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Single Site Supported Cationic Rhodium(I) Complexes for the Selective Redox Isomerization of Allylic Alcohols

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The isomerization of allylic alcohols to carbonyl compounds by a heterogeneous rhodium complex is reported. Different silica material supports and catalyst/ligand systems were evaluated. The most efficient catalyst in terms of catalytic activity and stability was found to be a cationic rhodium(I) complex with sulfonated phosphine ligands anchored on a mesoporous aluminosilica AISBA-15. The heterogeneous complex catalyzed the

isomerization of a variety of allylic alcohols in excellent yields with very low catalyst loadings (0.5 mol%). The catalyst could be recycled without significant loss of activity or selectivity. The optimized catalyst was characterized by N₂ sorption, powder X-ray diffraction, transmission electron microscopy, as well as solution and solid-state nuclear magnetic resonance, and Fourier Transform infrared spectroscopies.

Introduction

The transition-metal catalyzed isomerization of allylic alcohols provides a straightforward synthetic route to valuable carbonyl compounds, which are important raw materials in organic synthesis.^[1–5] This transformation is atom-economical because the use of stoichiometric amounts of reducing or oxidizing reagents is avoided. Transition-metal complexes of the groups 8–10 have been widely used in the isomerization of allylic alcohols under homogeneous conditions.^[4,5] It is only in the last few years that metal complexes were found to catalyze the reaction under mild reaction conditions with high efficiency and selectivity.^[6–13] Previously, we reported the use of Ru–Cl^[10,11] and Rh–Cl^[12] complexes together with potassium *tert*-butoxide (KO^tBu) as a cocatalyst for this reaction in organic solvents. Very recently, we found a cationic Rh^I complex that catalyzes the isomerization of allylic alcohols with low catalyst loadings and water as the sole solvent at ambient temperatures.^[13]

Although excellent results have been achieved in the isomerization of allylic alcohols using the abovementioned complexes (up to 99% yield under mild reaction conditions), we observed that the separation of the products from trace amounts of the metal catalysts was sometimes difficult. Immobilization of the transition-metal complexes onto an inorganic support could overcome this problem.

During the last decade, great efforts have been made towards the heterogenization of transition-metal complexes.^[14–16] Complexes covalently bonded to the supports is the most commonly used immobilization technique.^[17,18] However, this technique usually requires complicated synthesis procedures. More recently, the use of noncovalent immobilization procedures to anchor metal complexes onto mesoporous silica has attracted much attention.^[19,20]

Only a few heterogeneous catalysts for the isomerization of allylic alcohols have been reported to date. The majority of these are water soluble complexes used in biphasic solvent systems (water/organic solvent).^[13,21] To the best of our knowl-

edge, there is only one example in which a transition-metal complex (Ru(OH)₂) was immobilized onto an inorganic support (Al₂O₃) and used in the isomerization of allylic alcohols.^[22] The catalytic system was intrinsically heterogeneous and could be recycled.

As part of our on-going research program, we aimed at synthesizing a heterogeneous catalyst that could isomerize allylic alcohols efficiently and be recycled. In particular, we were in-

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terested in the isomerization of primary allylic alcohols and allylic alcohols with a high degree of substitution on the double bond. These types of substrates have been difficult to isomerize using Ru and Rh complexes under homogeneous conditions.^[4,5] Several complexes of rhodium have been successfully immobilized on mesoporous silica materials and used as catalysts in different reactions, such as hydrogenations,^[23,24] hydroformylations,^[25] acetylene cyclotrimerization,^[26] and transfer hydrogenation.^[27] These results, together with our experience on the isomerization of allylic alcohols using a cationic rhodium complex in water,^[13] prompted us to evaluate the activity of such complexes immobilized on inorganic supports.

Here, we communicate the evaluation of different anchoring strategies to immobilize a cationic rhodium(I) complex on various inorganic mesoporous supports, with the aim of preparing a highly active and selective heterogeneous catalyst for the isomerization of allylic alcohols to carbonyl compounds. The catalytic behavior of the best heterogeneous catalyst was further studied.

Results and Discussion

We chose 1,3,5-triaza-7-phosphaadamantane (PTA, **1a**)^[28] and sodium (4-methoxy-3-sulfonatophenyl)diphenylphosphine (MeO-TPPMS, **1b**,^[29,30] Figure 1) as the ligands, and the cationic Rh^I complex [Rh(cod)(MeCN)₂]BF₄ (**2**, cod = cyclooctadiene)^[12] as the rhodium source.

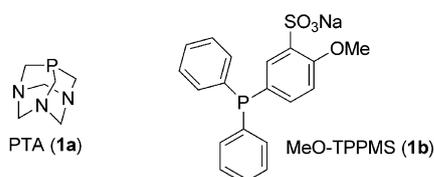


Figure 1. Ligands used in combination with the Rh^I complex [Rh(cod)-(MeCN)₂]BF₄ (**2**).

