



A new specifically designed calix[8]arene for the synthesis of functionalized, nanometric and subnanometric Pd, Pt and Ru nanoparticles

V. Huc^{a*}, K. Pelzer^{b*}

^aUniversité de Paris-Sud, ICMO, Bâtiment 420, 15 rue Georges Clémenceau, 91440 Orsay, France

^bFritz-Haber-Institute of the Max-Planck-Society, Department of Inorganic Chemistry, Faradayweg 4-6, 14195 Berlin, Germany

* Corresponding author: e-mail Pelzer@fhi-berlin.mpg.de

Received 19 February 2007; accepted 31 July 2007; Available online 24 August 2007

Abstract

A new thioester functionalized calix[8]arene derivative is used for the synthesis of metallic Pd, Pt and Ru nanoparticles, exhibiting several interesting features such as stability and remarkable surface functionalization. Crystalline particles of very small dimensions and good dispersion have been obtained.

Keywords: Calixarenes; Nanoparticles; Surface functionalization

There is presently a considerable interest for the study and the use of metallic or semiconducting nanoparticles because of their novel and attractive physical [1–5] and chemical properties [6,7]. In most cases, the solution-phase synthesis of metallic nanoparticles involves the controlled self-condensation of reduced metal centers in the presence of a suitable ligand. This ligand usually acts a stabilizer for the coordinatively unsaturated metal centers, prevents the agglomeration of the nanoparticles and controls the particle's size [8–17]. The stabilization of nanoparticles by ligands containing multiple anchoring groups is interesting, as it may improve the stability of the ligand shell due to the cooperative binding of all these groups. Moreover, this cooperativity-based strategy may also open the possibility to use individually weakly bonded ligands, without compromising the stability of the nanoparticles. The lability of each individual weak bond between the anchoring group and the surface of the metal may allow for a much greater reactivity of these nanoobjects in catalysis, along with a good stability due to these cooperative effects. Some examples of nanoparticles with ligands containing multiple anchoring groups such as veratrole or calixarene derivatives [18] have been already described.

Most of the interesting properties of calixarenes are directly related to their conformational behavior. The graft-

ing of calixarenes onto nanoparticles may ultimately lead to a better conformational control and thus to new properties for these molecules. New properties may also be expected for these nanoparticles/calixarene nanocomposites, for example, in catalysis, where the reactivity of metallic surfaces may be combined with the molecular recognition properties of calixarenes. We show here that a conformationally very flexible calix[8]arene derivative alone leads to the formation of very stable palladium, platinum and ruthenium nanoparticles of small dimensions. This calix[8]arene is functionalized with both thioester and hydroxyl groups. The former allows for the anchoring of the molecules onto the metallic surfaces, the later may be used for an easy post-derivatization of these nanoobjects. A stability test showed that the nanoparticles are not affected by heating for hours in strongly acidic organic solutions.

The synthesis of the sulfur functionalized calix[8]arene used in this study is depicted in Fig. 1.

Starting from the commercially available 4-(benzyloxy)phenol, the corresponding calix[8]arene is easily obtained by basecatalyzed condensation with paraformaldehyde [19]. From this calixarenic platform the thioacetate functionalized macrocycle is attained with an overall yield of 30% (see Supplementary material for experimental details).

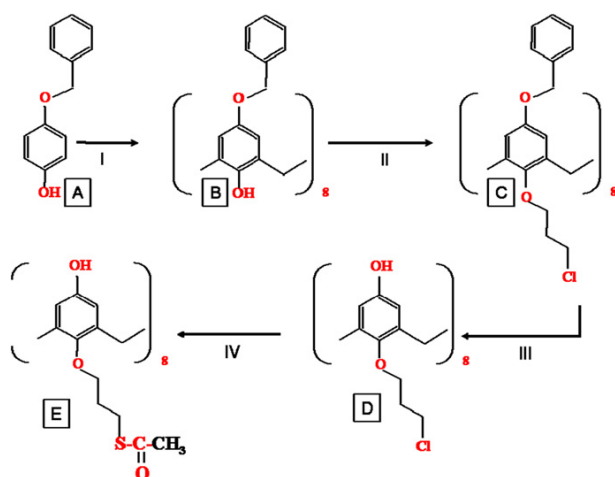


Fig. 1: Synthesis of a thioester-functionalized calix[8]arene. I: Paraformaldehyde/tBuOK (catalytic)/refluxing xylene, 70%. II: Bromochloropropane/NaH/THF/DMF, 51%. III: H_2 /Pd(OH) $_2$ (on carbon)/THF/MeOH (80/20 v/v), quantitative. IV: Potassium thioacetate/DMSO/RT, quantitative.

