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Efficient, Recoverable, and Durable Polymer-anchored Bifunctional Pincer Catalysts for Chemoselective Transfer Hydrogenation and Related Reactions

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Abstract: A series of polymer-supported cooperative PC(sp^3)P pincer catalysts was synthesized and characterized. Their catalytic activity in the acceptorless dehydrogenative coupling of alcohols and the transfer hydrogenation of aldehydes with formic acid as a hydrogen source was investigated. This comparative study, examining homogeneous and polymer-tethered species, proved that carefully designing a link between the support and the catalytic moiety, which takes into consideration the mechanism underlying the target transformation, might lead to superior heterogeneous catalysis.

Introduction

The grand challenge in modern organic chemistry is to achieve an ideal synthesis in terms of selectivity, atom-, and step-efficiency.[1] This goal led us to develop new catalytic methodologies allowing us to achieve clean and sustainable production of chemicals in such a way that the price of the catalysts, the use of toxic reagents and stoichiometric promoters, the investment in time and energy, as well as the production of wastes are well balanced. Among such methodologies, a one-pot operation using heterogeneous catalysis is important, because it saves time and energy owing to the straightforward separation and purification procedures, as well as the easy recycling of the catalyst.[2] From the perspective of environmentally friendly organic synthesis, alternative reaction pathways, based on C-H activation, and hydrogen transfer reactions, which occur via either H-X or H_2 evolution, rather than via production of high molecular weight by-products, have recently attracted much attention, since they are both waste- and atom-economical.[3] [4]

The most spectacular examples of homogeneous catalysts capable of promoting such processes belong to an emerging class of catalysts in which the ligand backbone actively participates in the bond-breaking and bond-making processes via a reversible structural transformation of the catalyst during substrate activation and product formation.[5] The concept of metal–ligand cooperativity has been exploited to develop a new generation of bifunctional catalysts (Figure 1). Each of these systems operates via a unique ligand-metal cooperation mechanism; however, it is inapplicable for large-scale synthesis due to the high direct costs of the transition metals and the even higher costs of the sophisticated ligands.[6] Therefore, replacing these current homogeneous catalysts with new, efficient heterogenized equivalents has attracted much interest.

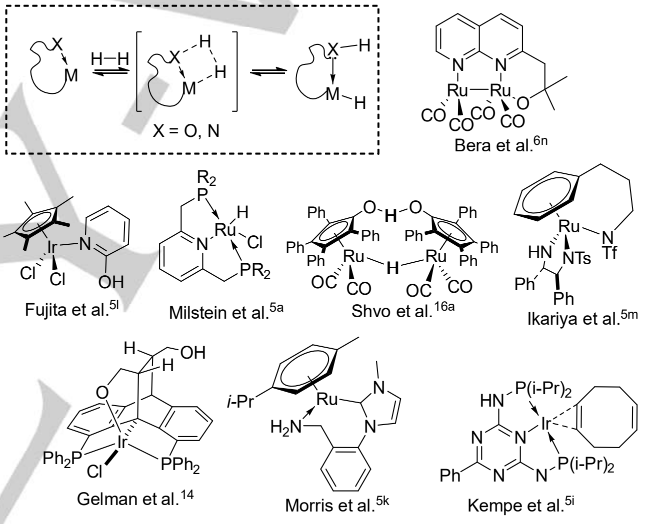

Figure 1. Ligand-metal cooperating systems.

The strategies for sustainable catalysis are numerous and include covalent anchoring to inorganic and organic supports, physical immobilization in inorganic or hybrid matrices,[7] liquid/liquid or solid/liquid biphasic conditions,[8] and others.[9] All these strategies are successful in recycling transition metal catalysts as well as removing metal complexes from waste products. However, unfortunately, when compared with their homogeneous counterparts, the heterogenized catalysts often suffer from lower performance and diminished selectivities due to poorly defined catalytic sites, thus nullifying all the benefits.

Organic polymers are arguably among the most versatile catalyst supports available because of the tunability of various parameters such as molecular weight, polydispersity, support flexibility, solubility, and others.[10] However, careful design of the polymer support alone does not guarantee the desired catalytic activity and selectivity. Clearly, fine-tuning the link between the support and the catalytic moiety, while taking into consideration the mechanism underlying the target catalysis as well as possible catalyst decomposition pathways, could achieve this goal. A

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Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) detailed understanding of the support/catalyst interface is even more important when the aim is to immobilize transition metal catalysts bearing so-called non-innocent (actor) ligands, because even a slight structural modification toward their anchoring may have pronounced deleterous effects on the performance.