Different mesoporous materials, silica MCM-41,^[31] MCM-48,^[31] and SBA-15,^[32] aluminosilica AISBA-15,^[33] and tungstophosphoric acid (TPA) modified Al₂O₃ [(TPA)-Al₂O₃] and SBA-15 [(TPA)-SBA-15] were synthesized and tested as the catalyst supports. In addition alumina (Merck) and amorphous silica with a surface area of 200 m²g⁻¹ (Sigma Aldrich) were also tested as catalyst supports. Mesoporous silica MCM-41 and MCM-48 were synthesized as reported in the literature (see Supporting Information). When the sulfonated phosphine (MeO-TPPMS, **1b**) is used, the immobilization can take place through hydrogen bonding between the silanol groups on the silica support and the sulfonate group in the ligand (Figure 2a).^[34] Further ionic interactions can occur between the positively charged Rh^I complex and a negatively charged support, such as AISBA-15 (Figure 2b).^[35] If heteropolyacids are anchored on a silica support, immobilization can take place through a noncovalent interaction between the cationic rhodium(I) complex and the heteropolyacids (Figure 2c).^[36] The immobilization can take place simultaneously through several different noncovalent in-

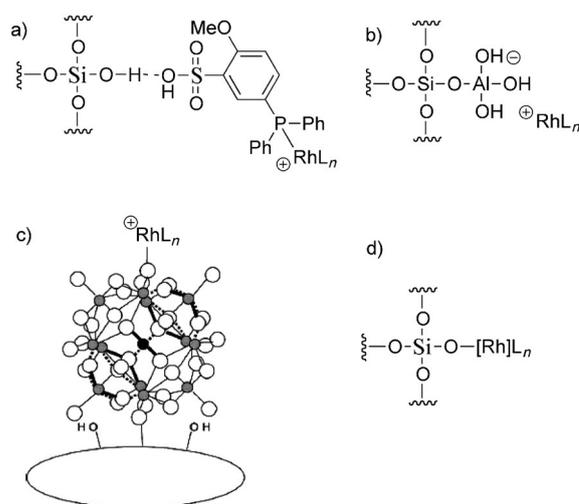


Figure 2. Different immobilization strategies: a) by hydrogen bonding, b) by cation exchange, c) using tungstophosphoric acid (TPA) as an anchoring agent, d) formation of siloxide rhodium complexes.

teractions (Figure 2a–c) by proper selection and matching of the ligand with a support. Covalently bonded rhodium siloxide complexes could also be formed (Figure 2d).^[37]

We immobilized two catalytic systems, Rh(2)/PTA(**1a**) (abbreviated as system I) and Rh(2)/MeO-TPPMS(**1b**) (abbreviated as system II) onto the various supports described above. Their synthesis and characterization are described in the Experimental Section and the Supporting Information. The following heterogeneous complexes were prepared with 1) catalytic system I [Rh(2)/PTA(**1a**) = 1:2]: I/AISBA-15, I/(TPA)-SBA-15, and I/(TPA)-Al₂O₃; and 2) catalytic system II [Rh(2)/MeO-TPPMS(**1b**) = 1:2]: II/SBA-15, II/AISBA-15, II/MCM-41, II/MCM-48, and II/SiO₂ (amorphous).

Characterization of the heterogeneous complex II/AISBA-15

Catalyst II/AISBA-15, which afforded the best results in the catalytic tests (see below), was further characterized by powder X-ray diffraction (PXRD), nitrogen adsorption/desorption, and electron microscopy to confirm the retention of the structural integrity of the parent support after immobilization. ³¹P cross polarization magic-angle spinning (CPMAS) nuclear magnetic resonance (NMR) and Fourier Transform infrared (FTIR) spectroscopies were used to confirm the successful immobilization of the Rh^I complex onto the AISBA-15 support.

Analysis by nitrogen adsorption/desorption

N₂ adsorption measurements showed that SBA-15, AISBA-15, and II/AISBA-15 displayed a type IV isotherm (as defined by IUPAC) with a H₁ hysteresis and a sharp increase in adsorbed volume at P/P₀ = 0.7 (Figure 3), which is characteristic of highly ordered mesoporous materials. A decrease in the surface area (from 915 m²g⁻¹ to 780 m²g⁻¹) was observed after modification of SBA-15 with AlCl₃ (Entries 1 and 2, Table 1). After immobilization of system II on AISBA-15, a further decrease in the

