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# Palladium nanoparticles stabilised by polyfluorinated chains

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**Palladium nanoparticles can be prepared by reduction of palladium(II) chloride in the presence of different compounds featuring long perfluorinated carbon chains.**

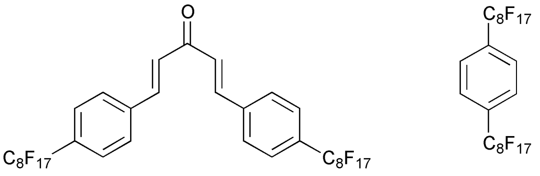
The preparation, structure determination, and possible applications of transition metal nanoparticles have attracted a great deal of attention in the past decade.[1] Several approaches have been reported for their preparation, such as chemical and electrochemical reduction, thermal decomposition, metal vapour deposition, photolysis, and sonochemical decomposition.[1] The method most generally used is the chemical or electrochemical reduction of a metal salt by a suitable reducing agent in the presence of stabilisers, which absorb to the particle surface thus preventing agglomeration and controlling the particle size. In the case of monometallic or bimetallic nanoparticles involving palladium several stabilising agents have been used: ionic and non-ionic surfactants, polymers, dendrimers, β-cyclodextrins, solvents such as ethers and thioethers, and other ligands based on nitrogen, phosphorus or sulfur. To the best of our knowledge stabilisation based on the properties of polyfluorinated long carbon chains has never been reported. Only one related situation has been described, namely palladium nanoparticles encapsulated in a dendrimer with a periphery featuring amino groups which interact with polyfluorinated carboxylic acids, the total architecture being soluble in perfluorinated phases.[2] These architectures catalyse the hydrogenation of alkenes.

Recently we discovered that 1,5-bis(4,4′-bis(perfluorooctyl)-1,4-pentadien-3-one, **1a**, stabilises palladium nanoparticles of 4–5 nanometers in diameter.[3] These nanoparticles are active in Heck and Suzuki reactions and are recovered and reused without noticeable decrease of activity.

Now, we want to report that stabilisation by compounds featuring perfluorinated chains is not exceptional for **1a**: other compounds **1b–e**,[4] highly loaded with fluorine, possess the same property (Fig. 1). In all cases a solution of disodium hexachlorodipalladate, $Na_2(Pd_2Cl_6)$, was reduced in methanol at 60 °C.[8] However, other heavily fluorinated compounds did not form palladium nanoparticles under similar conditions. Thus, the same reduction in the presence of 1*H*,1*H*,2*H*-perfluoro-1-decene, (perfluorooctyl)benzene, 1,3-bis(perfluorooctyl)benzene, 1,2-bis(perfluorooctyl)benzene, heptadecafluorononanoic acid, its sodium salt, potassium perfluorooctanesulfonate, or 4-perfluorooctylbenzaldehyde, produced only precipitates of palladium black. We do not know the reasons for the different behaviour exhibited by otherwise similar compounds (*cf.* all bis(perfluorooctyl)benzene isomers). The preparation of nanoparticles stabilised by **1c** took a different course. Indeed, when 1*H*,1*H*-pentadecafluorooctylamine was added to the palladium(II) solution a yellow precipitate of dichlorobis(1*H*,1*H*-pentadecafluorooctylamino) palladium(II), presumably *trans* **2**, was formed.[9] Treatment of this complex with methanol in the usual way at 60 °C finally produced the nanoparticles.

Table 1 contains preparative and analytical data for all nanoparticles prepared. Material stabilised with **1e** afforded a TEM which was difficult to interpret indicating that the material probably presents a more complex organisation.

The sum of percentages for all elements is in all cases around 100% indicating that compound **1** is the only constituent of the



**1a** **1b**

$C_7F_{15}$-$CH_2$-$NH_2$ **1c**

$C_{10}F_{21}$-$(CH_2)_6$-$C_{10}F_{21}$ **1d**

$(C_6F_{13}CH_2CH_2S)_2$ **1e**

$[C_7F_{15}CH_2NH_2]_2PdCl_2$ **2**

**Fig. 1** Compounds **1** stabilise palladium nanoparticles.

**Table 1** Preparative and analytical data for nanoparticles

| **1** | Molar ratio $PdCl_2$/**1** | C + H + F + Pd + (O,N,S) (%)[a] | Molar ratio Pd/**1** in particles | Yield (%) | Size/nm[b] ± Std. dev. | Mp/°C |
|---|---|---|---|---|---|---|
| **1a** | 0.53 | 96.96 | 1.15 | 81 | 4 ± 0.6 | 140-145 |
| **1a** | 0.54 | 99.40 | 0.65 | 79 | [c] | 158–163 |
| **1a** | 4.65 | 104.14 | 4.00 | 99 | 5 ± 0.7 | 170 |
| **1a** | 4.65 | 92.66 | 6.67 | 100 | 4.5 ± 0.9 | 166–172 |
| **1b** | 1.50 | 99.29 | 1.72 | 93 | 16 ± 5.3 | 102–103 |
| **1b** | 0.50 | 100.35 | 0.54 | 96 | 13 ± 3.0 | 102–103 |
| **1c** | 0.50 | 91.44 | 4.00 | 79 | 4 ± 1.5 | 130–132 |
| **1d** | 1.00 | 99.05 | 0.35 | 12 | 9 ± 2.8 | 113–115 |
| **1e** | 2.26 | 98.01 | 2.85 | 43 | [d] | 155 |

[a] Percentage of Cl was always < 1%; percentages of fluorine and oxygen were calculated from percentage of carbon; percentage of Pd was determined by inductively coupled plasma (ICP). [b] Determined by transmission electron microscopy (TEM). [c] Not determined. [d] See text.

