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Microwave-promoted hydrogenation and alkynylation reactions with palladium-loaded multi-walled carbon nanotubes†

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Multi-walled carbon nanotubes loaded with Pd(0) clusters (average size distribution 9 nm) have been used under microwave irradiation as catalysts in hydrogenation and alkynylation reactions under "eco-friendly" conditions; reduced cinnamic esters and cross-coupled products were obtained in good yields; use of piperidine as the base provided, in a regiospecific process, novel doubly alkynylated compounds unambiguously characterized by NMR correlation experiments and X-ray diffraction.

The intriguing physicochemical properties of carbon nanotubes (CNTs),[1] principally their exceptional strength and stiffness allied to high thermal and electrical conductivity, have stimulated vigorous research for possible applications in different areas of engineering,[2] fuel cell technology,[3] catalysis[4] and charge transfer.[5] Various significant applications have already been demonstrated.[6] The low density of CNTs combined with their other properties have led to much attention being paid to the preparation of composites incorporating CNTs loaded with metal nano-particles of controlled size and shape[7] and we report in the present work catalytic reactions based on such material under microwave irradiation.

In principle, the addition of a terminal alkyne to another alkyne is a very simple and highly atom-economical method for forming enynes,[8] which are important precursors in organic synthesis. Unfortunately, despite the availability of a wide range of metal catalysts for the reaction, homodimerisation of the terminal alkyne is always favoured over alkyne to alkyne addition[9] and examples of successful applications are rare.[10,11] Here, we report a basis for the resolution of this problem through the use, under microwave irradiation (μWI*), of MWCNTs (multi-walled carbon nanotubes) loaded with Pd nanoparticles. Recognition of the fact that the large surface areas and good electrical and thermal conductivities of CNTs makes them ideal substrates for microwave absorption and concentration at metallic nanoparticle sites[12] was the origin of our unprecedented use of CNTs under microwave irradiation. An additional benefit of the procedures developed is that the reactions involved can be conducted under "eco-friendly" conditions.

MWCNTs were prepared by CCVD (catalysed chemical vapor deposition) by a known procedure.[13] TEM show no traces of carbon nanoparticles and the MWCNTs had diameters ranging from 15 nm to about 50 nm and lengths up to several micrometers. The as-prepared MWCNTs were loaded with Pd (10 wt%) by impregnation with $Pd(NO_3)_2$ in water–ethanol. After evaporation and calcination at 350 °C for 2 h, the Pd was reduced under hydrogen gas for 2 h at 400 °C. TEM confirmed the presence of Pd nanoclusters (NCs) deposited solely on the outside walls (Fig. 1 left). Without reduction, no NCs are observed by TEM. The NCs had diameters ranging from 5 to 10 nm, with an average ~9 nm, and they were clearly crystalline (Fig. 1 right). The measured interplanar separation of 2.70 Å was close to that of the [110] planes in Pd metal (d_{th} = 2.74 Å).[14]

We first tested the catalytic activity of this material (surface area 180 $m^2\ g^{-1}$), in the catalytic hydrogenation of cinnamate esters, a common structural framework in numerous compounds of biological interest.[15] The ester unit involves short and long saturated or unsaturated carbon chains as well as methylpyrene. The hydrogenation was attempted using $HCOONH_4$ as reductant in EtOH.[16] In all cases, chemoselective reduction of the C=C bonds was achieved. For **1** (0.31 mmol) quantitative conversion was obtained at 140 °C, using 10 mg Pd(10%)/MWCNTs (10%), providing a turnover frequency (TOF) of 400 h^{-1}. The conversion, measured as the percentage of product formed after 5 min reaction, was a linear function of the temperature (Fig. 2) and the catalyst was recycled at least five times without loss of activity. This reduction could not be achieved without Pd, $HCOONH_4$ or μWI* (Scheme 1).

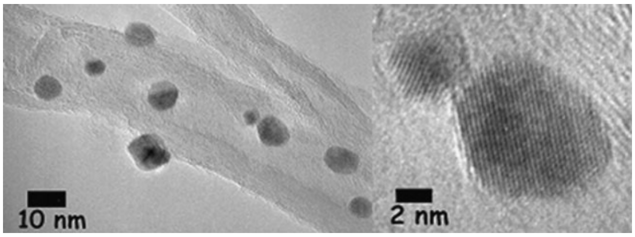

Fig. 1 TEM Images of MWCNT loaded Pd(0) NCs.

