Organometallic Synthesis of Bimetallic Cobalt-Rhodium Nanoparticles in Supported Ionic Liquid Phases (Co\textsubscript{x}Rh\textsubscript{100-x}@SILP) as Catalysts for the Selective Hydrogenation of Multifunctional Aromatic Substrates

Simon Rengshausen, Casey Van Stappen, Natalia Levin, Simon Tricard, Kylie L. Luska, Serena DeBeer, Bruno Chaudret, Alexis Bordet,* and Walter Leitner*

The synthesis, characterization, and catalytic properties of bimetallic cobalt-rhodium nanoparticles of defined Co:Rh ratios immobilized in an imidazolium-based supported ionic liquid phase (Co\textsubscript{x}Rh\textsubscript{100-x}@SILP) are described. Following an organometallic approach, precise control of the Co:Rh ratios is accomplished. Electron microscopy and X-ray absorption spectroscopy confirm the formation of small, well-dispersed, and homogeneously alloyed zero-valent bimetallic nanoparticles in all investigated materials. Benzylideneacetone and various bicyclic heteroaromatics are used as chemical probes to investigate the hydrogenation performances of the Co\textsubscript{x}Rh\textsubscript{100-x}@SILP materials. The Co:Rh ratio of the nanoparticles is found to have a critical influence on observed activity and selectivity, with clear synergistic effects arising from the combination of the noble metal and its 3d congener. In particular, the ability of Co\textsubscript{x}Rh\textsubscript{100-x}@SILP catalysts to hydrogenate 6-membered aromatic rings is found to experience a remarkable sharp switch in a narrow composition range between Co\textsubscript{25}Rh\textsubscript{75} (full ring hydrogenation) and Co\textsubscript{30}Rh\textsubscript{70} (no ring hydrogenation).

1. Introduction

The preparation of bimetallic nanoparticles (NPs) combining noble metals with their base metal 3d congeners has attracted significant attention as an effective strategy to produce materials with promising optical,[1,2] magnetic,[1,3] and catalytic[1,4] properties. The potential benefits are particularly pronounced in the field of catalysis, where combining metals to produce core–shell or alloyed nanostructures was shown to generate significant synergistic effects, providing access to activities and selectivities that are out of reach for the metals taken individually.[4] As a result, important technical applications such as catalytic reforming,[5] alcohol oxidation[6] and electrocatalysis in fuel cells[7] are now relying on the use of bimetallic catalysts. The use of bimetallic NPs to achieve the controlled activation of molecular hydrogen has also gained increased attention, with the goal of developing supported chemoselective catalysts capable of hydrogenating complex molecules possessing various functional groups.[6–d] While a wide range of supports and preparation techniques are available for the synthesis of monometallic NPs,[8] systematic approaches compatible with the preparation of bimetallic structures over a wide range of defined compositions are comparatively scarce.[9] Such studies would be highly desirable to arrive at a fundamental understanding of how the composition of bimetallic alloys in nanoparticles affects the performance of catalyst materials. In this context, the immobilization of metal NPs on supported ionic liquid phases (SILP) has emerged as a versatile molecular approach to producing multifunctional catalytic systems with tailored reactivity.[10] Recent studies have shown that SILPs provide suitable matrices for the synthesis and stabilization of monometallic and bimetallic NPs, producing catalytic systems possessing excellent properties for hydrogenation,[11] hydrodeoxygenation,[12] and hydrogenolysis[13] reactions. For example, bimetallic FeRu NPs immobilized on an imidazolium-based SILP have shown interesting reactivity for the selective hydrogenation of non-aromatic C=C
and C=O bonds while showing no activity toward aromatic rings.\[11c\]

In order to further explore the potential of bimetallic NPs, we have turned to systematically investigating NPs comprised of Rh and its 3d congener, Co, in defined compositions within a SILP matrix. Bimetallic CoRh NPs have previously been studied for their magnetic,[14] structural[15] and catalytic properties, e.g., in hydroformylation,[16] Pauson-Khand reaction,[16] and reductive cyclization.[17] However, their use in hydrogenation reactions has rarely been explored,[18] and versatile synthetic methods allowing the preparation of supported Co$_x$Rh$_{100-x}$ NPs with tunable Co:Rh ratios are lacking.

Herein, we present the synthesis, characterization, and application of supported bimetallic Co$_x$Rh$_{100-x}$ NPs. Co$_x$Rh$_{100-x}$ NPs were synthesized following an organometallic approach involving the co-reduction of the precursors [Co(cod)(cyclooctadienyl)] (with cod = 1.5 cyclooctadiene) and [Rh(allyl)$_3$] directly in presence of a SILP consisting of an imidazolium-based ionic liquid covalently grafted on silica. This SILP was chosen due to its proven potential as suitable matrix for the formation and stabilization of mono- and bimetallic nanoparticles (Figure 1a).\[11c,12c,e\] The selected organometallic metal complexes were chosen based on a combination of stability during handling and ligand lability upon hydrogenation, allowing the formation of well-defined NPs with a clean surface and tunable composition. In-depth characterization of the resulting Co$_x$Rh$_{100-x}$@SILP materials was achieved using a variety of techniques including electron microscopy, XRD, and XAS to collect information regarding NP size, dispersion, oxidation state and alloying extent (Figure 1b). The catalytic properties of the Co$_x$Rh$_{100-x}$@SILP materials towards hydrogenation of multifunctional aromatic substrates were investigated, with benzylideneacetone and bicyclic heteroaromatics used as chemical probes to study the influence of the Co:Rh metal ratio on activity and selectivity (Figure 1c).

