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A Case for Enantioselective Allylic Alkylation Catalyzed by Palladium Nanoparticles

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The use of well-defined metal nanoparticles for catalytic transformations of organic substrates is an exciting[1] and rapidly growing area.[2] Metal nanoparticles have been proven to be efficient and selective catalysts for reactions which are also catalyzed by molecular complexes such as olefin hydrogenation or C−C coupling, for example, as well as for reactions which are not or poorly catalyzed by molecular species such as aromatic hydrocarbons hydrogenation.[2d,3b] Unambiguous distinction between colloidal and true homogeneous catalysis is, however, often very difficult.[3] During the past few years, we have studied the synthesis of metal nanoparticles through an organometallic approach.[4] This method leads to nearly monodisperse particles of very small size displaying interesting surface coordination chemistry. This point can, in principle, be evidenced by spectroscopic methods (IR, NMR) or by the reactivity induced by the presence of ligands, for example, asymmetric induction. However, despite impressive progress in asymmetric catalysis,[5] only one colloidal system has been found to display an interesting activity, namely, Pt(Pd)/cinchonidine for the hydrogenation of ethyl pyruvate.[6] Palladium particles also recently attracted a high interest as catalysts for C−C coupling reactions (mainly Heck and Suzuki couplings).[7] Since Pd complexes are well-known catalysts for enantioselective allylic coupling reactions, we decided to examine the activity of palladium nanoparticles for this reaction. The ligand we chose is a chiral diphosphite with a xylose backbone, **1**[8] (Scheme 1), which has been successfully used for the stabilization of molecular Pd complexes involved in catalytic allylic alkylation.[9] It contains phosphite groups able to coordinate firmly at the surface of nanoparticles together with oxygen atoms able to interact weakly with this surface.

We describe hereafter the synthesis of palladium nanoparticles stabilized by the chiral xylofuranoside diphosphite **1** (Scheme 1), their catalytic activity in the Pd-catalyzed allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene (*rac*-**I**) with dimethyl malonate (Table 1), and experiments aiming at distinguishing these observations from a classical molecular catalysis. This is to the best of our knowledge the first report of a reaction catalyzed by nanoparticles giving rise to >95% ee outside the Pt/cinchonidine system.[6]

The Pd nanoparticles (**Coll.1**) were isolated as a black powder after decomposition of $[Pd_2(dba)_3]$ by H_2 (3 bar) at room temperature in THF in the presence of **1** (Pd/**1** = 1/0.2; Scheme 1). Transmission electron microscopy revealed the presence of small spherical, but in some cases agglomerated, particles of ca. 4 nm mean size (Scheme 1), while wide-angle X-ray scattering analyses evidenced the fcc structure of bulk palladium.[10]

Scheme 1. Synthesis and TEM Micrograph of Pd/1 Nanoparticles (**Coll.1**)

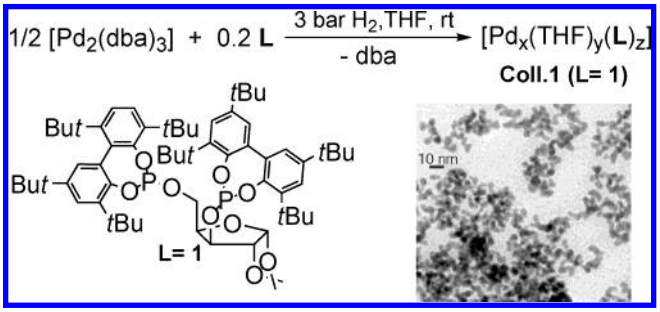
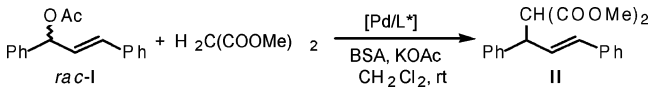


Table 1. Asymmetric Allylic Alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene (*rac*-**I**) with Dimethyl Malonate Catalyzed by **Coll.1**[a]



entry	catalyst	I/Pd/L*[a]	time (h)	conv. (%)[b]	ee **II** (%)[c]	ee **I** (%)[c]
1	**Coll.1**	100/1/0.2	24	56	97 (*S*)	89 (*S*)
2	**Coll.1**	100/1/0.2	168	59	97 (*S*)	89 (*S*)
3	**Coll.1**	100/1/1.05	168	61	97 (*S*)	89 (*S*)

[a] Molar ratio between **I**, Pd, and excess ligand added in the catalysis.[10] [b] Determined by ^{1}H NMR. [c] Determined by HPLC on a Chiracel-OD column. Absolute configurations of **I**[13c] and **II**[15] in parentheses.

The reaction of *rac*-3-acetoxy-1,3-diphenyl-1-propene (*rac*-**I**) with dimethyl malonate under basic conditions[11] was studied using as catalyst either **Coll.1** or a molecular complex (**Mol.1**) generated in situ by reaction of $[Pd(C_3H_5)Cl]_2$ and **1**, according to previous literature.[9,12] Both systems led to the expected alkylated product. The enantiomeric excess found using the molecular catalyst matched the published data, whereas that found using the colloid catalyst was slightly higher (ca. 97%(*S*) ee; see Table 1). The reactions observed using the two catalytic systems, however, displayed some clear differences, the most striking ones being the absence of completion of the reaction associated to a very high kinetic resolution (89% ee in the remaining substrate) when using **Coll.1** as a catalyst.[13] Thus, only ca. 55% product (**II**) was obtained after 24 h, and this value did not change after 168 h. In contrast, quasi total conversion but no kinetic resolution of the substrate was observed after 1.5 h using **Mol.1** as the catalyst.