The reaction between 0.1 equivalent of this thioacetate functionalized calix[8]arene and 1.0 equivalent of a suitable zerovalent Pd, Pt or Ru metallic complex [Pd(dba) $_2$, Pt(dba) $_2$ and Ru(Cod)(Cot), respectively] under hydrogen in THF leads in all three cases to the formation of well defined metallic nanoparticles (see supporting information for experimental details) [20]. Fig. 2 shows TEM pictures of these three systems (more TEM pictures are provided in Supplementary material, S1).

However, larger aggregated particles of about 2–3 nm are observed in the case of ruthenium.

The reason for this is unclear, although a similar behavior has already been observed for thiol-stabilized Ru nanoparticles [20]. This difference may be explained by the formation of Ru–O bonds between adjacent nanoparticles. Such a phenomenon is not observed in the case of Pt and Pd nanoparticles, due to their lower affinity for oxygen.

These nanoparticles are smaller than those obtained with more conventional monofunctional thiols at equivalent sulfur concentration. This may be explained by the very high local thioester concentration around the metallic centers during the growth of the nanoparticles. Indeed, the grafting of the first thioester group brings the seven remaining ones in close proximity with the nanoparticle's surface, resulting in an increase of thioester effective concentration. This results in both an improved coverage of the surface, and size reduction.

A striking feature is the reduced size distribution of the nanoparticles, especially for Pd and Pt, indicating that some Fig. 2. (a) Pd, (b) Pt and (c) Ru nanoparticles stabilized by the thioester functionalized calix[8]arene E. size-selection processes are occurring during the synthesis. A possible explanation may lie in the fixed number of 8 structuring thiolate-type ligands per calix[8]arene. Assuming that all the calix[8]arene's sulfur atoms are bonded to

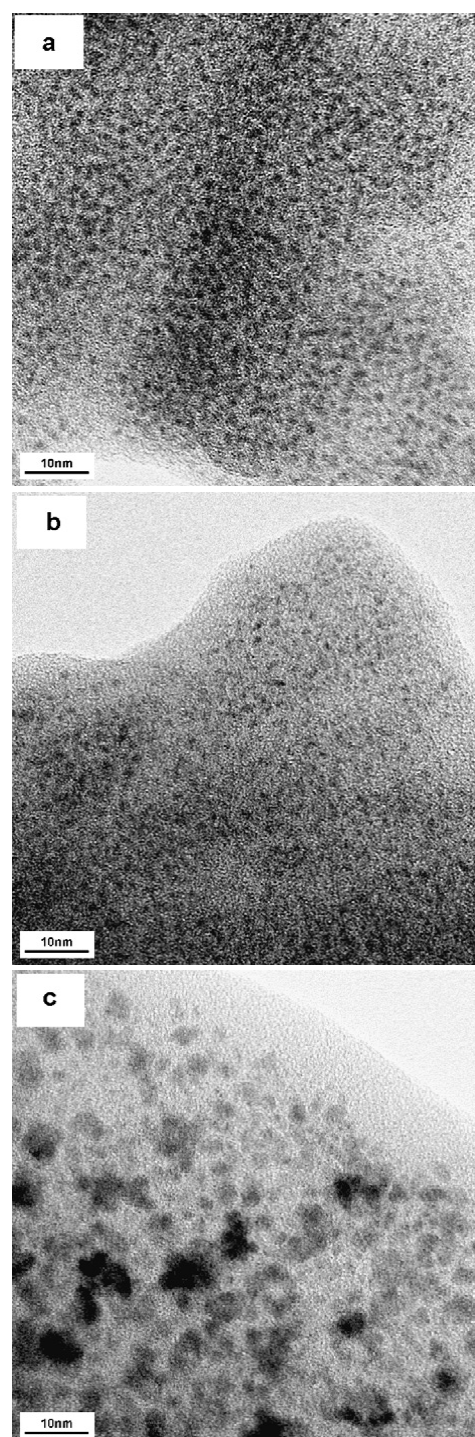


Fig. 2: (a) Pd, (b) Pt and (c) Ru nanoparticles stabilized by the thioester functionalized calix[8]arene E.

metallic surface atoms, the number of these surface atoms should thus be fixed as a multiple of 8. Such effect may result in a more defined geometry in comparison with monodentate ligands. As an example let us consider the case of a 1 nm cubooctahedral nanoparticle. In this case, the number of surface atoms (A_s) and total atoms (A_t) are 32 and 38, respectively.

