

Chemoselective Hydrogen Transfer Reduction of Unsaturated Ketones to Allylic Alcohols with Solid Zr and Hf Catalysts

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Dedicated to Roger Sheldon at the occasion of his 60th birthday.

Abstract: α,β -Unsaturated ketones were reduced to allylic alcohols with high chemo- and diastereoselectivity, using Zr and Hf compounds heterogenised on mesoporous molecular sieves.

Keywords: allylic alcohols; hafnium; heterogeneous catalysis; α,β -unsaturated ketones; zirconium

Introduction

Allylic alcohols are important intermediates in agrochemistry, pharmaceutical and fragrance chemistry. For instance, a new and elegant synthesis of morphine starts from an allyl-substituted cyclohexenol; the fragrance (S)- α -damascone can be prepared starting from a trimethyl-substituted cyclohexenol.^[1] Next to olefin autoxidation and oxygenation with singlet dioxygen,^[2,3] chemoselective reduction of α,β -unsaturated carbonyl compounds is an important synthetic entry to allylic alcohols.^[4] The stoichiometric $\text{NaBH}_4/\text{CeCl}_3$ system, and, most prominently, the ternary combination of Ru(phosphine) with a diamine and a base proved to be excellent for such reductions.^[5,6] In parallel to these homogeneous reagents or catalysts, considerable effort has been done to develop heterogeneous catalysts for this type of reduction. Especially the combination of group VIII metals (Pt, Rh, Ru) and some metal additives (Sn, Fe) is suited for the selective reduction of unsaturated aldehydes to allylic alcohols.^[7,8] However, when applied to the selective reduction of α,β -unsaturated ketones, these catalysts often show high selectivity for the saturated ketone or the alcohol.^[9] As an alternative to metal-catalysed hydrogenations, hydrogen transfer reactions of the Meerwein–Ponndorf–Verley (MPV) type form an attractive approach.^[10–12] This reaction is intrinsically selective since only the carbonyl group coordinates with the Lewis acid reaction centre, while the double bond remains unactivated. MPV reactions are often performed with stoichiometric amounts of soluble metal compounds.^[10] The use of heterogeneous catalysts has received much less attention,^[13–16] while reactions with unsaturated ketones have hardly been studied.^[12]

In this paper we report on the selective reduction of a variety of α,β -unsaturated ketones using heterogenised zirconium and hafnium catalysts. Heterogeneous MPV catalysts of this type have previously only been applied to the reduction of “simple” ketones, such as 4-*t*-butylcyclohexanone.^[17–19] As the hydride donor, either cyclopentanol or 1-indanol are employed. Mesoporous siliceous materials with mono- or tridimensional pore structure, functionalised with Zr or Hf, are useful catalysts. With truly catalytic amounts of the Zr or Hf catalyst, high yields of the allylic alcohol are obtained from unsaturated ketones with excellent chemo- and diastereoselectivities.

Results and Discussion

Survey of the General Reaction Parameters

In order to identify the best reaction conditions, the $\text{Zr}(\text{O}-n\text{-Pr})_n$ -MCM catalysts were tested with benzalacetone (*trans*-4-phenyl-3-buten-2-one). This unsaturated ketone is highly reactive in MPV reduction, probably due to the conjugation of the enone group with the aromatic nucleus. Initial reactions showed that with the solid catalyst and cyclopentanol as a hydrogen donor, complete selectivity for the allylic alcohol was obtained. Addition of molecular sieves strongly increased the rate, probably by efficient trapping of water traces (compare Table 1 entries 1 and 2). Particularly 4 Å molecular sieve is suitable; with the Ca-containing 5 Å material acid-catalysed side reactions such as etherifications or dehydrations may occur. An important reaction parameter is the reductant over enone ratio. An optimum was observed at a cyclopentanol over

Table 1. Effect of reaction conditions on MPV reduction of benzalacetone with solid Zr catalysts.

