Catalytic Hydrodechlorination of Benzyl Chloride promoted by Rh-NHC Catalysts

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Abstract: The rhodium(I) complexes [Rh(Cl)(COD)(R-NHC-(CH₂)₃Si(O*i*Pr)₃)] (COD = cyclooctadiene; R = 2,6-diisopropylphenyl (**1a**); n-butyl (**1b**)) are effective catalyst precursors for the homogeneous hydrodechlorination of benzyl chloride using HSiEt₃ as hydrogen source. This reaction is selective to the formation of toluene. However, in presence of a stoichiometric amount of K^tBuO the formation of mixtures containing toluene together with 17-19 mol% of the C-C homocoupling product, namely PhCH₂CH₂Ph, was observed. A mechanism proposal based on experimental insights and theoretical calculations at the DFT level which allows explanation of the experimental findings is included. Moreover, the heterogeneous catalytic system based on the supported catalyst **1a-MCM-41** has demonstrated to be effective for the solvent-free hydrodechlorination of benzyl chloride with HSiEt₃ and HSiMe(OSiMe₃)₂.

Introduction

The development of new catalytic systems effective for the transformation of hazardous molecules into harmless substances is a relevant goal of sustainable chemistry.^[1] In this regard, chloro alkanes in general, and benzyl chloride in particular, have been reported as pollutants^[2,3] Therefore, the design of active catalysts for hydrodechlorination of organochlorines is of particular interest.^[4,5] The driving force behind hydrodechlorination reaction is the balance between the activation energy of the E-H (E = H, SiR₃) and C-Cl bonds, and the energy of the new E-Cl and C-H bonds formed (Scheme 1). Hydrosilanes satisfy both requirements; on one hand Si-H bonds can be easily activated by a number of transition metal catalysts^[6] and on the other hand silicon and chloride form a strong covalent bond. Additionally, some environmentally innocuous, readily available and easy to handle hydrosilanes have been proposed as potential hydrogen molecular

storages.^[7]

Scheme 1. Hydrodechlorination of organic chlorides with hydrosilanes (E = SiR₃).

There are some examples of homogeneous catalytic systems based on rhodium complexes which have shown to be effective for catalytic hydrodechlorination of polychloroarenes^[8a] and hexachlorocyclohexane^[8b] using HSiEt₃ as reducing agent. Moreover, Pd(II) salts have proven to catalyze the reduction of organic chlorides including benzyl chloride with HSiEt₃.^[9a] P,P-chelated Pd(II) complexes have been reported as effective homogeneous catalysts for the reduction of organo chlorides using sodium formate as reductor.^[9b] In addition, P,N-chelated Pt(II) species also behave as active catalysts for the hydrodechlorination of alkyl chlorides with HSiMe₂Ph as hydrogen source.^[10] Recently, Yang and Brookhart have reported a cationic iridium(III) bis(phosphinite) pincer complex which has shown to be highly active for the catalytic reduction of alkyl chlorides to the corresponding alkane by HSiEt₃.^[11] However, the high price of these scarce precious late-transition metals (Pd, Pt, Rh or Ir) has attracted increasing interest into the design of easily recyclable catalytic systems. In this regard, it is worth noting that heterogeneous catalytic systems based on palladium nanoparticles have found application in hydrodehalogenation of organic halides using aqueous sodium formate^[12a,b] or molecular hydrogen^[12c-g] as reducing agents. Other heterogeneous catalytic systems based on copper^[13a] or rhodium^[13b] nanoparticles and H₂ have shown to be active for the reduction of organo chlorides. However, solid catalysts present some disadvantages as for instance: i) are difficult to characterize at the molecular level, and ii) may contain a wide distribution of catalytic sites with different activity and selectivity. One strategy to overcome this drawback could be the covalent immobilization of a single site homogeneous catalyst into an insoluble support to afford a heterogeneized catalyst.^[14] By the way, it should be noted that transition metal-NHC complexes with Si(OR)₃-functionalized NHC ligands are easy to immobilize on mineral supports by reaction between the Si-OH active sites present on the supports surface and the Si-OR bonds at the substituents of the NHC ligand.^[15,16] Particularly, we have recently described the synthesis of Rh(NHC)-based supported catalysts by immobilization of Si(O*i*Pr)₃-functionalized Rh-NHC (NHC = *N*-heterocyclic carbene) complexes on inorganic supports. A previous comparative study has shown that the support plays an important role on the catalytic

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performance of Rh-NHC supported catalyst. Indeed, it has been found that those catalysts prepared with MCM-41 (Figure 1) are more active than those prepared with KIT-6 or Aerosil as inorganic supports.^[17b]

Figure 1. Representation of a Rh-NHC catalyst supported on MCM-41.

