DOI: 10.1002/cctc.201402615



# A Rhodium Triphenylphosphine Catalyst for Alkene Hydrogenation Supported on Neat Superparamagnetic Iron Oxide Nanoparticles

Daniel Dehe,<sup>[a]</sup> Lei Wang,<sup>[a]</sup> Melanie K. Müller,<sup>[a]</sup> Gunder Dörr,<sup>[a]</sup> Zhou Zhou,<sup>[b]</sup> Robin N. Klupp-Taylor,<sup>[c]</sup> Yu Sun,<sup>[a]</sup> Stefan Ernst,<sup>[a]</sup> Martin Hartmann,<sup>[b]</sup> Matthias Bauer,<sup>[a]</sup> and Werner R. Thiel\*<sup>[a]</sup>

A phosphonic acid functionalized triphenylphosphine rhodium complex was synthesized and grafted onto neat superparamagnetic iron oxide nanoparticles. The material was investigated by elemental analysis, IR spectroscopy, thermogravimetric analysis, XRD,  $N_2$ -physisorption analyses, and TEM measurements. The obtained hybrid material could be used as a catalyst

for the hydrogenation of alkenes with excellent yields and a broad substrate scope. The catalyst can be reused ten times without any loss of activity. According to the results from X-ray absorption spectroscopy, it is likely that formation of Rh nanoparticles occurs during the reaction.

## Introduction

Separation and recycling are central problems that need to be solved to apply homogenous catalysts in industrial processes.<sup>[1,2]</sup> One way to overcome these problems, is to immobilize a homogenous catalyst onto an insoluble support material.<sup>[3]</sup> This strategy requires supports with large specific surface areas, which can be realized either by applying very small particles or porous materials. There are intrinsic advantages and disadvantages for both solutions; although for porous materials the overall rate of the reaction may become limited by pore diffusion, small particles may cause problems in the separation (filtration) procedure. To avoid classical filtration of tiny particles, superparamagnetic compounds may be considered as alternative support materials. Such materials lose their magnetization after removal of the external magnetic field, allowing an efficient redispersion of the catalyst. During the last years, the immobilization of organic molecules onto magnetically separable support materials has received wide interest and has been applied for catalytically active systems.<sup>[4]</sup> Most

1
6

- [b] Dr. Z. Zhou, Prof. Dr. M. Hartmann Erlangen Catalysis Resource Center (ECRC) Friedrich-Alexander-Universität Erlangen-Nürnberg Egerlandstraße 3, 91058 Erlangen (Germany)
- [c] Prof. Dr. R. N. Klupp-Taylor Institut für Partikeltechnologie Friedrich-Alexander-Universität Erlangen-Nürnberg Cauerstraße 4, 91058 Erlangen (Germany)
- [+] Present address: Fakultät für Naturwissenschaften, Department Chemie Universität Paderborn Warburger Str. 100, 33098 Paderborn (Germany)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201402615.

frequently, such catalyst supports consist of magnetic iron oxide nanoparticles covered by a layer of silica,<sup>[5]</sup> which prevents the aggregation of the nanoparticles and enables the grafting of organic molecules by using siloxanes as anchoring groups. However, preparing the silica layer requires an additional step and generally reduces the specific surface area of the material.<sup>[6]</sup> Furthermore, the magnetization of the material decreases drastically because only the relatively small core of a core-shell material is magnetic.<sup>[7]</sup> Therefore, applying neat nanoscale superparamagnetic iron oxides as supports could be a promising alternative. Notably, magnetic nanoparticles can themselves act as catalysts.<sup>[8]</sup> This factor has to be taken into account when using them as support materials. However, only a few examples have been reported to date in which organocatalysts or catalytically active metal complexes have been immobilized directly onto the surface of iron oxide nanoparticles. co-workers immobilized l in and several 2.2'-bis-(diphenylphosphino)-1,1'-binaphthyl (BINAP) complexes on Fe<sub>3</sub>O<sub>4</sub> nanoparticles and applied the obtained hybrid materials for the asymmetric hydrogenation of aromatic ketones, achieving excellent activity and enantioselectivity.<sup>[9]</sup> Alper and coworkers used magnetic-nanoparticle-supported proline as a ligand for a copper complex, which catalysed the amidation of various aromatic compounds.<sup>[10]</sup> Tucker-Schwartz and Garrell immobilized 2,2,4,4-tetramethylpiperdine-1-oxyl (TEMPO) sites on  $\mathsf{Fe}_3\mathsf{O}_4$  nanoparticles by using click chemistry.  $^{[11]}$  The resulting hybrid material was employed as a catalyst for the selective oxidation of alcohols. Polshettiwar, Baruwati, and Varma grafted glutathione on magnetite nanoparticles by using the thiol group of the internal cysteine moiety.<sup>[12]</sup> This organocatalyst was successfully used in the Paal-Knorr reaction and the aza-Michael addition. In a similar manner, Gawande and coworkers immobilized cysteine on Fe<sub>3</sub>O<sub>4</sub> and applied this catalyst for the synthesis of  $\beta$ -amino carbonyl compounds and hydroauinolines.<sup>[13]</sup>

Recently, our group reported the use of silica-coated magnetic nanoparticles as support materials for oxodiperoxo molybdenum complexes and palladium(II) phosphine complexes.<sup>[14]</sup> The hybrid materials obtained could be successfully used as catalysts for the epoxidation of olefins and for Suzuki-Miyaura coupling reactions, respectively. However, trialkoxysilyl-functionalized linkers have turned out to be sensitive to M-O-Si cleavage when applied with oxidic supports other than silica. For grafting organic molecules with high efficiency onto the surface of, for example,  $Fe_2O_3$ ,  $Fe_3O_4$ ,  $Al_2O_3$ ,  $ZrO_2$ , or TiO<sub>2</sub> alternative linker units have to be developed. The best linker groups for directly anchoring functional organic molecules onto these supports are phosphonic acids, carboxylic acids, or catecholes.<sup>[15–17]</sup> As outlined in the literature, grafted organic units will, furthermore, stabilize the nanoparticles and prevent aggregation.<sup>[18]</sup> Herein, we describe the direct covalent immobilization of a rhodium triphenylphosphine complex on neat superparamagnetic iron oxide by using phosphonic acid moieties as anchoring groups and demonstrate the application of this catalyst in the hydrogenation of alkenes.

## **Results and Discussion**

For the experiments described herein, maghemite  $(\gamma - Fe_2O_3)$ was chosen as the magnetic support. This material can be easily synthesized, is inexpensive, chemically sufficiently stable, and possesses a high specific magnetization.<sup>[19]</sup> We envisaged a convergent strategy for synthesizing the required ligand: The triphenylphosphine unit and the linker component were prepared separately and then linked by formation of an amide bond (Scheme 1). Unlike siloxane linkers, the assortment of commercially available phosphonic acid linkers is rather limited. We therefore decided to design and synthesize the desired linker 3, which is already known,<sup>[20]</sup> starting from 1,3-dibromopropane, by following a process modified from the literature.<sup>[21]</sup> Firstly, a diethyl phosphonate moiety was introduced by applying triethylphosphite (1) in an Arbusow reaction.<sup>[22]</sup> In the following step, the residual bromo group was substituted by an azido unit, giving diethyl azidophosphonate 2.[11] Using triphenylphosphine in a THF/water mixture allowed the reduction of the azide to the amine (Staudinger reaction).<sup>[23]</sup> To simplify further handling, the amine was transformed into its hydrochloride salt 3, which could be isolated in excellent yields. For the preparation of the triphenylphosphine component, 4-(diphenylphosphino)benzoic acid (6) was synthesized from diphenyltrimethylsilylphosphine and 4-fluorobenzoic acid utilizing a CsF-catalyzed C-P coupling reaction that we reported recently.<sup>[24]</sup> Protection of 4-fluorobenzoic acid by transforming it into the corresponding methyl ester, 4, allows the generation of phosphine 5. After saponification of the ester, phosphino acid 6 was obtained in an overall yield of more than 90%. The final coupling of 6 and amine 3 to create amide 7 was achieved by using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), triethylamine (NEt<sub>3</sub>), and 4-dimethylamino pyridine (DMAP) as the catalyst. Cleavage of the phosphonic acid diethylester was performed with bromotrimethylsilane, followed by treatment with water to yield phosphonic acid 8.