Entry	Conditions ^[a]	<i>t</i> [h]	Conversion [%] ^[b]
1	no 4 Å mol. sieve	22	26
2	with 4 Å mol. sieve	22	91
3	2 equiv. cyclopentanol	22	42
4	5 equiv. cyclopentanol	22	55
5	10 equiv. cyclopentanol	22	29
6	10 g heptane solvent	22	79
7	Zr(O- <i>n</i> -Pr) ₄	3	10
8	Zr(O- <i>n</i> -Pr) _n -MCM-41	3	22
9	Zr(O- <i>n</i> -Pr) _n -MCM-48	3	30

^[a] General conditions for substrate, catalyst, reductant, solvent, unless specified otherwise: 2 mmol benzalacetone, 0.1 mmol Zr catalyst as 50 mg Zr(O-*n*-Pr)_n-MCM-41, 10 mmol (5 equiv.) cyclopentanol, 100 mg 5 Å molecular sieve (entries 3–9) or 4 Å (entry 2), 6 g heptane, 75 °C.

^[b] Chemoselectivity was in all cases superior to 98%, hence the enone conversion practically equals the allylic alcohol yield.

benzalacetone ratio of about 5 (entries 3–5). This optimum can be explained by competitive adsorption of the reactants on the surface; a too high alcohol concentration probably impedes sufficient adsorption of the enone. Solvent composition is important as well; thus the enone conversion is faster if the volume of the heptane solvent is increased (entries 6 vs. 4). This agrees with the idea that coordination of alcohol and ketone on MPV catalysts is easiest in apolar media.^[10]

The presence and the nature of the siliceous support have a remarkable effect on the activity of the catalyst (Table 1, entries 7–9). In experiments with identical total Zr concentrations, a homogeneous catalyst was compared with heterogeneous Zr catalysts based on MCM-41 or MCM-48. With Zr(O-*n*-Pr)_n-MCM-41 and Zr(O-*n*-Pr)_n-MCM-48, the reaction is between 2 and 3 times faster than with the homogeneous Zr compound. The rather low catalytic activity of dissolved Zr(O-*n*-Pr)₄ is probably due to self-association of the homogeneous alkoxides or even to formation of oxide particles in solution. These phenomena considerably lower the Lewis acidity of the metal centres and the number of available free coordination sites. In contrast, the surface of the MCM materials provides many docking points for the Zr alkoxides, resulting in a more dispersed and reactive material.^[16] The tridimensional pore architecture of MCM-48 seems to facilitate the access to the large internal surface area. Together with the observation that the reaction practically stops when the Zr-loaded MCM-41 is removed from the reaction suspension, the acceleration of the Zr catalysis by the MCM supports is a clear indication that surface-associated, heterogeneous Zr species are responsible for the catalytic activity. Summarising, critical reaction

parameters are the presence and nature of the support and the molecular sieve, as well as the amount and the nature of the reducing alcohol. A discussion of the influence of the nature of the metal and of the precursor follows.

Scope of the Reaction

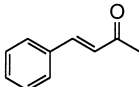
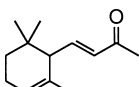
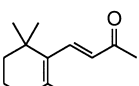
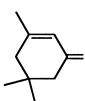
The extension of the scope of the reaction from benzalacetone to other groups of enones is shown in Table 2. Clearly aliphatic as well as alicyclic unsaturated enones can be reduced smoothly to allylic alcohols. Even if the enone group is not activated, but simply part of an aliphatic chain, as in α -ionone, an 89% yield is eventually obtained (entry 6). Remarkably not only the C=C double bond in the enone group of α -ionone, but also the endocyclic C=C bond are left totally intact. In the initial phase of the reaction, where kinetics dominate thermodynamics, the relative reactivity order can be written as follows: isophorone < 3,5-dimethyl-2-cyclohexen-1-one < α -ionone $\approx$ 3-methyl-2-cyclohexen-1-one $\approx$ *R*-carvone < β -ionone < 2-cyclohexen-1-one $\leq$ benzalacetone.

