

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201916385 Angew. Chem. 10.1002/ange.201916385

Link to VoR: http://dx.doi.org/10.1002/anie.201916385 http://dx.doi.org/10.1002/ange.201916385

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Selective Hydrogenation and Hydrodeoxygenation of Aromatic Ketones to Cyclohexane Derivatives Using a Rh@SILP Catalyst

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Abstract: The selective hydrogenation and hydrodeoxygenation of aromatic ketones is achieved using rhodium nanoparticles immobilized on an acid-free triphenylphosphonium-based supported ionic liquid phase (Rh@SILP(Ph3-P-NTf2)). The flexible molecular approach used to assemble the individual catalyst components (SiO₂, ionic liquid, nanoparticles) allows for the formation of a catalytic system possessing outstanding catalytic properties. In particular, an intimate contact between the nanoparticles and the phosphonium ionic liquid is required to enable the deoxygenation reactivity. Using the Rh@SILP(Ph₃-P-NTf₂) catalyst, benzylic ketones are hydrodeoxygenated under mild conditions, while for non-benzylic ketones the product distribution is controlled with high selectivity between the hydrogenated (alcohol) and hydrodeoxygenated (alkane) products by adjusting the reaction temperature. The Rh@SILP(Ph3-P-NTf₂) catalyst possesses excellent activity, versatility and stability, and opens the way to the production of a wide range of high-value cyclohexane derivatives via the hydrogenation and/or hydrodeoxygenation of Friedel-Crafts acylation products and ligninderived aromatic ketones. In addition, the catalyst's temperature controlled selectivity is a key feature broadening the scope of accessible products and potential applications.

The synthesis of alkyl cyclohexane derivatives has attracted considerable attention in the past decade due to the importance of these compounds in the transportation sector^[1] (kerosene-type fuels) and as building blocks for the production of coating agents,^[2] liquid crystals^[3] and pharmaceuticals.^[4] The traditional method for the synthesis of alkyl cyclohexanes consists in the hydrogenation of alkyl aromatics^[5] commonly produced through Friedel-Crafts alkylation reactions. However, this pathway suffers from the limited substrate scope and often low selectivity of Friedel-Crafts alkylation (overalkylation, carbocation rearrangements),^[6]. In this context, the hydro(deoxy)genation of aromatic ketones obtained for example through Friedel-Crafts acylation^[7] or oxidative depolymerization of lignin^[8] appears as an attractive alternative. In addition, using aromatic ketones as substrates gives the opportunity to access two classes of compounds, i.e. alkyl cyclohexanes and hydroxyl containing cyclohexane derivatives, broadening significantly the scope of

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products and potential applications (Figure 1). Despite recent efforts^[9] the development of versatile catalytic systems able to effectively hydrogenate and/or hydrodeoxygenate a large panel of aromatic ketones remains a major challenge and constitutes the focus of this study.



Figure 1. A) Pathways for the synthesis of cyclohexane derivatives through temperature-controlled hydrogenation or hydrodeoxygenation of aromatic ketones. B) Examples of applications for cyclohexane derivatives.

While in heterogeneous catalysis, hydrogenation reactions are mainly performed in the presence of transition metal nanoparticles (Ni,^[10] Ru,^[11] Rh,^[12] Pt,^[13] etc.), the subsequent hydrodeoxygenation typically requires the presence of both a metal and a strong Brønsted or Lewis acidic catalyst.^[14] Metal nanoparticles immobilized on Supported Ionic Liquid Phases (SILPs) were demonstrated to open a molecular approach to multifunctional catalytic systems with tailor-made reactivity.[15,16] SILPs are suitable matrices for nanoparticle synthesis and stabilization. The ionic liquid structure can be easily functionalized to bring different types of actives sites in intimate contact with the active metal. Recent studies described the synthesis of monometallic^[16a-c] bimetallic^[15f,16d] and nanoparticles on imidazolium-based SILPs to produce catalytic systems possessing excellent catalytic properties for hydrogenation and hydrodeoxygenation reactions. In particular, the choice of the acid, and a close proximity between the metal and acid sites were shown to be key factors in the development of effective hydrodeoxygenation catalysts.[16b,c,e]

We report here the synthesis of Rh nanoparticles immobilized on a triphenylphosphonium-based SILP. Using the resulting Rh@SILP(Ph₃-P-NTf₂) catalyst, aromatic ketones were effectively hydrogenated and hydrodeoxygenated without the need for an additional acid functionality. While benzylic ketones were readily hydrodeoxygenated under mild conditions, non-benzylic ketones could be selectively hydrogenated or hydrodeoxygenated

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depending on the temperature applied, providing flexible access to a wide range of substituted cyclohexanes.

