Brief Communications

Palladium nanocarbon catalysts (Pd/CNT) as potential enantioselective heterogeneous systems. The behavior in the hydrogenation and hydroarylation of unsaturated substrates

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Hydroxy-CNT were modified with optically active α-amino acids. The resulting chiral derivatives were directly palladated with Pd_2dba_3 and used to catalyze the hydrogenation of α-acetamidostyrene and α-phenylcinnamic acid as well as the hydroarylation of norbornene with iodoarenes. All the catalytic reactions afforded products containing a new chiral carbon center in high yields, though as racemates. Apparently, asymmetric induction is precluded because the palladium sites on the CNT surface are spatially apart from the chiral carbon centers in amino acid groups.

Key words: carbon nanotubes, palladium nanoclusters, hydroarylation, hydrogenation, catalysis.

Enantioselective synthesis and catalysis are among the most important challenges in organic chemistry, first of all because chiral molecules are essential constituents of most drugs and different enantiomers or diastereomers produce substantially different effects on the human body. For this reason, the synthesis of pure enantiomers is of primary importance for medicinal chemistry and pharmaceutics.

The most intriguing results in this area have been obtained in the last few decades when dealing with homogeneous catalysts based on transition metal complexes. Novel ligands for these catalysts have been proposed and synthesized. Many of these ligands show directional effects in the sense that they provide the desired stereochemical outcome only for a particular group of compounds. As for heterogeneous catalysts, Oosthuizen and Nyamori in their recent review[1] concerned with carbon-supported platinum metals made no reference to chiral palladium nanocarbon catalysts (Pd/CNT).

Novel nanocarbon materials (fullerenes, nanotubes, *etc.*) make it possible to prepare catalysts with an active metal as nanoclusters immobilized on a carbon material. This material acts as both a catalyst carrier and a ligand.

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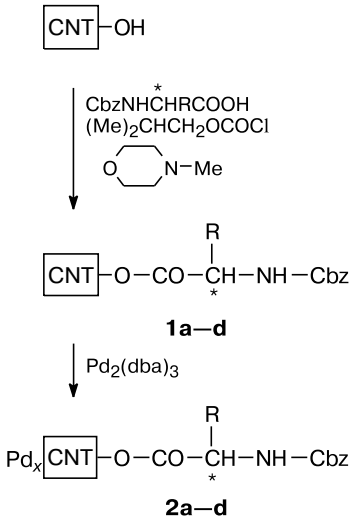
Earlier,[2] we have proposed a new straightforward method for the synthesis of a catalyst in a neutral medium from the zero-valent palladium complex $Pd_2(dba)_3$. Originally, this method has been used to deposit palladium on carbon nanotubes (CNT). The resulting catalyst is highly effective in cross-coupling (Suzuki, Heck, and Sonogashira) reactions. Later,[3–7] we have examined the catalytic activities of palladium catalysts based on fullerene C_{60}, nanodiamond, graphene, and a purely superparamagnetic inorganic complex made up of Fe_3O_4 and a double salt layer and studied the hydrogenation of unsaturated hydrocarbons. However, all those catalysts were *a priori* achiral.

To obtain potentially enantioselective catalysts, we performed chiral modification of single-walled hydroxy-CNT. Earlier,[8] we have described in detail the starting material and its acylation with optically pure natural α-amino acids. The reaction sequence is shown in Scheme 1.

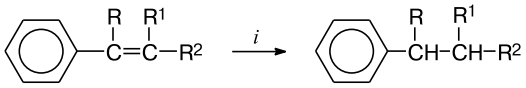
Scheme 1



R = $CH(Me)_2$ (**a**), CH_2CH_2SMe (**b**), $(CH_2)_3$ (proline) (**c**), CH_2Ph (**d**)

Here we presented the results of the use of catalysts **2a—d** in those reactions that allow asymmetric induction through the formation of a new chiral center on the carbon atom. Such reactions include hydrogenation of prochiral substituted olefins (Scheme 2) and hydroarylation of norbornene (Scheme 3). The Suzuki and Heck reactions were not considered because of their poor stereochemical scope.

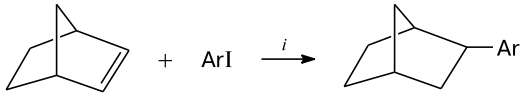
Scheme 2



3: R = NHAc, $R^1 = R^2 = H$; **4:** R = H, R^1 = Ph, R^2 = COOH

Reagents and conditions: *i.* catalyst, $p(H_2)$ = 19 atm, 60 °C, 5 h.

