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Stabilized $Ru[(H_2O)_6]^{3+}$ in Confined Spaces (MOFs and Zeolites) Catalyzes the Imination of Primary Alcohols under Atmospheric Conditions with Wide Scope.

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ABSTRACT: Imines are ubiquitous intermediates in organic synthesis and the metal–mediated imination of alcohols is one of the most direct and simple method for their synthesis. However, reported protocols lack compatibility with many other functional groups since basic supports/media, pure oxygen atmospheres and/or released hydrogen gas are required during reaction. Here we show that, in contrast to previous metal–catalyzed methods, hexa–aqueous Ru(III) catalyzes the imination of primary alcohols with very wide functional group tolerance, at slightly acid pH and under low oxygen atmospheres. The inorganic metal complex can be supported and stabilized, integrally, within either a faujasite–type zeolites (Y and X) or a metal organic framework (MOF), to give a reusable heterogeneous catalysts which provides an industrially viable process well–below the flammability limit of alcohols and amines.

KEYWORDS: imine • ruthenium • catalysis • zeolite • metal–organic framework.

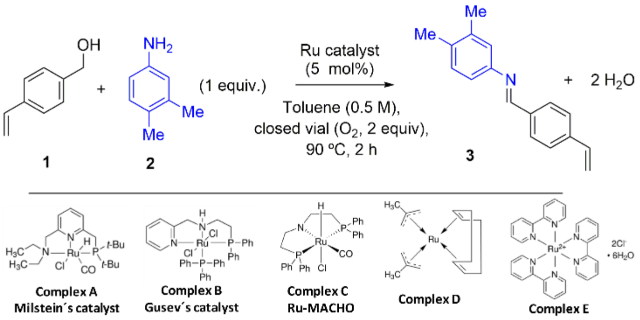
Ru is one of the most used and versatile metal catalysts for the dehydrogenation of alcohols,[1] however, it is barely used for the dehydrogenating imination reaction.[2] In one hand, acceptorless catalytic Ru(II) complexes (i.e. pincer–type organoRu(II) complexes)[3] produce H_2 during the reaction, which reduces the imine, and in the other hand, high–valent Ru (IV) and (VI) compounds (i.e. tetrapropylammonium perruthenate, TPAP, and RuO_2)[4] and Ru(II) catalysts (i.e. $Ru(PPh)_3Cl_2$ and Ru(p–cymene)Cl_2)[5] use sacrificial oxidants to quench the Ru–hydrides, which are not compatible with many functional groups.

Indeed, it is difficult to find functional group tolerant protocols for the imination of alcohols for any metal catalyst.[2a,6] The metal catalyst faces the challenge of avoiding hydrogen borrowing mechanisms by rapidly quenching or releasing the so–formed hydrides and, at the same time, shifting the equilibrium towards the imine product. These combined redox/acid–base requirements are even more hampered for aldimines, key intermediates for the synthesis of a plethora of commercially–relevant nitrogen–containing organic molecules,[7] since the dehydrogenation of primary alcohols requires strong basic conditions and promote decarbonylation reactions.[8] Should any powerful Ru catalyst for the dehydrogenation of alcohols operate in non–basic media and engage amines without giving hydrogen atoms back nor using strong oxidizing conditions, an inherently very active and selective metal catalyst for the direct imination of alcohols will arise.

Table 1 (entries 1–14) shows the imination of 4–vinylbenzyl alcohol (**1**) and 3,4–dimethylaniline (**2**) catalyzed by a 5 mol% of 15 representative Ru catalysts, in toluene at 90 ºC, and with 2 equivalents of O_2, which corresponds to the amount of air in the vial. Notice that these atmospheric conditions are extremely mild and fulfill flammability limitations in industry for organic compounds. The first results in Table 1 confirm the difficulties mentioned above, and Ru(II) or (III), salts and complexes (entries 1–5), pincer–type complexes (entries 7–10) and supported Ru nanoparticles (entries 11–12) do not give imine **3** (complex A Milstein´s aceptorless dehydrogenating catalyst gives 35% of the amine product, entry 6),[2c] while high–valent Ru compounds (entries 13–14) act as stoichiometric rather than catalytic agents, to yield the amount of imine **3** corresponding to reducible Ru.

In contrast, $[Ru(H_2O)_6]^{3+}$ (entry 15) shows truly catalytic activity and achieves 21% of imine **3**. This Ru species, prepared in HBF_4 solutions in the 60´s[9] and later supported in faujasite–type zeolites by simple cation exchange,[10] has rarely been reported for catalysis,[11] despite its simplicity. The combination of acidity, accessibility and water–compatibility in a same Ru site seems favorable for the imination of alcohols. Unfortunately, monitoring the homogeneous reaction by in–situ ultraviolet–visible (UV–vis) spectroscopy combined with kinetic experiments (Figure S1), with non–chromophoric reagents, showed

Table 1. Results for the imination of 4–vinylbenzyl alcohol (1) and 3,4–dimethylaniline (2) with Ru catalysts.



