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Asymmetric Nanocatalysis: N-Heterocyclic Carbenes as Chiral Modifiers of Fe_3O_4/Pd nanoparticles**

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Although asymmetric homogeneous catalysis has been a major focus of academic research over the past decades, only very few catalytic systems have proven suitable for large-scale industrial production.[1] Heterogeneous catalytic systems are favored by industry because of the ease of handling, workup, and purification of products, in addition to the robustness and reusability of the catalyst itself. In order to overcome problems of homogeneous catalytic reactions, many different concepts have been developed to generate chiral heterogeneous catalysts.[2]

Nanoparticles (NPs)[3] can be considered a semi-heterogeneous support,[4] as they are readily dispersed in the reaction medium, exhibit an intrinsically high surface area, and display highly accessible surface-bound catalytic sites. Fe_3O_4 NPs[5] have been increasingly recognized as an attractive support for applications in (asymmetric)[2g,6] catalysis;[7] these NPs are readily available, robust, and magnetically recoverable (thereby obviating tedious catalyst filtration after the reaction).

N-Heterocyclic carbenes (NHCs) are known to form exceptionally stable complexes with many metals. Consequently, they have emerged as versatile donor ligands in transition-metal catalysis[8] and several highly selective applications in asymmetric catalysis have been reported.[9] However, to the best of our knowledge, the successful use of enantiomerically pure NHCs as chiral modifiers[2,10] for heterogeneous catalysts has not yet been reported.

Herein, we report the formation of Pd NPs on magnetite (Fe_3O_4) and subsequent surface modification of the resulting bimetallic NPs by chiral, enantiomerically pure NHCs. This readily accessible catalyst was both successfully applied in asymmetric heterogeneous catalysis and also recycled several times.

The Fe_3O_4/Pd NPs were prepared by the so-called wet impregnation method as reported in the literature.[11] In order to explore the possibility of achieving asymmetric catalytic reactions on active NPs, the surface was modified with chiral, enantiomerically pure imidazolinium salts **L1**–**L5** (Figure 1, Scheme 2) under basic conditions. These modifiers were selected because they are easily prepared from the corresponding amino alcohols (thus allowing ample structural diversity) and because they can be readily converted to the free NHCs using base.[12]

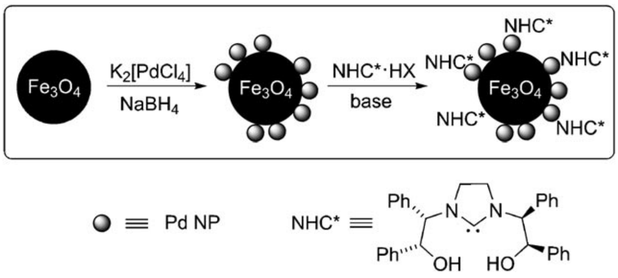

Figure 1. Preparation of Fe_3O_4/Pd NPs modified by chiral NHC; for clarity, the sizes are not represented proportionally.

Initially, the Fe_3O_4/Pd/**L1** nanocatalyst[13] was characterized by X-ray photoelectron spectroscopy (XPS): the spectrum showed binding energies for the Pd 3d electrons of 335.7 and 340.7 eV, which corresponds to Pd in the 0 oxidation state. Further signals at 400 and 285 eV were attributed to the N 1s and C 1s energy levels, respectively.[13] ATR-IR spectroscopy further supported the presence of an NHC-modified surface, since marked differences between the spectra of the free salt **L1** and of Fe_3O_4/Pd/**L1** are evident.[13] Similarly, different BET surfaces were obtained for Fe_3O_4, Fe_3O_4/Pd and Fe_3O_4/Pd/**L1** (43, 21, and 35 $m^2 g^{-1}$, respectively).[13]

The scanning electron microscopy/energy-dispersive X-ray analysis (SEM-EDX) spectrum of the NHC-modified surface also indicated the presence of all expected elements (Fe, Pd, O, and C) and more precisely a Pd content of 0.9 wt %. Inductively coupled plasma optical emission spectroscopy (ICP-OES) also showed a Pd loading of 0.92 wt %. Additionally, the NPs were characterized by transmission

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electron microscopy (TEM) after the surface had been modified with **L1**. The TEM images show iron oxide NPs 25–35 nm in diameter (Figure 2).