To the best of our knowledge the application of Rh-NHC catalysts in dehydrochlorination processes has not been studied so far. This work expands the scope of our previous research to explore the potential of Rh-NHC species as catalysts for hydrodechlorination processes. In particular, on the hydrodechlorination of benzyl chloride using hydrosilanes as hydrogen source.

Results and Discussion

Homogeneously catalyzed hydrodechlorination of benzyl chloride with HSiEt₃. Preliminary studies showed that the reactions of 1,4-dioxane solutions of benzyl chloride with HSiEt₃ using complex **1a** (or **1b**) (1.0 mol%) as catalyst precursor at 70 °C selectively affords toluene in 70% yield after 16 h. Increasing the catalysts loading up to 2.0 mol% and the temperature to 120 °C it was possible to reach the complete conversion of benzyl chloride in 2 hours with excellent selectivity to toluene together with traces of the C-C homocoupling product PhCH₂CH₂Ph (around 3-4 mol%), as a side reaction product (Table 1, entries 1 and 2). A comparison of both homogeneous catalysts shows that **1a** is slightly more active than **1b** with turnover frequencies (TOF) of 24.0 and 23.5 h⁻¹, respectively. This is in agreement with the tendency observed for acetophenone hydrosilylation,^[17b] and could be attributed to the greater steric influence provided by the 2,6-diisopropylphenyl *N*-substituent in **1a** in comparison with the *n*Bu *N*-substituent in **1b**.

It is worth mentioning that ¹H NMR studies of the reaction of species **1a** (or **1b**) with HSiEt₃ in C₆D₆ evidenced the formation of Rh-H containing complexes when the reaction mixture is heated above 70 °C, presumably **2a** (or **2b**) in Scheme 2. The formation of these Rh-hydrido species has been proposed as the rate determining step in the catalytic hydrosilylation of acetophenone using **1a** (or **1b**) (1.0 mol%) as catalyst precursor.^[17b] Thus, it is reasonable to assume that the formation of species **2a** (or **2b**) could also constitute the activation step in

the Rh-NHC catalyzed hydrodechlorination processes described in Table 1 (entries 1-6).

Table 1. Homogeneous Rh-catalyzed hydrodechlorination of benzyl chloride with HSiEt₃.^[a]

Entry	catalyst	selectivity ^[b]	conversion ^[c]	TON ^[d]	KtBuO (mmol)
1	1a	97.0	99.0	48.0	-
2	1b	96.0	98.0	47.0	-
3	1a	98.5	91.0	44.8	0.03
4	1b	99.0	87.0	43.0	0.03
5	1a	65.0	86.0	28.0	1.0
6	1b	62.0	80.5	25.0	1.0
7	6b	98.0	48.5	24.0	-

[a] General reaction conditions: 1,4-dioxane (1.0 mL), benzyl chloride (115 μL, 1.0 mmol), HSiEt₃ (0.8 mL, 0.5 mmol), 2.0 mol% of catalyst, hexamethyl benzene (4.0 mg) as internal standard, 120°C and 2 hours of reaction. [b] Selectivity to toluene based on NMR and expressed in % ± 0.5.^[18] [c] based on NMR and expressed in % ± 0.5. [d] Turnover number after 2 hours of reaction calculated as [mmol toluene / mmol of catalyst].

Scheme 2. In situ generation of active [Rh(H)(COD)(NHC)] species.

Based on that findings we proposed that a Rh(I)/Rh(III) mechanism could be operative for this Rh-catalyzed benzyl chloride hydrodechlorination process (Scheme 3, Path I). In a first step, the reaction of species **1** with HSiEt₃ affords the active rhodium(I)-hydrido species **2** which reacts with benzyl chloride to give the Rh(III) intermediate **3**. The reductive elimination of toluene from **3** regenerates the catalyst precursor **1**. The mechanism proposal showed in Scheme 3 also explains the formation of PhCH₂CH₂Ph as reaction side product (Scheme 3, Path II). The reductive elimination of toluene or HCl from the intermediate [Rh(Cl)(H)(CH₂Ph)(COD)] (**3**) determines the formation of the hydrodechlorination or C-C homocoupling products, that is toluene or 1,2-diphenylethane, respectively. On the other hand the catalytic reactions carried out in the presence of catalytic amounts of KtBuO led to a slight increase of the selectivity of the process but a falloff of the reaction yield (Table 1, entries 3 and 4). Interestingly, using one equivalent of KtBuO (0.1 mmol) the selectivity of the reaction changes and the concentration of PhCH₂CH₂Ph increases up to a value of around

17–19 mol% (Table 1, entries 5 and 6). This behaviour could be explained by assuming that an excess of KtBuO promotes HCl reductive elimination, thus favoring Path II in Scheme 3.