2. Results and Discussion

2.1. Synthesis

Preparation of the imidazolium-based SILP was achieved following a previously published procedure.[12a] Briefly, the silane-functionalized IL [1-butyl-3-(3-triethoxysilylpropyl)imidazolium] NT$_2$ was condensed on dehydroxylated SiO$_2$ with a loading of 0.7 mmol·g$^{-1}$ to produce the corresponding SILP. The preparation of Co$_x$Rh$_{100-x}$ NPs was achieved by adapting the organo-metallic approach developed in our group for bimetallic FeRu@SILP.[11c] This synthesis involved the decomposition of metal precursors ([Rh(allyl)$_3$] and [Co(cod)(cyclooctadienyl)]) via hydrogenation of the hydrocarbon ligands directly in presence of the SILP material under mild reaction conditions (total metal loading = 0.4 mmol·g$^{-1}$, $T$ = 150 °C, $p$ = 3 bar H$_2$, $t$ = 18 h, solvent = mesitylene). The syntheses of Co$_x$Rh$_{100-x}$@SILP catalysts were carried out in Fischer-Porter bottles allowing for the observation of the reaction progress, starting with a brownish-yellow colored suspension and ending with a black powder and a clear supernatant after 18 h. This approach provided access to a wide range of well-defined bimetallic Co$_x$Rh$_{100-x}$@SILP catalysts (See Figure 2a for illustration) with tunable Co:Rh ratios through the accurate adjustment of the relative quantities of metal precursors introduced in the reaction mixture (Table S1, Supporting Information).

2.2. Characterization

BET measurements showed that the Co$_x$Rh$_{100-x}$@SILP catalysts possess a surface area of about 297 m$^2$·g$^{-1}$. This is significantly lower than for the starting dehydroxylated silica (343 m$^2$·g$^{-1}$), which is anticipated due to the presence of the chemisorbed ionic liquid. The theoretical total metal loading and Co:Rh ratios were confirmed by scanning electron
microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) (for details see Table S1 in the Supporting Information). Characterization of the Co$_{x}$Rh$_{100-x}$@SILP materials by transmission and scanning transmission electron microscopy evidenced the formation of small (2–3 nm) and well-dispersed NPs on the SILP (example for Co$_{80}$Rh$_{20}$@SILP in Figure 2b, additional details in Table S1 and Figures S1–S6 in the Supporting Information). Elemental mapping using STEM-HAADF-EDX confirmed the formation of NPs containing both Rh and Co, as exemplified for Co$_{80}$Rh$_{20}$@SILP in Figure 2c–e (See Figure S7 in the Supporting Information). Interestingly, the elemental mapping revealed a higher concentration of sulfur around the NPs than on the rest of the support, suggesting a strong interaction between the ionic liquid (especially the S-containing anion) and the NPs. Overall, these data confirm the versatility of the organometallic approach in the controlled formation of bimetallic NPs on SILP.

To characterize the oxidation state and alloying properties of the Co$_{x}$Rh$_{100-x}$@SILP materials, a series of materials with $x = 100, 80, 30, 25,$ and 0 were characterized using Co and Rh K-edge X-ray absorption spectroscopy (XAS). Full details regarding data collection, processing, and analysis are given in the Supporting Information. The Co K-edge XAS spectra show minor modulations in the pre-edge ($\approx 7709–7713$ eV) and white-line ($\approx 7723$ eV) regions upon addition of Rh (Figure 3a).

The lack of significant increase in white-line intensity in our Co$_{x}$Rh$_{100-x}$@SILP materials relative to the Co$^0$ foil is indicative of the fact that the bulk oxidation state of Co remains zero-valent throughout the series (Figure S8, Supporting Information). The spectral changes anticipated with increased valency are demonstrated by comparisons of Co$_{100}$@SILP before and after O$_2$ exposure, where large increases in the white line region ($\approx 7723$ eV) are accompanied by significant decreases in pre-edge intensity ($7709–7713$ eV) (Figure S8, Supporting Information). Similarly, little modulation of the Rh K-edge is

![Figure 2](image1.png)

**Figure 2.** a) Illustration of bimetallic CoRh NPs immobilized on SILP (Co$_{100}$Rh$_{0}$@SILP, 100% = 0.4 mmol $g^{-1}$), b,c) STEM-HAADF image of Co$_{80}$Rh$_{20}$@SILP, d) STEM-HAADF-EDX elemental mapping of Co$_{80}$Rh$_{20}$@SILP looking at Co and e) STEM-HAADF-EDX elemental mapping of Co$_{80}$Rh$_{20}$@SILP looking at Rh.

![Figure 3](image2.png)

**Figure 3.** Comparison of normalized a) Co K-edge and b) Rh K-edge XAS for Co$_{x}$Rh$_{100-x}$@SILP, $x = 100, 80, 30, 25,$ and 0. The Rh K-edge spectrum of Co$_{25}$Rh$_{75}$@SILP is partially obscured due to its nearly complete overlap with that of Co$_{20}$Rh$_{80}$@SILP.
observed along the Co_{x}Rh_{100-x}@SILP series (Figure 3b). Based on the similar overlap of these spectra with that of the Rh\(^{0}\) foil (Figure S9, Supporting Information), in terms of both edge position and spectral shape, the bulk oxidation state of Rh in our Co_{x}Rh_{100-x}@SILP materials also remains zero-valent (Figure S9, Supporting Information). Interestingly, the oxidation state of Rh does not appear oxygen sensitive, as exposure of the Rh\(_{100}@SILP\) to ambient O\(_2\) does not result in any major deviations from the established Rh\(^{0}\) foil.

