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Facile generation and morphology of Pd nanoparticles from palladacycles and carbon monoxide

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Abstract

Treatment of PdCys or palladium salts with carbon monoxide (1 atm) in DMF or toluene at room temperature results in a solution of palladium nanoparticles whose morphology depends on the PdCy or palladium salt. Unusual triangular shaped 2–12 nm nanoparticles result from PdCys **1** and **3**.
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A great variety of, largely reductive, methods have been reported for the preparation of metal nanoparticles [1]. These include reduction of metal salts with hydrogen [2], alcohols [3] and hydride [4]. Carbon monoxide has been used to reduce $HAuCl_4$ [5] and PtO_2 [6] and $(Et_3P)_2PdCl_2$ was reported to give giant palladium clusters containing both Et_3P and CO when contacted with CO in DMF [7].

During the course of our research we observed that when PdCys were used as precatalysts in carbonylation reactions the solution rapidly turned black suggesting formation of palladium black. Further study of this effect led to a convenient and rapid synthesis of palladium nanoparticles from PdCys, palladium acetate or palladium trifluoroacetate and carbon monoxide (1 atm) at room temperature. Structural studies of several of the nanoparticle preparations by transmission electron mi-

croscopy (TEM) [1] revealed interesting morphological differences in addition to establishing the size range of the nanoparticles.
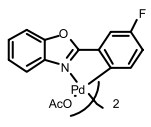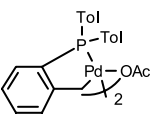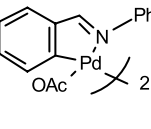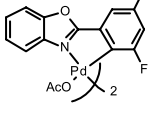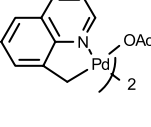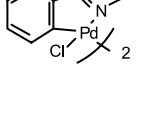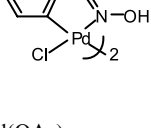
First, we examined the reduction of acetate bridged PdCys **1–5** by stirring their solutions in DMF and toluene under carbon monoxide (1 atm) at room temperature. Reactions in DMF (Table 1, entries 1, 3, 5, 7, 9) resulted in rapid formation of nanoparticles immediately after the introduction of CO. The generation of nanoparticles is signalled by the formation of black solutions which do not sediment. The reductions in toluene were slightly slower (entries 2, 6, 8, 10). Herrmann's catalyst **2**, the only P-donor, was particularly slow in toluene (entry 4), whilst chloride bridged imine PdCys **6** and **7** either gave very little nanoparticle formation (entry 11) or none (entries 12–14).

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[1] Preparation and examination of TEM images: The samples were examined to assess the size, morphology and particle distribution. A small portion of sample was taken and dried on a holey carbon coated copper TEM grid. The samples were examined in the FEI Tecnai F20 electron miscroscope using the following experimental conditions: voltage (kV): 200; C_2 aperture (μm): 50; analytical take-off angle: +15° and mode: microprobe.

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Table 1
Synthesis of Pd nanoparticles by treatment of PdCys with CO (1 atm) at room temperature[a]

Entry	PdCy	Solvent	Nanoparticles formation (min)[b]
1		DMF	5
2		Toluene	10
3		DMF	10
4		Toluene	360
5		DMF	5
6		Toluene	10
7		DMF	5
8		Toluene	10
9		DMF	5
10		Toluene	10
11		DMF	c
12		Toluene	d
13		DMF	c
14		Toluene	d
15	Pd(OAc)$_2$	DMF	5
16		Toluene	c
17	Pd(CO$_2$CF$_3$)$_2$	DMF	5
18		Toluene	360
19	Na$_2$PdCl$_4$	DMF	d
20		Toluene	d

[a] Treating a solution of PdCys or Pd salts in toluene or DMF (0.1 mmol/20 ml) with CO (1 atm, via balloon) at r.t. for 24 h.
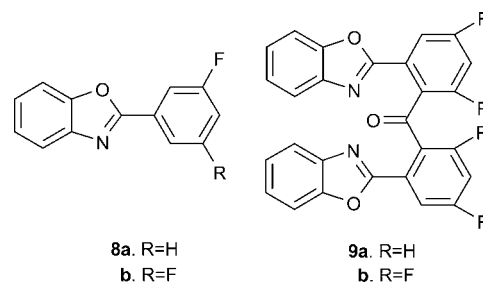[b] Diagnosed by formation of a non-sedimentry black solution.
[c] Very little nanoparticle formation after 24 h.
[d] No nanoparticle formation.