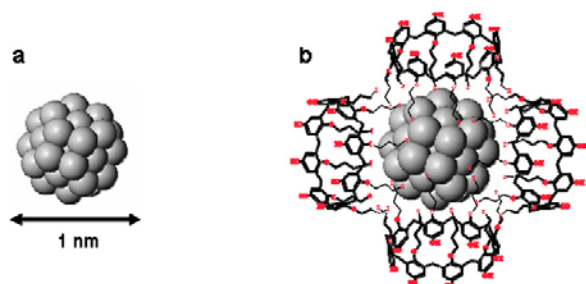


Fig. 3: (a) Model used for the description of the metallic core of the nanoparticles; (b) proposed structure for the palladium nanoparticles.

Considering (as a rough approximation) that all the 32 metal surface atoms are bonded to a sulfur atom from the calix[8]arene, 4 calixarenic ligands are likely to be grafted on the surface (Fig. 3). The observed sulfur-to-palladium ratio is close to the expected one in the case of the proposed model (32 sulfur atoms and 32 surface palladium atoms), as shown by elemental analysis (see Supplementary material). The same holds true for platinum and ruthenium nanoparticles. In these cases, elemental analysis shows a sulfur-to-metal ratio close to the expected one if all the surface atoms are bonded to sulfur.

To the best of our knowledge, such ligand-induced size selection mechanism was not yet reported.

The IR spectra of all these nanoparticles (S2) shows the presence of the expected signals associated with the calix[8]arene stabilizing ligand and the disappearance of the characteristic thioester C=O peak at 1690 cm^{-1} . It can thus be concluded that (i) the calix[8]arene macrocyclic framework is not affected by the synthetic procedure (no hydrogenation of the hydroquinone group for all three metals used in this study), and (ii) the thioester is cleaved during the growth of the nanoparticles (hydrogenolysis), most likely with formation of a transient thiol group which then adsorbs onto the surface of these nanoobjects. In the case of Pt and Ru nanoparticles this reaction probably occurs along with a decarbonylation of the starting thioester, as $\text{C}\equiv\text{O}$ is observed with these two metals (see below).

In the case of the Pd and Pt systems, signals associated with occluded solvents (THF) are observed around 1100 cm^{-1} even after vacuum drying at ambient temperature.

Such a solvent inclusion phenomena is commonly observed with most calixarenes [18].

More interestingly, for Pt and Ru nanoparticles, new signals are also observed at 2061 cm^{-1} (Pt) and 2025 cm^{-1} and 1917 cm^{-1} (Ru). The signals around 2060 cm^{-1} (Pt) and 2025 cm^{-1} (Ru) are attributed to the presence of CO groups (most likely from a decarbonylation of the thioester group) adsorbed in a terminal geometry [21,22]. Additionally, the large band observed at 1917 cm^{-1} for Ru nanoparticles could be assigned to the presence of Ru–H species, as adsorbed hydrogen atoms give peaks in the $1900\text{--}1960\text{ cm}^{-1}$ region [23]. This band is unsymmetrical and displays

shoulders. The vibration can be assigned to twin or dihydrogen-like types which are terminally bonded on the metal crystal [24].

It can thus be concluded that in the case of Pt nanoparticles, two different kinds of ligands (CO groups and thiolates from the calix[8]arene) are grafted at the same time onto the surface. In the case of the Ru ones, three different species (the calix[8]arene as its thiolate derivative, CO and hydrogen) are bonded to the surface. The presence of different species onto the surface may first be explained by different coordination modes for these ligands. Considering that the most stable binding modes of the thiolate ligand are generally the so called “hollow” or “bridging” ones, other “on top” coordination sites are still available (e.g., corners or edges) for extra species. A preferential binding of carbon monoxide and hydrogen onto the coordinatively unsaturated metal atoms located at the edges or corners of the nanoparticles is thus likely. The very small size of the nanoobjects points in the same direction, as in this case the number of “edge” or “corner type metallic centers” (“on top” sites, available for CO or hydrogen) is of the same order as the “face” ones (defining “hollow” or “bridging” sites, available for the thiolate ligands).

Moreover, once grafted onto the surface of the nanoparticles, the calix[8]arene ligand is conformationally restricted, resulting in an increased rigidity for this molecule. Accordingly, the mobility of calix[8]arene’s thiolate groups on the surface is reduced, as is their ability to saturate all the available coordination sites (compared with a more classical monodentate thiol). More metal atoms may thus remain available for coordination to other ligand species.

The different combinations of ligands observed for Ru, Pd and Pt nanoparticles may be explained first by the fact that although Ru–CO, Pt–CO, and Pd–CO bonds on one hand and Ru–H, Pt–H, and Pd–H bonds on the other hand are well documented in literature, they do not exhibit the same relative chemical stability. A competition is likely to occur between H, CO (and sulfur) for the surface atoms of the nanoparticles. Only the most stable combinations (in our experimental conditions) are observed at the end of the growth process.