Entry	Ru catalyst	Yield of 3 (%)[a]
1	$RuCl_3$	0
2	$Ru(acac)_3$	0
3	$RuCl_2(PPh)_3$	0
4	$RuCl_2(NH_3)_6$	0
5	$RuCl_2$(*p*–cymene)	0
6[b]	Complex A	0
7	Complex B	0
8	Complex C	5
9	Complex D	0
10	Complex E	0
11	Ru (5 wt%)–C	0
12	$Ru–Al_2O_3$	0
13	TPAP	36
14	RuO_2	14
15	$Ru[(H_2O)_6]\cdot 3BF_4$	21 (18)
16	$Ru(H_2O)_6–Al_2O_3$ (0.1 wt% Ru)	27
17	$Ru(H_2O)_6–SiO_2$ (0.1 wt% Ru)	26
18	$Ru(H_2O)_6–TiO_2$ (0.1 wt% Ru)	23
19	$Ru(H_2O)_6$–MgO (0.1 wt% Ru)	20
20[c]	$Ru[(H_2O)_6]^{3+}$–NaY (1 wt% Ru)	73 (65)
21[d]	$[RuH_2O)_6]^{3+}$–MOF (~3 wt% Ru)	97 (90)
22	$Ru(OH)_3– Al_2O_3$ (1 wt% Ru)	7

[a] 2 equivalents of O_2 corresponds to the air in the vial. GC yields. Between parentheses, isolated yields. [b] Hydrogenated imine as only product found. [c] 63% isolated yield in 2 gram–scale; 58% after 5 uses. A 3 wt% sample gives 56% isolated yield. [d] Bare zeolites and MOF do not give any product.

the rapid degradation and the loss of catalytic activity of $[Ru(H_2O)_6]^{3+}$ in toluene solution.

A plausible way to overcome such a catalyst degradation in solution is to support the Ru active species onto a solid. However, this degradation is not avoided when supporting $[Ru(H_2O)_6]^{3+}$ on different amorphous inorganic oxides such as alumina, silica, titania and magnesia (entries 16–19), since the progressive loss of the fragile hexa–aqueous Ru(III) cation still occurs.

$[Ru(H_2O)_6]^{3+}$ depletion may come from the loss of ionic interaction in the organic medium between the soft Ru(III) cation and the BF_4^-/inorganic oxide counterbalancing anion, and, perhaps, a confining anionic solid with a delocalized charge and an intimate interaction with $[Ru(H_2O)_6]^{3+}$ may preserve its integrity and catalytic activity for longer. Indeed, $Ru[(H_2O)_6]^{3+}$–NaY (1 wt% Ru in the zeolite, entry 20) gives a 65% of isolated imine **3**, 63% in 2 gram–scale, and the solid is recyclable for at least 5 times without significant depletion in catalytic activity (58%). Hot–filtration experiments, at 20% conversion, show no catalytic activity after solid catalyst filtration, and ICP analysis confirm that the Ru loading keeps constant on NaY after use. A NaY sample exchanged with 3 wt% instead of 1 wt% Ru (see footnote in Table 1) works similarly, thus saving catalytic solid material. Diffuse reflectance (DR) UV–vis and infrared (IR) spectroscopy, together with Ru3*p* X–ray photoelectron spectroscopy (XPS) of $[Ru(H_2O)_6]^{3+}$–NaY treated with air in the XPS chamber at 100 ºC, confirms the stability of the Ru(III) site (Figures S2 and S3).[12] These results strongly support the heterogeneous character of the catalysis.

Hydrophobic solvents (hexane, α,α,α–trifluorotoluene and toluene) work better than polar solvents (Table S1), plausibly by enhancing zeolite–$Ru[(H_2O)_6]^{3+}$ ionic interaction. In order to assess that this zeolite–$Ru[(H_2O)_6]^{3+}$ interaction is crucial for the catalysis, faujasite electronics was varied by cation exchange, from electron poor (thus highly acid, HY) to electron–rich (thus highly basic, CsX). DR UV–vis and IR spectra of the zeolites show the expected peaks for $[Ru(H_2O)_6]^{3+}$ and the absence of direct oxo–Ru bonds with the zeolite walls (Figures S2 and S5), which supports the integrity of the hexa–aqueous complex. The catalytic activity of the different $[Ru(H_2O)_6]^{3+}$–zeolite catalysts changes with the electronics, peaking for NaY and KY (Figure S4).[13] The fact that the quasi neutral faujasite KY confers the better catalytic activity to the extraframework Ru(III) site discards the participation of zeolite Brönsted sites during the imination reaction[14] and strongly supports $[Ru(H_2O)_6]^{3+}$ as the intrinsic catalyst, stabilized in the zeolite. Following this hypothesis, it seemed highly promising to prepare new active solid catalysts by supporting $[Ru(H_2O)_6]^{3+}$ in other delocalized anionic solids, such as MOFs.