Within the group of cyclohexenones, it is clear that an increasing number of alkyl substituents leads to a decreased reactivity, partially due to electronic effects. In, e.g., 3-methyl-2-cyclohexen-1-one, the presence of an alkyl group in the β position to the C=O group decreases the susceptibility of the carbonyl group to hydrogen transfer. On the other hand, steric effects are probably important as well, as demonstrated by the low reaction rate of the trimethyl-substituted isophorone.

Effect of Metal Precursor and Nature of the Metal

Catalysts prepared from different Zr sources, *viz.* Zr(O-*n*-Pr)₄ and ZrCp₂Cl₂ were compared in several enone reductions. If a strong reductant such as indanol is used in a facile reaction with, e.g., benzalacetone, differences between both catalysts are minor (Table 3, entry 2a). However, if a less potent reductant or a less reactive substrate is used, the zirconocene-based catalyst shows better performance than the material based on the alkoxide. For instance, in the reduction of isophorone with 1-indanol, Zr(Cp)_n-MCM-41 is more active than Zr(O-*n*-Pr)_n-MCM-41 (Table 3, entry 1). Similarly, the former catalyst gives better product yields in benzalacetone reduction with cyclopentanol (Table 3, entry 2b). The high activity of the zirconocene-based catalyst is likely related to the high dispersion degree of Zr, and to its slightly higher metal content. Anchoring of metallocene chlorides to a siliceous surface is known to result in mononuclear species,^[21] while clusters are easily formed when large amounts of metal alkoxides are supported on SiO₂ type materials.^[22]

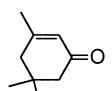
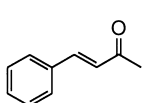
Table 2. MPV reduction of a variety of α,β -unsaturated ketones over a heterogenised $\text{Zr}(\text{O}-n\text{-Pr})_n\text{-MCM-41}$ catalyst.^[a]

Entry	Substrate		Reductant	<i>t</i> [h]	Yield, [%]	Chemoselectivity ^[b] [%] (de, %)
1	benzalacetone		1-indanol	4	94	98
2	2-cyclohexen-1-one		1-indanol	4	89	94
3	<i>R</i> -carvone		1-indanol	5	62	97 (92 <i>cis</i>)
4	3-methyl-2-cyclohexen-1-one		1-indanol	5	68	95
5	3,5-dimethyl-2-cyclohexen-1-one		1-indanol	5	52	95 (83 <i>cis</i>)
6	α -ionone		1-indanol	9	89	93
7	β -ionone		1-indanol	9	80	94
8	isophorone		1-indanol	29	23	97
9	<i>R</i> -carvone		cyclopentanol	48	20	98 (78 <i>cis</i>)

^[a] Reaction conditions: 2 mmol substrate, 10 mmol 1-indanol, 6 g heptane, 50 mg catalyst (Si/Zr = 5), 100 mg molecular sieve 4 Å, 75 °C.

^[b] Chemoselectivity to allylic alcohol.

Table 3. Comparison between zirconocene [$\text{Zr}(\text{Cp})_n\text{-MCM-41}$] (=A) and Zr-alkoxide [$\text{Zr}(\text{O}-n\text{-Pr})_n\text{-MCM-41}$] (=B) based catalysts in the reduction of enones to allylic alcohols.^[a]

Entry	Substrate	Reductant	<i>t</i> [h]	Yield [%] with A	Yield [%] with B	
1	isophorone		1-indanol	24	20	33
2a	benzalacetone		1-indanol	4	90	94
2b		cyclopentanol	3	32	53	

^[a] Reaction conditions: 1 mmol substrate, 5 mmol 1-indanol or cyclopentanol, 6 g heptane, 25 mg catalyst, 100 mg molecular sieve 4 Å, 75 °C; yields are given for allylic alcohols.