The Fourier-transform (FT) of the Co K-edge extended X-ray absorption fine structure (EXAFS) region of Co\(_{100}@SILP\) exhibits a single, dominating feature at 2.1 Å, along with several long-range features at 3.8 and 4.6 Å (Figure 4a). The presence of a proportionally small amount of Rh to form Co\(_{80}Rh_{20}@SILP\) similarly produces a single main feature, but with dramatically decreased intensity in the FT (relative to Co\(_{100}@SILP\)) and a decrease in position to 1.9 Å. Furthermore, no clear long-range features appear.

Increasing Rh content to Co\(_{30}Rh_{70}@SILP\) and Co\(_{25}Rh_{75}@SILP\) produces a clear second feature in the FT \(\approx 2.45\) Å, indicative of the presence of an additional scatterer. Again, no clear long-range scatterers are observed for either of these materials. The decrease in total FT intensity of the Co EXAFS for all Rh-containing materials relative to Co\(_{100}@SILP\) may arise from the presence of additional scattering pathways that result in partial phase-cancellation, and/or from increased disorder within the material. The possibility of increased disorder, previously observed by Chaudret et al. in the case of Co-rich CoRh nanocrystals with a polytetrahedral structure,[14] is further supported by the disappearance of any clear features in the FT at higher R (3.5–5 Å), which would otherwise arise from ordered long-range single scattering or multi-scattering pathways.

The Rh K-edge FT-EXAFS exhibits similar trends to those observed for the Co K-edge FT-EXAFS (Figure 4b). The Rh\(_{100}@SILP\) produces a single major feature at 2.4 Å with a shoulder at 1.9 Å, and two minor long-range features at 4.4 and 4.9 Å. Decreasing Rh content to Co\(_{25}Rh_{75}@SILP\) and Co\(_{30}Rh_{70}@SILP\) results in an overall decreased FT intensity and an increased intensity of the 1.9 Å relative to that at 2.4 Å. Similar to the Co FT-EXAFS, the long-range features at 4.4 and 4.9 Å are no longer clearly present. Further decreasing Rh content to Co\(_{80}Rh_{20}@SILP\) produces a single clear feature at 2.0 Å, still with a significantly decreased FT intensity relative to Rh\(_{100}@SILP\).

To further analyze these trends, EXAFS analysis was performed involving simultaneous fitting of the Co and Rh K-edge spectra for a given material composition (detailed in the Supporting Information). Over a range of R = 1–3 Å, both Co\(_{100}@SILP\) and Rh\(_{100}@SILP\) could be reasonably fit using single Co-Co and Rh-Rh scattering paths. The Rh K-edge EXAFS of Co\(_{30}Rh_{70}@SILP\), Co\(_{30}Rh_{70}@SILP\), and Co\(_{25}Rh_{75}@SILP\) could also be adequately modeled using Rh-Rh and Rh-Co scattering paths. However, additional scatterers were required to obtain reasonable fits of the Co K-edge EXAFS for all three bimetallic samples. In Co\(_{30}Rh_{70}@SILP\) and Co\(_{25}Rh_{75}@SILP\), a longer Co-Co scattering path with a distance of \(\approx 3.15\) Å was required in addition to the Co-Rh and shorter Co-Co scattering paths. In Co\(_{80}Rh_{20}@SILP\), fits performed using solely Co-Co and Co-Rh scatterers revealed a significant unaccounted for short scatterer with a maximum at R \(\approx 1.7\) Å in the non-phase shifted FT spectrum. Based on the elemental composition of the SILPs, a variety of Co-X scattering pathways were tested including X = O, N, C, F, S, and Si. Of these, only a Co-S scatterer with a distance of 2.16 Å could provide a reasonable fit. This scatterer may arise from partial degradation of the NTF\(_2\) (bis(trifluoromethane)sulfonimide) anion contained in the ionic liquid phase during synthesis, which could either form Co-S at the surface of the Co\(_{80}Rh_{20}@SILP\), or independently SILP-deposited cattiereite or limnaeite-like Co\(_{x}\)S\(_{y}\) clusters. Regardless, the presence of this possible Co-S scatterer does not appear to modulate catalytic selectivity, as discussed later.

EXAFS fitting results are summarized in Tables S2 and S3 in the Supporting Information. The Co-Co distance does not appear significantly modulated when moving between Co\(_{100}@SILP\) and Co\(_{30}Rh_{70}@SILP\) (\(\approx 2.48\) Å), but expands to \(\approx 2.53\) Å in Co\(_{30}Rh_{70}@SILP\) and Co\(_{25}Rh_{75}@SILP\). Similarly, the Co-Rh/Rh-Co distance increases from 2.55 Å in Co\(_{80}Rh_{20}@SILP\) to \(\approx 2.60\) Å in Co\(_{30}Rh_{70}@SILP\) and Co\(_{25}Rh_{75}@SILP\). This is generally consistent with an expanding lattice, and is supported by our X-ray powder diffraction measurements (Figure S10, Supporting Information). The fit Rh-Rh distances range between 2.65 and 2.69 Å across the series, appearing slightly contracted in the Co\(_{30}Rh_{70}@SILP\) and Co\(_{25}Rh_{75}@SILP\) samples. These
was observed. Yields were determined by GC-FID using tetradecane as internal standard.

