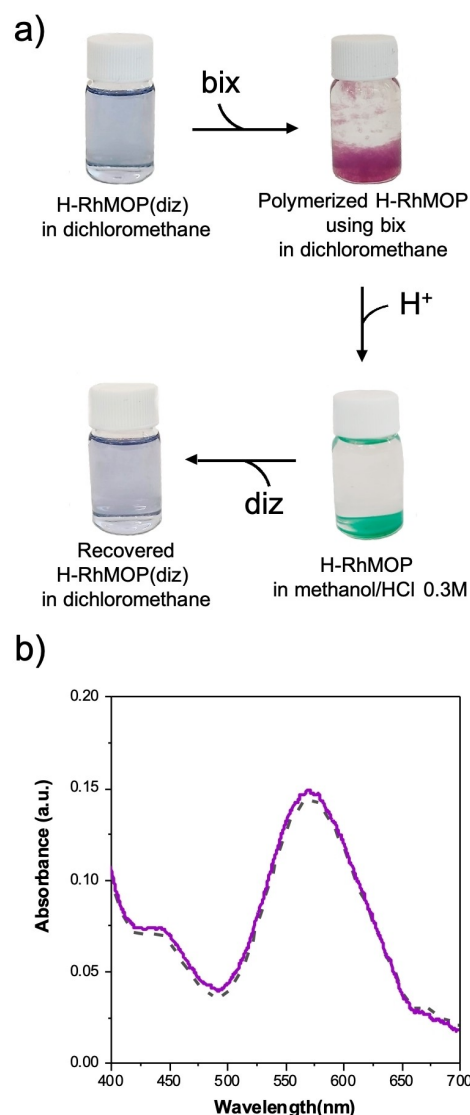


Figure 5. (a) Schematic representation depicting a complete linker-mediated precipitation and re-solubilisation cycle. (b) UV-Vis spectra of a H-RhMOP(diz)₁₂ in dichloromethane before (line) and quantitatively recovered (dash line) after the cyclopropanation reaction using the linker-mediated precipitation and re-solubilisation strategy.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

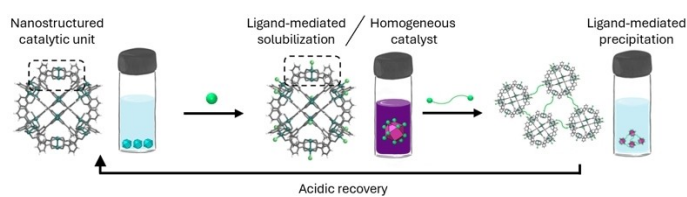
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The post-synthetic coordinative functionalization of Rh(II)-based metal-organic polyhedra (Rh-MOPs) is employed to engineer homogeneous catalysts for styrene aziridination and cyclopropanation reactions. This

dynamic coordinative functionalization does not hinder the catalytic activity of the Rh(II) sites and it can be coupled to ligand-exchange reactions to precipitate the Rh-MOP catalyst, facilitating its recovery and reuse.

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