In order to evaluate metal leaching and catalyst reusability, a test was performed for the benzalacetone reduction with indanol in heptane, using $\text{Zr}(\text{Cp})_n\text{-MCM-41}$ as the catalyst. At 30 minutes and an enone conversion of 32%, solution and catalyst were separated by centrifugation. Further conversion of the enone in

the filtrate is negligible (33% after 90 minutes), while addition of fresh reactants to the recuperated catalyst shows that the latter still has a high reactivity (from 0 to 66% conversion in 90 minutes). Thus, the reaction is truly heterogeneously catalysed by the solid material.

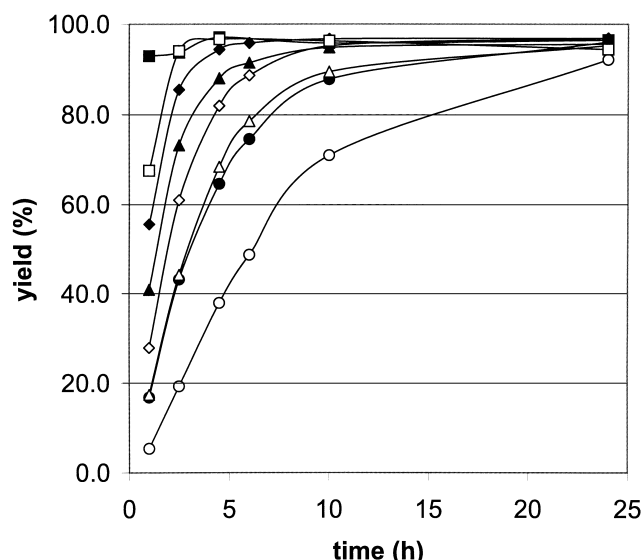


Figure 1. Yields of allylic alcohols vs. time, for the reduction of enones with 5 mol % of $\text{Zr}(\text{Cp})_n$ (open symbols) and $\text{Hf}(\text{Cp})_n$ (filled symbols) catalysts grafted on MCM-41 and with 1-indanol as hydride donor, starting from following enones: benzalacetone ($\square$, $\blacksquare$), α -ionol ($\diamond$, $\blacklozenge$), β -ionol ($\triangle$, $\blacktriangle$), and mesityl oxide ($\circ$, $\bullet$). Conditions as in Table 2.

As shown for different substrates in Figures 1 and 2, the rates can also be substantially increased by substitution of Zr for Hf. Catalysts based on the metallocenes ZrCp_2Cl_2 and HfCp_2Cl_2 were compared. Depending on the substrate, the rate increase in the initial phase of the reaction is on the average 1.5- to 3-fold, except for sterically hindered substrates such as isophorone. With indanol as a reductant, high yields are obtained within reasonable time with relatively small amounts of catalyst (5 mol %). Recommended standard MPV protocols with homogeneous catalysts employ regularly between 20 and 100 mol % of metal catalyst.^[10]

Diastereoselective and Enantioselective Reactions

With complex enones such as terpenic substrates, the reactions not only display high chemoselectivity, but also proceed diastereoselectively. For instance, *R*-carvone and 3,5-dimethyl-2-cyclohexen-1-one after 4 h gave rise to a diastereomeric excess (de) of 92 and 83%, respectively (Table 2, entries 3 and 5). Interestingly, the diastereomeric excess proved to be dependent on the nature of the reductant: a higher de value was obtained with the sterically more demanding 1-indanol than with cyclopentanol (Table 2, entries 3 and 9). This indicates that for the heterogeneous MPV reaction, reductant and enone must simultaneously coordinate to the reactive centre, in analogy to what happens in homogeneous catalysis. Similarly, initial de values are significantly