Conversion (to a combination of 1b, 1c) > 99% of 1a/1d Figure CoRh100@SILP was under an identical set of reaction conditions (T = 16 h, mesitylene). Fitting results generally support a fully alloyed bimetallic structure in these materials based on the determined values of J and S (Table S2, Supporting Information).

2.3. Catalysis

The catalytic properties of the CoRh100−x@SILP materials were investigated using first the hydrogenation of benzylideneacetone (1) as a model reaction. Substrate 1 possesses an aromatic ring, a conjugated double bond, and a non-benzylidene ketone, giving the opportunity to probe the reactivity of CoRh100−x@SILP for a wide range of prototypical functional groups. Hydrogenation of 1 can lead to the ketones 4-phenyl-2-butanone (1a) and 4-cyclohexyl-2-butanone (1b) as well as to the alcohols 4-phenyl-2-butanol (1c) and 4-cyclohexyl-2-butanol (1d) (Figure 5; Table S4, Supporting Information). These products are connected through a network of sequential and parallel hydrogenation pathways. Figure 5 shows the product yields as a function of the Co:Rh ratio in CoRh100−x@SILP obtained under an identical set of reaction conditions (T = 150 °C, p(H2) = 50 bar, t = 16 h, solvent = heptane).

Starting with monometallic Rh100@SILP, 1 was completely hydrogenated to give 1d in quantitative yield, which corresponds to the expected reactivity for pure Rh NPs. No change in product distribution was observed under these conditions with addition of Co up to Co25Rh75. However, "diluting" Rh content further to Co30Rh70 resulted in a sharp switch in selectivity, leading to production of the unsaturated alcohol 1c in high yield (92%). Excellent selectivity towards the formation of 1c was conserved across a broad range of Co:Rh ratios, reaching a maximum (>99%) at Co20Rh80. Further lowering Rh content led to a progressive decrease in total hydrogenation activity, resulting in mixtures of 1a (65%) and 1c (35%) for the monometallic Co90@SILP catalyst.

To gain further insight into the catalysts reactivity, the initial rate for C=O hydrogenation of Co80Rh20@SILP, Co90Rh30@SILP and Co95Rh5@SILP were determined by recording time profiles of product formation (Figure 6). To do so, reduced temperatures of 100 °C were used to slow down the reaction. Under these conditions, the C=O hydrogenation was extremely fast (completed in the first few minutes) and the three catalysts considered led only to the observable formation of 1c as a product from 1a during the first 4 h, allowing for a direct comparison. The activity for C=O hydrogenation increases with increasing Co content in the order kC=O(Co25Rh75) < kC=O(Co30Rh70) < kC=O(Co80Rh20). Further increasing the Co content led to a drop in C=O hydrogenation activity as evidenced by formation of mixtures of 1a and 1c already for Co95Rh5@SILP (Figure 5). Interestingly, the incorporation of Co in Rh NPs also appears to modify the sequence of hydrogenation of the different functional groups (Table S5, Supporting Information). Rh100@SILP exhibits a preference for hydrogenating C=C > aromatic > C=O, and thus displays
a product pathway of 1 → 1a → 1b → 1d. Meanwhile, the presence of Co changes the order to C=C > C=O > aromatic, resulting in a 1 → 1a → 1c → 1d product pathway for all three Co80Rh20@SILP catalysts, albeit with almost complete shut down of aromatic ring hydrogenation for Co contents above Co25Rh75. This last point was confirmed through the determination of the initial rate for aromatic ring hydrogenation of Co80Rh20@SILP, Co60Rh40@SILP, and Co25Rh75@SILP. Time profiles were recorded for the conversion of 1c to 1d under standard conditions, evidencing no or extremely low activity for Co80Rh20@SILP (k_{aromatic} = 0 h^{-1}) and Co60Rh40@SILP (k_{aromatic} = 0.009 h^{-1}) in contrast to Co25Rh75@SILP (k_{aromatic} = 0.104 h^{-1}) (Figure S11, Supporting Information).

As aforementioned, XAS analysis suggested the presence of a Co-S scattering path in Co80Rh20@SILP. The further lack of any significant Rh-S scattering indicated that such an interaction would arise from either coordination of sulfur with Co on the surface of the NP, or from independently formed Co-S-type clusters deposited on the SILP. To test whether the presence of a sulfur-containing anion impacts catalytic properties, Co80Rh20@SILP NPs were prepared additionally using a sulfur-free SILP (SILP-BPh4) as well as an unmodified SiO2 support. The resulting Co80Rh20@SILP-BPh4 catalyst displays reactivity largely identical to the standard Co80Rh20@SILP (Table S6, Supporting Information). This indicates that even if some form of Co-S interaction occurs when using the NTf2 anion, as suggested by XAS, this does not significantly influence the reactivity of the bimetallic NPs. More importantly, however, using unmodified SiO2 as a support rather than the 1L-grafted SILP – produced very different results. Specifically, use of unmodified silica did not allow for generation of homogeneously dispersed bimetallic CoRh NPs, as evidenced by the big aggregates observed in TEM (Figure S12, Supporting Information). Instead, material prepared using a 80:20 ratio of the Co and Rh precursor complexes displayed activity typical for catalysts with very high Rh content (Co25Rh75 and above), leading to deep hydrogenation and producing 1d as main product (Table S6, Supporting Information). This activity is indicative of the failure of the controlled formation of Co80Rh20 NPs on the SiO2 (Table S6, Supporting Information). In contrast, no evidence for agglomeration or segregation was obtained by TEM and SEM-EDX analysis of the CoRh100-x@SILP materials even after catalysis (Figures S13–S14 and Tables S7–S8, Supporting Information). These results highlight the importance of the ionic liquid layer in the controlled preparation and structural stability of these alloy-type bimetallic particles.