Scheme 3. Mechanism proposal for the Rh-NHC-catalyzed hydrodechlorination of benzyl chloride with HSiEt_3 .

The decrease of the conversion observed when KtBuO was added to the reaction mixture suggests a catalyst deactivation process. Indeed, using **1b** as catalyst precursor the conversion drops from 98.0% (Table 1, entry 2) to 80.5% (Table 1, entry 6). Therefore, we decided to study the reactivity of the less active catalyst precursor, **1b**, with KtBuO in THF. Treatment of **1b** with a stoichiometric amount of KtBuO in THF affords a brown solution after 24 h from which compound $[\text{Rh}\{\kappa^2\text{C}, \text{O}-(n\text{Bu-NHC}-(\text{CH}_2)_3\text{Si}(\text{O}i\text{Pr})_2\text{O})\}(\text{COD})]$ (**6b**) was isolated, after purification, as a yellow microcrystalline solid in 60% yield (see Experimental Section) (Scheme 4). Complex **6b** was fully characterized by means of elemental analysis, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy, mass spectrometry and its molecular structure determined by X-ray diffraction methods. It is worth noting that using **6b** as catalyst precursor under the same reaction conditions used for **1b**, in absence of KtBuO , a decrease of the catalytic performance was observed (Table 1, entry 7).

Scheme 4. Reaction of compound **1b** with KtBuO .

The molecular structure of **6b** is depicted in Figure 2, together with the most significant bond lengths and angles. The rhodium atom displays a slightly distorted square planar coordination, with the metal bonded to the two olefinic bonds of the COD ligand in a $\eta^2\text{-C}=\text{C}$ fashion, to the carbon atom C(15) of the NHC ligand and to the oxygen atom O(1). The distortion from an ideal square-planar coordination geometry is evidenced by the *trans* bond angles $\text{O}(1)\text{-Rh-Ct}(1)$ $173.67(12)^\circ$ and $\text{C}(15)\text{-Rh-Ct}(2)$ $178.12(14)^\circ$ and by the fact that the metal atom lies $0.0514(3)$ Å out of the mean coordination plane. The imidazol plane is placed almost perpendicular to the mean coordination plane (dihedral angle $81.49(10)^\circ$). Geometrical parameters of the fragment $[\text{Rh}(\text{COD})(\text{NHC})]$ compare well with those reported for complexes $[\text{Rh}(\text{Cl})(\text{COD})(\text{R-NHC}-(\text{CH}_2)_3\text{Si}(\text{O}i\text{Pr})_3)]$ ($\text{R} = 2\text{-methoxyethyl}$ ^[17a] or $2,6\text{-}i\text{Pr}_2\text{Ph}$ ^[17b]). Interestingly, the NHC ligand exerts a high structural *trans* effect producing a significant elongation of the Rh-C bonds situated in relative *trans* position (mean Rh-C bond $2.193(2)$ Å) if compared to those *trans* to O(1) atom (mean Rh-C bond $2.101(2)$ Å). This effect, which also influences the olefinic bond distances ($\text{C}1=\text{C}2$ $1.413(5)$ and $\text{C}5=\text{C}6$ $1.369(5)$ Å), has already been pointed out in related complexes.^[17,19a,19b]

The Rh-O(1) bond distance ($2.056(2)$ Å) is in the range of $2.030(2) - 2.065(3)$ Å found for the Rh-OSi bond in $[\text{Rh}(\text{OSiR}_3)(\text{PCy}_3)(\text{COD})]$ complexes.^[20a] The coordination of O(1) atom to the rhodium in **6b** leads to the formation of a 8-membered metallacycle. Noteworthy, this leads to a significant shortening of the Si-O(1) bond length ($1.579(2)$ Å), compared to Si-O(2) and Si-O(3) values ($1.654(3)$ and $1.648(3)$ Å, respectively) indicating a certain multiple character of this bond. However, structural differences between transition metal-siloxides^[21] and silanone complexes^[22] are quite subtle. It should be noticed that the nature of silicon-chalcogen bonds has recently attracted considerable interest.^[23]

Figure 2. Molecular structure of complex **6b**. Hydrogen atoms and the minor components of disordered fragments have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Rh-O(1) $2.056(2)$, Rh-Ct(1) $1.979(3)$, Rh-Ct(2) $2.084(3)$, Rh-C(15) $2.027(4)$; O(1)-Rh-Ct(1) $173.67(12)$, O(1)-Rh-Ct(2) $89.80(13)$, O(1)-Rh-C(15) $91.78(11)$, Ct(1)-Rh-Ct(2) $87.66(15)$, Ct(1)-Rh-C(15) $90.88(14)$, Ct(2)-Rh-C(15) $178.12(14)$. Ct(1) and Ct(2) represent the midpoints of the olefinic bonds C(1)-C(2) and C(5)-C(6) bonds, respectively.