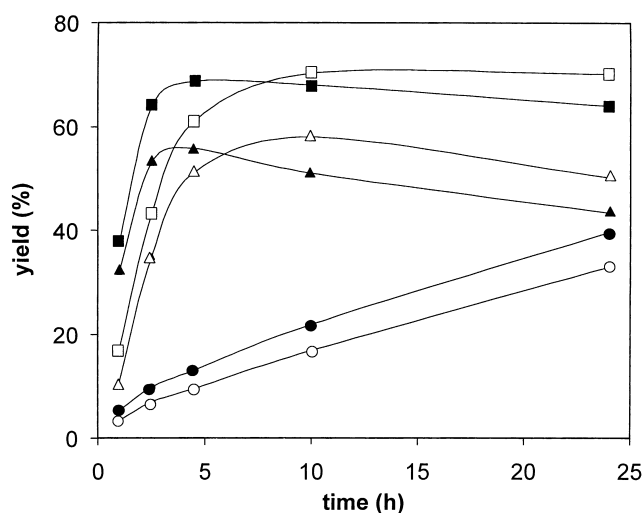


Figure 2. Yields of allylic alcohols vs. time, for the reduction of enones with 5 mol % of $\text{Zr}(\text{Cp})_n$ (open symbols) and $\text{Hf}(\text{Cp})_n$ (filled symbols) catalysts grafted on MCM-41 and with 1-indanol as hydride donor, starting from following enones: carvone ($\square$, $\blacksquare$), 3,5-dimethyl-2-cyclohexen-1-one ($\triangle$, $\blacktriangle$) and isophorone ($\circ$, $\bullet$). Conditions as in Table 2.

higher for the Zr catalyst than for the Hf catalyst. For instance in the reduction of 3,5-dimethyl-2-cyclohexen-1-one, the initial de in the allylic alcohol product for Zr and Hf amounts to 89% and 83%, respectively. This is clearly due to the smaller size of the Zr ion, which causes more steric crowding in the coordination sphere, hence yielding higher de values. This effect is less pronounced in the reduction of carvone, for which the de is only 2% smaller with Hf than with Zr (90 vs. 92%). Clearly, the larger size of the isopropenyl group in carvone results in a more effective stereocontrol of the ketone reduction.

As shown in Figure 3, the diastereomeric excess values change in time. In the initial, kinetically controlled phase of the reaction, the de is high and almost constant and the *cis*-allylic alcohols prevail. When towards the end of the reaction thermodynamics start to control the product distribution, the de decreases as more of the *trans*-products are formed, such as *trans*-3,5-dimethyl-2-cyclohexen-1-ol and *trans*-carveol. The epimerisation seems to be a catalytic process; it is clearly faster with the heterogeneous Hf catalyst than with the Zr material. This trend is essentially the same as for the actual enone reduction, and may be related to a higher ligand exchange rate on the larger Hf metal centre. The lowering of the de is probably due to back-reaction of the initially formed carveol, with predominant *cis*-configuration, with either carvone or indanone. In control reactions of pure *cis*-carveol (91% de) with 1-indanone or carvone over the $\text{Zr}(\text{Cp})_n$ -MCM-41 catalyst, a substantial lowering of the carveol de was observed, proving that the loss of de is related to the reversibility of the reaction.