The in-depth characterization of the pristine NPs and catalytic studies clearly indicate that the bimetallic alloy-type NPs with both metals in the formal oxidation state zero are the catalytically active components across the whole range of Co-Rh compositions. A possible explanation for the pronounced activity and selectivity effects might be a dynamic modification of the CoRh NPs surface composition under reaction conditions due to the attraction of the oxophilic Co atoms by the polar substrate, leading to a Co enrichment in the CoRh surface of the alloys. Similar examples of dynamic surface enrichment with 3d metals have been reported for related bimetallic systems including, for example, Cu-Pd and Co-Pd alloys.[20] For Co contents below 25%, the surface of the NPs can still be rich enough in Rh atoms to allow the arrangement of 3–4 adjacent Rh atoms necessary to hydrogenate 6-membered aromatic rings.[21] However, once the Co content is increased above 30%, the surface of the alloyed CoRh NPs becomes too Co rich when under dynamic conditions, thus preventing the necessary Rh ensembles and hence leaving the aromatic ring intact under hydrogenation conditions. The enhancement of the C=O hydrogenation rate upon further increase of the Co content can be rationalized by a more efficient activation of the C=O bond on the increasingly oxophilic CoRh surface together with an increasingly polarized activation of H2.[4] At very high Co:Rh ratios, the noble metal is no longer available to enhance the H2 activation and the reactivity of pure Co prevails. The rigorous investigation of this hypothesis by characterization of the catalysts under dynamic conditions using operando X-Ray spectroscopies is underway and will be the subject of future reports.

Based on this rationale, the generality of the selectivity switch between Co80Rh20@SILP and Co25Rh75@SILP was investigated by expanding the substrate scope to a variety of probe molecules also comprising a polar functional group and a C6 aromatic ring, i.e., bicyclic heteroaromatics. Achieving the selective partial or deep hydrogenation of such compounds in a controllable manner is very attractive because of the widespread use of these motifs as building blocks in the production of various fine chemicals and pharmaceuticals.[22] Benzofurans, indoles, and quinolines were chosen as representatives of this group and the results are summarized in Table 1. Hydrogenation using Co80Rh20@SILP under standard conditions (50 bar H2, 16 h reaction time) without further optimization resulted in formation of the partially saturated products (dihydrobenzofurans, dihydroindoles, and tetrahydroquinolines, respectively) in good to excellent yields. The hydrogenation of the C6 aromatic ring
was suppressed with very high selectivity, substrate 6 being the only exception. In this case, the methyl substituent adjacent to the NH seems to reduce the selectivity in general, as evidenced by the somewhat lower selectivity also found for quinaldine 9.

In contrast, use of Co25Rh75@SILP led to complete hydrogenation of the substrates considered, providing the corresponding octahydrobenzofurans, octahydroindoles and decahydroquinolines in particularly excellent yields for unsubstituted C6 rings. The degree of deep hydrogenation was reduced by the presence of electron-donating methoxy groups, specifically for substrates 4 and 7. Interestingly, partial cleavage of the methoxy group was observed for these substrates, suggesting that the Co25Rh75@SILP material also exhibits significant hydrogenolysis activity.

These results are consistent with those described above for benzylideneacetone, and confirm the existence of a sharp switch in the catalysts’ ability to hydrogenate 6-membered aromatic rings depending on the Co:Rh ratio. Importantly, this

| Substrate | T [°C] | Products | Co30Rh70 | Co25Rh75 |
|-----------|-------|----------|----------|----------|
|           |       |          | X [%]    | S<sub>a/b</sub> [%] | X [%]    | S<sub>a/b</sub> [%] |
| 1         | 150   | 2a 99    | >99 0/99 (89) | >99 0/99 (90) |
| 2         | 180   | 3a 60 98/2 | >99 0/99 |
| 3         | 180   | 4a 35/77  | >99 35/47 |
| 4         | 150   | 5a 86 97/3 | >99 35/42 |
| 5         | 150   | 6a 70 97/3 | >99 35/42 |
| 6         | 150   | 7a 70 97/3 | >99 35/42 |
| 7         | 150   | 8a 70 97/3 | >99 35/42 |
| 8         | 150   | 9a 98 83/17 | >99 0/99 (88) |
| 9         | 150   | 9b 98 83/17 | >99 0/99 |

<sup>a</sup>Reaction conditions: Catalyst (20.0 mg, 0.008 mmol [m]), H<sub>2</sub> (50 bar), substrate (0.20 mmol, 25 eq.), decalin (0.5 mL), 16 h. Conversion and selectivity determined by GC-FID using tetradecane as internal standard; p<sup>b</sup> (18%); q<sup>b</sup> (23%). X = conversion, S = selectivity, (isolated yields).
selectivity switch occurred systematically between the 30:70 and 25:75 ratios for all substrates considered, suggesting this is a general characteristic of Co$_{x}$Rh$_{100-x}$@SILP catalysts under these conditions.