MOFs[15] are porous crystalline materials showing a large variety of interesting properties –most of which arise from their porous character and amazing host–guest chemistry[16]– and find application in many different important fields.[15b] In particular, MOFs have already shown excellent results in supporting and stabilizing small metal clusters[17] or metal complexes[18] within their channels, showing high catalytic activity.[19] In this context, we thus selected a highly robust anionic MOF of formula $Ni_2^{II}\{Ni^{II}_4[Cu^{II}_2(Me_3mpba)_2]_3\} \cdot 54H_2O$, capable to exchange the Ni^{2+} cations hosted within its pores by $[Ru(H_2O)_6]^{3+}$, in a similar procedure to cation exchange in zeolites. The post–synthetic[20] single crystal to single crystal (SC to SC) process[21] was monitored through SEM–EDX and ICP–AES (Table S2), whereas Ru oxidation state and oxygen atom electronics were determined by X–ray photoelectron spectroscopy (XPS, Figures S6–S7). Figure 1 shows the single crystal X–ray crystallography (SC–XRC) results for the new MOF, with formula

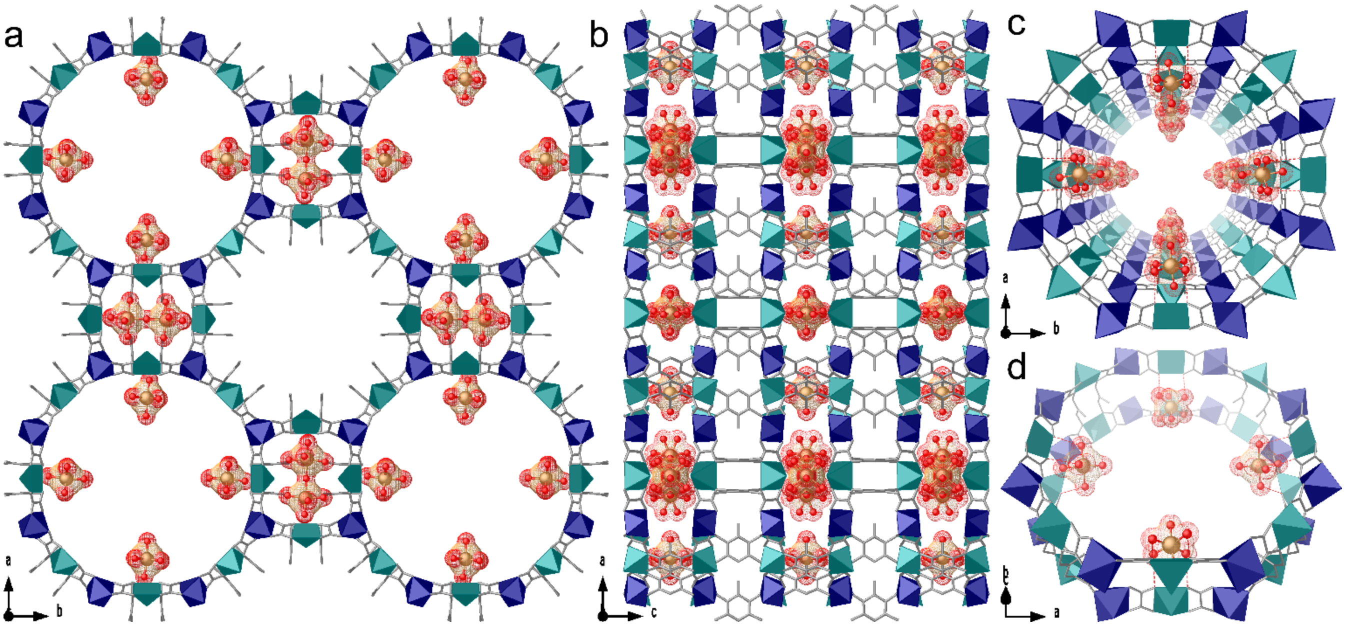


Figure 1. Views of the porous crystal structures, determined by single crystal X–ray diffraction, of $[Ru(H_2O)_6]^{3+}$–MOF in the *ab* (a) and *bc* (b) planes, respectively. (c) Perspective view one single channel of $[Ru(H_2O)_6]^{3+}$–MOF along the c (left) axis. d) Perspective view of a fragment of a single channel emphasizing the hydrogen bonds interactions. Cu(II) and Ni(II) cations from the coordination network are represented by cyan and blue polyhedra, respectively, whereas the ligands are depicted as gray sticks. Ru(III) cations and water molecules hosted in the channels are represented by gold and red spheres with surface, respectively.

$[Ru^{III}(H_2O)_6]_{0.83}[Ru^{III}_2(\mu\text{–}H_2O)(H_2O)_{10}]_{0.25}\{Ni^{II}_4[Cu^{II}_2(Me_3mpba)_2]_3\} \cdot 61H_2O$ ($[Ru(H_2O)_6]^{3+}$–MOF).