The functionalized support material SILP(Ph₃-P-NTf₂) was synthesized through the condensation of a triethoxysilanefunctionalized phosphonium ionic liquid, ([triphenyl(3-(triethoxysilyl)propyl)phosphonium]NTf₂), on dehydroxylated silica following a modified established procedure^[17]. Analysis by DRIFT IR (Figure S1-S3) showed signals at 1440, 1484, 1590 cm-1 and 2897, 2930, 2977, 3072 cm⁻¹ characteristic of the triphenylphosphine moiety. ²⁹Si solid state (Figure S4) shows the presence of two types of Si species: (1) tetra-functionalized (Q) signals at -110 ppm (Q4 = $Si(OSi)_4$) and -102 ppm (Q3 = Si(OSi)₃OH); and (2) tri-functionalized signals at -61 ppm (T2 = R-Si(OSi)₂OR') and -53 ppm (T1 = R-Si(OSi)(OR')₂). The T2 and T1 signals correspond to the Si atoms of IL bound to the SiO₂ surface and thus substantiate the covalent attachment of the IL on the silica support. ¹H, ¹³C, ³¹P and ¹⁹F solid state NMR further confirmed the presence of the desired triphenylphosphonium-NTf₂ ionic liquid in SILP(Ph₃-P-NTf₂) (Figure S5-8A).

Rhodium nanoparticles were generated on the SILP *via* impregnation with a solution of [Rh(allyl)₃] in dichloromethane, followed by a reduction of the dried and impregnated SILP under hydrogen atmosphere (100 bar H₂, 100 °C, 2h) to give a black powder.^[16b] The Rh loading on Rh@SILP(Ph₃-P-NTf₂) was determined to be 0.1 mmol/g by ICP-AAS, well in agreement with the theoretical value. The BET surface area of the support decreases slightly from 292 to 271 m²/g upon Rh-loading (Table S2). Analysis of Rh@SILP(Ph₃-P-NTf₂) (illustrated schematically in Figure 2A) by transmission electron microscopy shows that the NPs are small (1.2 nm) and well dispersed over the SILP support (Figure 2B).



Figure 2. Schematic representation (A) and transmission electron microscopy image (B) of $Rh@SILP(Ph_3-P-NTf_2)$.

The catalytic activity of Rh@SILP(Ph₃-P-NTf₂) and several reference catalysts for hydrogenation and hydrodeoxygenation was first studied using acetophenone (1) as model substrate (Table 1). The use of SiO₂-supported Rh NPs resulted in the hydrogenation of acetophenone (1) to form the saturated alcohol 1a in 95% yield (Entry 1). In contrast, Rh@SILP(Ph₃-P-NTf₂) produced the fully hydrodeoxygenated alkane 1b in quantitative yield (Entry 2). Since neither Rh NPs nor phosphonium salts are known to catalyze the deoxygenation of ketones/alcohols individually, we investigated this intriguing reactivity by systematically modifying the catalyst's structure.

 Table 1. Hydrogenation and hydrodeoxygenation of acetophenone using Rh and Ru nanoparticles immobilized on various supports.

Catalyst

		H ₂ (50 bar), 18 h, n-heptane	\bigcirc	† U	
4				Product Yield [%] ^[a]	
Ę	intry	Catalyst	Temp. [°C]		
	1	Rh@SiO ₂	100	95	5
	2	Rh@SILP(Ph ₃ -P-NTf ₂)	100	0	> 99
	3	Rh@SILP(Oct-n ₃ -NTf ₂)	100	95	5
	4	Rh@SILP(Oct-n ₃ -NTf ₂) + SILP(Ph ₃ -P-NTf ₂)	100	97	3
	5	$Rh@SILP(Oct_3-P-NTf_2)$	100	87	13
	6	Rh@SILP(Ph ₃ -P-BPh ₄)	100	> 99	0
	7	Rh@SILP(Ph ₃ -P-BF ₄)	100	91	9
	8	Ru@SILP(Ph ₃ -P-NTf ₂)	100	89	11
	9	Ru@SILP(Ph ₃ -P-NTf ₂)	175	92	8