Scheme 1. Synthesis of 8.

Strong absorptions in the IR spectra of compounds 1-3 and **7** at approximately 1225 ( $\nu_{P=0}$ ), 1020 and 950 cm<sup>-1</sup> (2× $\nu_{P=0}$ ) clearly demonstrate the presence of the phosphonate moieties. The according resonance in the  $^{31}\mbox{P}\{^1\mbox{H}\}$  NMR spectra appears at 31-33 ppm, whereas the resonance of the phosphine phosphorous atom in compounds 5-8 is observed at -4 to -5 ppm, allowing doubtless discrimination of the two phosphorous sites. The free phosphonic acid in compound 8 gives a resonance at 30.54 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum measured in a mixture of CDCl<sub>3</sub> and CD<sub>3</sub>OH. In the IR spectrum of 8, there are two very strong absorptions at 998 and 944 cm<sup>-1</sup>, which are assigned to the PO(OH)<sub>2</sub> unit. Recrystallization of compound 7 from methanol gave single crystals suitable for X-ray structure analysis (Figure 1). Compound 7 crystallizes in the space group  $P2_1/n$ . In the solid state, compound **7** forms dimers by hydrogen-bond interactions between the hydrogen atom of the amide group and the P=O oxygen atom of a neighboring molecule. Because one of the phenyl groups

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



**Figure 1.** Molecular structure of **7** in the solid state, exhibiting a dimeric structure by formation of intermolecular hydrogen bonds. The disordering is omitted for clarity.

and both ethoxy units are disordered (see the Supporting Information), a detailed interpretation of bond lengths and angles would not make sense.

The molecule is found in an almost perfectly stretched conformation, leading to a P1–P2 distance of 11.50 Å, which gives an impression about the maximum distance between a metal site coordinated to P1 and the surface of the support. The torsion angle between the planar amide group and the phenyl ring is  $19.13^{\circ}$  and the NH···O distance is 2.12 Å, a typical value for a hydrogen bond of this kind.<sup>[25]</sup>

Phosphine **8** was reacted with  $[(CO)_2Rh(\mu^2-CI)]_2$  in a mixture of dichloromethane and methanol, leading to the carbonyl chlorido complex **9** (Scheme 2).

The successful synthesis of **9** is confirmed by its  ${}^{31}P{}^{1}H{}$  NMR spectrum (Figure 2), which shows one broad peak for the



Scheme 2. Synthesis of 9 and its grafting onto the nanoparticles.



Figure 2. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 9.

phosphonic acid moiety at 30.48 ppm and a doublet for the triphenylphosphine function coordinated to the rhodium center at 30.38 ppm ( ${}^{1}J_{Rh,P}$  = 127.0 Hz). The IR absorption of the carbonyl ligand is found at 1974 cm<sup>-1</sup>, which is typical for carbonyl chlorido rhodium(I) species bearing two phosphine ligands in *trans* orientation.<sup>[26]</sup>

The decision to synthesize the rhodium complex first, instead of immobilizing the phosphine ligand on the support, followed by treatment with  $[(CO)_2Rh(\mu^2-CI)]_2$  was made to receive a molecularly well-defined catalyst on the support. Grafting only the ligand would yield statistically distributed phosphine molecules on the surface, all of which might not be in an ideal position to coordinate to the rhodium(I) center in the given manner. In 2010, we synthesized a structurally closely related system covalently supported on SBA-15, which could completely be characterized spectroscopically.<sup>[27]</sup>

The superparamagnetic iron oxide nanoparticles were prepared by reacting ferrous chloride and ferric chloride with aqueous ammonia in isopropyl alcohol following an established procedure. Detailed studies of the magnetic properties of the superparamagnetic nanoparticles obtained this way have been conducted by our group.<sup>[14a]</sup> The iron oxide nanoparticles exhibit a saturation magnetization (Ms) of 56 emu g<sup>-1</sup>.

Grafting of **9** onto the support material was achieved by stirring both components in a 1:1 mixture of methanol and dichloromethane for 24 h. The amount of grafted complex was determined by elemental analysis. Furthermore, the obtained hybrid material was examined by IR, TEM, XRD, TGA, and BET measurements.

The hybrid material exhibits a nitrogen content of 0.43%, from which a loading of 0.15 mmol  $g^{-1}$  can be computed. The specific surface area of 88 m<sup>2</sup>g<sup>-1</sup> was calculated from the N<sub>2</sub> adsorption–desorption isotherms (Figure 3), resulting in a mean density of 1.35 complex molecules per nm<sup>2</sup>. The distance between the two phosphonic acid groups of **9** can be estimated to about 11 Å, assuming a parallel alignment of the propylene chains, which is required for surface functionalization, resulting in a calculated required space of at least 1 nm<sup>2</sup> per complex molecule. A possible explanation for the high value of 1.35 molecules of **9** per nm<sup>2</sup> could be the partial for-

 $<sup>\</sup>ensuremath{^{\odot}}$  2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 3. N<sub>2</sub> physisorption isotherms of 9@Fe<sub>2</sub>O<sub>3</sub>.

mation of a double layer. The hybrid material exhibits a type II isotherm (as defined by IUPAC), typical for a non-porous material showing a slight hysteresis, which is caused by capillary condensation in the gaps between the nanoparticles.<sup>[28]</sup>

Powder XRD examinations, as well as the TEM imaging, confirmed the successful synthesis of the nanoparticles and proved the expected morphological properties. The powder XRD pattern of  $9@Fe_2O_3$ , shown in Figure 4, exhibits the char-



Figure 4. Powder XRD pattern of 9@Fe<sub>2</sub>O<sub>3</sub>.

acteristic diffraction peaks of the maghemite phase ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>):  $2\theta = 29.5^{\circ}$  (220), 35.0° (311), 42.8° (400), 56.8° (511), and 62.4 (440).<sup>[4b, 19a, 29]</sup> TEM images show separated iron oxide nanoparticles of an average size of 10 nm (Figure 5).

Hybrid material  $9@Fe_2O_3$  appears as a brown powder and gives a black suspension when stirred in isopropanol (Figure 6, left). The catalyst shows the expected superparamagnetism and can quickly and completely be separated from the solvent by using a simple magnet (Figure 6, right).



Figure 5. TEM images of 9@Fe<sub>2</sub>O<sub>3</sub>.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 6.  $9@Fe_2O_3$  suspended in isopropanol (left) and magneto filtration after 1 min (right).



Figure 7. TGA plot of 9@Fe<sub>2</sub>O<sub>3</sub>.

By means of thermogravimetric analysis (TGA, Figure 7) applied to  $9@Fe_2O_3$ , a loss of physisorbed water and residual solvent molecules can be detected below 100 °C. At approximately 200 °C, the decomposition and desorption of compound **9** begins, resulting in a total weight loss of 13% (including 2% for the loss of volatiles). This result confirms the loading of the complex calculated from elemental analysis.