We recently disclosed a series of Ir- and Ru-based PC(sp^3)P pincer complexes that can be efficiently prepared in a combinatorial fashion via a Diels-Alder cycloaddition of anthracene-based pincer ligands or their corresponding complexes to a variety of symmetrical dienophiles.[5j, 11] The complexes proved themselves as active ligand-metal cooperating catalysts for efficient acceptorless dehydrogenative processes and other reactions.[12]

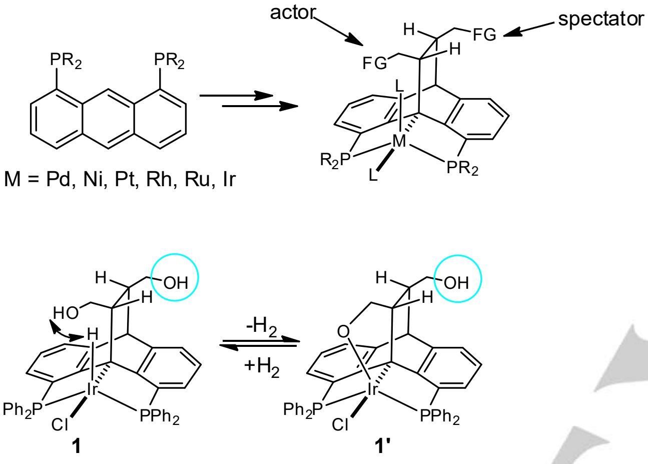


Figure 2. Catalysts developed by our groups.

Mechanistic studies revealed that these catalysts can activate/form chemical bonds via an intramolecular interaction between the metal center and the ligand's functional frontside arm of the catalyst, whereas the backside is a spectator, although it can be used as an anchor (Figure 2).[13] In this manner, immobilization is achieved with minimal perturbation of the catalyst, so that both the catalytic site and the support/catalyst interface remain well defined.

We wish to report the results of our comparative studies on the catalytic activity of Merrifield resin-anchored catalysts in several acceptorless dehydrogenative coupling reactions.

Results and Discussion

Immobilization. The previously described iridium-based **1** and ruthenium-based **2** materials were chosen as catalysts (Figure 3) and the standard commercially available Merrifield resin (200-400 mesh, 3.5-4.5 mmol/g of Cl-loading, 1% cross-linked) as a support for this study. The less sterically demanding backside hydroxyl group has been used for the immobilization of ligand on Merrifield. **L** has been tethered to microporous polystyrene via nucleophilic substitution of the chlorine atoms of a Merrifield resin (**PS**) in DMF for 24 hours at 60 °C, affording **PS-L** with a loading of 0.33 mmol/g (Scheme 1). The high regioselectivity of this step is usually dictated by a diminished steric demand of the backside group.

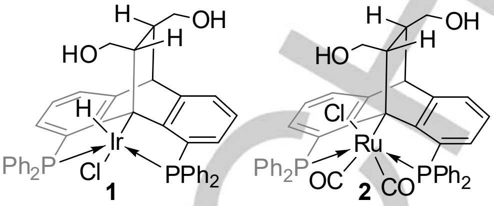
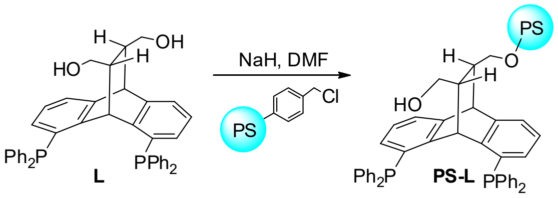


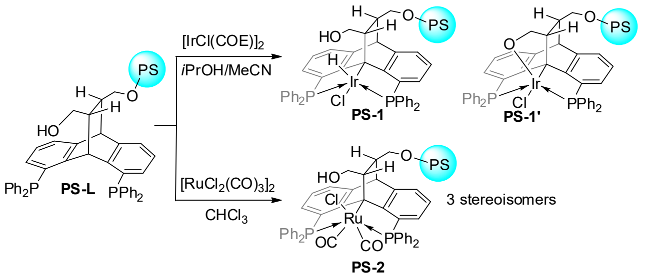
Figure 3. Complexes used in this work.

The ^{31}P NMR of the free ligand **L** possessed a pair of well-resolved doublets at -18.5 and -19.8 ppm in $CDCl_3$. ^{31}P CP-MAS of the supported ligand exhibits a single broad signal centered at -15 ppm, indicating the successful anchoring of the ligand to the support (Figure 4).