The most relevant resonances in the ^1H NMR spectra of C_6D_6 solutions of **6b** are those corresponding to the NCH_2 protons bounded to $\text{C}(18)$, which appear as multiplets at δ 5.54 and 3.60 ppm. Each of these two resonances show a direct C-H bond correlation in the heteronuclear single quantum correlation (HSQC) spectra with one signal in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, which can be assigned to the $\text{NC}(18)$ carbon atom that appear at δ 51.4 ppm. The remaining resonances of the ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are consistent with the structure shown in Figure 2 (see experimental and supporting information). The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **6b** in C_6D_6 exhibit a doublet resonance at δ -51.0 ppm

($^2J_{\text{Rh-Si}} = 4.0$ Hz) which shows a Si-H correlation in the heteronuclear multiple bond correlation ^1H - ^{29}Si HMBC spectra with the resonances assigned to the CH_2Si protons bounded to $\text{C}(20)$ in the ^1H NMR spectra of **6b**.

It is noteworthy that the reaction of **1a** with one equivalent of KtBuO in THF affords a mixture of compounds which contains complex $[\text{Rh}\{\kappa^2\text{C},\text{O}-(2,6\text{-iPr}_2\text{Ph-NHC}-(\text{CH}_2)_3\text{Si}(\text{O}i\text{Pr})_2\text{O-})\}(\text{COD})]$ **6a** (related to **6b**) as major component. All attempts to separate compound **6a** from that mixture of complexes were fruitless.

Figure 3. Relative Gibbs energy profile at 393.15 K (in kcal mol^{-1}) for the hydrodechlorination of benzylchloride versus the homocoupling reaction using the species $[\text{RhH}(\text{COD})(\text{NHC})]$ (**A**) ($\text{NHC} = 1,3\text{-}N,N'$ -dimethyl-2-ilydene-imidazol) as catalyst.

Computational studies. Theoretical calculations at the B3LYP-D3 level have been performed on the above described rhodium-catalyzed hydrodechlorination processes using the complexes $[\text{RhX}(\text{COD})(\text{NHC})]$ ($\text{X} = \text{H}$ (**A**), Cl (**E**); $\text{NHC} = 1,3\text{-}N,N'$ -dimethyl-2-ilydene-imidazol) as model of species **1** and **2**, respectively (see supporting information).

As a result from these studies it has been found that the formation of toluene and regeneration of species **E** from the reaction of **A** with benzyl chloride is thermodynamically favored by $53.8 \text{ kcal mol}^{-1}$ (Figure 3). The highest activation barrier of this path, $23.3 \text{ kcal mol}^{-1}$ (**TSB/C** in Figure 3, see Figure 4 for the molecular geometry), corresponds to the $\text{S}_{\text{N}}2$ nucleophilic attack of the metal to the C_{sp}^3 atom of benzyl chloride and concomitant breaking of the $\text{C}_{\text{sp}}^3\text{-Cl}$ bond. A metastable ionic pair between the metallic complex of $\text{Rh}(\text{III})$ and the chlorine anion is formed (**C**). Coordination of the anion to the metal vacancy is energetically favorable being the relative energy of $-17.2 \text{ kcal mol}^{-1}$ and leading to complex **D**. An alternative reaction mechanism for this step is the concerted $\text{C}_{\text{sp}}^3\text{-Cl}$ bond breaking of benzyl chloride and formation of Rh-C and Rh-Cl , however

the calculated energetic barrier for this step is much larger than the presented above (see SI).

Starting at intermediate **D**, two competitive reaction pathways are available. Path I corresponds to the reductive elimination of toluene through **TSD/E** transition structure (Figure 5) with an activation energy of $11.3 \text{ kcal mol}^{-1}$ to afford the $\text{Rh}(\text{I})$ complex **E** (related to **1**). Path II leads to the release of HCl followed by a stepwise mechanism that affords $\text{PhCH}_2\text{CH}_2\text{Ph}$ and species **E**. Hence, transition state **TSD/F** has been found for the migratory insertion of one of the olefin moieties of the COD ligand into the Rh-H bond. The activation energy of this process is low ($6.3 \text{ kcal mol}^{-1}$) leading to intermediate **F**. It is worth mentioning that examples of analogous migratory insertions in complexes containing the " $\text{Ir}(\text{H})(\text{COD})$ " moiety have been previously reported.^[24] In a subsequent step, chlorine anion is dissociated from the metal center and a proton transfer from the CH_2 moiety of the ligand to the chlorine anion takes place through **TSF/G** transition state (Figure 6) showing an activation barrier from the most stable intermediate **D** of $14.1 \text{ kcal mol}^{-1}$. After **TSF/G** is passed, HCl is released and complex **G** is obtained. Under the reaction conditions it is reasonable to assume that HCl reacts