3. Conclusions

In conclusion, we report a synthetic organometallic approach that is suitable for the preparation of small (2–3 nm) and well-dispersed bimetallic CoRh nanoparticles on an imidazolium-based SILP support. Investigation of the resulting Co$_{x}$Rh$_{100-x}$@SILP catalysts using STEM-HAADF-EDX and XAS confirmed the formation of homogeneous Co-Rh alloys in a zero-valent state over the entire composition range. The molecular approach to assemble the materials allows precise control over the Co:Rh ratio which in turn has a great influence on the catalytic properties of Co$_{x}$Rh$_{100-x}$@SILP materials for hydrogenation of substituted aromatics. In particular, while NPs with high Rh content (>75 at%) possess activity typical of Rh metal and can fully hydrogenate aromatic substrates, increasing Co content (30–80 at%) leads to a selectivity switch with nearly complete suppression of the arene hydrogenation accompanied by an enhancement of the C=O hydrogenation activity. The materials Co$_{x}$Rh$_{100-x}$@SILP and Co$_{x}$Rh$_{15}$@SILP were found highly active, selective and stable for the hydrogenation of benzylideneacetone and various bicyclic heteroaromatics to the corresponding partially and fully saturated products, respectively. As electron microscopy and XAS do not evidence major morphological, structural, or electronic differences between Co$_{x}$Rh$_{100-x}$@SILP and Co$_{x}$Rh$_{15}$@SILP catalysts, the selectivity switch observed is tentatively associated with the interrupion of the arrangement of Rh atoms necessary for aromatic ring hydrogenation above a specific Co content under dynamic catalytic conditions.

In general, the results presented here substantiate the opportunities offered by controlled “dilution” of noble metal nanoparticles with the respective first row base-metal congener. Provided that suitable support materials allow for the formation of defined and stable alloy-type materials, synergistic effects can result in catalytic properties that are not provided by any of the two metals individually and may be difficult—if not impossible—to be achieved with traditional supported metal catalysts in general. The combination of molecularly modified and in particular SILP-type support materials with the organometallic approach to nanoparticle synthesis provides an excellent platform to explore this opportunity in a wide parameter space.

4. Experimental Section

**Safety Warning:** High-pressure experiments with compressed H$_2$ (g) must be carried out only with appropriate equipment and under rigorous safety precautions.

**General:** If not otherwise stated, the synthesis of ionic liquids (ILs), supported ionic liquid phases (SILPs) and nanoparticles (NPs) supported on SILPs (NPs@SILP) were carried out under argon using standard Schlenk techniques or inside a glovebox. After synthesis, ILs, SILPs and NPs@SILPs were stored under argon. The substrates used in the catalytic study were purchased from commercial sources and stored under argon. Benzylideneacetone was sublimated prior to use. Mesitylene, toluene, heptane, DCM and acetone were distilled, dried over molecular sieves (4 Å) and stored under argon. Descalin was purchased commercially (from ACROS, 99% anhydrous), flushed with argon and stored over molecular sieves (4 Å). SiO$_2$ (Merck Grade 10184, pore size 100, 63–200 mm) was dehydroxylated in vacuo at 500 °C for 16 h prior to use. [Co(cod)(cyclooctadienyl)] was purchased from Nanomems and [Rh(allyl)]$_3$ was synthesized according to a literature procedure.$^{35}$ High-pressure experiments were performed using in-house engineered 10 and 20 mL stainless steel autoclaves equipped with a glass insert.

**Catalytic Reactions:** Gas chromatography (GC) was performed on a Thermo Scientific Chromatograph Trace GC Ultra equipped with a CP-Wax 52 CB column from Agilent and Rtx-1 from Restek. Conventional bright-field TEM images were taken using a JEOL JEM 1400 operated at 120 kV. Scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-HAADF/EDS) was performed on a JEOL JEM-ARM200F Cold FEG operated at 200 kV, and on a Hitachi HF-2000 Cold FEG operated at 200 kV. The NP size and distribution was determined from the measurement of >150 spherical particles chosen in arbitrary areas of enlarged micrographs. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) was performed on a JEOL JSM 7800F operated at 10 kV with a thermally assisted Schottky electron gun and equipped with a Bruker XFlash 66/60 detector (silicon drift detector technology), and on a Hitachi S-3500N using a 10 mm$^2$ Si(Li) detector (Oxford Instruments). Samples for SEM/EDS analysis were prepared by pressing powder of NPs@SILPs on carbon tape. BET was measured using a Quadrasorb station (7.01). Powder X-ray diffraction was performed using a X’Pert PRO powder diffractometer (PANalytical) equipped with a copper X-ray source. The data collection was performed with the aid of X’Celerator detectors. A detailed section on the characterization by X-ray absorption spectroscopy is available in the Supporting Information.