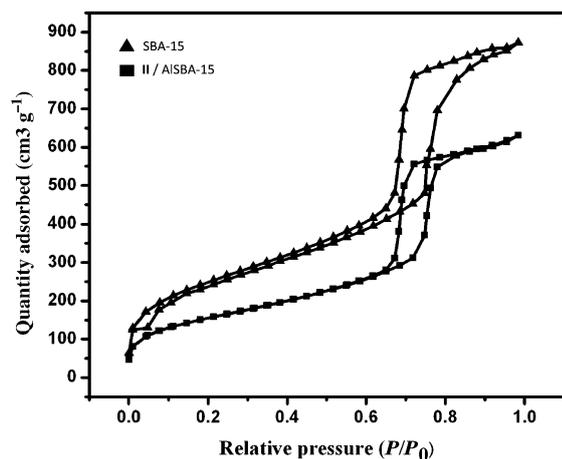


Figure 3. N_2 adsorption and desorption isotherms of SBA-15 and II/AISBA-15.

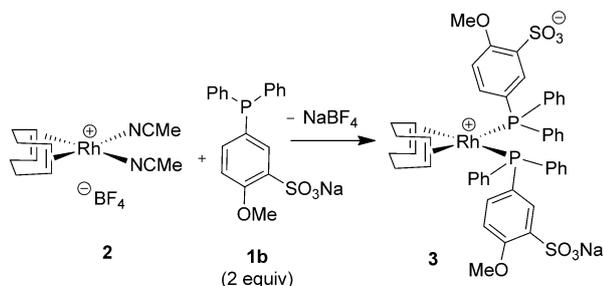
Table 1. Surface areas and pore size distributions of SBA-15 materials at different stages of functionalization.

Entry	Materials	BET surface area [$m^2 g^{-1}$]	Pore volume [$cm^3 g^{-1}$]	Pore diameter [nm]
1	SBA-15	915	1.29	5.9
2	AISBA-15	780	1.14	5.8
3	II/AISBA-15	567	0.94	5.8

surface area to $567 m^2 g^{-1}$ was observed. The average pore volume decreased from $1.29 cm^3 g^{-1}$ (for SBA-15) to $0.94 cm^3 g^{-1}$ (for II/AISBA-15, Entries 1 and 3, Table 1). There was a slight decrease in the average pore diameters, from 5.9 nm to 5.8 nm. The decrease in surface area and average pore volume after the immobilization indicates that the Rh^I -phosphine complex was immobilized within the pores.

Analysis by solution and solid-state ^{31}P NMR

Reaction of catalyst **2** with two equivalents of MeO-TPPMS (**1b**) in CH_2Cl_2 for 3 h afforded, after isolation, a new complex with a structure tentatively assigned as the zwitterionic complex **3** (Scheme 1). The solution 1H NMR spectrum of **3** showed very broad peaks, and the ^{31}P NMR spectrum did not show any sharp signals. Attempts to obtain crystals suitable for X-ray dif-



Scheme 1. Reaction and proposed zwitterionic structure of the homogeneous Rh^I phosphine complex **3**.

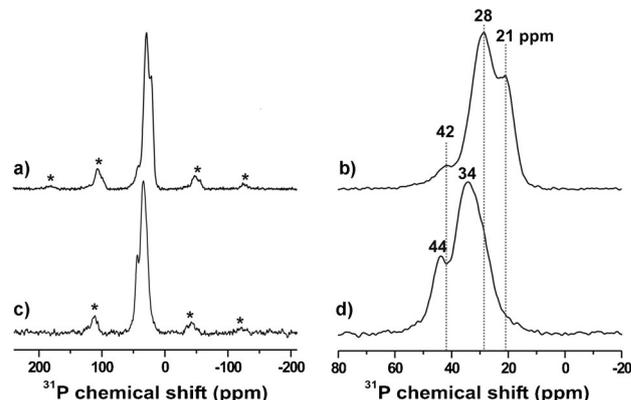


Figure 4. ^{31}P MAS NMR spectra recorded at 9.4 T of a, b) the Rh^I phosphine complex **3** and c, d) II/AISBA-15. The positions of the spinning sidebands are marked by *. Parts b and d show enlargements of the regions of each centerband with the peak maxima (in ppm) indicated.

fraction analysis were unsuccessful. We characterized **3** using ^{31}P solid-state NMR. A ^{31}P CPMAS NMR spectrum of complex **3** is shown in Figure 4a–b. It features a set of relatively minor spinning sidebands, spaced by the magic-angle spinning (MAS) frequency. The centerband revealed three components, marked by the dotted lines in the zoomed spectrum in Figure 4b. The two main peaks around 28 and 21 ppm stem from complex **3** and are tentatively assigned to each of the P atoms shown in Scheme 1. The widths of the relatively broad ^{31}P NMR peaks are primarily dictated by structural disorder, and unresolved scalar couplings to ^{103}Rh . Besides a minor ^{31}P NMR peak at about 42 ppm, attributed to an oxidation product impurity (such NMR signals appear typically above 40 ppm^[38,39]), the absence of additional resonances reflects a pure sample of complex **3**. The NMR spectrum reveals no traces of residual MeO-TPPMS (**1b**), which were observed to generate a sharp ^{31}P NMR peak at -10 ppm (data not shown).