Figure 1a shows the $[Ru(H_2O)_6]^{3+}$ and $[Ru^{III}_2(\mu\text{–}H_2O)(H_2O)_{10}]^{6+}$ units, respectively hosted in the two types of channels present in the anionic framework: the larger octagonal ones much more accessible for catalysis (*vide infra*) and the small square hindered channels. Both the hexa–aqua Ru(III) monomers, located in octagonal pores and $[Ru^{III}_2(\mu\text{–}H_2O)(H_2O)_{10}]^{6+}$ dimers, exhibit Ru–OH_2 bond distances [1.97(1) to 2.37(3) Å], very similar to the only one report found in the literature.[22] This lack of reports on crystallographically defined $[Ru(H_2O)_6]^{3+}$ monomers further supports an intrinsic stabilizing effect of MOF's confined space. The larger octagonal hydrophilic channels of the MOF, contain a much larger accessible void space (size of *ca.* 2.2 nm), which contrasts with the very small amount of room available in the small square channels, almost fully occupied by the $[Ru^{III}_2(\mu\text{–}H_2O)(H_2O)_{10}]^{6+}$ dimers (Figure 1c and 1d). This point suggests that the $[Ru(H_2O)_6]^{3+}$ monomers located in the larger channels are potential catalytic species. Apart from electrostatic interactions between Ru^{3+} units and the anionic framework, all $[Ru(H_2O)_6]^{3+}$ cations located in both types of channels are hydrogen–bonded – involving the carboxylate oxygen atoms of the framework and water molecules constituting the coordination environment of the Ru^{3+} ions [$O_{waters}\cdots O_{oxamate}$ 2.827(3) and 2.923(3) Å] to the anionic framework, which further fixes and stabilizes them within the pores (dashed lines in Figures 1c, 1d and S8–S10). These results definitely underline how the interplay between hydrophilic channels and the consequent vastly solvated confined nanospace–in which water molecules are noninnocent participants – is at the origin of $[Ru(H_2O)_6]^{3+}$ moieties stabilizations and unambiguously confirm the integrity of $[Ru(H_2O)_6]^{3+}$ within the porous solid.

The experimental powder X–ray diffraction (PXRD) patterns of a polycrystalline sample of $[Ru(H_2O)_6]^{3+}$–MOF is identical to the theoretical one (Figure S11), which confirms the purity of the bulk. Moreover, the chemical nature was further determined by elemental analysis (Supporting Information) and the water contents was established by thermogravimetric analysis (TGA, Figure S12). There is a continuously loss of mass before 150 °C, however, this corresponds to physisorbed water an organic solvent traces, and not to the aqueous complex, that decomposes at much higher temperature. Finally, the porosity of the MOF after the PS cation exchanged was confirmed by measuring the N_2 adsorption isotherm at 77 K (Figure S13).

The $[Ru(H_2O)_6]^{3+}$–MOF catalyst gives 90% isolated yield of imine **3** (entry 21 in Table 1), the highest among all Ru catalysts tested. Hot–filtration experiments and ICP analysis show that Ru remains on the MOF after reaction, and XPS confirms the stability of the Ru catalyst within the MOF (Figures S6–S7). Kinetic experiments show that the initial turnover frequency TOF_0 for soluble $Ru[(H_2O)_6]^{3+}\cdot 3BF_4^-$, $Ru[(H_2O)]_6^{3+}$–NaY and $Ru[(H_2O)_6^{3+}]$–MOF is similar, measured at initial reaction times when degradation is still no significant (Figure S14), and that product formation increases longer for the MOF catalyst. These results confirm that the catalytic activity is intrinsic

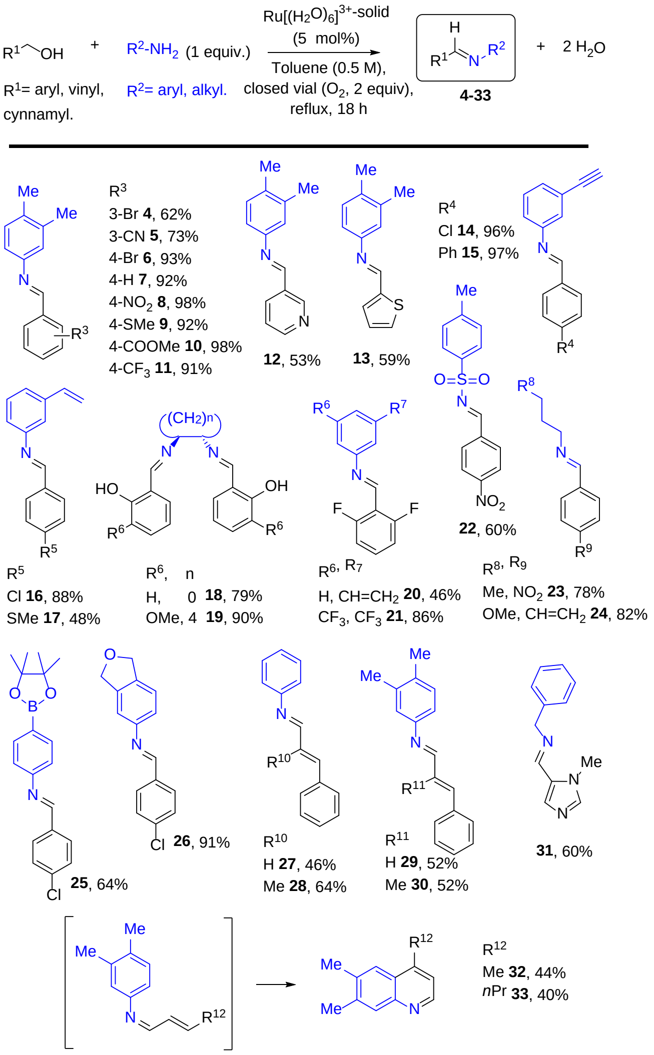


Figure 2. Scope for the imination of primary alcohols with amines using either $Ru[(H_2O)_6]^{3+}$–NaY, –KY or –MOF as a catalyst. Imines **6**, **7** and **9–10** were catalyzed by the MOF; imines **11–13** by KY, and the rest by NaY. The same yield of imine **4** is obtained with a 15–year old NaY catalyst, and the same occurs with imine **6** and the MOF. 2 equivalents of O_2 corresponds to the air in the vial.