**Synthesis of Co$_{x}$Rh$_{100-x}$@SILP (Example of Co$_{80}$Rh$_{20}$@SILP):** In a typical experiment [Rh(allyl)$_3$] (18.1 mg, 0.08 mmol) was dissolved in mesitylene (4 mL) and combined with a solution of [Co(cod)(cyclooctadienyl)] (8.84 mg, 0.32 mmol) in mesitylene (4 mL) in a Fischer-Porter bottle (70 mL). While stirring the solution in a glovebox, the SILP (1.00 g) was added and the suspension was stirred for 30 min at room temperature (RT). The Fischer-Porter bottle was placed into a preheated oil bath (150 °C), stirred for 15 min under argon and subsequently pressurized with H$_2$ (3 bar). The reaction mixture was then stirred for 18 h, yielding a black powder (the catalyst) and a clear supernatant. After cooling down, the mesitylene was decanted and the catalyst washed with toluene (dried and degassed, 5 mL) before drying in vacuo at RT for 1 h.

**Catalytic Reactions:** In a typical catalytic experiment, the catalyst (20 mg, 0.008 mmol metal) and the substrate (0.2–0.8 mmol, 25–100 eq.) were weighed into a glass insert and the solvent (heptane for benzylideneacetone, decalin for heteroaromatics) (0.5 mL) was added, as well as a stir bar. The inlet was placed in a high-pressure autoclave and pressurized with H$_2$ (50 bar). The reaction mixture was stirred at 150 °C for 16 h in a pre-heated aluminum heating cone. At the end of the reaction, the autoclave was cooled in a water bath, carefully vented and the reaction mixture was filtered into a GC vial for characterization, using tetradecane as an internal standard. Conversion and selectivity were determined by GC-FID.

**Supporting Information:** Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements:** The authors acknowledge financial support by the Max Planck Society and by the Deutsche Forschungsgemeinschaft (DFG, German Research...
Conflict of Interest
The authors declare no conflict of interest.

Keywords
bimetallic nanoparticles, catalytic hydrogenation, cobalt-rhodium, SILP, synergistic

Received: October 27, 2020
Revised: December 2, 2020
Published online:

[1] K. D. Gilroy, A. Ruditsky, H.-C. Peng, D. Qin, Y. Xia, Chem. Rev. 2016, 116, 10414.

[2] a) G. Mattei, P. Mazzoldi, M. L. Post, D. Buso, M. Guglielmi, A. Martucci, Adv. Mater. 2007, 19, 561; b) D. A. Garfinkel, G. Paketis, N. Tang, I. N. Ivanov, J. D. Fowlkes, D. A. Gilbert, P. D. Rack, ACS Omega 2020, 5, 19285; c) A. V. Soloveva, N. K. Eremenko, I. I. Obraztsova, A. N. Eremenko, S. P. Gubin, Russ. J. Inorg. Chem. 2018, 63, 444; d) S. Thota, Y. Wang, J. Zhao, Mater. Chem. Front. 2018, 2, 1074.

[3] a) S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, Science 2000, 287, 1989; b) I.-C. Chiang, D.-H. Chen, Adv. Funct. Mater. 2007, 17, 1311; c) K. I. M. da Silva, F. Bernardi, G. Abarca, D. L. Baptista, M. J. L. Santos, L. F. Barquin, J. Dupont, S. J. Sciutto, Phys. Chem. Chem. Phys. 2018, 20, 10247; d) V. Amendola, S. Scaramuzza, L. Litt, M. Meneghetti, G. Zuccolotto, A. Rosato, E. Nicolato, P. Marzola, G. Fracasso, C. Anselmi, M. Pinto, M. Colombatti, Small 2014, 12, 2476.

[4] a) D. Wang, Y. Li, Adv. Mater. 2011, 23, 1044; b) M. Sankar, N. Dimitratos, P. J. Miedziak, P. P. Wells, C. J. Kiely, G. J. Hutchings, Chem. Soc. Rev. 2012, 41, 8099; c) J. Lee, Y. T. Kim, G. W. Huber, Green Chem. 2014, 16, 708; d) D. M. Alonso, S. G. Wettstein, J. A. Dumesci, Chem. Soc. Rev. 2012, 41, 8075.

[5] a) G. A. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley, New York 1994, pp. 500–512; b) G. W. Huber, J. W. Shabaker, J. A. Dumesci, Science 2003, 300, 2075.

[6] D. I. Enache, J. K. Edwards, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, Science 2006, 311, 362.

[7] F. Maroun, F. Oznam, O. M. Magnusson, R. J. Behm, Science 2001, 293, 1811.

[8] a) L. Zhang, M. Zhou, A. Wang, T. Zhang, Chem. Rev. 2020, 120, 683; b) A. Sánchez, M. Fang, A. Ahmed, R. A. Sánchez-Delgado, Appl. Catal., A 2014, 477, 117; c) J. C. Matsubu, S. Zhang, L. DeRita, N. S. Marinkovic, J. G. Chen, G. W. Graham, X. Pan, P. Christopher, Nat. Chem. 2017, 9, 120; d) A. Karakulina, A. Gopakumar, Z. Fei, P. J. Dyson, Catal. Sci. Technol. 2018, 8, 5019; e) C. Deraedt, R. Ye, W. T. Ralston, F. D. Toste, G. A. Somorjai, J. Am. Chem. Soc. 2017, 139, 18084.