Reaction conditions: catalyst (20 mg, metal content: 0.002 mmol), acetophenone (0.1 mmol, 50 eq., 12.0 mg), n-heptane (375 mg), H_2 (50 bar), 18 h, 500 rpm. ^[a] Product distribution determined by GC-FID using tetradecane as an internal standard, conversion > 99%. ^[b] Catalyst details in SI. ^[c] 20 mg SILP(Ph₃-P-NTf₂) added (physical mixture).

With Rh NPs synthesized on an imidazolium-based SILP (SILP(Oct-n₃-NTf₂), see SI for details and Figure S9 for TEM characterization), the substrate was converted to the alcohol **1a** (95%) without any significant hydrodeoxygenation activity, suggesting that SILP(Ph₃-P-NTf₂) plays a key role in the deoxygenation step (Entry 3). However, a physical mixture of Rh@SILP(Oct-n₃-NTf₂) and SILP(Ph₃-P-NTf₂) also gave **1a** as main product (97%), evidencing the importance of the intimate contact of metal and support (Entry 4). Using Rh NPs immobilized on a different phosphonium-based SILP (Rh@SILP(Oct₃-P-NTf₂),

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see SI for synthetic details and Figure S10 for TEM characterization) lead to a mixture of products with the alcohol 1a as main product (87%) (Entry 5). Using a fluorine-free counter anion (BPh₄, Entry 6) resulted in the selective conversion of the substrate to the alcohol 1a. In case of another fluorine-containing anion (BF₄, entry 7), no significant deoxygenation activity was observed, indicating that the deoxygenation-active species was not formed. These results demonstrate the importance of the NTf2 anion in the observed deoxygenation activity. Finally, the metal precursor was changed to [Ru(cod)(cot)] and Ru NPs were then synthesized on SILP(Ph₃-P-NTf₂) (see SI for synthetic details and Figure S11 for TEM characterization). The Ru@SILP(Ph₃-P-NTf₂) catalyst produced also the alcohol 1a, forming the hydrodeoxygenation product 1b only in low yield, even at high temperatures (11% at 100 °C, 8% at 175 °C) (Entry 8 and 9). Altogether, these results demonstrate that an intimate contact between Rh nanoparticles and the SILP(Ph₃-P-NTf₂) support is necessary to constitute an efficient hydrodeoxygenation catalyst. A time profile was recorded (Figure S12), evidencing a fast conversion of the substrate in the first hour to give a mixture of 54% 1a and 46% 1b. After that, 1a was gradually converted to 1b. producing quantitative yield of the fully hydrodeoxygenated product after 18h.

Recycling experiments showed that Rh@SILP(Ph₃-P-NTf₂) could be reused at least 5 times without any loss of activity or selectivity (Figure 3). For this assessment, the reaction conditions were intentionally tuned to yield a roughly 50:50 mixture of **1a** and **1b** in order to probe any change in performance. The catalyst could also be reused efficiently after 18h reactions (Table S1).



Figure 3. Product distribution for the hydrodeoxygenation of acetophenone using recycled Rh@SILP(Ph₃-P-NTf₂). Catalyst was washed with 1 mL n-heptane between cycles. Reaction conditions: Cat (20 mg, metal content: 0.002 mmol Rh), acetophenone (12.0 mg, 0.1 mmol, 50 eq.), n-heptane (375 mg), 100 °C, H₂ (50 bar), 1 h, 500 rpm. Distribution determined by GC-FID using tetradecane as an internal standard. Green: ethylcyclohexane (1b), grey: 1-cyclohexylethanol (1a). The conversion of the substrate was complete in all cases.