Scheme 3



Reagents and conditions: *i.* catalyst, HCOOH, Et_3N, DMSO.

Derivatives of L-valine, L-methionine, and L-proline were used as catalysts for the hydrogenation of such prochiral substituted olefins as α-acetamidostyrene (**3**) and α-phenylcinnamic acid (**4**). Conversions of these substrates varied appreciably, probably because of the inhomogeneity of the catalyst. The best results obtained are summarized in Table 1. One can see that the conversion of substrate **4** in the hydrogenation is lower than that of substrate **3**.

L-Proline and L-phenylalanine derivatives were employed for the hydroarylation of norbornene (Scheme 3). The results obtained are given in Table 2

Table 1. Hydrogenation of α-acetamidostyrene and α-phenylcinnamic acid on the palladium catalysts prepared from hydroxy-CNT acylated with enantiomeric α-amino acids[a]

Entry	Catalyst	Substrate (S)	S/Cat[b] (mol/g-atom)	MeOH /mL	Conversion (%)
1	3% Pd—CNT—L-valine[c]	$PhC(NHAc)=CH_2$	1000	3	92
2	3% Pd—CNT—L-valine[c]	$PhC(NHAc)=CH_2$	200	2	100
3	3% Pd—CNT—L-valine[c]	PhCH=C(Ph)COOH	200	2	71
4	6% Pd—CNT—L-methionine[d]	$PhC(NHAc)=CH_2$	200	2	65
5	6.7% Pd—CNT—L-proline[d]	$PhC(NHAc)=CH_2$	200	2	100
6	6.7% Pd—CNT—L-proline[d]	PhCH=C(Ph)COOH	200	2	68

[a] The hydrogenation conditions: $p(H_2)$ = 19 atm, 60 °C, 5 h.
[b] The substrate/catalyst ratio.
[c] The amount of the catalyst is 4 mg.
[d] The amount of the catalyst is 2 mg.

Table 2. Hydroarylation of norbornene on the palladium catalysts prepared from hydroxy-CNT acylated with enantiomeric α-amino acids

Amino acid residue	ArI	*t*/h	*T*/°C	Conversion (%)
L-Proline	C_6H_4MeI	7	65	69
L-Proline	C_6H_4MeI	7	75	97
L-Proline	C_6H_4MeI	7	120*	0
L-Phenylalanine	C_6H_4MeI	7	65	65
L-Phenylalanine	C_6H_5I	10	75	100

* The catalyst decomposes at 120 °C.

It is worth noting that all reaction products are racemates. Therefore, the catalysts under discussion show no enantioselectivity. Apparently, this is because palladium clusters are bound to strained double bonds[2] outside the zone of catalytic reactions. Their arrangement along CNT is random, regardless of the acylating amino acid as a chiral inductor. Clearly, the steric relations between the Pd atoms and the amino acid during the formation of the catalyst cannot be controlled. Now we are studying an alternative approach to the synthesis of a catalyst containing an enantiomeric acid directly bound to a palladium nanocluster.

Experimental

Modification of hydroxynanotubes with optically active amino acids. For the acylation of hydroxy-CNT as well as for the synthesis and characteristics of compounds **1a—c**, see Ref. 8. Compound **1d** was obtained as described earlier.[8] Found (%): C, 83.35; H, 1.29; N, 0.84.

Palladation of acylated hydroxy-CNT. Products **2a—c** were characterized earlier.[8] For the details of the synthesis of compound **2d**, see Ref. 8. Found (%): C, 80.09; H, 1.07; N, 0.72; Pd, 5.7.

Hydrogenation of unsaturated substrates was carried out as described earlier.[5]

Reactions of norbornene with iodoarenes (general procedure). Norbornene (3 mmol), iodoarene (1 mmol), formic acid (3 mmol), and triethylamine (3 mmol) were added with stirring to DMSO (5 mL). The mixture was stirred for 5 min, and then the catalyst (10 mg) was added. The reaction mixture was heated with stirring for 7—10 h and diluted with water. Organic products were extracted with diethyl ether. The extracts were dried with Na_2SO_4, concentrated, and chromatographed on SiO_2 with hexane—AcOEt (1 : 1) as an eluent. The compounds obtained were identified by comparing their ^{1}H NMR spectra with the literature data. The conversion was determined from the signal intensity ratios for the protons of the starting iodoarene and those of the hydroarylation product in the ^{1}H NMR spectrum.

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