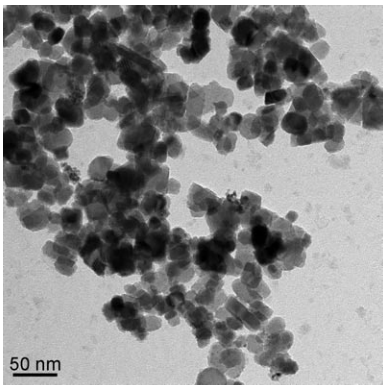
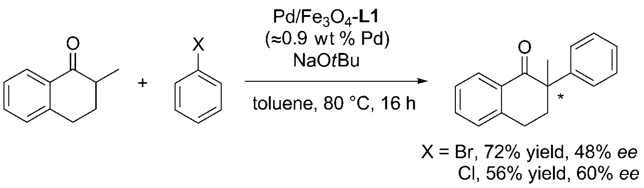


Figure 2. TEM image of Fe_3O_4/Pd NPs after modification with **L1**.

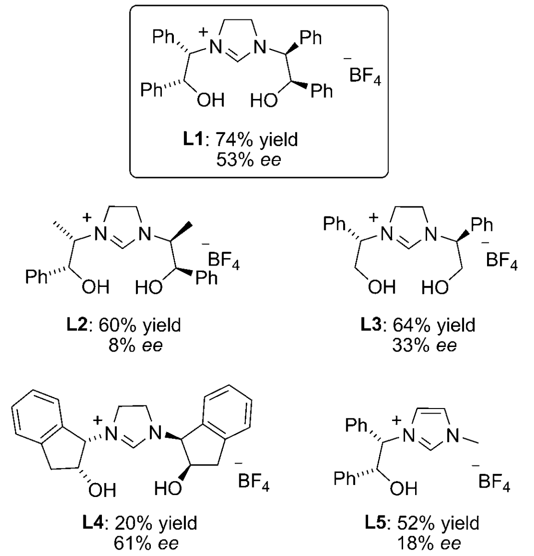
The catalytic properties of the surface-modified Fe_3O_4/Pd NPs were initially evaluated in the α-arylation reaction of 2-methyl-1-tetralone and various phenyl halides in toluene at 80 °C using NaO*t*Bu as the base (Scheme 1). This Pd-catalyzed asymmetric transformation provides valuable intermediates for the pharmaceutical industry.[14–16]



Scheme 1. The asymmetric α-arylation of 2-methyl-1-tetralone using chloro- and bromobenzene.

We found that the Fe_3O_4/Pd/**L1** NPs performed as a versatile chiral nanocatalyst in the reaction with bromobenzene, furnishing the corresponding α-arylated product in 72 % yield and with pronounced selectivity of 48 % *ee*; the reaction with chlorobenzene proceeded in 56 % yield and 60 % *ee*. There was no reaction in the absence of Pd when only **L1**-modified Fe_3O_4 was employed. To better understand the effect of modifier on the surface, we also conducted the reaction without any chiral modifier (Fe_3O_4/Pd only); this reaction furnished the expected α-arylated product in 22 % yield (naturally, in racemic form) along with a significant number of by-products, one of which was identified (GC–MS) as biphenyl.

We continued our study by preparing the catalysts in situ, mixing Fe_3O_4/Pd NPs with one of the corresponding imidazolinium salts **L1**–**L5** in the presence of base. All further experiments were run using this in situ protocol, obviating the isolation/purification of the desired NHC-modified NPs. The NPs with 2.5 mol % of **L1** were found to be optimal in terms of selectivity and reactivity. Increasing the amount of **L1** to 10 mol % led to a dramatically decreased activity, and lowering to 1.25 mol % resulted in a significantly lower enantioselectivity.[13] Thus, when we used 2.5 mol % **L1** and followed the indicated in situ protocol, the α-arylated product was isolated in 74 % yield with 53 % *ee* (Scheme 2). Alternatively, prior mixing of the imidazolium salt **L1** with the base and stirring for 1 h, followed by addition of the Fe_3O_4/Pd NP resulted in an equally active and selective (48 % *ee*) catalyst.