No changes in the textural properties of the catalyst were evidenced by BET surface analysis (Table S2). TEM characterization after catalysis suggests that the nanoparticles stay small and well-dispersed on the support with only a slight increase of their size to 1.7 nm (Figure S13). Elemental analysis by ICP-AAS did not evidence any leaching of the metal during the reaction (Table S2). Small amounts of IL were removed from the catalyst after the first cycle. After this initial loss, no further IL leaching could be evidenced even after six consecutive runs (Table S2). ¹H, ¹³C and ³¹P solid state NMR of Rh@SILP(Ph₃-P-NTf₂) measured before and after catalysis showed partial hydrogenation of the phenyl groups of the phosphonium cation during Rh NP synthesis and catalysis (Figure S5-7). Interestingly, an additional peak at -122.5 ppm was observed in the ¹⁹F

spectrum after catalysis (Figure S8), indicating the partial conversion of the NTf₂ anion into other F-containing species. This signal has been previously ascribed to decomposition of the NTf2 anion under formation of metal fluorides.^[18] No signal corresponding to silicon fluoride species^[19] are visible on the ²⁹Si solid state NMR spectrum (Figure S4). We thus suspect the formation of Rh fluoride species through the partial breakdown of the NTf₂ anion during the hydrogenation of the IL. The formation of acidic Rh fluoride species at the surface of the nanoparticles could explain the catalyst's hydrodeoxygenation activity. This is consistent with the observation made by Forsyth and co-workers who evidenced the formation of magnesium fluoride species during the decomposition of the NTf₂ anion under electrochemical conditions.^[18] Interestingly, the thermal decomposition of the NTf₂ anion is known to occur at high temperature (ca. 300°C).^[20] This is observed in the present case at much lower temperature, indicating that the Rh nanoparticles promotes the process. The absence of deoxygenation activity observed when using Ru as metal suggests that the Ru NPs do not promote the anion decomposition under these conditions.

To gain more insight into the mechanism of formation of the active species - presumably rhodium fluoride - reference experiments were carried out. Heterogeneous catalysts are known to possess high hydrodefluorination activity, leading to the release of HF when hydrogenating fluoroaromatic substrates.^[21] Taking advantage of this reactivity, we performed a first reaction involving the hydrogenation of fluoroacetophenone with Rh@SiO2. This resulted in the formation of a mixture of hydrogenated and hydrodefluorinated products, with the release of small quantities of HF (Table S3). The catalyst was recovered, washed carefully and characterized by ¹⁹F solid state NMR, evidencing the apparition of a signal at -122.3 ppm, similar to what was previously observed for the Rh@SILP(Ph₃P-NTf₂) catalyst (Figure S14). In addition, applying this recycled catalyst to the conversion of acetophenone lead to the formation of ethylcyclohexane, thus evidencing deoxygenation activity that the starting Rh@SiO2 did not possess (Table S3). This demonstrates that the deoxygenation activity is related to the formation of RhF species, which can be generated by the action of small quantities of HF on Rh nanoparticles. This supports that the RhF species observed on Rh@SILP(Ph₃P-NTf₂) are formed through the decomposition of the NTf₂ anion, process which is known to generate HF among other products.^[20] The involvement of free HF in catalysis can however be ruled out, as recycling experiment did not show any decrease in activity (Figure 3). Furthermore, the supernatant obtained after a catalytic reaction did not catalyze the deoxygenation of 1-phenylethanol under standard conditions (Table S1).

The hydrodeoxygenation activity of Rh@SILP(Ph₃-P-NTf₂) was further studied for a wide range of acetophenone derivatives with different steric and electronic properties (Table 2). All the substrates considered were effectively hydrodeoxygenated under mild reaction conditions, giving cyclohexane derivatives in high yields. The catalyst was found tolerant to various functional though partial even ether cleavage aroups. and hydrodefluorination were observed for substrates 6 and 7, respectively. In some cases, an increase of the temperature to 175°C was necessary to reach full conversion (substrate 4 and 8) or to limit the formation of dimers (substrates 9 and 10). To get

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more insight into the influence of the presence of electronwithdrawing and -donating substituents on the catalytic activity, substrates 1, 5, 6 and 8 were considered for a reaction time reduced to 1h.