to [Ru(H2O)6]3 and that keeps for longer on solids that stabilize better the catalyst. Notice that a related catalyst, $Ru(OH)_3$–Al_2O_3, prepared in highly alkaline solutions and very active for dehydrogenations of alcohols,[23] is merely inactive here since amine condensation is hampered under strong basic conditions.

Figure 2 shows that $Ru[(H_2O)_6]^{3+}$–NaY, –KY and –MOF catalyze the imination of primary benzyl and allyl alcohols with different amines in good isolated yields and selectivity under aerobic conditions, tolerating halogen (imines **4**, **6**, **14**, **16**, **20–21**, **25–26**), cyano (**5**), alkene (**7**, **16–17**, **20** and **24**), nitro (**8** and **22–23**), thioether (**9** and **17**), ester (**10**), trifluoromethane (**11** and **21**), heteroaromatic (**12–13** and **31**), alkyne (**14–15**), phenol (**18–19**), ether (**19**, **24** and **26**), sulfonamide (**22**), boronic ester (**25**) and enamine (**27–30**) functionalities in the molecule. For alkyl enamines, cyclization occurs to give the corresponding Doebner–Miller quinoline products **32–33**, which reflects the acidity imparted by the Ru^{3+} aqueous cation. A sample of $[Ru(H_2O)_6]^{3+}$–NaY stored for 15 years in the bench shows the same catalytic activity than a fresh sample, and the same occurs for $[Ru(H_2O)_6]^{3+}$–MOF stored for 1 year. These results illustrate the robustness of the supported $[Ru(H_2O)_6]^{3+}$ catalysts. Notice that flammability limits in industry for organic compounds generally restrict O_2 concentration below 20%, thus the results here presented are not only of interest for imine synthesis in the laboratory but also for a plausible industrial scale production.

The imination reaction shown in Table 1 does not proceed in complete absence of O_2, and H_2 is not detected in the reaction atmosphere, even at $[O_2] << $ air. If 1–dodecene and Pd/C (5 wt%) are added from the beginning to a reaction under optimized conditions (>80% of **3**), no alkene hydrogenation occurs. These results discard acceptorless mechanisms and support a very efficient Ru–hydride quenching by O_2 during reaction. The corresponding kinetic equation, according to kinetic results at initial times, is $v_o=k_{app}[\mathbf{1}][O_2][Ru]$ at $[O_2]<$air, and simply $v_o=k'_{app}[\mathbf{1}][Ru]$ at higher $[O_2]$ (Figure S15), which reflects a rapid saturation of the catalytic site for $[O_2]>$air and that amine **2** does not participate in the rate–determining step (r.d.s.) of the reaction. In accordance, the dehydrogenation initial rate of **1**, without adding amine **2**, is very similar to the imination initial rate when **2** is present, and a kinetic isotopic effect (*KIE*)= 2.8 is obtained when α,α–deuterated benzyl alcohol ($PhCD_2OH$) is used, regardless if amine **2** is present or not. These results strongly support that alcohol dehydrogenation is the rate–limiting step of the imination, and that amine condensation and Ru–hydride capture by O_2, to form water, are much faster processes.

A possible general mechanism for the $Ru[(H_2O)_6]^{3+}$ imination reaction, either supported or not, is shown in Figure 3. Notice that the confining solids maximize the synthesis and lifetime of the $Ru[(H_2O)_6]^{3+}$ species, but do not have a direct role in the reaction mechanism. The bigger pore size of the MOF respect to the zeolite can explain the better catalytic activity of the former (>20% yield increase for product **3**), however, the porosity of both solids is enough for reactants/products diffusion and does not hamper the reaction outcome.

The proposed mechanism involves that the alcohol displaces one water ligand on Ru^{3+} to trigger a beta–hydrogen elimination, and that the intermediate Ru–H species is rapidly quenched by O_2. The so–formed aldehyde condensates with the amine under acid catalysis to give the final imine product.

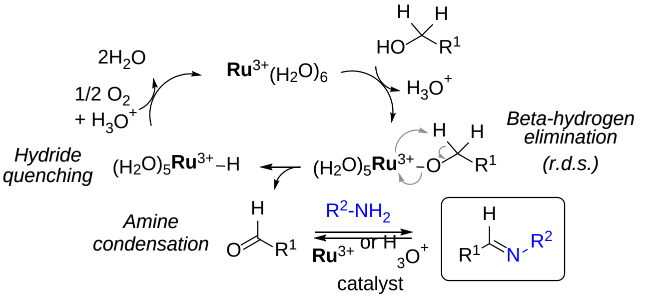


Figure 3. Mechanism of the $[Ru(H_2O)_6]^{3+}$-catalyzed imination of primary alcohols with amines.