Metalation of **PS-L** with $[IrCl(COE)]_2$ proceeds at 60 °C in a *i*-PrOH/acetonitrile mixture to afford **PS-1** as a light-cream powder (Scheme 2). The ^{31}P CP-MAS spectrum shows the presence of some unreacted ligand in addition to two overlapping signals centered at 30 and 12 ppm (Figure 4). The major signal (30 ppm) presumably belongs to **PS-1** - the unsupported **1** that appears in the ^{31}P NMR as a virtual double doublet centered at 28 ppm. The second peak (12 ppm) may be assigned to a **PS-1**-derived iridium alkoxide species that formed as a result of the intramolecular proton-hydride interaction described in Scheme 2. The chemical shift of this minor peak correlates well with the previously reported **1'** that features a pair of doublets at 15 and -1 ppm.[14] MP-AES analysis shows 0.15 wt % of iridium in **PS-1**. The species **PS-1** and **PS-1'** are interconvertible and are both catalytically active as was demonstrated by us previously, [14] thus no isolation or purification is required.



Scheme 1. The immobilization step of **L** on Merrifield resin.



Scheme 2. Synthesis of **PS-1** and **PS-2**.

Synthesis of the ruthenium-based **PS-2** proceeded smoothly as well. Thus, exposing **PS-L** to $[RuCl_2(CO)_3]_2$ in chloroform at room temperature for 24 hours (Scheme 2) resulted in the formation of three stereoisomers of the target compound, different from the location of the chloride ligand, as was described by us previously (50, 16, and 0 ppm, respectively). The ^{31}P CP-MAS spectrum shows the presence of nonmetalated sites in addition to the latter. MP-AES analysis revealed 0.5 wt % ruthenium in **PS-2**.

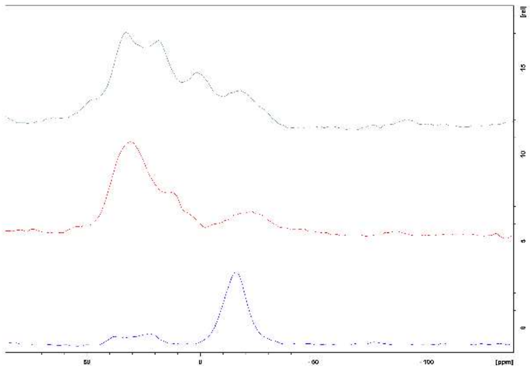
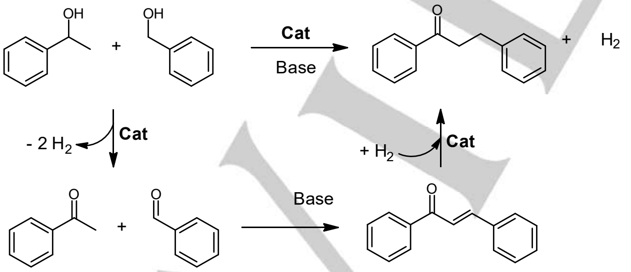


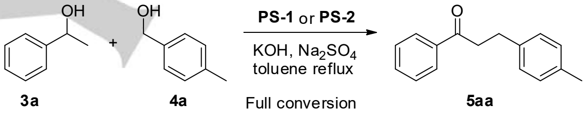
Figure 4. ^{31}P CP-MAS spectrum of **PS-1** (red line), **PS-2** (green line) in comparison with **PS-L** (blue line).

Catalysis. The functional resins **PS-1** and **PS-2** were then tested in the acceptorless dehydrogenative cross-coupling of primary and secondary alcohols to form β-alkylated ketones.[13c] This one-pot dehydrogenation of alcohols to the corresponding carbonyl compounds was followed by aldol condensation and subsequent partial double bond hydrogenation under the same reaction conditions using the unsupported **1** and **2**, which were described by us in the past and, therefore, they appear to be a good benchmark now for comparison purposes (Scheme 3 and Table 1).



Scheme 3. Acceptorless dehydrogenative cross-coupling of primary and secondary alcohols forming β-alkylated ketones.