Figure 4c–d show the corresponding ^{31}P CPMAS NMR results from the immobilized complex II/AISBA-15. Evidence of immobilization of the Rh^I phosphine complex on AISBA-15 is reflected by the two main ^{31}P CPMAS NMR signals observed around 44 ppm and 34 ppm, which were assigned to surface-bound oxidized phosphine and phosphine-rhodium(I) complexes, respectively. The latter peak position conforms well with previously reported ^{31}P chemical shifts (35–37 ppm) observed from different silica-surface immobilized Rh^I phosphine complexes.^[40,41] The presence of silica bound phosphine oxide observed in the ^{31}P CPMAS NMR spectra indicates that complex **3** undergoes structural changes when binding to the mesoporous surface and that the supported catalyst may contain only one phosphine ligand bound to rhodium, the other having been oxidized during the immobilization process or upon storage (the samples were kept in air). Nevertheless, two equivalents of phosphine **1b** were needed to prepare II/AISBA-15. The complex obtained when reacting phosphine **1b** with equimolar amounts of Rh (**2**) had a lower solubility in organic solvents than that of **3**, which resulted in an unsuccessful immobilization. The presence of phosphine oxide in II/AISBA-15 does not seem to diminish its catalytic activity.

Analysis by FTIR

The FTIR spectrum of the rhodium(I) phosphine complex **3** (Figure 5a) showed peaks at $\tilde{\nu}=2935$ and 3050 cm^{-1} , which correspond to the C–H stretching frequencies of the aromatic rings, and at $\tilde{\nu}=1485$ and 1583 cm^{-1} attributed to aromatic C=C bending. All of these peaks were also observed in the FTIR spectra of the immobilized rhodium(I) complex **II**/AISBA-15 (Figure 5b). The broad peak in the region of $\tilde{\nu}=3000\text{--}3800\text{ cm}^{-1}$ (Figure 5b) corresponds to adsorbed water molecules and to the O–H groups of the silanols from the AISBA-15 support.

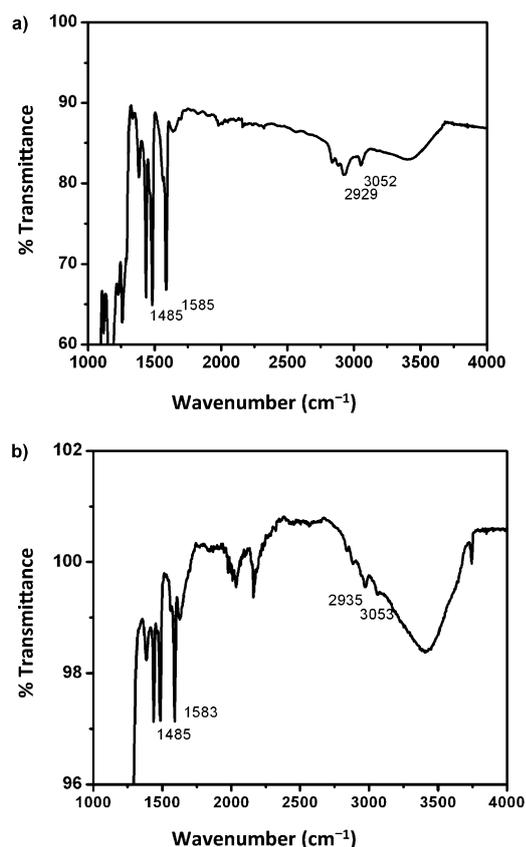


Figure 5. FTIR spectra of a) Rh^I phosphine complex **3** and b) immobilized complex **II**/AISBA-15.

Analysis by powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM)

PXRD data (see Supporting Information) and TEM (Figure 6) data revealed that AISBA-15 retained its long range mesoporous order after immobilization of the Rh^I complex.

Comparison and evaluation of the immobilized catalysts

The isomerization of allylic alcohol **4a** (Scheme 2) was performed to evaluate the activity of the different heterogeneous rhodium catalysts. When the reaction was run with system **I** [Rh(**2**)/PTA(**1a**)=1:2, 0.5 mol%] immobilized on AISBA-15,

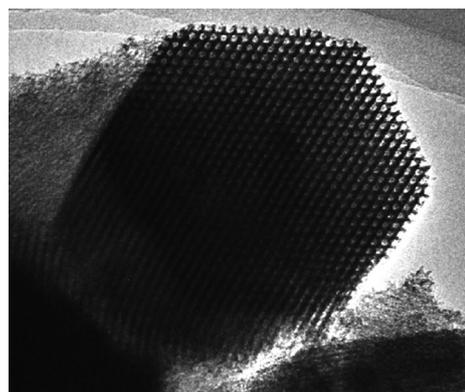
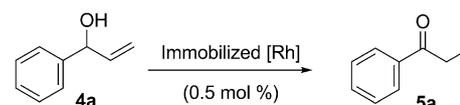


Figure 6. A TEM image of **II**/AISBA-15.