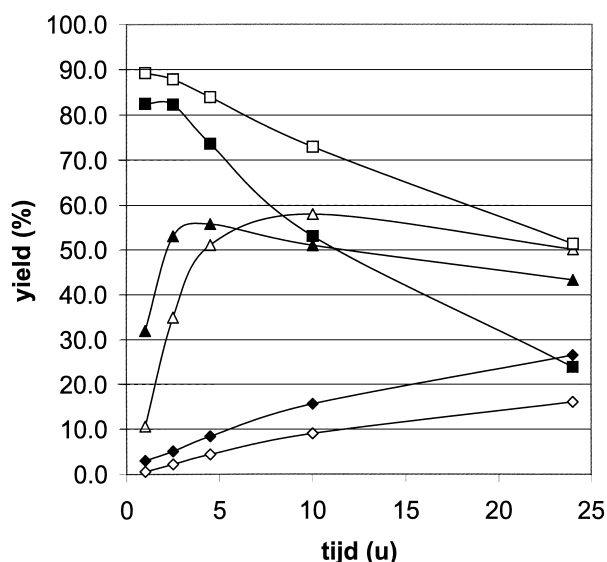


Figure 3. MPV reduction of 3,5-dimethyl-2-cyclohexen-1-one with as catalysts $\text{Zr}(\text{Cp})_n\text{-MCM-41}$ (open symbols) and $\text{Hf}(\text{Cp})_n\text{-MCM-41}$ (filled symbols), and with 1-indanol as hydride donor: yield of *cis*-3,5-dimethyl-2-cyclohexen-1-ol (Δ , $\blacktriangle$), yield of *trans*-3,5-dimethyl-2-cyclohexen-1-ol ($\diamond$, $\blacklozenge$), and diastereomeric excess ($\square$, $\blacksquare$). Conditions as in Table 2.

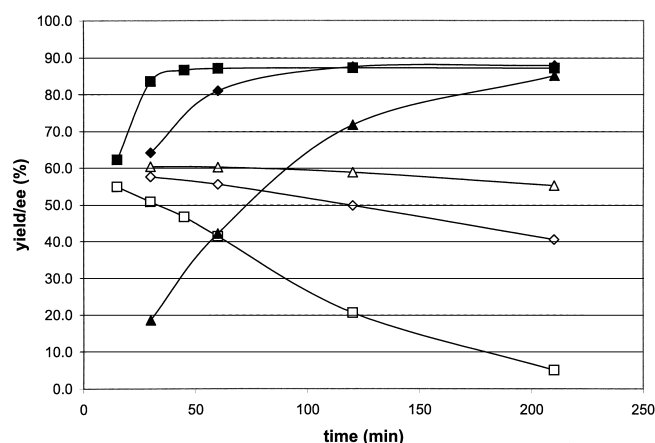


Figure 4. Influence of the temperature on the allylic alcohol yield (filled symbols) and the enantiomeric excess (open symbols) in the reduction of 2-cyclohexen-1-one with a 3-fold excess of (*S*)-1-indanol as hydride donor and with 5 mol % $\text{Hf}(\text{Cp})_n\text{-MCM-41}$ as the catalyst: 60 °C ($\blacktriangle$, Δ), 80 °C ($\blacklozenge$, $\diamond$), 100 °C ($\blacksquare$, $\square$). Other conditions as in Table 2.

Finally, the Hf and Zr MPV catalysts were not only applied to diastereoselective but also to enantioselective reactions. In the reduction of 2-cyclohexen-1-one, enantiomerically pure (*S*)-1-indanol was used as a reductant instead of the racemic alcohol. The results show that it is indeed possible to transfer chirality onto the allylic alcohol in an effective way. The ee value depends on the used excess of (*S*)-1-indanol as well as on the temperature. A high concentration of the chiral hydride donor and low temperature are the most

beneficial conditions for obtaining ee's up to 60% (Figure 4). This is to our knowledge the first example of a heterogeneously performed enantioselective transfer reaction using an MPV type of catalyst. Moreover, even in homogeneous MPV catalysis few reports exist of effective chiral transfer reactions; often the substrate scope is limited, or ee values are rather low.^[23,24]

Conclusion

Zr and Hf catalysts were prepared by immobilisation of alkoxide or metallocene precursor complexes on ordered siliceous matrices such as MCM-41. In optimised reaction conditions, and with suitable alcohols as reductants, these materials catalyse the chemoselective reduction of most unsaturated ketones to the corresponding allylic alcohols. The materials based on Hf are more active catalysts than those containing Zr. Moreover, the metallocene preparation procedure yields more active materials than the metal-alkoxide routes. In addition to the high chemoselectivity, a high diastereoselectivity is observed for reactions with natural chiral molecules such as carvone. Finally, it is demonstrated that chirality can be efficiently transferred from a chiral reductant to a substrate enone, resulting in ee's up to 60% for the allylic alcohol.