The optimal reaction conditions derived for the unsupported catalysts **1** and **2** were used as the starting point for our initial experimentation. As we found previously, the ruthenium-based **2** was less efficient than **1** so that complete conversion could only be achieved at a higher catalyst loading (2 mol% versus 1 mol% for **1**) after heating in boiling xylene for 24 hours (12 h for **1**) in the presence of equimolar KOH. Applying these reaction conditions for the cross-coupling of 1-phenylethanol and 4-methylbenzyl alcohol, catalyzed by the Merrifield-supported **PS-1** and **PS-2** in amounts that corresponded to 1 and 2 mol%, respectively, showed full conversion of the starting material to 1-phenyl-3-(p-tolyl)propan-1-one in both cases, implying that catalyst loading may be reduced (Scheme 4). Indeed, a brief optimization revealed that full conversion of the model substrates could be achieved using only 0.02 mol% of **PS-1** and 0.2 mol% of **PS-2**, indicating TONs of 5000 and 500, respectively. These high TON values are especially remarkable because they are at least one order of magnitude higher than for the corresponding non-supported complexes and comparable to the most effective heterogeneous systems described in the recent years and featuring high efficiency in terms of recoverability, recycle and durability.[16] Experimentation with different bases such as KO*t*-Bu, Cs_2CO_3, DBU, or Et_3N, as well as different reaction media such as DMF or DME led to no further improvement. Thus, a stoichiometric mixture of 4-methylbenzyl alcohol and 1-phenyl ethanol resulted in the formation of 1-phenyl-3-(*p*-tolyl)propan-1-one in 92 and 86% yield, after being catalyzed by 0.02 mol% of **PS-1** and 0.2 mol% of **PS-2**, respectively (Table 1, entry 1).



3a 4a 5aa

Full conversion
PS-1: 0.02 mol% 16h
PS-2: 0.2 mol% 24h

Scheme 4. The optimized conditions in the acceptorless dehydrogenative cross-coupling of primary and secondary alcohols with **PS-1** and **PS-2**.

The optimized reaction conditions are applicable to the cross-coupling of a variety of primary and secondary alcohols according to the same scheme. Excellent isolated yields (89-97%) of the corresponding cross-coupled products were obtained using 1-phenyl ethanol and electron-rich to electron-deficient benzyl alcohols as coupling partners and 0.02 mol% of **PS-1** as a catalyst (Table 1, Entries 1-4). The reactions catalyzed by 0.2 mol% of **PS-2** exhibited generally lower selectivity toward the cross-coupled product (63-86% isolated yield) because of the completive homo-coupling of the primary alcohol to the corresponding Tischenko product, benzyl benzoate (Table 1, Entries 1-4).

The same reactivity trend was observed when benzyl alcohol was reacted with a series of 1-phenylethanols possessing electron withdrawing and electron-donating groups – complete conversion to the cross-coupled products in excellent selectivity and isolated yield were obtained using the iridium-based **PS-1** (Table 1, Entries 5-7), whereas only moderate to poor yields were observed using the ruthenium-based **PS-2**. We also found that aliphatic primary alcohols are suitable coupling partners despite that upon dehydrogenation they acquire an enolizable nature.

Here, no self-coupling was observed under iridium or ruthenium catalysis (Table 1, entry 8-9). Finally, homo-coupling of the secondary 1-phenyl ethanol was carried out, also with moderate selectivity (ca. 70% isolated yield of the coupled product accompanied by acetophenone as a major by-product). It is remarkable that at least for the iridium-based supported catalyst, **PS-1**, the performance is comparable to that of the unsupported **1**, whereas its stability is significantly higher (5000 TONs for **PS-1** versus 830 for **1**).

Table 1. Representative coupling of the primary and secondary alcohols catalyzed by **1-2** and **PS-1-2.**[a-b]

[a] **PS-1** (0.02 mol%) or **PS-2** (0.2 mol%), $R^1OH/R^2OH/KOH = 1/1/1$, toluene.
[b] Yield of the isolated compounds as an average of two runs in entries 1-10.

Recovery and reusability of the supported catalysts were demonstrated. Thus, homo- and cross-coupling of alcohols was performed up to five consecutive runs without a notable decline in the performance of the catalyst **PS-1** (Table 2, runs 1-3), whereas the catalyst **PS-2** (Table 2, entries 2-3), as expected, exhibited poorer durability. Owing to the good properties of the catalysts, in terms of stability and reusability, high TON values have been reached, from 24200 to 20200 (Table 2, entries 1-3) when **PS-1** was employed and 1735 and 1935 (Table 2, entries 2-3) using **PS-2**. High efficiency and TONs values of heterogeneous supported catalysts **PS-1** and **PS-2** are expected due to a higher concentration induced on the catalyst surface as a results of the immobilization of the active catalyst. This effect also suggests that the after the immobilization, the combination polymeric support/reaction medium used are effective for regulating the swelling phenomenon and as a results, the catalytic sites are easily accessible active.