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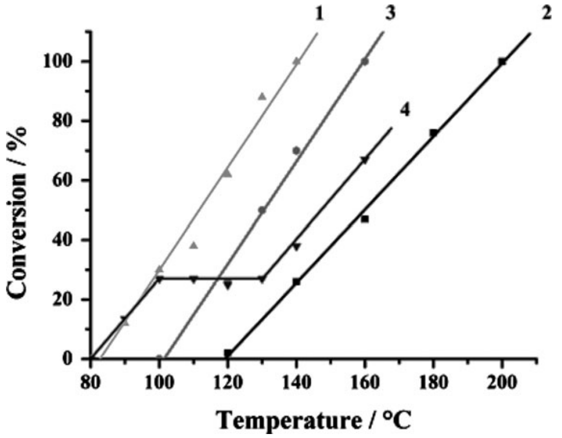
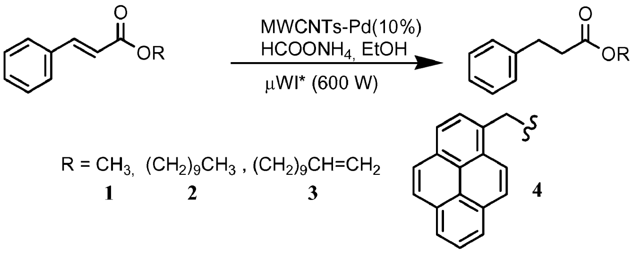


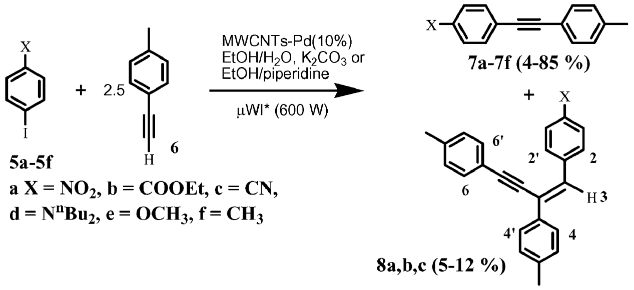
Fig. 2 Reduction of esters (0.31 mmol), using 10 mg Pd(10%)/MWCNTs (10%), 10 mL EtOH, 10 equiv. $HCOONH_4$, during 5 min under μWI*, 600 W, 9 bar: (▲) **1**, (■) **2**, (●) **3**, (▼) **4**.

Increasing the chain length from C_1 (methyl cinnamate **1**) to C_{10} (decyl cinnamate **2**) resulted in a decrease of the activity from 100 to 25% at 140 °C. Complete conversion was achieved at 200 °C (Fig. 2). With a terminal double bond in the ester chain (10-undecenyl cinnamate **3**), reduction of both double bonds occurs but more slowly than with **1**. The decrease in catalytic activity with increasing chain length may reflect decreased surface mobility of the substrate due to interaction of the carbon chains with the CNT walls. In line with this hypothesis is the total inhibition of the reduction of **1** when an anionic surfactant *e.g.* AOT (1 equiv. with respect to **1**) or dodecane (1 equiv.) are added to the reaction mixture. With the pyrene derivative **4** (Fig. 2), unusual activity changes were seen above 100 °C. Between 100 and 130 °C, the reactivity was constant but an increase began above 140 °C. This reproducible behaviour may be due to the strong adsorption of the pyrene unit on the CNT walls[17] being disrupted at higher temperatures. TEM images recorded for the Pd/MWCNTs catalyst before and after the catalytic cycles showed no evidence of sintering of the Pd–NCs, a result in keeping with the absence of detectable loss of catalytic activity during recycling. It was noticed that when Pd (10%)/charcoal under microwave irradiation was used under the standard experimental reaction conditions (*e.g.* EtOH, $HCOONH_4$, 5 min under μWI* at 600 W under 9 bar), a lot of degradation products were observed during the work-up of the reaction mixture.