Scheme 2. Isomerization of allylic alcohol **4a**.

(TPA)-SBA-15, and (TPA)-Al₂O₃ using different solvents at temperatures between RT and 80 °C, the desired product, ketone **5a**, was not formed (Supporting Information, Table S1). On the other hand, the catalytic system **II** containing Rh^I complex **2** and the sulfonated phosphine MeO-TPPMS (**1b**) immobilized on various supports (amorphous SiO₂, MCM-41, MCM-48, SBA-15, and AISBA-15) gave the isomerization product (**5a**) in good yields (Entries 1, 3, 5, 7 and 9, Table 2) with THF as the solvent. All of the catalysts gave >99% selectivity.

Table 2. Catalyst screening and recyclability study.^[a]

Entry	Catalyst ^[b]	Run	Yield of 5a [%] ^[c,d]	Selectivity [%] ^[c]	TON ^[e]
1	II /amorphous SiO ₂	1	>95	>99	190
2	II /amorphous SiO ₂	2	66	>99	132
3	II /MCM-41	1	>95	>99	190
4	II /MCM-41	2	70	>99	140
5	II /MCM-48	1	>95	>99	196
6	II /MCM-48	2	75	>99	150
7	II /SBA-15	1	>95	>99	190
8	II /SBA-15	2	85	>99	170
9	II /AISBA-15	1	>95	>99	190
10	II /AISBA-15	2	>95	>99	190
11	II /AISBA-15	3	>95	>99	190
12	II /AISBA-15	4	>95	>99	190
13	II /AISBA-15	5	95	>99	190

[a] Reaction conditions: A mixture of **4a** (0.4 mmol, 52 μL) and the heterogeneous catalyst (≈ 0.002 mmol of Rh as estimated by ICP, ≈ 0.5 mol%) in THF (1 mL) was heated under stirring at 80 °C for 20 h. Then, the catalyst was filtered, washed repeatedly with THF, dried under vacuum and used in the next catalytic run. The filtrate was evaporated and analyzed by ¹H NMR spectroscopy. [b] System **II**=Rh(**2**)/MeO-TPPMS. [c] Determined by ¹H NMR spectroscopy. [d] Only the product (**5a**) was observed by ¹H NMR spectroscopy in those entries where the yields are >95%. The starting material (**4a**) was not detected. [e] TON=number of moles of product formed per mole of catalyst.

Only the supported complex **II**/AISBA-15 could be recycled at least five times without losing its catalytic activity (Entries 9–13, Table 2). The turnover number (TON) of each run was 190. Inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis of the **II**/AISBA-15 catalyst before and after the reaction showed similar rhodium content (0.606 wt% and 0.605 wt% Rh, respectively). Over the five runs, the total turnover number reached 950. The catalyst **II**/AISBA-15 gave the best performance in anhydrous THF (Table S1, Supporting Information). A control reaction, in which **II**/AISBA-15 was substituted by AISBA-15 or amorphous silica (i.e., without rhodium), did not afford any product at 80 °C after 16 h. Moreover, the solid **II**/AISBA-15 kept its yellow color after being reused for five times and the reaction solutions obtained after filtration of the heterogeneous catalysts were colorless, which was not the case for the unsuccessful catalytic systems (i.e., indicating rhodium leaching from these catalysts). Although studies performed on silica supported hydroformylation catalysts using a flow reactor have demonstrated that even the most stable heterogeneous complexes decrease their metal content after several cycles,^[42] the immobilization of system **II** on AISBA-15 appears to be very efficient, and no appreciable leaching occurred. The heterogeneity of **II**/AISBA-15 was confirmed by a "filtration test".^[43] The solid catalyst was removed by filtration at the reaction temperature (80 °C) when the reaction had reached 40% conversion. The filtrate was allowed to stir at 80 °C, and the mixture was analyzed after 24 h. The conversion remained the same as before filtration (40%), confirming that the isomerization is catalyzed by the supported rhodium complex.