In summary, the imination of primary alcohols catalyzed by $[Ru(H_2O)_6]^{3+}$ supported on structured porous solids occurs in high yields and with a wide functional group tolerance under aerobic conditions, which is a step forward for imine synthesis. This work constitutes an example of cross–fertilization between zeolites and MOFs to support catallytically active metal species.

ASSOCIATED CONTENT

Supporting Information. CCDC–1841425 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Additional experimental procedures, X–ray crystallographic data collection, Figures, Tables and compound characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

(1) For reviews see a) Guillena, G.; Ramón, D. J.; Yus, M. Hydrogen Autotransfer in the *N*-Alkylation of Amines and Related Compounds using Alcohols and Amines as Electrophiles. *Chem. Rev.* **2009**, *110*, 1611–1641. b) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols. *Chem. Rev.* **2018**, *118*, 372–433. c) Corma, A.; Navas, J.; Sabater, M. J. Advances in One-Pot Synthesis through Borrowing Hydrogen Catalysis. *Chem. Rev.* **2018**, *118*, 1410–1459.

(2) For a review see a) Chen, B.; Wang, L.; Gao, S. Recent Advances in Aerobic Oxidation of Alcohols and Amines to Imines. *ACS Catal.* **2015**, 5, 5851–5876. For representative examples see b) Jung Won, K.; Jinling, H.; Kazuya, Y.; Noritaka, M. Heterogeneously Catalyzed One-pot Synthesis of Aldimines from Primary Alcohols and Amines by Supported Ruthenium Hydroxides. *Chem. Lett.* **2009**, *38*, 920–921. c) Gnanaprakasam, B.; Zhang, J.; Milstein, D. Direct synthesis of imines from alcohols and amines with liberation of H_2. *Angew. Chem. Int. Ed.* **2010**, *49*, 1468–1471. d) Cano, R.; Ramon, D. J.; Yus, M. Impregnated Ruthenium on Magnetite as a Recyclable Catalyst for the N-Alkylation of Amines, Sulfonamides, Sulfinamides, and Nitroarenes Using Alcohols as Electrophiles by a Hydrogen Autotransfer Process. *J. Org. Chem.* **2011**, *76*, 5547–5557. e) Saha, B.; Wahidur Rahaman, S. M.; Daw, P.; Sengupta, G.; Bera, J. K. Metal–Ligand Cooperation on a Diruthenium Platform: Selective Imine Formation through Acceptorless Dehydrogenative Coupling of Alcohols with Amines. *Chem. Eur. J.* **2014**, *20*, 6542–6551. f) Oldenhuis, N. J.; Dong, V. M.; Guan, Z. Catalytic acceptorless dehydrogenations: Ru-Macho catalyzed construction of amides and imines. *Tetrahedron* **2014**, *70*, 4213–4218. g) Higuchi, T.; Tagawa, R.; Iimuro, A.; Akiyama, S.; Nagae, H.; Mashima, K. Tunable Ligand Effects on Ruthenium Catalyst Activity for Selectively Preparing Imines or Amides by Dehydrogenative Coupling Reactions of Alcohols and Amines. *Chem. Eur. J.* **2017**, *23*, 12795–12804.

(3) a) Gunanathan, C.; Milstein, D. Metal–Ligand Cooperation by Aromatization–Dearomatization: A New Paradigm in Bond Activation and “Green” Catalysis *Acc. Chem. Res.* **2011**, *44*, 588–602. b) Gunanathan, C.; Milstein, Applications of Acceptorless Dehydrogenation and Related Transformations in Chemical Synthesis. *Science* **2013**, *341*, 1229712. c) Crabtree, R. H. Homogeneous Transition Metal Catalysis of Acceptorless Dehydrogenative Alcohol Oxidation: Applications in Hydrogen Storage and to Heterocycle Synthesis. *Chem. Rev.* **2017**, *117*, 9228–9246.

(4) a) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. Tetrapropylammonium Perruthenate, $Pr4N^+RuO4^-$, TPAP: A Catalytic Oxidant for Organic Synthesis. *Synthesis* **1994**, *7*, 639–666. b) Lenz, R.; Ley, S. V. Tetra-*n*-propylammonium perruthenate (TPAP)-catalysed oxidations of alcohols using molecular oxygen as a co-oxidant. *J. Chem. Soc., Perkin Trans.* **1997**, *1*, 3291–3292. c) Over, H. Surface Chemistry of Ruthenium Dioxide in Heterogeneous Catalysis and Electrocatalysis: From Fundamental to Applied Research. *Chem. Rev.* **2012**, *112*, 3356–3342.