In a second trial we tested the catalytic activity of these materials in alkynylation reactions using "eco-friendly" conditions, *i.e.*, the absence of copper salts, organic bases and phosphine ligands, and of toxic organic solvents. Cross-coupling of the iodo-arenes **5a–f** with 4-ethynyltoluene **6** in a mixture of ethanol–water and potassium carbonate as base, gave the tolanes **7a**, **7d**, **7e** and **7f** in 40–82% yields with Pd/MWCNTs and 5 min microwave irradiation, providing a TOF of 900 h^{-1} (Scheme 2 and Table 1). No conversion could be achieved without aryl halide, Pd, base or μWI* over the 5 min period. An optimal conversion of the reactants was found between 135 and 160 °C after 5 min reaction. The catalyst was recovered by simple filtration and recycled at least five times without loss of activity. Furthermore, TEM images carried out on the Pd/MWCNTs before and after the catalytic cycles showed no evidence of sintering of the Pd–NCs, a result in keeping with this retention of activity. XRD investigations have been carried out on the support, and on the Pd-loaded MWCNTs before and after catalysis. No significant changes on the Pd crystallinity and particle size distribution were observed after the catalytic conversion of **5a** to **7a** and **8a** (Fig. S1, ESI†). This result is in keeping with the absence of loss of catalytic activity. Sheldon tests[18] carried out after the catalysis (experimental conditions of Table 1) revealed moderate leaching of Pd 1.1% in the case of Pd(10%)/MWCNTs, whereas 3.8% were found for Pd/charcoal. After the catalysis, the solution was filtered and evaporated and the obtained residue was mineralized with concentrated acid. After evaporation of the acid, the resulting solid, was redissolved in aqueous solution and analyzed by ICP-mass (4.6 and 15.0 μg of Pd were analyzed, respectively for Pd/MWCNTs and Pd/C).



Scheme 1



Scheme 2

When commercially available Pd (10%)/charcoal catalyst was used under the same experimental conditions, the conversion was significantly poorer (Table 1). Longer irradiation times with Pd/C does not increase the yield of cross-coupled compounds **7a–f** because after 5 min irradiation no iodo starting materials **5a–f** were present in the reaction mixture as checked by thin-layer-chromatography and proton NMR analysis in solution. Note that in the absence of μWI*, catalysis with Pd on charcoal require much longer reaction times.[19] Other catalytic systems based on supported Pd nanoparticles that promote Sonogashira reaction with comparable efficiency are known.[20] However, in the absence of MWI* much longer irradiation times are needed, for instance preparation of an analogue of compound **7a** was produced in 98% yields after heating at 80 °C during 180 min.

The ill-defined structures of activated charcoal provide a broad size distribution of Pd particles (average diameter around 15 nm).[21] The results obtained with the present Pd/MWCNTs probably reflect the greater efficacy of well-

Table 1 Optimized Pd (10 wt%)/MWCNTs catalyzed alkynylation with 4-ethynyltoluene and comparison with Pd(0) (10 wt%)/charcoal (Aldrich)[a]

	K_2CO_3–EtOH–H_2O[b]		Piperidine–EtOH[c]			
	Yield (%) of **7**		Yield (%) of **7**		Yield (%) of **8**	
Iodo substrate	Pd/CNT	Pd/C	Pd/CNT	Pd/C	Pd/CNT	Pd/C
p-NO_2–C_6H_4–I **5a**	82	53	65	60	12	—
p-COOEt–C_6H_4–I **5b**	—[d]	—[d]	85	48	5	—
p-CN–C_6H_4–I **5c**	—[d]	—[d]	85	20	8	—
p-$N^{n}Bu_2$–C_6H_4–I **5d**	45	17	6	3	—	—
p-MeO–C_6H_4–I **5e**	45	18	6	9	—	—
p-CH_3–C_6H_4–I **5f**	40	17	4	3	—	—