		R^2 –	Rh@SILP(Ph ₃ -P-NTf H ₂ (50 bar), n-heptan	r_{2} r_{R}^{2} R^{2}	
Entry	Substrate	Temp. [°C]	Time [h]	Product	Yield [%] ^{a]}
1		100	1	\bigwedge	52 ^[b]
	V 1	100	18	✓ 1b	>99
2		100	18	C) 2b	>99
3		100	18		>99 (73) ^[e]
	~ ^ Å	100	18		79 ^[b]
4		175	18	4b	>99
_	A H	100	1	\sim	58 ^[b]
5	5	100	18	5b	>99
		100	1		40 (6b) ^[c] 10% (1b
6		100	18		62 (6b) 24 ^[d] (1b
	0	175	18	0 1 10	25 (6b) 75 (1b)
7		100	18	F 7b 01b	20 (7b) 80 (1b)
	<u>^</u>	100	1		50 ^[b]
8	E-C 8	100	18	F ₃ C 8b	91
F ₃ C ⁻ ∽ ⊍		175	18		>99
9	HO B	175	18		87 (1b) 13 (dimer
10		175	18		>99

Reaction conditions: Rh@SILP(Ph₃-P-NTf₂) (20 mg, metal content: 0.002 mmol Rh), substrate (0.1 mmol, 50 eq.), n-heptane (375 mg), H₂ (50 bar), 18 h, 500 rpm. ^[a]Determined by GC-FID using tetradecane as an internal standard, conversion > 99%. ^[b]Remaining product: corresponding saturated alcohol. ^[c]Total hydrodeoxygenation products: 71%. 40% **6b**, 22% 4-ethyl-cyclohexan-1-ol, 10% **1b**, 25 % 1-(4-methoxycyclohexyl)ethan-1-ol, 3% cyclohexylethanol. ^[d]Remaining: 4-ethyl-cyclohexan-1-ol (10%), cyclohexylethanol (3%), (1-methoxyethyl)cyclohexane (2%). ^[e](Isolated yield)

While electron-donating substituents have been reported to have a positive effect on the hydrodeoxygenation activity,^[22] we could not identify a clear trend in our particular case (Table S4). Part of the substrates from Table 2 was then used to evaluate the catalytic activity of Ru@SILP(Ph₃-P-NTf₂) as comparison to Rh@SILP(Ph₃-P-NTf₂). In agreement with the preliminary results shown in Table 1 for acetophenone, the ruthenium-based catalyst was barely active for the hydrodeoxygenation of the various aromatic ketones





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considered even at high temperature (Table S5 and S6). The catalytic properties of Rh@SILP(Ph₃-P-NTf₂) were further studied for the conversion of non-benzylic ketones, which are known to be more challenging to hydrodeoxygenate than acetophenone derivatives.^[23] Benzylideneacetone (11) was used as model substrate for this class of ketones (Scheme 1). Keeping the conditions previously used for the hydrodeoxygenation of acetophenone derivatives led to the almost exclusive formation of the saturated alcohol (11a). However, the conversion of 11 to the hydrodeoxygenated product 2b was achieved with excellent selectivity at higher temperatures (175 °C). By adjusting the reaction temperature, both products (hydrogenated and hydrodeoxygenated) were produced in quantitative yields. Again, the hydrodeoxygenation activity could not be switched on for Ru@SILP(Ph₃-P-NTf₂)

and **11a** was the only product at both 100 °C and 175 °C (Table S6). In order to see whether such a "temperature switch" between hydrogenation and hydrodeoxygenation could be more generally applied to other substrates, a selection of non-benzylic ketones was converted at 100 °C and 175 °C using Rh@SILP(Ph₃-P-NTf₂) as catalyst (Table 3). At 100 °C, substrates **11-16** (Entries 1-6) possessing a phenyl ring in beta or gamma position to the carbonyl group were converted to the saturated alcohols in high yields (81-99%). Substrate **13** however, was converted into a mixture of the saturated alcohol (**13a**, 32%) and partially hydrodeoxygenated product **11a** (50%).

Table 3. Temperature-controlled hydrogenation or hydrodeoxygenation of non-benzylic ketones using Rh@SILP(Ph₃-P-NTf₂).

	R1 OH	Hn@SILP(Ph ₃ -P-NTf ₂) H ₂ (50 bar), 100 °C, n-heptane	R ¹ O R ₂	Rh@SILP(Ph ₃ -P-NTf ₂) H ₂ (50 bar), 175 °C, n-heptane	→ ^H _n -R ₂
Entry	Yield [%] ^[a]	Product 100 °C	Substrate	Product 175 °C	Yield [%] ^[a]
1	>99 ^[b] (87) ^[f]	OH 11a		<u> 2b</u>	>99
2	>99 ^(b)	OH 11a		2b	>99
3	50 (11a) 32 ^[c] (13a)	OH OH OH 11a OH OH 13a		2b	>99
4	81 ^[d]		0 14	14b	97
5	92	ОН 15а		15b	>99
6	96 (92) ^[1]	OH 16a		16b	>99 (99) ^[1]
7				0 ^{-17b} 2b	20 (17b) 80 (2b)
8	Dimerization	-	0 18	0 18b 0 18c	61 (18b) 22 (18c) ^[e]