Since the reaction rates were found to be very different in the two systems, a comparison proved difficult, and the formation from the particles of a small amount of an active molecular catalyst could not be excluded. To be able to rule out this possibility and, more generally, to better characterize the colloidal system, control

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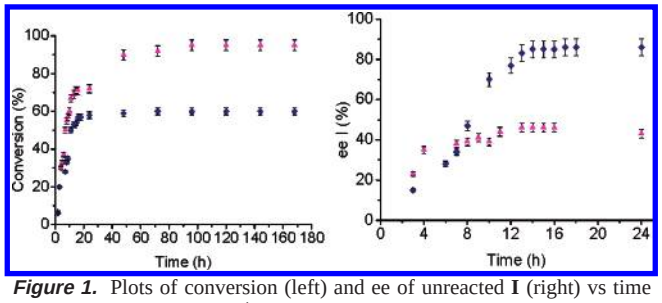

Figure 1. Plots of conversion (left) and ee of unreacted **I** (right) vs time using as catalysts **Coll.1** (◆) and **Mol.1** 1/10 000 (▲).

experiments were carried out which have all been found reproducible and are described in the Supporting Information. The results are the following: (i) Excess ligand added to the colloidal system changed neither the course nor the selectivity and kinetic resolution of the reaction. (ii) Addition of excess substrate after 24 h (time for stabilization of the reaction) led to a further conversion of the (*R*)-**I** enantiomer and, consequently, accumulation of the *S*-one with the same enantiomeric excess (97%); this operation could be reproduced three times with the same activity and selectivity. (iii) The molecular catalyst-to-substrate ratio (Pd/**I**) was varied between 1/100 (original literature report)[9] and 1/10 000. For the latter ratio, the initial reaction rate was found comparable to that of the colloidal system but, interestingly, the conversion of the substrate was quasi complete and the enantiomeric excess of the substrate remained limited and constant at ca. 40%. For less dilute systems, the ee was smaller (1/2000: 27%; 1/500: 0). For higher dilutions (1/100 000), the catalytic system became very slow and the data became doubtful; notably, the ee of the substrate remained low (ca. 16%). (iv) Conversion of an enriched substrate was achieved with both the colloidal and the very dilute molecular systems (1/10 000). After 30 h, only 10% of substrate (84% (*S*) ee) was converted in the colloidal case to be comparable to 67% in the molecular one leading to products of ca. 95% ee in both cases. (v) Plots of $k((R)\text{-}\mathbf{I})/k((S)\text{-}\mathbf{I})$[14] versus time calculated for both the colloidal and the molecular 1/10 000 catalysts revealed two different stable values, namely ca. 12 for the colloidal and 2 for the dilute molecular system (a similar value was obtained for the 1/100 000 system). (vi) Poisons[3b] were added to the different catalytic systems: addition of mercury or CS_2 at the beginning of the reaction totally inhibited the reactions catalyzed by colloids, whereas it had little or no effect on the molecular ones (CS_2 slowed down the reaction but no kinetic resolution was observed). Addition of CS_2 after a 3-h reaction time stopped the colloidal catalytic system. However, addition of mercury after the same reaction time had only a slowing effect. (vii) Potential degradation products of **1** were used as ligands to prepare **Coll.2** and **Coll.3**; these species were found inactive in catalysis.[10] (viii) Finally, TEM analyses of the colloids did not show any significant change in the size and shape of the particles after 7 days of catalytic reactions. Figure 1 shows conversion and ee of unreacted **I** versus time using catalysts **Coll.1** and **Mol.1**.

The main difference between the colloidal and the molecular systems lay in the relative rates of alkylation of the two enantiomers of the substrate. The kinetic preference for the *R*-substrate was only a factor of 2 in the molecular system, whereas it was clearly higher in the colloidal one (12 to 20). This induced an apparent absence of reaction with the sample enriched in the *S* substrate for the colloidal catalyst. This apparent lack of reactivity observed at 58−60% conversion was not due to catalyst deactivation, as demonstrated by further addition of substrate which led to its alkylation at the same rate and with the same selectivity. The result was a very high kinetic resolution yielding at the end of the reaction both nearly enantiomerically pure substrate and product. Furthermore, poisoning experiments, although questionable,[3b,c] agreed with the colloidal character of the catalysts prepared from nanoparticles.

In conclusion, this communication reports a facile synthesis of novel palladium nanoparticles of low size dispersity and stabilized by an asymmetric diphosphite. These particles display a high selectivity as catalysts for an asymmetric allylic alkylation reaction. The reaction mainly proceeds with one enantiomer of the substrate, hence demonstrating a very high degree of kinetic resolution. The same reaction catalyzed by a corresponding molecular species accommodating the same diphosphite ligand and in conditions of dilution where the rates of both catalysts match proceeds at similar rates with both enantiomers. This demonstrates that two different mechanisms operate according to the nature of the catalyst. This is to the best of our knowledge the first report of an asymmetric C−C coupling reaction catalyzed by nanoparticles with a high enantiomeric excess and, moreover, the first nanoparticle-catalyzed reaction outside hydrogenation with the Pt/cinchonidine system leading to high enantioselectivity.

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Supporting Information Available: Synthesis and characterization procedures for nanoparticles, and full description of catalytic reactions, control experiments, and kinetic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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