Isomerization of allylic alcohols with the heterogeneous catalyst **II**/AISBA-15

A variety of allylic alcohols were isomerized using the best heterogeneous catalyst, **II**/AISBA-15, with a catalyst loading of about 0.5 mol% (determined by ICP-AES analysis, Table 3). Allylic alcohols bearing aromatic substituents (**4a–4d**) were isomerized in excellent yields (91–95%, Entries 1–4, Table 3). The α -naphthyl substituted allylic alcohol **4e** (Entry 5, Table 3) could be isomerized in high yields (85%). Allylic alcohol **4f**, with a higher degree of substitution on the olefin, was isomerized with a yield of >95% (Entry 6, Table 3). Aliphatic allylic alcohol **4g** afforded 2-octanone (**5g**) in >95% yield after only 4 h (Entry 7, Table 3). It is worth noting that the primary allylic alcohol **4h** afforded the aldehyde **5h** in >95% yield, although a longer reaction time (24 h) was needed (Entry 8, Table 3). The isomerization of cinnamyl alcohol **4i** and of cyclic allylic alcohol **4j** were very sluggish (Entries 9–10, Table 3). For comparison, we ran two experiments under homogeneous conditions. The isomerization of **4a** in THF under reflux using system **II** [i.e., Rh(**2**)/MeO-TPPMS(**1b**) = 1:2, 1.7 mol% Rh] afforded 40% of the isomerization product after 18 h (Entry 11, Table 3). When instead water was used as the solvent (Entry 11 in parenthesis), **5a** was formed with a yield of >95% at 80 °C after 20 h, but a high catalyst loading was needed (5 mol%). Thus,

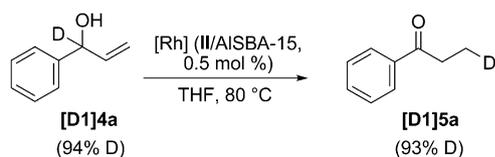
Table 3. Isomerization of a variety of allylic alcohols with the heterogeneous catalyst **II**/AISBA-15.^[a]

Entry	Substrate	Product	t [h]	Yield [%] ^[b]	TON ^[c]
1			18	> 95	198
2			20	95	189
3			20	> 95	190
4			24	91	180
5			20	85	170
6			20	> 95	198
7			4	> 95	198
8			24	> 95	190
9			24	6	10
10			24	52	104
11 ^[d]			18 (20)	40 (> 95)	23 (20)

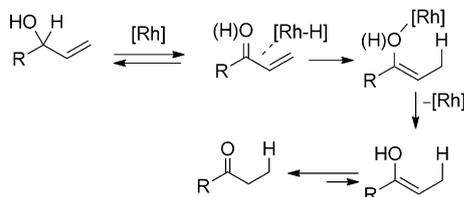
[a] Reaction conditions: A mixture of **4a–j** (0.4 mmol) and the heterogeneous catalyst **II**/AISBA-15 (0.04 g, \approx 0.002 mmol of Rh as estimated by ICP analysis, \approx 0.5 mol%) in THF (1 mL) was heated under stirring at 80 °C for the time indicated. The catalyst was filtered, and the filtrate was evaporated. Unless otherwise stated, 100% selectivity was always obtained. [b] Determined by ¹H NMR spectroscopy. [c] TON = number of moles of product formed per mole of catalyst. [d] Reaction carried out under homogeneous conditions using **2** (1.7 mol%) and **1b** (3.4 mol%) in THF. In parenthesis, reaction run using **2** (5 mol%) and **1b** (10 mol%) in H₂O.

the activity of the heterogeneous system is superior to that of the homologous homogeneous catalysts.

The isomerization of deuterated allylic alcohol [D₁]**4a** using the same conditions as those for **4a** took place quantitatively in 18 h affording deuterated ketone [D₁]**5a**, in which the deuterium label was exclusively shifted to the methyl group (Scheme 3, Figure S2–3, Supporting Information), indicating a 1,3-hydrogen (deuterium) shift. Cleavage of the C–OH bond was not observed for any of the substrates. We propose the mechanism shown in Scheme 4, similar to that proposed by Trost^[44] and us,^[11–13] and studied theoretically by Cadierno, Sordo, and Gimeno^[7] for homogeneous complexes. It involves



Scheme 3. Isomerization of deuterium labeled allylic alcohol [D1]4a.



Scheme 4. Proposed mechanism.

the oxidation of allylic alcohols to α,β -unsaturated carbonyl compounds with concomitant formation of a [Rh–H] species. Reduction of the enone double bond by the metal hydride forms an enol (enolate) that tautomerizes to the carbonyl compound.