Reaction conditions: Rh@SILP(Ph₃-P-NTf₂) (20 mg, metal content: 0.002 mmol Rh), substrate (0.1 mmol, 50 eq.), n-heptane (375 mg), 100 °C or 175 °C, H₂ (50 bar), 18 h, 500 rpm. ^[a] Determined by GC-FID using tetradecane as an internal standard, conversion > 99%. ^[b] 1h. ^[c] Determined via protection of the diol with benzaldehyde (see Scheme S1). ^[d] 80 °C, 30 eq.^[e] Additional products: Octanol (10%), Octane (7%).^[f] (Isolated yield)

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As expected, the hydrodeoxygenation of the benzylic alcohol was favored over the non-benzylic, resulting in high amounts of 11a (50%) compared to 1-cyclohexylbutanol (8%). In the case of substrate 17, only low mass balances were observed indicating probably competing acid-mediated condensation reactions of the enone substrate. All the substrates were efficiently hydrodeoxygenated at 175°C to give the corresponding alkanes in excellent yields (97-99%). In agreement with what was previously observed for substrate 6, the methoxy group of substrate 17 was partially cleaved at 175 °C (Entry 7). Using biomass derived 4-(tetrahydrofuran-2yl)butan-2-ol (18, obtained from the complete hydrogenation of furfuralacetone) as substrate, only various dimers were obtained when performing the reaction at 100°C. However, the substrate was efficiently hydrodeoxygenated at 175°C, producing a mixture of 2-butyltetrahydrofuran (18b), 2propyltetrahydro-2H-pyran (18c), octanol and octane (Entry 8). Interestingly, these products are currently discussed as potential alternative fuels and fuel additives.^[24]

In conclusion, we show that immobilizing Rh nanoparticles on а triphenylphosphonium-based SILP produces а $Rh@SILP(Ph_3-P-NTf_2)$ catalyst possessing excellent properties for the hydrogenation and hydrodeoxygenation of a wide range of aromatic ketones with various substituents. The required bifunctionality is enabled by a specific interaction between the Rh NPs and the SILP(Ph₃-P-NTf₂)) support, presumably leading to the formation of acidic Rh fluoride species. Using Rh@SILP(Ph₃-P-NTf₂), acetophenone derivatives were readily hydrodeoxygenated under mild conditions. For non-benzylic ketones, the product distribution could be switched with high selectivity between the hydrogenated and hydrodeoxygenated products simply by tuning the temperature. The flexibility and modularity of the molecular approach used to prepare NPs@SILP catalysts allows for the assembly of the exact key components required to achieve this unique reactivity. This opens the way to an efficient production of highly valuable cyclohexane derivatives from readily available aromatic ketones.

Acknowledgements

The authors acknowledge financial support by the Max Planck Society and by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – Exzellenzcluster 2186 "The Fuel Science Center" ID: 390919832.. Furthermore, the authors would like to thank Teresa Stamm for BET absorption measurements, Alina Jakubowski, Annika Gurowski and Justus Werkmeister for GC and GC-MS measurements, Norbert Pfänder (MPI for Chemical Energy Conversion, Mülheim an der Ruhr), Adrian Schlüter (MPI for Kohlenforschung, Mülheim an der Ruhr) for TEM analysis.

Keywords: Hydrodeoxygenation • Ionic liquids • Nanoparticles • Rhodium • SILP

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Rhodium nanoparticles immobilized on an acid-free triphenylphosphonium-based supported ionic liquid phase (Rh@SILP(Ph₃-P-NTf₂)) enable the easy access to high-value cyclohexane derivatives starting from aromatic ketones. The product distribution can be switched with high selectivity between the completely hydrogenated (alcohol) and hydrodeoxygenated (alkane) products by changing the reaction temperature.

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Selective Hydrogenation and Hydrodeoxygenation of Aromatic Ketones to Cyclohexane Derivatives Using a Rh@SILP Catalyst