In the IR spectrum of  $9@Fe_2O_3$  (Figure 8), a band at 1980 cm<sup>-1</sup> can be assigned to the C=O stretching vibration of the carbonyl ligand coordinated to the rhodium center.<sup>[27]</sup> This band is only shifted by a few cm<sup>-1</sup> towards higher energy compared to the data of the rhodium precursor 9. This finding can be explained by a weak interaction of the carbonyl oxygen site with the Lewis acidic support. Typical absorptions for the



Figure 8. IR spectra of 9 (dashed line) and 9@Fe2O3 (solid line).

ChemCatChem 0000, 00, 1 - 11

amide unit at 1632 (amide I) and 1545 cm<sup>-1</sup> (amide II) can also be detected. The aryl phosphine vibration and the C–H deformation vibrations of the methylene units of the propyl chain are visible in the band at 1437 cm<sup>-1</sup>.<sup>[30]</sup> The extinction of the P–OH stretching vibration at 933 cm<sup>-1</sup> proves the formation of covalent bonds between the complex and the support.<sup>[31]</sup> Additional evidence for the bonding is the shift of the PO<sub>3</sub> stretching vibration from 982 cm<sup>-1</sup> to a higher wavenumber, together with the broadening of this band.<sup>[10]</sup>

Catalytic hydrogenation of alkenes plays an important role in industrial fine-chemical synthesis, therefore, it has been intensively investigated over the last decades.<sup>[32]</sup> To evaluate the activity and selectivity of our catalyst, cyclohex-2-enone was used as the model substrate because it contains both, a C=C and a C=O double bond. The reaction was carried out with 1.0 mol% of catalyst (with respect to the Rh content) in isopropanol under an ambient pressure of hydrogen. Before use, the catalyst was stored for one week in air because such a pretreatment turned out to have a positive effect on the catalytic reactivity in preceding investigations.<sup>[29]</sup> Hybrid material 9@Fe<sub>2</sub>O<sub>3</sub> exhibited good reactivity, providing a complete conversion of the substrate in 3 h. The only product of the reaction was cyclohexanone. Thus, although the C=C double bond is hydrogenated with high efficiency, the carbonyl group of the substrate remains untouched.

To demonstrate the scope of  $9@Fe_2O_3$  as a catalyst for hydrogenation reactions, a series of different alkenes was employed as starting materials (Table 1). The catalyst exhibits a high activity and selectivity: terminal as well as internal double bonds are hydrogenated, no byproducts such as isomerization products are observed, and carbonyl groups are not affected. Even sterically hindered alkenes are completely converted (see Table 1, entries 2 and 6). Vinyl benzoate, cinnamyl alcohol, and benzylidene acetone exhibit only a low reactivity (entries 7, 8, and 9).

In 2010, we published a study on the synthesis and the catalytic activity of a structurally closely related system in which we grafted a Rh(CO)Cl complex coordinated by two functionalized triphenylphosphine ligands, each equipped with a -C(O)NH(CH<sub>2</sub>)<sub>3</sub>Si(OMe)<sub>3</sub> linker, covalently onto the surface of a neat silica SBA-15 support.<sup>[27]</sup> The catalytic activity of this catalyst and 9@Fe<sub>2</sub>O<sub>3</sub> was investigated under identical conditions. Obviously all substrates that were converted quantitatively with the silica-supported material could also be converted quantitatively with 9@Fe<sub>2</sub>O<sub>3</sub>. However, the SBA-15-based catalyst provided poorer yields for several substrates; cyclooctene is hydrogenated in less than 15% (9@Fe2O3: quantitative), 3,5,5-trimethylcyclohex-2-enon showed conversion no (9@Fe<sub>2</sub>O<sub>3</sub>: quantitative), and 1,3-diphenylprop-2-enon also showed no conversion (9@Fe<sub>2</sub>O<sub>3</sub>: 17%). This observation can be assigned to the increased accessibility of the catalytically active sites located on the outer surface of the magnetic-nanoparticle support compared with sites that are located inside the pores of the SBA-15 material. The differences become evident for substrates that are more difficult to hydrogenate owing to steric hindrance (3,5,5-trimethylcyclohex-2-enon), or steric bulk (e.g. cyclooctene), and will give rise to pore-diffu-



sion hindrance. However, in the preceding study we also found that, for example, cinnamyl alcohol, which is not hydrogenated at 40 °C and 1 bar  $H_2$ , can be quantitatively converted into 3-phenylpropan1-ol by changing the conditions to 60 °C and 15 bar  $H_2$ .

To prove that the catalysis is in fact conducted by the heterogenized rhodium sites present on 9@Fe<sub>2</sub>O<sub>3</sub> and not by a rhodium species leached out in solution, a filtration experiment was carried out. The solution containing cyclohex-2enone as the substrate and the catalyst were separated by filtration after the conversion had reached 20%. The filtrate was again set under an atmosphere of hydrogen and stirred for additional 20 h. The yield versus time curve of the filtration experiment and the normal course of the reaction are shown in Figure 9. In the first hours after the filtration no further reaction is observed, however after 20 h an additional increase of 25% was discovered. These findings show that the reaction is significantly slowed down by the separation of the catalyst. For the additional turnovers after the separation there are two possible explanations. Either, detached complex molecules in solution are responsible for the catalytic activity to a very small extent, or the filtration was incomplete and small support particles caused the additional conversion. In both cases, the rhodium complex was perhaps transformed into rhodium nanoparticles, which then are responsible for the activity, after a certain period of time (see discussion below).

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 9. Filtration experiment and normal course of reaction for the hydrogenation of cyclohex-2-enone with  $9@Fe_2O_3$  as the catalyst.

To gain further insight into the recyclability of the catalyst, the material was separated, by magneto filtration, from the reaction mixture, washed twice with ethyl acetate, dried under reduced pressure, and reused for catalysis. Even after ten runs the catalyst showed no signs of losing reactivity (Table 2). In contrast, there is a steady increase of activity the more often the catalyst is reused. Several explanations for this behavior seem plausible (see below).

Table 2. Recycling experiments for the hydrogenation of cyclohex-2-enone with $9@Fe_2O_3$ as the catalyst. $^{[a]}$							
Run	Time for complete conversion [min]						
1	180						
2	180						
3	160						
4	150						
5	150						
6	120						
7	45						
8	20						
9	15						
10	15						
[a] Reaction conditions: 1 mmol cyclohex-2-enone, $10^5$ Pa H <sub>2</sub> , 1.0 mol% <b>9@Fe<sub>2</sub>O<sub>3</sub></b> , 10 mL isopropanol, rt, reaction monitoring by GC-MS analysis.							

To further investigate this issue, the reaction and washing solutions of the first, second, third, and tenth run were analyzed by atomic absorption spectroscopy (AAS). No rhodium species could be detected down to the limit of detection  $(0.01 \text{ mg L}^{-1})$ . This proves that the maximum loss of the rhodium species present in the catalyst is 0.016%, higher losses would have exceeded the detection limit. Additionally, the reused catalyst was examined by elemental analysis after the first and the tenth run. The results reveal that the loading remains constant. A pronounced loss of immobilized molecules can, therefore, be excluded.

During the reaction the rhodium site loses its carbonyl ligand, as documented by the IR spectra of the reused catalyst (Figure 10).



Figure 10. IR spectra of fresh  $9@Fe_2O_3$  and of reused  $9@Fe_2O_3$  after the first and tenth run.