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stabilising layer. On the other hand IR and $^1H$ NMR spectra of all nanoparticles are identical to those of the corresponding **1**. Chlorine is always below the limits of detection. All nanoparticles were soluble in perfluorooctane, perfluorooctyl bromide, and 1,1,2-trichloro-1,2,2-trifluoroethane.

The two first experiments of the table, both with **1a**, show that in spite of the same $PdCl_2$/**1a** ratio of starting materials, the Pd/**1a** ratios in the final nanoparticles can be significantly different. The most important difference between these two reactions is the working scale, three-fold in the first experiment with respect to the second. Also 2 h elapsed in the first experiment between addition of **1a** and addition of sodium acetate whereas 7 h elapsed in the second experiment. We feel that the working scale can determine some characteristics of the obtained nanoparticles. We have not yet addressed this problem.

## Notes and references

1 L. N. Lewis, *Chem. Rev.*, 1993, **93**, 2693; J. S. Bradley, in *Clusters and Colloids, From Theory to Applications*, ed. G. Schmid, VCH, Weinheim, 1994, pp. 523–536; P. P. Edwards, R. L. Johnston and C. N. R. Rao, in *Metal Clusters in Chemistry*, ed. P. Braunstein, L. Oro, P. R. Raithby, Wiley-VCH, Weinheim, 1998; J. H. Fendler, *Nanoparticles and Nanostructured Films, Preparation, Characterization and Applications*, Wiley-VCH, Weinheim, 1998; J. D. Aiken and R. G. Finke, *J. Mol. Catal. A*, 1999, **145**, 1; C. N. R. Rao, G. U. Kulkarni, P. J. Thomas and P. P. Edwards, *Chem. Soc. Rev.*, 2000, **29**, 27; M. T. Reetz, M. Winter, R. Breinbauer, T. Thurn-Albrecht and W. Vogel, *Chem. Eur. J.*, 2001, **7**, 1084.

2 V. Chechik and R. M. Crooks, *J. Am. Chem. Soc.*, 2000, **122**, 1243; R. M. Crooks, M. Zhao, L. Su, V. Chechik and L. K. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181; L. K. Yeung and R. M. Crooks, *Nanoletters*, 2001, **1**, 14.

3 M. Moreno-Mañas, R. Pleixats and S. Villarroya, *Organometallics*, 2001, **20**, 4524.

4 **1a**: see ref. 3. **1b**: mp 102–103 °C. It was prepared by the method of ref. 5. **1c** is commercially available. **1d**: mp 97–99 °C. It was prepared by the method of ref. 6. **1e**: all attempts to prepare the corresponding thiol according to ref. 7 failed. Instead disulfide **1e** was obtained, mp 37–38 °C, MS (*m*/*z*): 758 ($M^+$, 20), 425 (21), 411 (18), 327 (18), 119 (23), 65 (100%).

5 V. C. R. McLoughlin and J. Thrower, *Tetrahedron*, 1969, **25**, 5921.

6 R. J. Twieg and J. F. Rabolt, *Macromolecules*, 1998, **21**, 1806.

7 C. Naud, P. Calas, H. Blancou and A. Commeyras, *J. Fluorine Chem.*, 2000, **104**, 173.

8 Typical procedure. A mixture of palladium chloride (0.180 g, 1.017 mmol), sodium chloride (0.058 g, 1.025 mmol) and methanol (10 mL) was stirred at room temperature for 24 h. The mixture was filtered through a glass wool plug. Additional methanol (10 mL) was added to the filtrate. The solution was heated at 60 °C under stirring, 1,4-bis(perfluorooctyl)benzene, **1b**, (0.600g, 0.656 mmol) was added, and the mixture heated (60 °C) under stirring for 24 h. Then sodium acetate (1 g) was added and stirring was maintained at room temperature for 1 h. The formed black solid was filtered, washed successively with methanol, water, and acetone, and dried to afford 0.605 g of a black solid, mp 102–103 °C, soluble in perfluorooctane, perfluorooctyl bromide, and 1,1,2-trichloro-1,2,2-trifluoroethane. Extraction of the methanolic filtrate with perfluorooctane did not give additional material. The IR and $^1H$-NMR spectra of the solid were identical to those of **1b**. Elemental analysis: C, 23.93; H, 0.34; Cl, $< 1$; Pd, 16.51%. Size of nanoparticles is 15–20 nm as determined by transmission electron microscopy (TEM).

9 Compound **2** had mp 243 °C; IR (KBr): 3274, 3215, 3125, 1245, 1210, 1145, 1104 $cm^{-1}$; IR (polyethylene): 315 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3 + C_8F_{17}Br$): $\delta$ 1.28 (s, 2H), 1.61 (s, 2H). Calcd. for $C_{16}H_8N_2Cl_2F_{30}Pd$: C, 19.69; H, 0.83; N, 2.87; Cl, 7.27. Found: C, 19.67; H, 0.86; N, 2.84; Cl, 7.52%.