Next we examined the reduction of palladium salts using carbon monoxide (1 atm) at room temperature in DMF and toluene. The reduction of palladium acetate and palladium trifluoroacetate with CO was fast in DMF (entries 15 and 17) but was very slow in toluene

(entries 16 and 18), whilst sodium chloropalladate did not give any nanoparticles in either DMF or toluene (entries 19 and 20).

8a. R=H
b. R=F

9a. R=H
b. R=F

We investigated the fate of the palladacycle ligands from the reactions between PdCys **1** and **4** and CO. Work up of the nanoparticle solutions afforded ca. 3:1 mixtures of the ligand **8** and ketone **9** [8] derived from insertion of CO into the ligand [9]. The structure of the ketones **9a** and **9b** were confirmed by X-ray crystallography, e.g., Fig. 2.[2]

TEM technology was utilized to determine the morphology of the nanoparticles [1]. The results show the nanoparticles derived from **1** (Fig. 1(a)) and **3** (Fig. 1(b)) to consist of triangular palladium nanoparticles [10] from 2 to 12 nm in size which tend to exist as small clusters. In contrast the nanoparticles generated from Pd(OAc)$_2$ (Fig. 1(c)), Herrmann's catalyst **2** (Fig. 1(d)) and **5** (Fig. 1(e)) exhibited conventional morphology and were faceted palladium particles from 3 to 10 nm which tend to exist as small clusters.

Studies of the growth and morphology of three-dimensional metal clusters of catalytically active transition metals on inert crystal surfaces has underpinned advances in the mechanisms of heterogeneous catalysts [10]. A recent paper [11] concerned with the high temperature formation of palladium nanoparticles on natural graphite single crystals reports palladium clusters comprised of mixed morphology including some apparent triangular shaped particles. In this work, TEM experiments in the weak beam dark field mode showed them to be regular tetrahedra. Thus it appears likely that our triangular shaped particles are also tetrahedra.

The precise factors that control the shapes of the palladium nanoparticles in our case are not clear. However, triangular nanoparticles were derived from **1** and **3** both of which are sp^2 carbon metallated PdCys whilst faceted nanoparticles were derived from
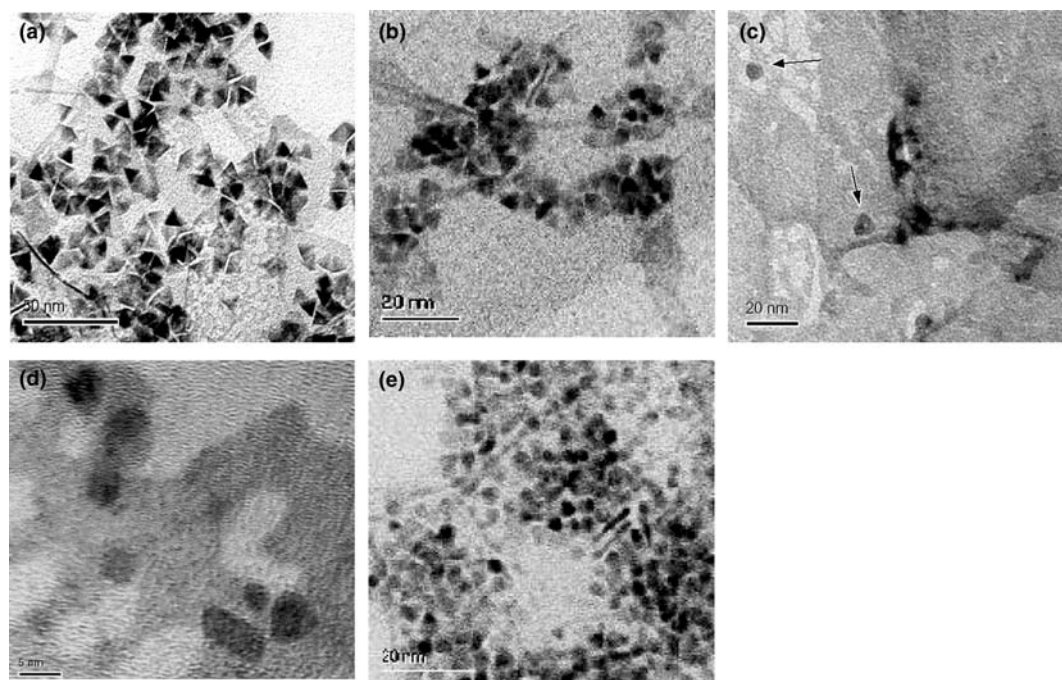
Fig. 1. TEM of nanoparticles arising from treatment of PdCys **1–3**, **5** and Pd(OAc)$_2$ with (1 atm) in DMF: (a) nanoparticles from **1**, (b) nanoparticles from **3**, (c) nanoparticles from Pd(OAc)$_2$, (d) nanoparticles from **2** and (e) nanoparticles from **5**.
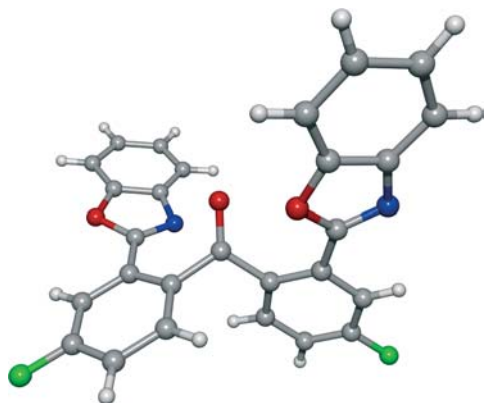