The ageing in air only slightly affects the intensity of the carbonyl absorption of the catalyst, and the band is still clearly visible after ten months. However, after the first run the band at 1980 cm<sup>-1</sup> ( $\nu_{CO}$ ) had almost disappeared. By a detailed spectroscopic investigation, Gao and Angelici proved that the carbonyl ligand in such complexes can be replaced by one molecule of water.<sup>[33]</sup> In our experiments, residual water from the solvent or from the support may be responsible for this effect. However, if the dissociation of the carbonyl ligand is responsible for the increasing activity of the catalyst, this increase should be observed even after the first run, which is not the case. Alternatively, the formation of rhodium nanoparticles or structural changes of the support material could explain the ongoing increase of the reactivity, but TEM images (Figure 11) of the used  $9@Fe_2O_3$  catalyst did not show any signs of the formation of rhodium nanoparticles.



Figure 11. TEM images of 9@Fe<sub>2</sub>O<sub>3</sub> after the first run.

The IR measurements also prove that cleavage of the immobilized complex from the support does not occur. Even after the tenth run the characteristic bands are still present (Figure 10). The broadening of the bands is caused by changes in the support, rendering the environment of the immobilized molecule more heterogeneous.

To gain further insight into the fate of the rhodium sites, X-ray absorption spectroscopy (XAS)<sup>[34]</sup> measurements were performed on the [(CO)<sub>2</sub>Rh( $\mu^2$ -Cl)]<sub>2</sub> precursor and on the catalyst,

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



**Figure 12.** XANES (top) and Fourier transformed EXAFS (bottom) spectra of the samples 1) [(CO)<sub>2</sub>Rh( $\mu^2$ -Cl)]<sub>2</sub>, 2) as prepared **9@Fe<sub>2</sub>O<sub>3</sub>**, and 3) **9@Fe<sub>2</sub>O<sub>3</sub>** after application in catalytic hydrogenation. In the EXAFS graphs, the experimental spectra are shown as black solid lines, the simulated spectra according to the parameters in Table 3 are presented as grey dotted dashed lines.

9@Fe<sub>2</sub>O<sub>3</sub>, before and after the catalytic hydrogenation. The corresponding X-ray absorption near edge structure (XANES) spectra are shown in Figure 12, together with the Fourier transformed extended X-ray absorption fine structure (EXAFS) spectra. The structural parameters obtained by fitting the experimental EXAFS functions with theoretical models are displayed in Table 3. The precursor could be fitted with a fourshell model according to the molecular structure.<sup>[35]</sup> Important for the structural assignments is the Rh-C pair from the CO ligand at 1.84 Å and the Rh-Cl contribution found at a distance of 2.4 Å. For **9**@**Fe**<sub>2</sub>**O**<sub>3</sub>, significant changes in the XANES spectrum can be observed, indicating an altered coordination environment. This is also reflected in the structural parameters given in Table 3. Approximately two Rh-P pairs, one Rh-C contribution from the CO ligand, and 1.5 remaining Cl neighbor can be assigned. The distance between the rhodium site and the CO ligand is increased by approximately 0.15 Å, whereas the Rh--Cl distance is identical to that of the precursor. The Rh–P distance of approximately 2 Å is, by 0.2 Å, shorter than the expected value. This is explained by interference effects of the P and CI backscatter, caused by their close proximity in the

Table 3. Neighbor atoms, coordination numbers, and distances calculated from the EXAFS data.							
Sample	Abs-Bs <sup>[a]</sup>	N(Bs) <sup>[b]</sup>	R(Abs-Bs) [Å] <sup>[c]</sup>	$\sigma_{[\text{\AA}^{-1}]^{[d]}}$	R [%] <sup>[e]</sup>		
[(CO) <sub>2</sub> Rh(µ <sup>2</sup> -Cl)] <sub>2</sub>	Rh—C Rh—Cl Rh—Rh Rh—O <sup>[f]</sup>	$\begin{array}{c} 2.3 \pm 0.2 \\ 2.1 \pm 0.2 \\ 1.1 \pm 0.2 \\ 9.1 \pm 1.8 \end{array}$	$\begin{array}{c} 1.87 \pm 0.02 \\ 2.39 \pm 0.02 \\ 2.95 \pm 0.02 \\ 3.25 \pm 0.03 \end{array}$	$\begin{array}{c} 0.059 \pm 0.012 \\ 0.067 \pm 0.014 \\ 0.067 \pm 0.021 \\ 0.110 \pm 0.042 \end{array}$	15.8		
9@Fe <sub>2</sub> O <sub>3</sub> as prepared	Rh—P Rh—C Rh—Cl	$\begin{array}{c} 2.6 \pm 0.3 \\ 1.5 \pm 0.2 \\ 1.5 \pm 0.2 \end{array}$	$\begin{array}{c} 1.94 \pm 0.02 \\ 2.02 \pm 0.02 \\ 2.40 \pm 0.02 \end{array}$	$\begin{array}{c} 0.105 \pm 0.021 \\ 0.055 \pm 0.011 \\ 0.039 \pm 0.008 \end{array}$	27.8		
9@Fe <sub>2</sub> O <sub>3</sub> after the reaction	Rh—O Rh—P Rh—Cl Rh—Rh	$\begin{array}{c} 2.1 \pm 0.2 \\ 1.1 \pm 0.1 \\ 1.1 \pm 0.1 \\ 1.9 \pm 0.2 \end{array}$	$\begin{array}{c} 2.05 \pm 0.02 \\ 2.20 \pm 0.02 \\ 2.32 \pm 0.02 \\ 2.67 \pm 0.03 \end{array}$	$\begin{array}{c} 0.095 \pm 0.019 \\ 0.055 \pm 0.011 \\ 0.055 \pm 0.011 \\ 0.071 \pm 0.014 \end{array}$	25.8		
[a] Abs=X-ray absorbing atom, Bs=backscattering atom. [b] Number of							

[a] Abs=X-ray absorbing atom, Bs=backscattering atom. [b] Number of backscattering atoms. [c] Distance between absorbing atom and back-scattering atom. [d] Debye-Waller-like factor. [e] Fit index. [f] Signal composed by Rh–(C)O and multiple scattering signal from the carbonyl group.

periodic table. Nevertheless, the structure proposed in Scheme 2 was confirmed by the XAS results.

After the reaction, further changes in the XANES spectrum become apparent. To understand this, the EXAFS analysis has to be considered first. In Figure 12, the Fourier transform of the EXAFS functions shows an enlarged intensity at around 2.7 Å. This can only be interpreted by including the formation of a Rh-Rh shell, which yields an exact distance of 2.7 Å, typical for metallic Rh. Because this is unambiguous proof for the presence of Rh<sup>0</sup>, the XANES spectrum of **9@Fe<sub>2</sub>O<sub>3</sub>** after the catalytic reaction was subjected to a linear combination XANES fit (LC-XANES fit).<sup>[36]</sup> In this fit, the XANES spectra of the as prepared 9@Fe<sub>2</sub>O<sub>3</sub> and a bulk Rh foil were fitted to the spectrum of 9@Fe2O3 after application in catalysis, yielding a content of 25%  $Rh^0$  and 75% of the as prepared **9**@**Fe**<sub>2</sub>**O**<sub>3</sub>. This finding is in rough agreement with the parameters extracted from the EXAFS analysis, in which 1.1 instead of 1.5 Rh-Cl neighbors were found. A light-atom shell is still present at 2 Å. IR results exclude the presence of CO ligands, therefore, this light-atom contribution could be attributed, for example, to water, and is consequently denoted Rh-O in Table 3. Because two of these neighbors were found, the Rh-P coordination is reduced to one. Summarizing the XAS results for 9@Fe<sub>2</sub>O<sub>3</sub> after the reaction, it can be concluded that part of the Rh centers are reduced to Rh<sup>0</sup>, whereas the main fraction is transformed into species that cannot be further identified by XAS.