with the silane to give ClSiMe_3 which produces additional stabilization.^[25] Path II continues with the coordination of a second molecule of benzyl chloride to the metal through **TSH/I** with an activation energy of $26.9 \text{ kcal mol}^{-1}$. This process can be described as a $\text{S}_{\text{N}}2$ mechanism similar to the one described at **TSB/C**, the higher energy is due to the replacement of the hydride by the CH_2Ph ligand and leads also to a metastable intermediate **I**. Chlorine coordination to the metal leads to the dibenzylchlorido intermediate **J** and, finally, reductive elimination of $\text{PhCH}_2\text{CH}_2\text{Ph}$ via **TSJ/E** leads to complex **E** closing the catalytic cycle for Path II. Comparison of the highest energetic barriers of path I (**TSD/E**, $-5.9 \text{ kcal mol}^{-1}$) and path II (**TSF/G**, $-3.1 \text{ kcal mol}^{-1}$) reveals that the energy barrier for path I is $2.8 \text{ kcal mol}^{-1}$ lower than the corresponding for path II. This energetic difference is in agreement with the selectivity observed experimentally and with the mechanism proposal shown in Scheme 3 and Figure 3.

Figure 4. Geometrical representation of transition state **TSB/C**.

Figure 5. Geometrical representation of transition state **TSD/E**.

Figure 6. Geometrical representation of transition state **TSF/G**.

Solvent-free Heterogeneously Rh-catalyzed hydrodechlorination of benzyl chloride with hydrosilanes.

The development of solvent-free catalytic processes is of wide interest in the context of sustainable chemistry. Thus, based on the above described homogeneous catalytic studies we decided to explore the catalytic potential of **1a-MCM-41** (Figure 1) as heterogeneous hydrodechlorination catalyst. This supported catalyst was prepared by reaction of complex **1a** with the Si-OH active sites at the surface of MCM-41.^[17b] The resulting solid was characterized by ICP analysis and N_2 -physisorption/desorption studies (Table 2). The results of these studies show that the surface area, pore volume and pore diameter of **1a-MCM-41** are lower than the corresponding values obtained for the parent MCM-41, and agree with the anchoring of **1a** inside the channels of the mesoporous material.

Table 2. N_2 -physisorption/desorption studies and ICP analysis for the support and different preparations of the supported catalyst.

Material	Rh (mg/g) ^[a]	SA (m ² /g) ^[b]	PD (Å) ^[c]	PV (cm ³ /g) ^[d]
MCM-41	-	1070	40.9	1.00
1a-MCM-41	5.12	796	31.1	0.61
1a-MCM-41	9.10	780	31.8	0.68

[a] obtained by ICP analysis. [b] Surface area. [c] Pore diameter. [d] Pore volume.

In addition, Transmission Electron Microscopy (TEM) studies of samples of **1a-MCM-41** evidenced that the mesoporous structure of MCM-41 is maintained after the immobilization process (see Figure 7 and supporting information). The only particles that we are able to detect by TEM are those corresponding to MCM-41 and no evidence of Rh particles was observed. This fact constitutes further evidence of the covalent anchoring of the Rh-containing molecules to MCM-41.^[15,16]

Figure 7. Transmission Electron Microscopy (TEM) images of **1a-MCM-41**.

The hybrid material **1a-MCM-41** was used as heterogeneous catalyst for the solvent-free hydrodechlorination of benzyl chloride using HSiEt_3 or the environmentally innocuous and easily available siloxane $\text{HSiMe(OSiMe}_3)_2$ as hydrogen sources. Interestingly, the results from these studies showed that **1a-MCM-41** effectively catalyzed the hydrodechlorination of benzyl chloride (Table 3). However, a slight decrease of the activity in comparison to that achieved by the parent homogenous catalyst, **1a**, was observed. Indeed, using the heterogeneous catalyst **1a-MCM-41** five hours were needed to accomplish the full transformation of the starting benzyl chloride.