[9] a) A. Wong, Q. Liu, S. Griffin, A. Nicholls, J. R. Regalbuto, Science 2017, 358, 1427; b) K. Ding, D. A. Cullen, L. Zhang, Z. Cao, A. D. Roy, N. I. Ivanov, D. Cao, Science 2018, 362, 560; c) S. H. Hakim, C. Sener, A. C. Alba-Rubio, T. M. Gostanian, B. J. O’Neill, F. H. Ribeiro, J. T. Miller, J. A. Dumesci, J. Catal. 2015, 238, 75.

[10] P. Migowski, K. L. Luska, W. Leitner, In Nanocalotysis in Ionic Liquids (Ed: M. H. G. Prechtl), Wiley VCH, Weinheim 2016; b) R. Fehmann, A. Rissager, M. Haumann, Supported Ionic Liquids: Fundamentals and Applications, Wiley-VCH Verlag GmbH, Weinheim 2014.

[11] a) M. A. Gelesky, S. S. X. Chiaro, F. A. Pavan, J. H. Z. dos Santos, J. Dupont, Dalton Trans. 2007, 5549; b) M. Ruta, G. Laurenzcy, P. J. Dyson, K.-L. Minsker, J. Phys. Chem. 2008, 112, 17814; c) K. L. Luska, A. Bordet, S. Tricard, I. Sinev, W. Grünert, B. Chaudret, W. Leitner, ACS Catal. 2016, 6, 3719; d) S. El Sayed, A. Bordet, C. Weidenthaler, W. Hetaba, K. L. Luska, W. Leitner, ACS Catal. 2020, 10, 2124; e) A. Bordet, C. Welsh, P. Lience, K. L. Luska, W. Leitner, ACS Catal. 2020, 10, 13904.

[12] a) K. L. Luska, J. Julis, E. Stavitski, D. N. Zakharov, A. Adams, W. Leitner, Chem. Sci. 2014, 5, 4895; b) K. L. Luska, P. Migowski, S. El Sayed, W. Leitner, Angew. Chem., Int. Ed. 2015, 54, 15750; c) L. Offner-Marko, A. Bordet, G. Moos, S. Tricard, S. Rengshausen, B. Chaudret, K. L. Luska, W. Leitner, Angew. Chem., Int. Ed. 2018, 57, 12721; d) G. Moos, M. Emondis, A. Bordet, W. Leitner, Angew. Chem., Int. Ed. 2020, 59, 11977; e) L. Goclik, L. Offner-Marko, A. Bordet, W. Leitner, Chem. Commun. 2020, 56, 9509.

[13] S. Rengshausen, F. Etscheidt, J. Großkühr, K. L. Luska, A. Bordet, W. Leitner, Synlett 2019, 30, 405.

[14] D. Zitoun, C. Amiens, B. Chaudret, M.-C. Froment, P. Lecante, M.-J. Casanove, M. Respaul, J. Phys. Chem. B 2003, 107, 6997.

[15] H. F. Van’t Blik, D. C. Koningsberger, R. Prins, J. Catal. 1986, 97, 210.

[16] J. H. Park, Y. K. Chung, Dalton Trans. 2008, 18, 2369.

[17] I. Choi, H. Chung, J. W. Park, Y. K. Chung, Org. Lett. 2016, 18, 5508.

[18] a) F. Benseradj, F. Sadi, M. Chater, C. R. Chim. 2004, 7, 669; b) X. Zheng, Y. Lin, H. Pan, L. Wu, W. Zhang, L. Cao, J. Zhang, L. Zheng, T. Yao, Nano Res. 2018, 11, 2357; c) H. Kusama, K. Okabe, K. Sayama, H. Arakawa, Appl. Organomet. Chem. 2000, 14, 836.

[19] B. J. Hwang, L. S. Sarma, J. M. Chen, C. H. Chen, S. C. Shin, Q. R. Wang, D. G. Liu, J. F. Lee, M. T. Tang, J. Am. Chem. Soc. 2005, 127, 11140.

[20] a) J. S. Bradley, E. W. Hill, B. Chaudret, A. Duteil, Langmuir 1995, 11, 693; b) M. Cokoja, H. Parala, A. Birkner, R. A. Fischer, O. Margeat, D. Ciuculescu, C. Amiens, B. Chaudret, A. Falqui, P. Leconte, Eur. J. Inorg. Chem. 2010, 11, 1599; c) C. H. Wu, C. Liu, D. Su, H. L. Xin,
H.-T. Fang, B. Eren, S. Zhang, C. B. Murray, M. B. Salmeron, Nat. Catal. 2019, 2, 78; d) F. Tao, M. E. Grass, Y. Zhang, D. R. Butcher, J. R. Renzas, Z. Liu, J. Y. Chung, B. S. Mun, M. Salmeron, G. A. Somorjai, Science 2008, 322, 932.

[21] C. Fan, Y.-A. Zhu, X.-G. Zhou, Z.-P. Liu, Catal. Today 2011, 160, 234.

[22] a) D.-S. Wang, Q.-A. Chen, S.-M. Lu, Y.-G. Zhou, Chem. Rev. 2012, 112, 2557; b) A. Karakulina, A. Gopakumar, I. Akçok, B. L. Roulier, T. LaGrange, S. A. Katsyuba, S. Das, P. J. Dyson, Angew. Chem., Int. Ed. 2016, 55, 292; c) R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, Angew. Chem., Int. Ed. 2017, 56, 3216.