Table 2. Recycle of **PS-1-2** in homo- and cross-coupling of alcohols [a-b]

[a] **PS-1** (0.02 mol%) or **PS-2** (0.2 mol%), $R^1OH/R^2OH/KOH = 1/1/1$, toluene.
[b] Yield of the isolated compounds as an average of two runs in entries 1-3.

Encouraged by the excellent performance of the supported catalyst, we decided to apply it to another transformation in order to demonstrate the broad applicability of the approach. Based on the efficient decomposition of formic acid by some of our complexes, we decided to focus on some generic transformations utilizing formic acid as a hydrogen source, such as the selective transfer hydrogenation of carbonyl compounds.[12b, 13a] Although numerous examples of transfer hydrogenation from formic acid (FA) to aldehydes are known, many of them suffer from low chemoselectivity.[17] The most frequent problem in these reactions is aldol-type side-reactivity under basic reaction conditions, which are typically required in transfer hydrogenation. In addition, Tishchenko-type by-products may form under these conditions.[18] Another possible side-reaction is the decarbonylation of aldehydes, which is known to proceed with rhodium and iridium complexes. Finally, uncontrollable hydrogenation of unsaturated aldehydes often accompanies the hydrogenation of the carbonyl group.[19] Therefore, to develop highly selective protocols, new catalysts operating via alternative mechanisms may be employed. Initially, the reaction conditions were optimized using unsupported **1**. In the initial experiment, benzaldehyde as a model substrate was hydrogenated with equimolar formic acid in DME. Interestingly, only incomplete conversion of the model substrate was obtained under these conditions with or without inorganic basic additives. We suspected that premature decomposition of

FA to the corresponding H_2 and CO_2 causes an incomplete reaction. We found, however, that addition of 10 mol% of triethylamine impedes FA decomposition, thus, achieving a complete reduction of the model substrate by **1**. Replacing triethylamine with 5% K_2CO_3 or 20% of sodium formate dramatically lowered the conversion. We also investigated the influence of different solvents on the benchmark reaction. Whereas a low hydrogenation rate was observed in toluene, affording low to moderate conversions, in THF, dioxane, and DME the desired product formed equally well. The reaction temperature had a major effect on the reactivity of the system, for example, an increase from 60ºC to 80ºC raised the conversion rate from 19% to 96%.

Next, we investigated the general applicability of our catalyst system using both supported and unsupported catalysts. To explore the functional group tolerance in more detail, we started to investigate the reactions of different substituted benzaldehydes (Table 3). First, unsubstituted benzaldehydes were fully converted to benzyl alcohols (Table 3, entries 1 and 8) using both **PS-1** and **1** in nearly equal selectivity and efficiency. Benzaldehydes bearing electron-donating (alkyl, *p-,* and *o*-methoxy groups) and electron-withdrawing (bromo- and nitro-) groups yielded the desired products in nearly quantitative yields (Table 3, entries 2-7). Remarkably, benzaldehydes with sensitive functional groups such as nitro were reduced with excellent chemoselectivity under these conditions (Table 3, entries 6).

Table 3. Representative transfer hydrogenation of aldehydes catalyzed by **1** and **PS-1**.[a-b]

[a] **PS-1** or **1** (0.01 mol%), RCHO/FA/TEA = 1/2/1, DME, 80 ºC. [b] Yield of the isolated compounds as an average of two runs in entries 1-9.

Similarly, the hydrogenation aliphatic aldehydes were efficiently accomplished (Table 3, entry 9). Remarkably, decarbonylation, Cannizzaro, and aldol condensation reactions were not observed in this run using both supported **PS-1** and unsupported **1**, stressing again the fact that heterogenization of the molecular catalysts can be performed without a significant loss of their activity.

Finally, recovery and reusability of the catalyst was tested by repeatedly employing **PS-1** as a catalyst in the transfer hydrogenation of benzaldehyde, *p*-bromo-, and *p*-nitrobenzaldehyde. In all the reactions, some decline in the reactivity was observed only after 5 consecutive runs.

Conclusions

In conclusion, we showed that careful design of the link between the support and the catalytic moiety, which takes into consideration the mechanism underlying the target transformation, may lead to very efficient and stable heterogenized catalysts that maintain their high performance in direct comparison with the homogeneous ones and may even exceed them. In particular, we synthesized and characterized a series of polymer-supported cooperative PC(*sp*^{3})P pincer catalysts and demonstrated their excellent catalytic activity in the acceptorless dehydrogenative coupling of alcohols and the transfer hydrogenation of aldehydes with FA as a hydrogen source. Remarkably high TONs were achieved using these sophisticated catalysts after heterogenization.