### Conclusions

A rhodium triphenylphosphine complex could be successfully immobilized on superparamagnetic iron oxide nanoparticles by applying a novel ligand with a phosphonate-based linker unit. This magnetically separable catalyst exhibits excellent activity for the hydrogenation of alkenes and high selectivity towards C=C double bonds. It can be recycled ten times without

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

any loss of activity. The observed increase of reactivity during the recycling process might indicate the formation of rhodium nanoparticles. This indication is supported by X-ray absorption spectroscopy. However, according to TEM investigations, the particle diameters have to be far below 2 nm. No cleavage of the organic ligand from the support takes place during the catalysis and no leaching of rhodium could be detected by AAS. We assign these findings to the strategy of synthesizing the rhodium complex before tethering it onto the iron oxide surface. Hereby, at least two of the phosphine units are in close proximity to each other, stabilizing the complex on the surface as well as the small rhodium nanoparticles. Furthermore, the phosphonate linker strongly binds to the maghemite surface. These promising results open up new opportunities for the immobilization of other homogenous catalysts on nonsilica-based inorganic oxides. We are currently investigating the immobilization of different metal complexes on various metal oxides by using the phosphonic acid bearing ligand 8.

# **Experimental Section**

#### **General remarks**

All manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques unless otherwise specified. Solvents were dried by standard methods. Reagents were purchased from ACROS, Alfa Aesar, or Sigma-Aldrich and used without further purification, unless otherwise noted. NMR spectra were recorded with a Bruker DPX 400 and a Bruker Avance 600 spectrometer. Elemental analyses were carried out at the Fachbereich Chemie (TU Kaiserslautern). The infrared spectra were recorded by using a PerkinElmer FT-ATR IR 1000 spectrometer equipped with a diamond-coated ZnSe window. Rhodium leaching was determined by atomic adsorption spectroscopy with a PERKIN ELMER AAnalyst 300. XRD patterns were obtained on a Siemens D5005 diffractometer with Cu K\_{\alpha} radiation (40 kV, 30 mA,  $\lambda = 0,15405$  nm). Nitrogen physisorption isotherms were measured at liquid nitrogen temperature by using a Quantachrome Autosorb 1 sorption analyzer. The specific surface areas were calculated by the BET equation at a relative pressure of 0.05 to 0.5 (p/p). Thermogravimetric analyses (TGA) were carried out on a Setaram Setsys 16/18. TEM images were recorded on a Philips CM 300 UltraTwin microscope with a LaB6 cathode at an acceleration voltage of 300 kV. The samples were deposited onto commonly used copper TEM grids coated with a continuous carbon film. For the procedures used for the synthesis of compounds 1–6 and of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, as well as for the assignment of the NMR resonances and further details on X-ray structure analysis and X-ray spectroscopy, see the Supporting Information.

**Diethyl (3-(4-(diphenylphosphino)benzamido)propyl)phosphonate (7):** Diethyl (3-aminopropyl)phosphonate hydrochloride (**3**) (10.86 g, 44.6 mmol) and triethylamine (11.7 mL, 84.4 mmol) were dissolved in dichloromethane (20 mL). In a different Schlenk tube, 4-(diphenylphosphino)benzoic acid (**6**) (9.60 g, 31.3 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, 7.20 g, 37.6 mmol), and 4-dimethylaminopyridine (DMAP, 150 mg, 1.22 mmol) were dissolved in dichloromethane (50 mL). The content of the first Schlenk tube was added to the second tube and the resulting mixture was stirred for 72 h at rt. Then, the solvent was removed under reduced pressure and the residue was combined with HCl (1 m, 150 mL) and diethylether (100 mL). The layers were separated and the aqueous layer was extracted twice with diethylether (100 mL). The combined organic layers were washed five times with HCl (1 м), once with saturated Na<sub>2</sub>CO<sub>3</sub> solution and twice with brine. After drying over MgSO<sub>4</sub> the solvent was removed under reduced pressure and a colorless solid was obtained (yield: 11.4 g, 23.6 mmol, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.83–7.76 (m, 2 H, H-3), 7.37– 7.27 (m, 12H, ArH), 4.14-3.99 (m, 4H, H-9), 3.59-3.52 (m, 2H, H-6), 2.01-1.79 (m, 4H, H-7, H-8), 1.32-1.26 ppm (m, 6H, H-10);  $^{13}C{^{1}H}$  NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 167.2$  (s, C-5), 141.8 (d,  $^{1}J(P,C) =$ 13.1 Hz, C-1), 136.5 (d, <sup>1</sup>J(P,C) = 10.7 Hz, C-i), 134.6 (s, C-4), 134.0 (d, <sup>2</sup>J(P,C) = 20.0 Hz, C-o), 133.6 (d, <sup>2</sup>J(P,C) = 18.9 Hz, C-2), 129.1 (s, C-p), 128.7 (d, <sup>3</sup>J(P,C) = 7.3 Hz, C-m), 127.1 (d, <sup>3</sup>J(P,C) = 6.5 Hz, C-3), 61.9 (d,  ${}^{2}J(P,C) = 6.6$  Hz, C-9), 40.3 (d,  ${}^{3}J(P,C) = 12.1$  Hz, C-6), 23.6 (d,  $^{1}J(P,C) = 141.4 \text{ Hz}, C-8), 22.5 \text{ (d, } ^{2}J(P,C) = 4.6 \text{ Hz}, C-7), 16.5 \text{ ppm} \text{ (d, }$  $^{3}J(P,C) = 6.0 \text{ Hz}, C-10); ^{31}P\{^{1}H\} \text{ NMR} (162 \text{ MHz}, \text{ CDCI}_{3}): \delta = 32.93 \text{ (s,}$ PO(OEt)<sub>2</sub>), -5.02 ppm (s, PPh<sub>2</sub>R); IR (ATR):  $\tilde{\nu} = 3287$  (m) (NH), 2984 (w), 2937 (w), 1655 (vs) (CO), 1597 (m), 1550 (s), 1479 (m), 1434 (m), 1391 (m), 1302 (s), 1235 (vs), 1219 (s), 1174 (m), 1091 (m), 1023 (vs), 961 (vs), 852 (m), 817 (s), 743 (vs), 696 cm<sup>-1</sup> (vs); elemental analysis calcd. (%) for C<sub>26</sub>H<sub>31</sub>NO<sub>4</sub>P<sub>2</sub> (483.48): C 64.59, H 6.46, N 2.90; found: C 64.38, H 6.60, N 2.86.