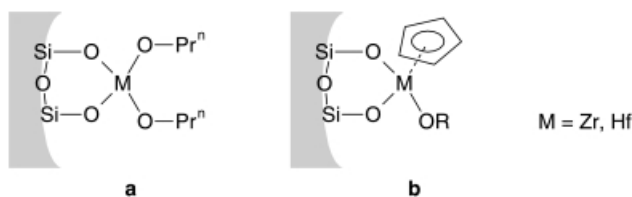
Experimental Section

Preparation of Mesoporous Supports

MCM-41 was prepared as follows. 19.43 g of a 20 wt. % tetraethylammonium hydroxide (TEAOH) solution, 16.16 g cetyltrimethylammonium chloride (CTMACl) and 20 mL of water were consecutively added to 19.27 g of LUDOX AS-40 (Dupont) under vigorous stirring. After 15 minutes an additional amount of 32.33 g CTMACl and 20 mL H_2O were added. The resulting mixture was stirred for another 15 minutes. The mixture was transferred into a stainless steel autoclave. The rotating autoclave was heated at 110 °C for 24 h. MCM-48 was prepared according to the procedure reported by Kevan et al.^[20]

Grafting of Alkoxides

After calcination, 1 g of siliceous MCM material was predried at 200 °C, and contacted with a solution of 0.936 g $\text{Zr}(\text{O-}n\text{-Pr})_4$ (as a 70 wt % solution in 1-propanol) in 10 g of hexane for 3 h at room temperature. The solid was filtered under N_2 , washed with an excess of hexane and finally dried under a helium flow. Elemental analysis indicated a typical Si/Zr ratio of 6. XRD measurements, as well as SEM, show that the structure of the MCM-41 or MCM-48 materials remains unaltered. The material containing the grafted alkoxides is denoted as $\text{Zr}(\text{O-}n\text{-Pr})_n\text{-MCM}$ (Scheme 1, a); $\text{Zr}(\text{O-}n\text{-Pr})_n\text{-MCM-41}$ typically contains 0.81 mmol Zr per g.



Scheme 1.

Grafting of Metallocenes

After calcination, 0.5 g of predried (200 °C) siliceous MCM material was contacted with a solution of 1 mmol of ZrCp_2Cl_2 or HfCp_2Cl_2 in 13 g CHCl_3 for 1 h at room temperature. Subsequently a small excess of triethylamine (3 mmol) in 1 mL of CHCl_3 was added and the solution was kept stirring for another 3 h. After filtering, washing with excess CHCl_3 and drying under He, the $\text{Zr}(\text{Cp})_n\text{-MCM}$ or $\text{Hf}(\text{Cp})_n\text{-MCM}$ catalysts are obtained (Scheme 1, b). For $\text{Zr}(\text{Cp})_n\text{-MCM-41}$, a typical Zr content was 1.21 mmol per g.

Reaction Conditions

Typically a mixture of the substrate (1 mmol) and the hydride donor (5 mmol) was first dissolved in 6 g of heptane at 75 °C. After cooling to room temperature the catalyst (25 mg) and the molecular sieve (4 Å, 100 mg) were added consecutively. The reaction was performed at 75 °C.

Preparation of Reference Compounds and Analysis

Reference allylic alcohols, if not commercially available, were synthesised according to a literature procedure.^[5] Typically, 1 mmol of enone was dissolved in 2 mL of methanol, and stoichiometric amounts of CeCl_3 and NaBH_4 were added at 25 °C. Extraction with ether after 3 min yields the allylic alcohols. Routine product analysis was performed on a GC, equipped with a 50 m CP-Wax-58 capillary column (Chrom-pack). The identity of the products was as well confirmed by ^1H NMR.

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