Experimental Section

All manipulations were performed using standard Schlenk techniques under dry N_2 or Ar. All reagents were purchased from the usual suppliers and used without further purification. All reagents were weighed and handled in air. Flash column chromatography was performed with Merck ultra-pure silica gel (230-400 mesh). All catalytic reactions were carried out under N_2. Yields refer to isolated compounds with greater than 95% purity, as determined by proton Nuclear Magnetic Resonance spectroscopy (1H-NMR) analysis. The CAS numbers of the known compound were listed. Spectroscopy data of the known compounds match the data reported in the corresponding reference. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded on Bruker 400 or 500 MHz instruments with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane. Elemental analysis of phosphorous for loading calculations was carried out using PE analyzer 2400 Series II. Metal loading was measured using a MP-AES 4210 instrument.

Synthesis of ligand ***PS-L***. The 25 mL round bottom flask equipped with a double surface condenser was charged with **L1** (0.997 g, 1.57 mmol) in 10 mL of anhydrous DMF under N_2 flow. To clear the solution, NaH (251.2 mg, 60% oil dispersion, 6.28 mmol, 4 equiv.) was added portionwise and then the reaction mixture was heated at 50 °C for 30 minutes. After having been cooled to RT, the Merrifield resin (1.57 g, 5.52 mmol, 3.5 equiv.) was added and heating to 70 °C was resumed for another 36 hours. Filtration of the product afforded **PS-L** as a light-beige solid that was washed with 3 mL of milli-Q water, 3 mL of MeOH, 3 mL of THF, and 3 mL of hexane and dried under vacuum for 24 h. The loading was determined by Elemental Analysis on phosphorous (P: 2.05 %, 0.33 mmol/g).

Synthesis of ***PS-1****.* The supported ligand **PS-L** (800 mg) and $[IrCl(COE)_2]_2$ (122mg, 0.14 mmol, 0.5 equiv.) in an acetonitrile/isopropanol mixture was stirred for 24 hours at 60 °C under a constant flow of N_2. Filtration provided the product as a light-cream solid and then it was washed with 3 mL of THF and 3 mL of hexane.

*Synthesis of **PS-2***. The supported ligand **PS-L** (800 mg) and $[RuCl_2(CO)_3]_2$ (70 mg, 0.14 mmol, 0.5 equiv.) in $CHCl_3$ was stirred for 24 hours at RT under a constant flow of N_2. Filtration afforded the product as a yellow-orange solid and then it was washed with 3 mL of THF and 3 mL of hexane.

General reaction conditions for coupling of the primary and secondary alcohols. A flame-dried Schlenk tube was charged with **PS-1** or **PS-2** (0.02-0.2 mol%, 25-40 mg, respectively), KOH (1 equiv.), and Na_2SO_4 (200 mg) in toluene (1.5 mL) under Nitrogen. Alcohols (1 mmol of each) were added and the mixture was heated to 150 °C with stirring for the specified time. Filtration was performed and then the filtrate was evaporated under reduced pressure to obtain the product. The product was purified by Combi Flash Chromatography.

General reaction conditions for the transfer hydrogenation of aldehydes. A flame-dried Schlenk was charged with **PS-1** (0.01 mol%, 13 mg) and FA/TEA (2 equiv.) in DME (1 mL) under Nitrogen. The aldehyde (1 mmol) was added and the mixture was heated at 80°C with stirring for the specified time, followed by filtration. Then the filtrate was evaporated under reduced pressure to obtain the product, which was purified by Combi Flash Chromatography.

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Keywords: cooperative catalysis • heterogenized • pincer complexes • acceptorless dehydrogenation • transfer hydrogenation • formic acid

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Entry for the Table of Contents

Layout 1:

FULL PAPER

Durable and recyclable polymer-supported bifunctional cooperative PC(*sp*^{3})P pincer catalysts for acceptorless dehydrogenative coupling of alcohols and transfer hydrogenation of aldehydes.

Shuruq Mujahed, Federica Valentini, Shirel Cohen, Luigi Vaccaro, Dmitri Gelman**

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Efficient, Recoverable, and Durable Polymer-anchored Bifunctional Pincer Catalysts for Chemoselective Transfer Hydrogenation and Related Reactions.