Scheme 2. Effect of various chiral modifiers on the yield and enantioselectivity of the α-arylation of 2-methyl-1-tetralone with bromobenzene. Reaction conditions: Fe_3O_4/Pd (50 mg), ligand (2.5 mol %), 2-methyl-1-tetralone (0.3 mmol), PhBr (0.6 mmol), NaO*t*Bu (0.6 mmol), toluene (3.0 mL).

The heterogeneous nature of this catalyst system was demonstrated by a number of experiments:

Firstly, the Fe_3O_4/Pd/**L1** catalyst was used five times without any significant decrease in either activity or selectivity.[13] After completion of the first α-arylation reaction, the paramagnetic catalyst was removed with a magnet, washed sequentially with EtOH and CH_2Cl_2, and finally dried under high vacuum for 30 min. A new reaction was then performed with fresh reactants and NaO*t*Bu under the same conditions.[13] It is important to note that the residual solution (after the magnetic removal of the Fe_3O_4/Pd/**L1** NP) was no longer catalytically active (filtration test).[13]

Secondly, the leaching of the catalytically active Pd from the Fe_3O_4 support was studied by ICP-OES analysis of the catalyst before and after the second reaction cycle (Scheme 1, X = Br): the Pd concentration in the NP was found to be 0.92 wt % before and 0.88 % after the reaction. The liquid phase of the reaction mixture had a low Pd content of 0.232 ppm (ICP-OES). This negligible difference in the catalysts' Pd content shows the stabilizing effect of **L1**. For comparison, the unmodified catalyst (Fe_3O_4/Pd only) displayed a significantly decreased activity in the second cycle, and in the third cycle no reaction took place. This behavior can be attributed to the leaching of Pd into the solution (16.6 ppm, determined by ICP-OES) and depletion of the Pd content on the magnetite surface.

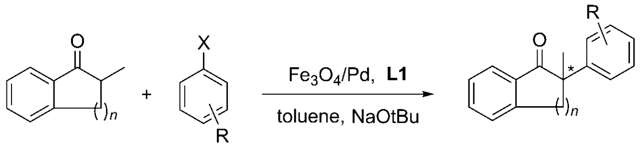
The mercury-poisoning experiment[17] is well established for the investigation of the heterogeneous nature of a catalyst system. While a homogeneous Pd–**L1** complex derived from [{Pd(allyl)Cl}$_2$] and **L1** did not lose its catalytic activity upon addition of elemental Hg, the same addition of Hg completely deteriorated the catalytic activity of the Fe_3O_4/Pd/**L1** NP catalyst by poisoning the surface—unequivocal proof of the heterogeneous nature of the catalyst.[13]

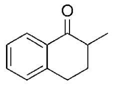
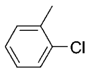
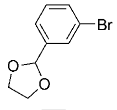
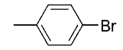
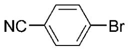
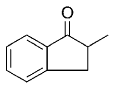
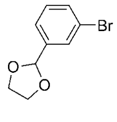
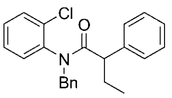
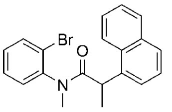
Finally, the heterogeneous nature of the Fe_3O_4/Pd/**L1** catalyst system is confirmed by the dramatically lower *ee* obtained with several homogeneous Pd–**L1** complexes. As a typical example, the combination of Pd(OAc)$_2$ and **L1** led to the formation of racemic α-arylation product only.[13] In addition, under all homogeneous reaction conditions examined, biphenyl and other products were also observed by GC–MS. Similarly, when magnetite NPs were added to the reaction mixture (again using Pd(OAc)$_2$ and **L1**) only the racemic product was obtained.[13] These experiments strongly emphasize the importance of the components of this novel catalyst system: a formed heterogeneous paramagnetic Fe_3O_4/Pd NP catalyst stabilized and activated by chiral NHCs bearing secondary hydroxy groups.[18] To the best of our knowledge, this represents the first successful use of NHCs as chiral modifiers of NP catalysts.[19]

Clearly, the success of the asymmetric reaction will strongly depend on the structure of the ligand. A screening of various alternative ligands showed pronounced effects not only with regard to the activity, but also with regard to the enantioenrichment of the α-arylated product (Scheme 2). Especially for the latter feature, hydroxy groups on the ligand seem to be crucial.[20]