(3-(4-(Diphenylphosphino)benzamido)propyl)phosphonic acid (8): Diethyl (3-(4-(diphenylphosphino)benzamido)propyl)phosphonate (7) (7.00 g, 14.5 mmol) was dissolved in dichloromethane (60 mL). Trimethylbromosilane (7.50 mL, 56.8 mmol) was added dropwise to the solution over a period of 1 h and the resulting mixture was stirred for 12 h at rt. Then, the solvent and the residual trimethylbromosilane were removed under reduced pressure. The residue was combined with NaOH solution (1 m, 150 mL). Dichloromethane (100 mL) was added to this suspension and the resulting two-phase mixture was stirred vigorously for 10 min, followed by the addition of HCl (1 M) until no further precipitation of a solid was observed and the pH value was 1. The solid was removed by filtration, washed several times with water, acetone, and dichloromethane before drying at 40 °C under reduced pressure. The colorless solid is prone to oxidation and should be stored in a cool place (yield: 6.05 g, 14.2 mmol, 98%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>+CD<sub>3</sub>OD):  $\delta$  = 7.77-7.73 (m, 2H, H-3), 7.36-7.25 (m, 12H, ArH), 3.47-3.41 (m, 2H, H-6), 1.92-1.83 (m, 2H, H-7), 1.79-1.71 ppm (m, 2H, H-8);  ${}^{13}C{}^{1}H$  NMR (101 MHz, CDCl<sub>3</sub>+CD<sub>3</sub>OD):  $\delta$  = 169.2 (s, C-5), 142.8 (d, <sup>1</sup>J(P,C) = 12.5 Hz, C-1), 136.8 (d, <sup>1</sup>J(P,C) = 9.9 Hz, C-i), 134.8 (s, C-4), 134.4 (d,  ${}^{2}J(P,C) = 19.5$  Hz, C-o), 133.9 (d,  ${}^{2}J(P,C) =$ 19.1 Hz, C-2), 129.7 (s, C-p), 129.2 (d, <sup>3</sup>J(P,C) = 7.9 Hz, C-m), 127.6 (d,  $^{3}J(P,C) = 7.0$  Hz, C-3), 40.8 (d,  $^{3}J(P,C) = 17.2$  Hz, C-6), 25.0 (d,  $^{1}J(P,C) =$ 138.8 Hz, C-8), 23.3 ppm (d,  ${}^{2}J(P,C) = 3.9$  Hz, C-7);  ${}^{31}P{}^{1}H}$  NMR (243 MHz, CDCl<sub>3</sub>+CD<sub>3</sub>OD):  $\delta$  = 30.54 (s, PO(OH)<sub>2</sub>), -4.66 ppm (s,  $\text{PPh}_2\text{R}\text{)};$  IR (ATR):  $\tilde{\nu}\!=\!3313$  (m) (NH), 3051 (m), 2927 (m), 2693 (m) (POH), 2205 (m), 1815 (w), 1708 (m) (CO), 1596 (m), 1541 (s), 1481 (m), 1434 (s), 1319 (m), 1278 (m), 1197 (m), 1141 (m), 1030 (m), 998 (vs), 944 (vs), 851 (m), 744 (vs), 724 (s), 692 cm<sup>-1</sup> (vs); elemental analysis calcd. (%) for  $C_{22}H_{23}NO_4P_2 \cdot (CH_2Cl_2)_{0.1}$  (435.86): C 60.90, H 5.37, N 3.21; found: C 60.36, H 5.66, N 3.30.

#### Carbonyl chloridobis [ (3-(4-(diphenyl phosphino) benzamido) pro-

**pyl)phosphonicacid]rhodium(I)** (9): (3-(4-(Diphenylphosphino)benzamido)propyl)phosphonic acid (8) (220 mg, 514  $\mu$ mol) was suspended in dichloromethane (5 mL). A solution of tetracarbonyldi( $\mu$ -chlorido)dirhodium(I) (50.0 mg, 129  $\mu$ mol) in dichloromethane (5 mL) was added to this mixture. The resulting suspension was combined with methanol (1 mL) and the now clear yellow solution was stirred for 40 min. After filtration and removal of the solvent under reduced pressure, the yellow residue was washed twice with

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

dichloromethane (20 mL) and four times with diethylether (40 mL). The obtained yellow solid was dried under vacuum for 5 h. The complex decomposes slowly at rt and, therefore, should be stored in a cool place (yield: 254 mg, 249 µmol, 97%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>+CD<sub>3</sub>OD):  $\delta = 7.83-7.78$  (m, 4H, H-3), 7.75-7.66 (m, 12H, ArH), 7.47-7.36 (m, 12 H, ArH), 3.45-3.40 (m, 4 H, H-6), 1.91-1.83 (m, 4H, H-7), 1.79–1.70 ppm (m, 4H, H-8); <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub> + CD<sub>3</sub>OD):  $\delta$  = 187.4 (dt, <sup>1</sup>J(Rh,C) = 73.4 Hz, <sup>2</sup>J(P,C) = 16.8 Hz, CO), 168.7 (s, C-5), 137.4 (m, C-1), 136.4 (s, C-4), 135.3 (m, C-o), 135.1 (m, C-2), 132.6 (m, C-i), 131.2 (s, C-p), 129.0 (m, C-m), 127.4 (m, C-3), 40.9 (d,  ${}^{3}J(P,C) = 16.9 \text{ Hz}$ , C-6), 25.1 (d,  ${}^{1}J(P,C) = 138.7 \text{ Hz}$ , C-8), 23.3 ppm (d, <sup>2</sup>J(P,C) = 4.7 Hz, C-7); <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CDCl<sub>3</sub>+CD<sub>3</sub>OD):  $\delta$  = 30.48 (s, PO(OH)<sub>2</sub>), 30.38 ppm (d, <sup>1</sup>J(Rh,P) = 127.0 Hz, P-Rh); IR (ATR):  $\tilde{\nu}$  = 3299 (w), 3053 (w), 2867 (w), 2281 (w), 1974 (vs) (CO), 1630 (m), 1599 (m), 1535 (s), 1482 (m), 1434 (s), 1390 (w), 1307 (m), 1150 (s), 1114 (m), 1094 (vs), 979 (vs), 932 (vs),  $845 \text{ cm}^{-1}$ (s); elemental analysis calcd. (%) for C45H46CIN2O9P4Rh·(H2O)3 (1075.15): C 50.27, H 4.87, N 2.61; found: C 50.62, H 5.08, N 2.48.

Grafting of 9 on superparamagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles (9@Fe<sub>2</sub>O<sub>3</sub>): The iron oxide nanoparticles prepared according to the procedure given in the Supporting Information were transferred to a Schlenk tube and the supernatant methanol was discarded. The particles were suspended in a mixture of methanol (8 mL) and dichloromethane (8 mL), followed by the addition of carbonylchloridobis[(3-(4-(diphenylphosphino)benzamido)propyl)phosphonic

acid]rhodium(I) (9) (100 mg, 98  $\mu$ mol). This mixture was stirred for 24 h and placed five times, for 15 min, in an ultrasonic bath. The nanoparticles were magnetically separated and washed three times with a 1:1 mixture of methanol and dichloromethane. The resulting hybrid material was dried under vacuum at 50 °C and stored under air.

General procedure for the hydrogenation of alkenes: The alkene (0.5 mmol) and  $9@Fe_2O_3$  (1.0 mol% of Rh) were mixed with isopropanol (3 mL) in a small Schlenk tube equipped with a rubber balloon as hydrogen reservoir. The mixture was degassed and purged with hydrogen ( $10^5$  Pa) three times. Afterwards, the mixture was stirred at the indicated temperature for the given time. The yields were determined by GC-MS. For the reusability test the catalyst was magnetically separated, washed twice with ethyl acetate and dried under reduced pressure.