Conclusions

We evaluated the effect of using different inorganic supports and ligands in the isomerization of allylic alcohols catalyzed by immobilized rhodium complexes. Out of all the heterogeneous catalysts reported here, the cationic Rh^I complex bearing sulfonated phosphines immobilized on AISBA-15 gave the best results. This complex could be recycled at least five times without losing its catalytic activity. The immobilized catalyst was highly active for the isomerization of allylic alcohols, even with loadings as low as 0.5 mol%. Furthermore, the immobilized catalyst was also active in the isomerization of allylic alcohols with a disubstituted double bond and in the isomerization of aliphatic primary allylic alcohols, which are usually more difficult to isomerize. Characterization of the heterogeneous Rh^I catalyst by N_2 sorption, PXRD, ^{31}P CPMAS NMR and FTIR supported the successful immobilization of the metal complex onto the mesoporous aluminosilica AISBA-15. The immobilization of the catalyst might have occurred by a combination of hydrogen bonding and ionic interactions. Nevertheless, and taking into account the robustness of the system, covalent bonding should also be considered.

Experimental Section

General information

All of the reactions were carried out under a nitrogen atmosphere. The solvents were used as received from the supplier (Sigma Aldrich, puriss p. a.) unless otherwise noted. Anhydrous THF was obtained using a VAC solvent purifier system. All of the allylic alcohols were purchased from Sigma–Aldrich. 1,3,5-Triaza-7-phosphadamanantane and $[\text{Rh}(\text{cod})(\text{MeCN})_2]\text{BF}_4$ were purchased from Strem.

Sodium (4-methoxy-3-sulfonatophenyl)-diphenylphosphine was synthesized in two steps from chlorodiphenylphosphine as described elsewhere.^[29,30] The Si/Al molar ratio of AISBA-15 and the Rh contents of the resulting solids were estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Nitrogen adsorption and desorption isotherms were measured at -196°C on a Micromeritics ASAP 2020 system. The samples were degassed for 10 h at 100°C under vacuum before the measurements. Specific surface areas were calculated using the BET model. Pore size distributions were obtained from the adsorption branches of the nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) method. Powder X-ray diffraction (PXRD) was performed on a PANalytical X'Pert PRO MRD using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FTIR) spectroscopy was performed on a Varian 670-IR spectrometer. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2000FXII microscope operated at 200 kV.

Mesoporous silica MCM-41 and MCM-48 were synthesized as reported in the literature^[31] (see the Supporting Information). The syntheses of other supports are described below.

Syntheses of SBA-15

Mesoporous silica SBA-15 was synthesized according to the procedure by Zhao and co-workers.^[32] In a typical synthesis, tetraethyl orthosilicate (8.0 g, 38 mmol) was added under stirring to a homogeneous solution of pluronic P123 (4.0 g, 4.0 mmol), distilled water (30 mL), and hydrochloric acid (2 M, 240 mmol, 120 mL) at 40°C . The reaction mixture was stirred at 40°C for 24 h, and then heated at 100°C for 48 h under static conditions. The resultant white precipitate was filtered, washed with distilled water and dried at 100°C overnight. The as-synthesized SBA-15 samples were calcined at 540°C for 10 h in air.

Syntheses of AISBA-15

Mesoporous aluminosilica AISBA-15 was synthesized by post-synthesis.^[33] A mixture of silica SBA-15 (2.0 g, approx. 32 mmol) and AlCl_3 (0.134 g, 1.10 mmol) was heated to reflux in anhydrous ethanol at 80°C for 10 h. The resulting solid was filtered, washed repeatedly with anhydrous ethanol, and dried in air at room temperature. The material was calcined in air at 550°C for 10 h. The Si/Al ratio of the final product AISBA-15 was 9:1, determined by ICP-AES.

Syntheses of tungstophosphoric acid modified silica, (TPA)- Al_2O_3 and (TPA)-SBA-15

To a solution of tungstophosphoric acid (TPA, 0.2 g, 0.7 mmol) in ethanol (10 mL), pre-dried alumina (0.9 g) was added under stirring. The mixture was stirred for 18 h at room temperature. The solid was filtered, washed several times with ethanol, dried, and kept in a desiccator until further use. A similar procedure was used for the synthesis of tungstophosphoric acid (TPA)-SBA-15, in which alumina was replaced by SBA-15.

Immobilization of I/AISBA-15

$[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ (**2**, 22.8 mg, 0.06 mmol) and 1,3,5-triaza-7-phosphadamanantane (**1a**, 18.9 mg, 0.12 mmol) were dissolved in CH_2Cl_2 (10 mL). After 30 min, pre-dried AISBA-15 (0.6 g) was added

and the mixture was stirred at room temperature for 8 h. After filtration, the white solid was washed several times with CH_2Cl_2 and ethanol (EtOH) and dried under vacuum to provide the supported complex (I/AISBA-15, 0.60 g).