[a] Average of triplicates. CNT accounts for multi-walled-CNTs. [b] Reactions performed on 0.858 mmol of iodo substrate and 2.145 mmol of 4-ethynyltoluene in EtOH–H_2O (1 : 1, v/v), K_2CO_3 (3 equiv.), 10 mg Pd (10 wt%)/MWCNTs or Pd (10 wt%)/C at 160 °C, 12–13 bar for 5 min μWI*. [c] Reactions were performed on 0.858 mmol of iodo substrate and 2.145 mmol of 4-ethynyltoluene in EtOH (10 mL) with 3 equiv. of piperidine and 40 mg Pd (10 wt%)/MWCNTs or Pd (10 wt%)/C at 120 °C, 6–7 bar for 30 min μWI*. [d] Hydrolysis of the cyano and the ester compounds into the acid derivatives.

dispersed, small Pd particles in catalyzing C–C coupling.[22,23] With electron donating substituents such as CH_3, MeO or $^{n}Bu_2$, the efficiency decreases to 45% with Pd (10%)/MWCNTs but more dramatically to 17% with Pd (10%)/charcoal. The use of cyano or ester groups is not possible in the presence of water due to hydrolysis.

With piperidine in place of the mineral base, **7a–c** were also formed in acceptable yields but for the reactants with electron-donating groups, the yields were much poorer, being <6% for **7d–f**. More interestingly, with electron-withdrawing substitutents (NO_2, COOEt or CN), novel highly fluorescent, doubly alkynylated products **8a–c** were isolated (Table 1), as confirmed by MALDI-TOF MS peaks at *m*/*z* 353.1, 381.2 and 334.2, respectively for **8a**, **8b** and **8c**. To the best of our knowledge, these compounds are unknown and no clear synthetic routes could be foreseen.[10] Note that with Pd on charcoal, these bis-alkynylated compounds could not be isolated.

For these unexpected enyne products **8a–c**, the reaction regio-selectivity and alkene geometry were first assigned on the basis of COSY and NOESY NMR correlations. The 2D NOESY spectra exhibited pronounced cross-peaks between the vinyl proton 3 and the two protons 2,2′ and 4,4′ of the surrounding phenyl rings. The absence of cross-peaks with the two protons 6,6′ excluded the other regio-isomer (Fig. S2. ESI†). In all cases, only a single peak was observed near δ 7.2 ppm for the enyne proton (H2 in Fig. 3) along with a single vinylic-carbon resonance near δ 119.5 ppm, both observations indicating the presence of a single isomer.

Ultimately, the regio-selectivity and alkene geometry were unambiguously assigned by an X-ray structure of **8b** (Fig. 3). A noteworthy feature of the crystal structure is the quasi-planarity of the molecule with the largest dihedral angle between *Ar1* and *Ar2* of 11.3° and a small tilt between *Ar1* and *Ar3* of 4.3°. The C1–C2 and C19–C20 distances are characteristic of carbon double and triple bonds, respectively. The geometrical parameters around the vinylic atoms C1 and C2 are in good agreement with sp^2 hybridization. Only a slight deviation of 6.3° between the C19–C21 and the C1–C19 axes is apparent, showing that there is no constraint in the binding of the *p*-toluylacetylene fragment to the vinyl bond.

Changing the ratio of 4-ethynyltoluene **6** in the cross-coupling reaction with **5a** from (1.5 to 10 equiv.) have no significant impact of the isolated yields of compounds **7a** (60–65%) and compound **8a** (9–12%).

These new compounds resulting from an alkynylation/carbopalladation sequence are formed only when electron-withdrawing groups (NO_2, COOEt, CN) are present on the iodophenyl substrate (Table 1). In *no* case was a bis-*p*-toluylbutadiyne derivative observed and, significantly, the doubly cross-coupled products **8a–c** are *not* formed by mixing **6** with the mono-cross coupled compounds **7a–c** under the standard experimental conditions in the presence of Pd(10%)/MWCNTs and μWI*. These experiments have been