The catalytic activity of the supported catalyst **1a-MCM-41** (Table 3) is lower than that reported for catalytic systems based on Pd-nanoparticles and H_2 .^[12c,12g] However, It is worth noting that those Pd-based catalytic systems operate using alcohols as solvent and need excess of base (NaOH) in order to achieve a good performance while the heterogeneous catalyst **1a-MCM-41** presents the advantage of being active under solvent-free conditions. Furthermore, as is shown in Table 3 can be reused after recycling keeping the catalytic activity. It should be mentioned that in all the studied reactions the selectivity values found for the heterogeneous catalyst were slightly higher than those found for the homogeneous reactions (Table 1).

Table 3. Solvent-free heterogeneous Rh-catalyzed hydrodechlorination of benzyl chloride with HSiEt_3 .^[a]

Entry	Silane	cycle	selectivity ^[e]	conversion ^[f]	TON ^[g]
1	HSiEt_3	Fresh ^[b]	100	39.91	20.0
2	HSiEt_3	Fresh ^[c]	100	59.11	12.0
3	HSiEt_3	Fresh ^[d]	99.5	98.0	19.5
4	HSiEt_3	2 ^[d]	98.0	96.0	19.0
5	HSiEt_3	3 ^[d]	97.5	94.0	18.5
6	HSiEt_3	4 ^[d]	98.0	96.5	19.0
7	HMTS ^[e]	Fresh ^[d]	100	92.0	18.5
8	HMTS	2 ^[d]	100	93.0	18.5
9	HMTS	3 ^[d]	99.5	94.5	19.0
10	HMTS	4 ^[d]	99.5	96.0	19.0

[a] General reaction conditions: 120 °C, benzyl chloride (11.5 μL , 0.1 mmol), silane (1.0 mL), hexamethyl benzene (2.0 mg) as internal standard. [b] **1a-MCM-41** (2.0 mol%), 2 hours of reaction. [c] **1a-MCM-41** (5.0 mol%), 2 hours of reaction. [d] **1a-MCM-41** (5.0 mol%), 5 hours of reaction. [e] Selectivity to toluene based on NMR and expressed in % ± 0.5 .^[18] [f] Consumption of benzyl chloride based on NMR and expressed in % ± 0.5 . [g] Turnover number at the end of the reaction calculated as [mmol toluene / mmol of catalyst]. [e] HMTS = $\text{HSiMe(OSiMe}_3)_2$.

Conclusions

The rhodium(I) complexes $[\text{Rh}(\text{Cl})(\text{COD})(\text{R-NHC}(\text{CH}_2)_3\text{Si}(\text{O}i\text{Pr}_3)_3)]$ ($\text{R} = 2,6\text{-diisopropylphenyl}$ (**1a**); $n\text{Bu}$ (**1b**)) are effective catalyst precursors for the homogeneous hydrodechlorination of benzyl chloride to toluene using HSiEt_3 as hydrogen source. In presence of one equivalent of KfBuO the formation of the C-C homocoupling product, $\text{PhCH}_2\text{CH}_2\text{Ph}$, and a decrease of the catalytic performance was observed. A Rh(I)/Rh(III) mechanism, based on theoretical calculations at the DFT level and on experimental insights, has been proposed for explaining the homogeneous hydrodechlorination of benzyl chloride to toluene and the formation of traces of $\text{PhCH}_2\text{CH}_2\text{Ph}$ as side reaction product. Interestingly, the heterogeneous catalytic system based on the supported catalyst, **1a-MCM-41**, has demonstrated to be effective for the solvent-free selective hydrodechlorination of benzyl chloride with HSiEt_3 and $\text{HSiMe(OSiMe}_3)_2$.

The supported catalyst **1a-MCM-41** is easily handled and it can be stored for long time in air. Furthermore, the heterogeneous catalyst could be reused maintaining the effectivity. In addition, the reducing agent, namely $\text{HSiMe(OSiMe}_3)_2$, which was also used as reaction solvent is environmentally innocuous, cheap and available in ton scale.

Experimental Section

General information. All manipulations were performed with rigorous exclusion of air at an argon/vacuum manifold using standard Schlenk-tube techniques or in a dry-box (MB-UNILAB). Solvents were dried by the usual procedures and distilled under argon prior to use or taken under argon from a Solvent Purification System (SPS). The reagents triethylsilane, HSiMe(OSiMe₃)₂, benzylchloride and the solid MCM-41 were purchased from commercial sources. The complexes **1a**, **1b** and the supported catalyst **1a-MCM-41** were prepared according to methods reported in the literature.^[17b] NMR spectra were recorded on a Varian Gemini 2000, Bruker ARX 300, Bruker Avance 300 MHz or Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (¹H, ¹³C{¹H}). Coupling constants, J, are given in hertz. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectrometry was measured on an Esquire 3000+ with ion trap detector interfaced to an Agilent 1100 series HPLC system. TEM microscopy images were collected with a INCA 200 X-Sight from Oxford Instruments with a resolution in energy between 136 eV and 5.9 KeV. Isotherms were obtained on a Quantachrome AUTOSORB by measuring the volume of N₂ absorbed at relative pressures between 0.05 and 0.99 at 77.3 K after drying the sample at 120 °C *in vacuo*. Surface Area Data, pore volume data and pore size data were obtained by Non Localized Density Functional Theory (NLDFT) method.