(5) a) Zhang, S.–Y.; Tu, Y.–Q.; Fan, C.–A.; Jiang, Y.–J.; Shi, L.; Cao, K.; Zhang, E. Cross-Coupling Reaction between Alcohols through sp^3 C-H Activation Catalyzed by a Ruthenium/Lewis Acid System. *Chem. Eur. J.* **2008**, *14*, 10201–10205.

(6) a) Tian, H.; Yu, X.; Li, Q.; Wang, J.; Xua, Q. General, Green, and Scalable Synthesis of Imines from Alcohols and Amines by a Mild and Efficient Copper-Catalyzed Aerobic Oxidative Reaction in Open Air at Room Temperature. *Adv. Synth. Catal.* **2012**, *354*, 2671–2677. b) Zhang, G.; Hanson, S. K. Cobalt-catalyzed acceptorless alcohol dehydrogenation: synthesis of imines from alcohols and amines. *Org. Lett.* **2013**, *15*, 650–653. c) Bain, J.; Cho, P.; Voutchkova–Kostal, A. Recyclable hydrotalcite catalysts for alcohol imination via acceptorless dehydrogenation. *Green Chem.* **2015**, *17*, 2271–2280. d) Mukherjee, A.; Nerush, A.; Leitus, G.; Shimon, L. J. W.; Ben David, Y.; Espinosa Jalapa, N. A.; Milstein, D. Manganese-Catalyzed Environmentally Benign Dehydrogenative Coupling of Alcohols and Amines to Form Aldimines and H_2: A Catalytic and Mechanistic Stud. *J. Am. Chem. Soc.* **2016**, *138*, 4298–4301. e) Jaiswal, G.; Landge, V. G.; Jagadeesan, D.; Balaraman, E. Sustainable iron-catalyzed direct imine formation by acceptorless dehydrogenative coupling of alcohols with amines. *Green Chem.* **2016**, *18*, 3232–3238.

(7) a) Pruett, R. L.; Keenan, M. J.; Mozeleski, E. J. US patent US 5103058, **1992**, 8 pp., Exxon Chemical Patents, Inc. USA. b) Martin, S. F. Recent applications of imines as key intermediates in the synthesis of alkaloids and novel nitrogen heterocycles. *Pure Appl. Chem.* **2009**, *81*, 195–204.

(8) a) Cho, C. S.; Kim, B. T.; Kim, H.–S.; Kim, T.–J.; Shim, S. C. Ruthenium-Catalyzed One-Pot β-Alkylation of Secondary Alcohols with Primary Alcohols. *Organometallics* **2003**, 22, 3608–3610. b) Fujita, K.; Yoshida, T.; Imori, Y.; Yamaguchi, R. Dehydrogenative Oxidation of Primary and Secondary Alcohols Catalyzed by a Cp*Ir Complex Having a Functional C,N-Chelate Ligand. *Org. Lett.* **2011**, *13*, 2278–2281. c) Sik Cho, C.; Tae Kim, B.; Kim, T.–J.;

Chul Shim, S. An Unusual Type of Ruthenium-Catalyzed Transfer Hydrogenation of Ketones with Alcohols Accompanied by C–C Coupling. *J. Org. Chem.* **2001**, *66*, 9020–9022. d) Mazziotta, A.; Madsen, R. Ruthenium-Catalyzed Dehydrogenative Decarbonylation of Primary Alcohols. *Eur. J. Org. Chem.* **2017**, 5417–5420.

(9) Merceras, E. E.; Buckley, R. Hexaaquoruthenium(II). *Inorg. Chem.* **1965**, *4*, 1692–1695.

(10) Wan, B.–Z.; Lunsford, J. H. An EPR study of ruthenium(III) aquo complexes in water and in zeolite-Y. *Inorg. Chim. Acta Lett.* **1982**, *65*, L29–L30.

(11) Cürdaneli, P. E.; Özkar, S. Ruthenium(III) ion-exchanged zeolite Y as highly active and reusable catalyst in decomposition of nitrous oxide to sole nitrogen and oxygen. *Micropor. Mesopor. Mater.* **2014**, *196*, 51–58.

(12) a) Liang, H.; Chen, G.; Desinan, S.; Rosei, R.; Rosei, F.; Ma, D. In situ facile synthesis of ruthenium nanocluster catalyst supported on carbon black for hydrogen generation from the hydrolysis of ammonia-borane. *Inter. J. Hydrogen Energy* **2012**, *37*, 17921–17927. b) Maximov, A.; Zolotukhina, A.; Murzin, V.; Karakhanov, E.; Rosenberg, E. Ruthenium Nanoparticles Stabilized in Cross-Linked Dendrimer Matrices: Hydrogenation of Phenols in Aqueous Media. *ChemCatChem* **2015**, *7*, 1197–1210.

(13) a) Corma, A.; García, H.; Leyva, A. Controlling the softness–hardness of Pd by strong metal–zeolite interaction: cyclisation of diallylmalonate as a test reaction. *J. Catal.* **2004**, *225*, 350–358. b) Rubio–Marqués, P.; Rivero–Crespo, M. A.; Leyva–Pérez, A.; Corma, A. Well-Defined Noble Metal Single Sites in Zeolites as an Alternative to Catalysis by Insoluble Metal Salts. *J. Am. Chem. Soc.* **2015**, *137*, 11832–11837.