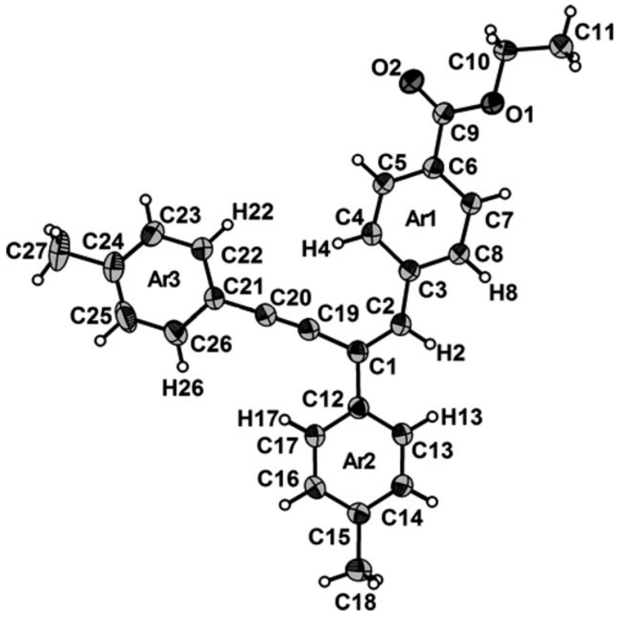


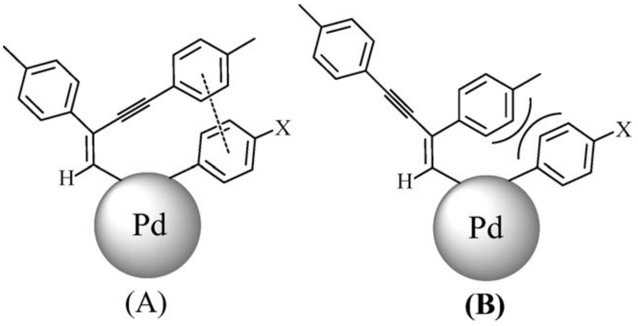
Fig. 3 ORTEP view of compound **8b** (50% probability displacement ellipsoids). Selected distances (Å) and angles (°): C1–C2, 1.354(33); C19–C20, 1.200(25); C12–C1–C19, 115.03(17); C12–C1–C2, 121.99(17); C19–C1–C2, 122.98(18); C1–C2–C3, 131.57(18); C1–C2–H2, 114.18(19); C3–C2–H2, 114.25(19). Dihedral angles (°): C19–C1–C2–H2, 177.18(19); C12–C1–C2–C3, 178.34(19)°. For clarity, only the key hydrogen atoms are labeled.

reproduced several times with various substrates without any detectable traces of derivatives **8a–c**. For the same reasons mentioned above no starting materials **5a–f** are present at the end of the reaction cycle, consequently longer irradiation times would not change the isolated yields nor the selectivity of the catalytic process. The role of piperidine is unclear compared to the mineral base. The use of a tertiary amine (triethylamine) instead of piperidine in ethanol gives 55% of **7a** and 7% of **8a** which compares favourably with the yields found with piperidine. We do believe that the presence of water (case with K_2CO_3 see Table 1) is the key point which might have a crucial impact in the transition state of the catalytic process. Further work is planned to understand this interesting observation.

From a mechanistic view point this is a key point which confirm the novelty of the herein described catalytic system. Our working hypothesis as to the reaction mechanism is that the presence of 2.5 equiv. of *p*-toluylacetylene would favour the formation of a highly reactive enyne–Pd intermediate (**A**) resulting from homodimerization of the terminal alkyne. Oxidative addition of the iodophenyl reagent followed by reductive elimination would lead to the final product. The regio-selectivity might at this stage be governed by unfavourable steric crowding in the intermediate (**B**) and favourable π–π interactions in intermediate (**A**) (Scheme 3).

Aliphatic diyne cross-coupling reactions have previously been shown to occur in solution when using reactive Pd-phosphine and electron deficient derivatives but no mention was made of homodimerization/carbo-palladation reactivity.[10] The present use of highly dispersed Pd(0) particles, with microwave irradiation generating pronounced local heating on the reactive Pd-clusters, might be at the origin of the formation of these unusual compounds. The operating pressures used, as high as 13 bar (Table 1), presumably accelerated the reactions by favouring adsorption of the reactants on the catalysts. The small size of the Pd nano-particles and efficient microwave energy transfer by the CNT may be other factors augmenting their catalytic function.[23]