Homogeneous catalytic reactions. In a MB-UNILAB glove box (argon atmosphere) a cylindrical vessel (7.5 mL) for operating in batch mode was charged with HSiEt₃ (0.80 mL, 5.0 mmol), the corresponding catalyst precursor (14.0 mg (**1a**) or 12.0 mg (**1b**), 0.02 mmol), ClCH₂Ph (115.0 μL, 1.0 mmol), 4.0 mg of hexamethylbenzene as internal standard and 1,4-dioxane (1.0 mL). The vessel was closed, taken out of the glove box and placed in an isothermal bath at 120 °C and continuously stirred for 2 hours, after which the reaction mixture was studied by NMR, quantitative GC and qualitative GC-MS (see supporting information).

Homogeneous catalytic reactions in presence of K^tBuO. The procedure for the preparation of the reaction samples was the same as above described for homogeneous catalytic processes but adding K^tBuO (112.0 mg, 1.0 mmol or 3.4 mg, 0.03 mmol) to the reaction mixture.

Heterogeneous catalytic reactions. The procedure for the preparation of the reaction samples was the same as it was above described for the homogeneous catalytic process but using **1a-MCM-41** (54 mg, Rh loading 9.104 mg g⁻¹) as catalyst precursor and the corresponding hydrosilane (1.0 mL) as solvent and hydrogen source, ClCH₂Ph (11.5 μL, 0.1 mmol) and 1.6 mg of hexamethylbenzene as internal standard. Under these reaction conditions we can assume that the reagents and the reaction products have a high diffusion through the channels of **1a-MCM-41**.^[26]

Recycling of the heterogeneous catalyst. After the first catalytic run, the reaction mixture was centrifuged and the corresponding heterogeneous catalyst separated from the product by decantation, washed with CH₂Cl₂ (3 x 3.0 mL), Et₂O (3 x 3.0 mL), dried *in vacuo* and reused without further purifications.

Reaction of 1b with K^tBuO. THF (15 mL) was added to a mixture of **1b** (50.0 mg, 0.10 mmol) and K^tBuO (11.2 mg, 0.10 mmol). The reaction mixture was stirred at 45 °C for 16 h. The solvent was removed *in vacuo* and the residue thus obtained extracted with hexane (3 x 10 mL). The hexane solution was concentrated in vacuum to around 5.0 mL and cooled at -20°C to afford a yellow crystalline solid of **6b**. Yield 32 mg