Fig. 2. X-ray crystal structure of **9a**.

Herrmann's catalyst **2** and from **5** both of which are sp^3 carbon metallated PdCys. It is also known that dissociative adsorption can alter the shape/morphology of nanoparticles [12] and that in the reductive generation of nanoparticles in the presence of "capping" polymers the morphology is dependent on the "capping" polymer. Thus, a significant proportion (41%) of triangular Pt nanoparticles are produced from K$_2$PtCl$_4$ in the presence of sodium poly(acrylate) [13].

When toluene was used as solvent, the Pd nanoparticles aggregated and separated out, in our reductive protocol, whilst in DMF the nanoparticles did not aggregate which implies DMF is acting as a stabiliser.

We have previously reported excellent catalytic activity of nanoparticles derived from precursors of type **1**

in our cascade reaction chemistry [14] and have shown that these nanoparticles also allow π-allylpalladium species to exhibit nucleophilic chemistry rather than the normal electrophilic chemistry [15]. Most recently we have demonstrated the efficacy of nanoparticles generated by our protocol from PdCys in the [2 + 2 + 1]-cycloaddition of 1,6-dienes and CO [16] and in cyclative carbonylation/amination cascades [17].

In conclusion, a new protocol for generating palladium nanoparticles has been established which involves treating PdCys or selected palladium salts with carbon monoxide (1 atm) in DMF or toluene at room temperature. The possibility that the unusual morphology of the nanoparticles derived from **1** and **3** is a general feature for all sp^2 carbon cyclopalladated complex precursors is under study as are the mechanistic and synthetic implication of these observations.

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[8] Characteristic data: **9a**: colourless needles, m.p. 201–202 °C. (Found: HRMS m/z ($M^+ + 1$) 453.1048; $C_{27}H_{15}F_2N_2O_3$ requires 453.1050); δ_H (250 MHz, CDCl$_3$): 7.10–7.23 (m, 1H, ArH), 7.30–7.36 (m, 2H), 7.40–7.48 (m, 1H), 7.60–7.75 (m, 3H, ArH); ^{13}C NMR (CDCl$_3$), 193.6, 166.3, 162.1, 161.1, 151.3, 141.9, 135.5, 133.3, 133.2, 129.8, 129.7, 126.2, 125.2, 120.9, 118.3, 118.2, 117.9, 111.2; m/z (EI) (%): 452.2 (M^+), 306.2 (100). **9b**: colourless needles, m.p. 178–179 °C (Found: HRMS m/z ($M^+ + 1$) 489.0859; $C_{27}H_{13}F_4N_2O_3$ requires 489.0857); δ_H (250 MHz, CDCl$_3$): 6.89–6.95 (m, 1H, ArH), 7.30–7.37 (m, 2H), 7.45–7.58 (m, 2H), 7.70–7.75 (m, 1H, ArH); ^{13}C NMR (CDCl$_3$), 183.3, 164.5, 162.3, 160.02, 158.6, 149.5, 140.1, 128.6, 124.8, 123.7, 119.3, 112.7, 109.6, 105.7; m/z (ES) (%): 489.0 ($M^+ + H$).

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