**X-ray structure determination**: Detailed crystal data and refinement parameters for compound **7** are summarized in the Supporting Information. The structures was solved by using direct methods (SIR92<sup>[37]</sup>), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.<sup>[38]</sup> Semiempirical absorption corrections from equivalents (Multiscan) were carried out.<sup>[39]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined by using a riding model. CCDC-1031751 contains the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**XAS measurements**: XAS experiments were performed at beamline BM23 at the ESRF (European Synchrotron Radiation Facility) in Grenoble, France. The measurements were carried out at the Rhodium K-edge with a Si(311) double-crystal monochromator and a maximum synchrotron beam current of 200 mA. Spectra of undiluted powders between two Kapton windows were recorded in the fluorescence mode at ambient temperature. The second monochromator crystal was tilted for optimal harmonic rejection. Data evaluation started with background absorption removal from the experimental absorption spectrum by subtracting a Victoreen-type polynomial. Owing to several inflection points in the absorption edge, the threshold energy  $E_0$  was determined consistently by taking the energy at half of the edge jump. To determine the smooth part of the spectrum, corrected for pre-edge absorption, a piecewise polynomial was used. It was adjusted in such a way that the low-R components of the resulting Fourier transform were minimal. After division of the background-subtracted spectrum by its smooth part, the photon energy was converted to photoelectron wave numbers k. The resulting  $\chi(k)$ -function was weighted with  $k^3$  and Fourier transformed by using a Hanning window function. Data analysis was performed in the k-space on filtered data. The filtered range was chosen according to the range of the significant data (1-4 Å). Adjustment of the common theoretical EXAFS expression:

$$\chi(k) = \sum_{j} \frac{N_{j}}{kr_{j}^{2}} S_{0}^{2}(k) F_{j}(k) e^{-2k^{2}\sigma_{j}^{2}} e^{-2r_{j}/\lambda} \sin[2kr_{j} + \delta_{j}(k)]$$

 $(N_j:$  one type of neighbor atoms, j, in a shell.  $r_j:$  distance of atoms j from the X-ray absorbing atom.  $S_0^2:$  amplitude reduction factor.  $F_j:$  backscattering amplitude.  $\sigma^2:$  Debye-Waller-like factor.  $\delta_j:$  overall phase shift) according to the curved wave formalism of the EXCURV98 program with XALPHA phase and amplitude functions was carried out. The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI set to -4.00 eV). An inner potential correction,  $E_t$ , was introduced when fitting experimental data with theoretical models that accounts for an overall phase shift between the experimental and calculated spectra. The amplitude reduction factor was 0.8.

## Acknowledgements

This work was supported by the Uni-FH research cluster MAG-NENZ. The ESRF (Grenoble) is kindly acknowledged for provision of beamtime, Dr. Olivier Mathon is acknowledged for his help during the XAS measurements. M.B. thanks the Carl-Zeiss foundation for financial support.

**Keywords:** hydrogenation · iron · magnetic properties · phosphonate · rhodium

- Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Three Volumes, 2<sup>nd</sup> ed. (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, 2002.
- [2] Industrial Catalysis: A Practical Approach, 2<sup>nd</sup> ed. (Ed.: J. Hagen), Wiley-VCH, Weinheim, 2006.
- [3] a) D. E. De Vos, M. Dams, B. F. Sels, P. A. Jacobs, Chem. Rev. 2002, 102, 3615–3640; b) A. Corma, H. Garcia, Adv. Synth. Catal. 2006, 348, 1391–1412; c) Catalyst Separation, Recovery and Recycling: Chemistry and Process Design (Eds.: D. J. Cole-Hamilton, R. P. Tooze), Springer, Dordrecht, 2006; d) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, Angew. Chem. Int. Ed. 2006, 45, 3216–3251; Angew. Chem. 2006, 118, 3290–3328; e) C. Copéret, J. M. Basset, Adv. Synth. Catal. 2007, 349, 78–92; f) J. Blümel, Coord. Chem. Rev. 2008, 252, 2410–2423; g) A. F. Trindade, P. M. P. Gois, C. A. M. Afonso, Chem. Rev. 2009, 109, 418–514; h) Heterogenized Homogeneous Catalysts for Fine Chemicals Production: Materials and Processes (Eds.: P. Barbaro, L. Francesca), Springer, Dordrecht, 2010; i) A. Monge-

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Marcet, R. Pleixats, X. Cattoën, M. Wong, C. Man, *Catal. Sci. Technol.* 2011, *1*, 1544–1563.

- [4] a) A. Schätz, O. Reiser, W. J. Stark, Chem. Eur. J. 2010, 16, 8950–8967;
  b) S. Shylesh, V. Schünemann, W. Thiel, Angew. Chem. Int. Ed. 2010, 49, 3428–3459; Angew. Chem. 2010, 122, 3504–3537; c) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.-M. Basset, Chem. Rev. 2011, 111, 3036–3075; d) M. B. Gawande, P. S. Branco, R. S. Varma, Chem. Soc. Rev. 2013, 42, 3371–3393; e) R. B. N. Baig, R. S. Varma, Chem. Commun. 2013, 49, 752–770; f) D. Wang, D. Astruc, Chem. Rev. 2014, 114, 6949–6985.
- [5] S. B. Kalidindi, B. R. Jagirdar, ChemSusChem 2012, 5, 65-75.
- [6] Y.-H. Deng, C.-C. Wang, J.-H. Hu, W.-L. Yang, S.-K. Fu, Colloids Surf. A 2005, 262, 87–93.
- [7] a) M. Stjerndahl, M. Andersson, H. E. Hall, D. M. Pajerowski, M. W. Meisel, R. S. Duran, *Langmuir* 2008, 24, 3532–3536; b) J. Ge, Y. Hu, M. Biasini, W. P. Beyermann, Y. Yin, *Angew. Chem. Int. Ed.* 2007, 46, 4342–4345; *Angew. Chem.* 2007, 119, 4420–4423.
- [8] R. Hudson, Y. Feng, R. S. Varma, A. Moores, Green Chem. 2014, 16, 4493-4505.
- [9] a) A. Hu, G. T. Yee, W. Lin, J. Am. Chem. Soc. 2005, 127, 12486–12487;
   b) A. Hu, S. Liu, W. Lin, RSC Adv. 2012, 2, 2576–2580.
- [10] G. Chouhan, D. Wang, H. Alper, Chem. Commun. 2007, 4809.
- [11] A. K. Tucker-Schwartz, R. L. Garrell, Chem. Eur. J. 2010, 16, 12718-12726.
- [12] a) V. Polshettiwar, B. Baruwati, R. S. Varma, Chem. Commun. 2009, 1837– 1839; b) V. Polshettiwar, R. S. Varma, Tetrahedron 2010, 66, 1091–1097.
- [13] M. B. Gawande, A. Velhinho, I. D. Nogueira, C. a. A. Ghumman, O. M. N. D. Teodoro, P. S. Branco, *RSC Adv.* 2012, *2*, 6144–6149.
- [14] a) S. Shylesh, J. Schweizer, S. Demeshko, V. Schünemann, S. Ernst, W. Thiel, Adv. Synth. Catal. 2009, 351, 1789-1795; b) S. Shylesh, L. Wang, W. R. Thiel, Adv. Synth. Catal. 2010, 352, 425-432.
- [15] a) R. Ernstorfer, L. Gundlach, S. Felber, W. Storck, R. Eichberger, F. Willig, J. Phys. Chem. B 2006, 110, 25383–25391; b) E. Galoppini, Coord. Chem. Rev. 2004, 248, 1283–1297; c) P. Hirva, M. Haukka, Langmuir 2010, 26, 17075–17081; d) M. Nilsing, S. Lunell, P. Persson, L. Ojamäe, Surf. Sci. 2005, 582, 49–60; e) M. Nilsing, P. Persson, L. Ojamäe, Chem. Phys. Lett. 2005, 415, 375–380; f) J. S. Basuki, L. Esser, P. B. Zetterlund, M. R. Whittaker, C. Boyer, T. P. Davis, Macromolecules 2013, 46, 6038–6047; g) T. T. T. N'Guyen, H. T. T. Duong, J. Basuki, V. Montembault, S. Pascual, C. Guibert, J. Fresnais, C. Boyer, M. R. Whittaker, T. P. Davis, L. Fontaine, Angew. Chem. Int. Ed. 2013, 52, 14152–14156; Angew. Chem. 2013, 125, 14402–14406.
- [16] a) C. Queffélec, M. Petit, P. Janvier, D. A. Knight, B. Bujoli, *Chem. Rev.* 2012, *112*, 3777–3807; b) G. Guerrero, J. G. Alauzun, M. Granier, D. Laurencin, P. H. Mutin, *Dalton Trans.* 2013, *42*, 12569–12585.
- [17] a) F. Gonzàlez de Rivera, I. Angurell, M. D. Rossell, R. Erni, J. Llorca, N. J. Divins, G. Muller, M. Seco, O. Rossell, *Chem. Eur. J.* 2013, *19*, 11963 – 11974; b) C. Duanmu, L. Wu, J. Gu, X. Xu, L. Feng, X. Gu, *Catal. Commun.* 2014, *48*, 45–49.
- [18] Y. Sahoo, H. Pizem, T. Fried, D. Golodnitsky, L. Burstein, C. N. Sukenik, G. Markovich, *Langmuir* 2001, *17*, 7907–7911.
- [19] a) K. S. M. Salih, P. Mamone, G. Dörr, T. O. Bauer, A. Brodyanski, C. Wagner, M. Kopnarski, R. N. Klupp-Taylor, S. Demeshko, F. Meyer, V. Schünemann, S. Ernst, L. J. Gooßen, W. R. Thiel, *Chem. Mater.* 2013, *25*, 1430–1435; b) R. Dronskowski, *Adv. Funct. Mater.* 2001, *11*, 27–29.
- [20] a) W. L. Santos, B. H. Heasley, R. Jarosz, K. M. Carter, K. R. Lynch, T. L. Macdonald, *Bioorg. Med. Chem. Lett.* 2004, 14, 3473–3476; b) A. Rosowsky, R. A. Forsch, R. G. Moran, W. Kohler, J. H. Freisheim, *J. Med. Chem.*