(60 %). ¹H NMR plus COSY and HSQC (300 MHz, C₆D₆): δ 6.09 (d, J_{HH} = 2 Hz, 1H, CH_{ind}), 6.08 (d, J_{HH} = 2.0 Hz, 1H, CH_{ind}), 5.54 (m, 1H, CH₂N(3)), 5.24 (m, 2H, CH_{cod}), 4.65 (spt, J_{HH} = 6.0 Hz, 1H, CHOⁱPr), 4.61–4.55 (m, 1H, CH₂N(1)), 4.38 (spt, J_{HH} = 6.0 Hz, 1H, CHOⁱPr), 3.86–3.79 (m, 1H, CH₂N(1)), 3.60 (ddd, J_{HH} = 13.0, 4.0, and 3.0 Hz, 1H, CH₂N(3)), 3.08 (m, 1H, CH_{cod}), 2.79 (m, 1H, CH_{cod}), 2.58–2.48 (m, 1H, CH_{2cod}), 2.45 (m, 1H, CH_{2cod}), 2.41–2.33 (m, 1H, CH₂CH₂CH₃), 2.29 (m, 1H, CH_{2cod}), 2.11 (m, 1H, CH₂CH₂Si), 1.98 (m, 1H, CH_{2cod}), 1.94 (m, 1H, CH_{2cod}), 1.90 (m, 1H, CH₂CH₂CH₃), 1.88–1.79 (m, 1H, CH_{2cod}), 1.79–1.67 (m, 1H, CH_{2cod} + 1H, CH₂CH₂Si), 1.61 (m, 1H, CH_{2cod}), 1.52 (d, J_{HH} = 6.0 Hz, 3H, CH₃OⁱPr), 1.47 (d, J_{HH} = 6.0 Hz, 3H, CH₃OⁱPr), 1.33 (d, J_{HH} = 6.0 Hz, 3H, CH₃OⁱPr), 1.27 (d, J_{HH} = 6.0 Hz, 3H, CH₃OⁱPr), 1.39–1.15 (m, 2H, CH₂CH₃), 0.97 (t, J = 7.0 Hz, 3H, CH₂CH₃), 0.82 (m, 1H, CH₂Si), 0.12 (m, 1H, CH₂Si). ¹³C NMR plus APT, HSQC and HMBC (126 MHz, C₆D₆): δ 184.5 (d, J_{RhC} = 54.6 Hz, NCHN), 120.4 (CH_{ind}), 118.8 (CH_{ind}), 98.9 (d, J_{RhC} = 7 Hz, CH_{cod}), 98.6 (d, J = 7 Hz, CH_{cod}), 64.6 (d, J_{RhC} = 14 Hz, CH_{cod}), 63.2 (CH, OⁱPr), 63.1 (CH, OⁱPr), 60.9 (d, J_{RhC} = 14 Hz, CH_{cod}), 51.4 (CH₂N(3)), 50.0 (s, CH₂N(1)), 34.7 (CH_{2cod}), 33.5 (CH₂CH₂CH₃), 32.8 (CH_{2cod}), 29.7 (CH_{2cod}), 27.9 (CH_{2cod}), 26.6 (CH₃, OⁱPr), 26.4 (CH₃, OⁱPr), 26.3 (2 x CH₃, OⁱPr), 25.4 (CH₂CH₂Si), 19.8 (CH₂CH₃), 13.7 (CH₂CH₃), 11.0 (CH₂Si). ²⁹Si NMR (60 MHz, C₆D₆): δ -51.04 (d, J_{RhSi} = 4.0 Hz).

X-ray crystal structure determination. Suitable crystals of complex **6b** were grown from a pentane/hexane solution. X-ray data collection was carried out at 100(2) K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using narrow ω rotations (0.3°) on a Bruker SMART APEX CCD diffractometer. Intensities were integrated with SAINT+ program^[27] and corrected for absorption effect with SADABS program^[28], integrated in APEX2 package. The structure was solved by direct methods with SHELXS-97.^[29] Refinement, by full-matrix least-squares on F², was performed with SHELXL-97.^[30]

Crystal data for 6b. C₂₄H₄₃N₂O₃RhSi, M = 538.61, yellow prism 0.190 x 0.084 x 0.050 mm³, triclinic, P-1, a = 7.2509(5), b = 9.7693(7), c = 18.8415(13) Å, α = 82.7690(10), β = 80.2570(10), γ = 82.1710(10)°; Z = 2; V = 1295.90(16) Å³; D_c = 1.380 g cm⁻³; μ = 0.731 cm⁻¹; min. and max. correction factors 0.841 and 0.943; 2θ_{max} = 52.88°; 13176 collected reflections, 5267 unique [R_{int} = 0.0313]; number of data/restraints/parameters 5267/1/363; final GoF 1.101; R₁ = 0.0417 [4676 reflections, I > 2σ(I)]; wR₂ = 0.1011 for all data; the largest difference peak: 1.504 e Å⁻³. Two carbon atoms of the nBu chain and an isopropyl fragment have been found to be disordered. They have been included in the model in two sets of positions with complementary occupancy factors (0.511/0.489(8) and 0.595/0.405(9)) and isotropically refined. All the hydrogen atoms of the non-disordered parts except those of terminal methyl groups have been included in observed positions and freely refined (with only one restraint in a C-H bond length). When convergence was achieved, a residual density peak of 1.50 e Å⁻³ was found close to Rh atom. It has no chemical sense. CCDC 1024308 contains the supplementary crystallographic data for complex **6b**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details. All DFT theoretical calculations have been carried out using the G09.D01 program package.^[31] Full citation is given in supporting information. The B3LYP method^[32] has been employed including the D3 dispersion correction proposed by Grimme^[33] and the “ultrafine” grid. The def2-SVP basis set^[34] has been selected for all atoms for geometry optimizations and calculation of free energy corrections. The nature of the stationary points has been checked by calculation of vibrational frequencies and intrinsic reactions paths have been traced connecting each transition state with the respective intermediates. Solvent effects have been including using the PCM continuum model for

dichloromethane on the optimized structures.^[35] All reported energies are Gibbs energies and relative to **B** and isolated molecules.

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