Immobilization of I/(TPA)- Al_2O_3

$[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ (**2**, 11.4 mg, 0.03 mmol) and 1,3,5-triaza-7-phosphadamantane (**1 a**, 9.45 mg, 0.06 mmol) were stirred in ethanol (15 mL). After 30 min, (TPA)- Al_2O_3 (0.4 g) was added to the solution and the mixture was stirred overnight. After filtration, the product was washed with EtOH several times to afford a pale yellow solid (0.41 g) of the anchored complex [I/(TPA)- Al_2O_3].

The immobilization of I/(TPA)-SBA-15 was achieved by following the same procedure as for I/(TPA)- Al_2O_3 .

Immobilization of II/AISBA-15

$[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ (**2**, 15 mg, 0.04 mmol) was added to a solution of MeO-TPPMS (**1 b**, 30 mg, 0.08 mmol) in CH_2Cl_2 (20 mL). After 30 min, AISBA-15 (0.5 g) was added and the mixture was stirred at room temperature for 7 h. Subsequently, the solid was filtered and the residue was washed several times with CH_2Cl_2 to afford a yellow solid (0.5 g) of II/AISBA-15.

Immobilization of II/SBA-15

A mixture of $[\text{Rh}(\text{COD})(\text{MeCN})_2]\text{BF}_4$ (**2**, 15 mg, 0.04 mmol) and MeO-TPPMS ligand (**1 b**, 30 mg, 0.08 mmol) in CH_2Cl_2 (10 mL) was stirred for 30 min. Then, SBA-15 (0.5 g, pre-dried) was added. The mixture was stirred for 6 h, filtered, washed several times with CH_2Cl_2 , and dried under vacuum to afford the immobilized complex II/SBA-15 (0.5 g).

Immobilization of II/MCM-41, II/MCM-48 and II/ SiO_2

A similar procedure to that described for the synthesis of II/SBA-15 was used to synthesize the immobilized complexes II/MCM-41, II/MCM-48, and II/ SiO_2 (amorphous) by replacing SBA-15 with MCM-41, MCM-48, or amorphous SiO_2 , respectively.

NMR spectroscopy

NMR chemical shifts (δ) are reported in ppm (deshielding scale) and scalar (J) coupling constants are given in Hz. ^{31}P chemical shifts are quoted relative to 85% H_3PO_4 (aq).

Solution NMR

Solution ^1H , ^{13}C , and ^{31}P NMR spectra were recorded at 9.4 T, corresponding to -400 MHz and -100 MHz Larmor frequencies for ^1H and ^{13}C , respectively, using a Bruker Avance II spectrometer. The residual solvent peaks in CDCl_3 were used as an internal standard for shift referencing ($\delta_{\text{H}} = 7.26$ ppm and $\delta_{\text{C}} = 77.00$ ppm relative to tetramethylsilane).

Solid-state NMR

MAS ^{31}P NMR data were recorded at 9.4 T using a Varian/Chemagnetics Infinity-400 spectrometer, giving a ^{31}P Larmor frequency of

-161.98 MHz. Finely ground powders of system II [Rh(**2**)/MeO-TPPMS(**1 b**) = 1:2, 7 mg] and II/AISBA-15 (21 mg) were packed in 4 mm zirconia rotors and spun at 12.50 kHz at room temperature. System II was mixed with NaCl to fill out the rotor volume (81 mg total mass). The experimental conditions were identical for both samples. $^1\text{H} \rightarrow ^{31}\text{P}$ CPMAS employed a 2.5 ms contact interval (optimized on system II). Proton nutation frequencies of 65 kHz and 85 kHz were used for CP and continuous-wave decoupling, respectively. A ramp was applied to the ^{31}P rf-field amplitude (around a mean value of 40.0 kHz) during CP.^[45] The ^{31}P NMR spectra shown in Figure 4 resulted from 3072 and 17 408 accumulated signal transients for systems II and II/AISBA-15, respectively, using relaxation delays of 6 s; the latter were selected from ^1H saturation-recovery experiments on system II. We also verified that the relative NMR peak intensities observed in the CPMAS spectra from systems II and II/AISBA-15 were reproduced by separate ^{31}P NMR acquisitions using single pulses (data not shown).

General method for catalytic isomerization of allylic alcohol

In a typical catalytic run, the catalyst (40 mg, 0.606 wt% of Rh estimated by ICP-AES analysis, ≈ 0.5 mol%) was placed in a Schlenk tube under vacuum at 80°C for 1 h. Then, the flask was filled with nitrogen gas, and anhydrous THF (1 mL) was added, followed by the allylic alcohol (0.4 mmol). The reaction mixture was immediately introduced into an oil bath at a specified temperature. After a certain time period, the catalyst was filtered and the mixture was analyzed by ^1H NMR spectroscopy. To test the recyclability of a catalyst, it was filtered after each catalytic reaction, washed several times with THF and dried at 80°C . The recycled material was then subjected to the next catalytic run with fresh allylic alcohol and THF.

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