To test the substrate scope of the Fe_3O_4/Pd/**L1**-catalyzed enantioselective α-arylation reaction, various aryl halides were examined (Table 1). Notably, unactivated aryl chlorides also reacted with 2-methyl-1-tetralone, furnishing the desired product in 56% yield with 61% *ee*, whereas in the same reaction with iodobenzene the product was formed with a slightly reduced enantioselectivity of 45% *ee* (Table 1, entries 2 and 3). The *meta*- and *para*-substituted aryl bromides gave good yields and moderate to good *ee* values. The reactions of 2-methyl-1-indanone with aryl bromides resulted in good yields with substantial enantioselectivities (Table 1, entries 8 and 9). Moreover, in challenging intramolecular α-arylation reactions (Table 1, entries 10 and 11) the **L1**-modified NP catalyst showed good activity and selectivity, providing the indanone products in up to 85% *ee*.

Table 1: Asymmetric α-arylation of ketones with aryl halides catalyzed by Fe_3O_4/Pd/**L1** (using the in situ protocol).[a]



Entry	Ketone	Aryl halide	Yield [%][b]	*ee* [%][c]
1		Ph–Cl	56	61
2		Ph–Br	74	53
3		Ph–I	70	45
4			58	33
5			90	61
6			83	60
7			78	57
8		Ph–Br	61	35
9			66	40
10			91[d,e]	81[e]
11			68[d]	85

[a] Reaction conditions: Ketone (0.3 mmol), aryl halide (0.6 mmol), NaO*t*Bu (0.6 mmol), Fe_3O_4/Pd NP (50 mg), ligand **L1** (2.5 mol%). [b] Yield of isolated product. [c] Determined by HPLC on a chiral stationary phase. [d] Substrate (0.3 mmol), NaO*t*Bu (0.6 mmol), Fe_3O_4/Pd modified with **L1** (50.0 mg), PhMe(3.0 mL). [e] Under homogeneous conditions ([{Pd(allyl)Cl}$_2$] (5.0 mol%), ligand **L1** (10 mol%), substrate (0.3 mmol), NaO*t*Bu (2.0 equiv), PhMe (3.0 mL)); the product was formed in 32% yield with 24% *ee*.

In conclusion, we have reported the formation of a heterogeneous catalyst from Fe_3O_4/Pd NPs and enantiomerically pure NHCs. The resulting NP catalyst with its new ensemble of catalytically active entities[21] catalyzed asymmetric α-arylation reactions with up to 85% *ee*. In addition, simple magnetic removal and recycling of the catalyst was shown to proceed without loss of activity and selectivity. We are currently working on the elucidation of the underlying active principle of this new class of heterogeneous catalysts for asymmetric catalysis.

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[19] It should be noted that Thomas et al. have reported that the combination of an immobilized chiral ligand together with SiO$_2$-supported bimetallic NPs can lead to enhanced enantioselectivity: for the positive effect of immobilization of chiral transition-metal catalysts in nanopores, see: a) R. Raja, J. M. Thomas, M. D. Jones, B. F. G. Johnson, D. E. W. Vaughan, *J. Am. Chem. Soc.* **2003**, *125*, 14982; b) J. M. Thomas, B. F. G. Johnson, R. Raja, G. Sankar, P. A. Midgley, *Acc. Chem. Res.* **2003**, *36*, 20; c) M. D. Jones, R. Raja, J. M. Thomas, B. F. G. Johnson, D. W. Lewis, J. Rouzaud, K. D. M. Harris, *Angew. Chem.* **2003**, *115*, 4462; *Angew. Chem. Int. Ed.* **2003**, *42*, 4326.

[20] A similar effect was observed in nanocrystalline aerogel-prepared MgO-catalyzed asymmetric epoxidation and Michael reactions using chiral modifiers: a) B. M. Choudary, M. L. Kantam, K. V. S. Ranganath, K. Mahender, B. Sreedhar, *J. Am. Chem. Soc.* **2004**, *126*, 3396; b) B. M. Choudary, K. V. S. Ranganath, U. Pal, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2005**, *127*, 13167.

[21] It is important to note that this is not simply the immobilization of a successful homogeneous catalyst, which, once immobilized, still follows the same activity principle. On the contrary, Fe$_3$O$_4$/Pd/**L1** is a novel catalyst with its own activity principle.