The present use of Pd(0)-loaded, multi-walled carbon nanotubes under microwave irradiation in catalysis of hydrogenation and alkynylation reactions could be summarized the following way: (i) the chemoselective reduction of the double bond in dihydrocinnamic esters; (ii) the successful use of an easily handled solid (ammonium formate) as reductant in pure ethanol; (iii) the C–C cross-coupling of various iodo-substrates with 4-ethynyltoluene under eco-friendly conditions (water–ethanol–K_2CO_3); (iv) the catalytic activity of Pd(0) deposited on MWCNT is higher than that of commercially available Pd(0) on charcoal for Sonogashira-type cross-coupling reactions; (v) the formation of novel enyne cross-coupled products is regio- and stereoselective when Pd(10%)/MWCNTs are used. We intend extending the present work to obtain additional conjugated enyne building blocks by a surface-controlled oligomerisation process. Initial experiments have provided some higher oligomers, the structures of which are currently under investigation.



Scheme 3

Experimental

Microwave irradiation experiments

Microwave irradiation experiments were performed using a multi-mode MARS System From CEM Corporation using standard Pyrex vessels (capacity 50 mL). The temperature profiles for microwave experiments were recorded using a fiber-optic probe protected by a sapphire immersion well inserted directly into the reaction mixture. Pressure profiles were recorded with a pressure sensor directly connected to the reaction vessel.

General procedure for the hydrogenation of various cinnamic esters

To a solution of cinnamic esters (0.31 mmol) dissolved in 10 mL of EtOH was added ammonium formate (250 mg, 3.10 mmol) and Pd/MWCNTs (10 mg, 10 wt%). The mixture was subsequently heated at different temperature with stirring during 5 min in a 50 mL reactor vessel. The crude reaction mixture was filtered on a glass frit and the Pd/MWCNTs were washed with 2 × 10 mL of EtOH and was recycled. The solution was diluted with 20 mL of dichloromethane and water was added. The phases were separated and the resulting aqueous phase was extracted with an additional 2 × 20 mL of dichloromethane. The combined organic phases were washed with 2 × 20 mL of distilled water and 1 × 20 mL of brine. The resulting organic phase was dried over $MgSO_4$ and the heterogeneous mixture was filtered. The filtrate was concentrated in vacuum to afford dark red oil. The target product was purified by flash chromatography on silica gel eluting with a dichloromethane–petroleum ether mixture as mobile phase.

General procedure for the cross-coupling between aryl iodide and 4-ethynyltoluene in EtOH–H_2O (1 : 1) and K_2CO_3 (Table 1)

To a solution of aryl iodide (0.858 mmol) dissolved in 10 mL (1/1, v/v) of EtOH–H_2O were added, 4-ethynyltoluene (2.145 mmol, 250 mg, 0.272 mL), K_2CO_3 (2.57 mmol, 300 mg) and Pd/MWCNTs or Pd/charcoal (10 mg, 10 wt%). The mixture was subsequently heated at 160 °C with stirring during 5 min (300 W, 12–13 bar) in a 50 mL reactor vessel. The crude reaction mixture was filtered and the Pd/MWCNTs or Pd/charcoal were washed with 2 × 10 mL of EtOH and recycled. The solution was diluted with 20 mL of dichloromethane and 15 mL of water were added. The phases were separated and the resulting aqueous phase was extracted with an additional 2 × 20 mL of dichloromethane. The combined organic phases were washed with 2 × 20 mL of distilled water and 1 × 20 mL of brine. The resulting organic phase was dried over $MgSO_4$ and the heterogeneous mixture was filtered. The filtrate was concentrated in vacuum to afford a dark red oil. The residue was purified by flash chromatography on silica gel eluting with a mixture of dichloromethane and petroleum ether to give the desired product.

Crystal data for 8b. $C_{27}H_{24}O_2$, M = 380.46, triclinic, space group $P\bar{1}$, a = 5.644(1), b = 12.047(2), c = 16.159(2) Å, α = 82.02(5), β = 82.48(5), γ = 81.90(4)°, V = 1070.2(3) $Å^3$, T = 293(2) K, Z = 2, μ = 0.073 mm^{-1}, 3081 unique (R_{int} = 0.025), Friedel pairs merged, R_1 [$I > 2\sigma(I)$] = 0.048, wR_2 (all data) = 0.144. CCDC reference number 661999.

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