**1988**, *31*, 1326–1331; c) H. Gali, K. R. Prabhu, S. R. Karra, K. V. Katti, *J. Org. Chem.* **2000**, *65*, 676–680; d) P. Bakó, T. Novak, K. Ludanyi, B. Pete, L. Toke, G. Keglevich, *Tetrahedron: Asymmetry* **1999**, *10*, 2373–2380; e) G. Fabre, N. Collignon, P. Savignac, *Can. J. Chem.* **1981**, *59*, 2864–2869.

- [21] a) L. Mercklé, A. de Andrés-Gómez, B. Dick, R. J. Cox, C. R. A. Godfrey, *ChemBioChem* **2005**, *6*, 1866–1874; b) J. M. van Gelder, J. Y. Klein, Y. Basel, A. Reizelman, S. Tchilibon, O. Mouallem, US2008/39456A1, **2008**.
- [22] a) A. K. Bhattacharya, G. Thyagarajan, Chem. Rev. 1981, 81, 415-430;
   b) B. A. Arbusow, Pure Appl. Chem. 1964, 9, 307-335.
- [23] a) D. M. Iula, Staudinger reaction in Name Reactions for Functional Group Transformations (Eds.: J. Li, E. J. Corey) Wiley, New York, 2007, pp. 129– 151; b) Y. G. Gololobov, I. N. Zhmurova, L. F. Kasukhin, Tetrahedron 1981, 37, 437–472; c) H. Staudinger, J. Meyer, Helv. Chim. Acta 1919, 2, 635– 646.
- [24] a) A. Reis, D. Dehe, S. Farsadpour, I. Munstein, Y. Sun, W. R. Thiel, New J. Chem. 2011, 35, 2488–2495; b) A. Reis, W. R. Thiel, DE 102008039167.
- [25] T. Steiner, Angew. Chem. Int. Ed. 2002, 41, 48–76; Angew. Chem. 2002, 114, 50–80.
- [26] C. L. Thurner, M. Barz, M. Spiegler, W. R. Thiel, J. Organomet. Chem. 1997, 541, 39–49.
- [27] L. Wang, M. Jia, S. Shylesh, T. Philippi, A. Seifert, S. Ernst, A. P. Singh, W. Thiel, *ChemCatChem* **2010**, *2*, 1477–1482.
- [28] K. S. W. Sing, Pure Appl. Chem. 1985, 57, 603-619.
- [29] T. Hyeon, S. S. Lee, J. Park, Y. Chung, H. B. Na, J. Am. Chem. Soc. 2001, 123, 12798–12801.
- [30] M. Hesse, H. Meier, B. Zeeh, Spectroscopic Methods in Organic Chemistry, 2<sup>nd</sup> ed., Thieme, Stuttgart, 2007.
- [31] a) W. Gao, L. Dickinson, C. Grozinger, F. G. Morin, L. Reven, *Langmuir* 1996, 12, 6429–6435; b) G. Guerrero, P. H. Mutin, A. Vioux, *Chem. Mater.* 2001, 13, 4367–4373.
- [32] a) O. Schmidt, Chem. Rev. 1933, 12, 363-417; b) R. A. W. Johnstone, A. H. Wilby, I. D. Entwistle, Chem. Rev. 1985, 85, 129-170; c) The Handbook of Homogeneous Hydrogenation (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, 2007; P. W. N. M. van Leeuwen, Homogeneous Catalysis—Understanding the Art, Kluwer Academic Publ., Dordrecht, 2004, chap. 4; d) S. Bhaduri, D. Mukesh, Hydrogenation of Alkenes, Wiley, New York, 2000; e) A. Börner, J. Holz, Homogeneous Hydrogenations, in Transition Metals for Organic Synthesis, Vol. 2, 2<sup>nd</sup> ed. (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, 2004.
- [33] H. Gao, R. J. Angelici, J. Mol. Catal. A 1999, 149, 63-74.
- [34] M. Bauer, H. Bertagnolli in *Methods in Physical Chemistry*, Wiley-VCH, Weinheim, 2012, pp. 231–269.
- [35] K. A. Potekhin, A. S. Batsanov, Y. S. Struchkov, *Rhodium Express* 1993, 1, 3-7.
- [36] M. Bauer, T. Kauf, J. Christoffers, H. Bertagnolli, Phys. Chem. Chem. Phys. 2005, 7, 2664–2670.
- [37] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 1994, 27, 435–435.
- [38] G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112-122.
- [39] CrysAlisPro, Agilent Technologies, Version 1.171.33.66, 2010.

Received: August 5, 2014 Revised: August 28, 2014 Published online on ■■ ■, 0000

# **FULL PAPERS**



A hybrid for hydrogenation: The grafting of a functionalized carbonyldichloridobis(triphenylphosphino)rhodium complex, by means of two phosphonate linker units, onto neat maghemite nanoparticles generates a magnetically separable catalyst for olefin hydrogenation. X-ray absorption spectroscopy shows that in the course of the catalysis rhodium nanoparticles are formed. D. Dehe, L. Wang, M. K. Müller, G. Dörr, Z. Zhou, R. N. Klupp-Taylor, Y. Sun, S. Ernst, M. Hartmann, M. Bauer, W. R. Thiel\*



A Rhodium Triphenylphosphine Catalyst for Alkene Hydrogenation Supported on Neat Superparamagnetic Iron Oxide Nanoparticles