(14) Cabrero–Antonino, J. R.; Leyva–Pérez, A.; Corma, A. Beyond acid strength in zeolites: soft framework counteranions for stabilization of carbocations on zeolites and its implication in organic synthesis. *Angew. Chem. Int. Ed.* **2015**, *54*, 5658–5661.

(15) a) Zhou, H.–C.; Kitagawa, S. Metal–Organic Frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, 5415–5418. b) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks *Science* **2013**, *341*, 1230444. d) Farha, O. K.; Hupp, J. T. Rational Design, Synthesis, Purification, and Activation of Metal–Organic Framework Materials. *Acc. Chem. Res.* **2010**, *43*, 1166–1175. d) Long, J. R.; Yaghi, O. M. The pervasive chemistry of metal–organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1213–4. e) Maurin, G.; Serre, C.; Cooper, A.; Férey, G. The new age of MOFs and of their porous-related solids. *Chem. Soc. Rev.* **2017**, *46*, 3104–3107.

(16) Kitagawa, S.; Matsuda, R. Chemistry of coordination space of porous coordination polymers. *Coord. Chem. Rev.* **2007**, *251*, 2490–2509.

(17) a) Mon, M.; Rivero–Crespo, M. A.; Ferrando–Soria, J.; Vidal–Moya, A.; Boronat, M.; Leyva–Pérez, A.; Corma, A.; Hernandez–Garrido, J. C.; López–Haro, M.; Calvino, J. J.; Ragazzon, G.; Credi, A.; Armentano, D.; Pardo, E. Synthesis of Densely Packaged, Ultrasmall Pt^0_2 Clusters within a Thioether-Functionalized MOF: Catalytic Activity in Industrial Reactions at Low Temperature. *Angew. Chem. Int. Ed.* **2018**, 57, 6186 –6191.

(18) a) Fortea–Pérez, F. R.; Mon, M.; Ferrando–Soria, J.; Boronat, M.; Leyva–Pérez, A.; Corma, A.; Herrera, J. M.; Osadchii, D.; Gascon, J.; Armentano, D., Pardo, E. The MOF-driven synthesis of supported palladium clusters with catalytic activity for carbene-mediated chemistry. *Nat. Mater.* **2017**, *16*, 760–766. b) Mon, M.; Ferrando–Soria, J.; Verdaguer, M.; Train, C.; Paillard, C.; Dkhil, B.; Versace, C.; Bruno, R.; Armentano, D.; Pardo, E. Postsynthetic Approach for the Rational Design of Chiral Ferroelectric Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2017**, *139*, 8098–8101. c) Liu, H.; Chang, L.; Bai, C.; Chen, L.; Luque, R.; Li, Y. Controllable Encapsulation of "Clean" Metal Clusters within MOFs through Kinetic Modulation: Towards Advanced Heterogeneous Nanocatalysts. *Angew. Chemie Int. Ed.* **2016**, 55, 5019–5023.

(19) Gascon, J.; Corma, A.; Kapteijn, F.; Llabrés i Xamena, F. X. Metal Organic Framework Catalysis: Quo vadis? *ACS Catal.* **2014**, *4*, 361–378.

(20) Cohen, S. M. The Postsynthetic Renaissance in Porous Solids. *J. Am. Chem. Soc.* **2017**, *139*, 2855–2863.

(21) a) Grancha, T.; Ferrando–Soria, J.; Zhou, H.–C.; Gascon, J.; Seoane, B.; Pasán, J.; Fabelo, O.; Julve, M.; Pardo, E. Postsynthetic Improvement of the Physical Properties in a Metal–Organic Framework through a Single Crystal to Single Crystal Transmetallation. *Angew. Chem. Int. Ed.* **2015**, 54, 6521–6525.

(22) Bernhard, P.; Buergi, H. B.; Hauser, J.; Lehmann, H.; Ludi, A. Syntheses and crystal and molecular structures of hexaaquaruthenium(II) *p*-toluenesulfonate and hexaaquaruthenium(III) *p*-toluenesulfonate, $[Ru(H2O)_6](C7H7SO3)_2$ and $[Ru(H2O)_6](C7H7SO3)_3.3H2O$. *Inorg. Chem.* **1982**, *21*, 3936–3941.

(23) a) Yamaguchi, K.; Mizuno, N. Supported ruthenium catalyst for the heterogeneous oxidation of alcohols with molecular oxygen. *Angew. Chem. Int. Ed.* **2002**, *41*, 4538–4542. b) Yamaguchi, K.; Mizuno, N. Development of Highly Active Heterogeneous Oxidation Catalysts Based on the Properties of Metal Hydroxides. *Top. Catal.* **2014**, 57, 1196–1207. c) Kim, Y.; Ahn, S.; Hwang, J. Y.; Ko, D.–H.; Kwon, K.–Y. Dehydrogenative Oxidation of Alcohols Catalyzed by Highly Dispersed Ruthenium Incorporated Titanium Oxide. *Catalysts* **2017**, *7*, 7–18.

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