Moreover, the formation of CO probably results from a decarbonylation of the starting thioester group. Although such decarbonylation processes are already known for some noble metals complexes, they are not easily observed for all noble metals. The absence of CO in the case of the palladium nanoparticles may be rationalized in this way, especially if one considers that the Pd–CO bond is less stable than the Ru–CO and Pt–CO bonds.

In the case of Pt and Ru nanoparticles, the presence of such catalytically relevant species as hydrogen and/or CO along with the calix[8]arene may lead to interesting catalytic behavior. The study of these systems is underway.

In order to test the chemical stability of the nanoparticles, a sample of these nanoparticles was heated for 2.5 h in a 0.3 M ethanolic solution of *p*-toluenesulfonic acid at $70\text{ }^{\circ}\text{C}$. For the palladium and platinum particles no precipitation was observed, showing the strong binding of the ca-

lix[8]arene ligand to the particles. These nanoparticles were then precipitated with pentane and dried under vacuum. These dried samples readily redissolve in organic solvents (such as dichloromethane, THF, ethanol) except pentane.

The IR spectra of Pd, Pt and Ru nanoparticles are similar to those observed before heating. As an example, the IR spectrum of the palladium nanoparticles after this acidic treatment is shown in S3. All the characteristic signals associated with the calix[8]arene are still observed, confirming the strong binding of the calix[8]arene ligand to the Pd surface. Additionally, the signals associated with included solvents (observed on the initial nanoparticles) have now disappeared. A TEM picture of the Pd nanoparticles after the acidic treatment shows that the size distribution of the nanoparticles remained essentially unaffected (S4).

In conclusion, a new sulfur-containing calix[8]arene derivative was synthesized and used for the synthesis of Pd, Pt and Ru nanoparticles. In all three cases, well defined, crystalline nanoobjects are obtained. In the case of Ru, 2–3 nm, aggregated nanoparticles are obtained. For palladium, 1 nm small, highly monodisperse nanoobjects are observed. In the case of platinum, discrete, subnanometric nanoparticles are present.

It is shown that surprisingly, although the presence of the calix[8]arene is observed as expected in all three cases (most likely as its thiolate derivative), carbon monoxide

and carbon monoxide plus hydrogen are also evidenced at the surface of platinum and ruthenium nanoparticles respectively.

As the calix[8]arene is functionalized with reactive hydroxyl groups, further derivatization of these nanoobjects should be possible, opening the way to a new family of tailor-made nanoparticles. This possibility is being investigated in our groups.

A first stability experiment using these nanoparticles revealed the high chemical stability (at least in acidic media) of these systems, opening the way to the derivatization of these nanoobjects and the study of their catalytic properties.

Supplementary material

Supplementary material for this article may be found on Science Direct, in the online version.

Please visit DOI: 10.1016/j.jcis.2007.07.083.

References

- [1] G. Schön, U. Simon, *Colloid Polym. Sci.* 273 (1995) 101.
- [2] V.L. Colvin, M.P. Schlamp, A.P. Alivisatos, *Nature* 370 (1994) 354.
- [3] A.P. Alivisatos, *Science* 271 (1996) 933.
- [4] K.A. Easom, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanyis, *Polyhedron* 13 (1994) 1197.
- [5] M.D. Musick, C.D. Keating, M.H. Keefe, M.J. Natan, *Chem. Mater.* 9 (1997) 1499.
- [6] G. Schmid, *Chem. Rev.* 92 (1992) 1709.
- [7] G. Schmid (Ed.), *Cluster and Colloids, from Theory to Application*, VCH, Weinheim, 1994.
- [8] T. Li, J. Moon, A.A. Morrone, J.J. Mecholsky, D.R. Talham, J.H. Adair, *Langmuir* 15 (1999) 4328.
- [9] K.V. Sarathy, G.U. Kulkarni, C.N.R. Rao, *Chem. Commun.* (1997) 537.
- [10] A. Rodriguez, C. Amiens, B. Chaudret, M.-J. Casanove, P. Lecante, J.S. Bradley, *Chem. Mater.* 8 (1996) 1978.
- [11] K. Naka, M. Yaguchi, Y. Chujo, *Chem. Mater.* 11 (1999) 849.
- [12] W. Shenton, D. Pum, U.B. Sleytr, S. Mann, *Nature* 389 (1997) 585.
- [13] T. Cassagneau, T.E. Mallouk, J.H. Fendler, *J. Am. Chem. Soc.* 120 (1998) 7848.
- [14] T. Yonezawa, T. Tominaga, D. Richard, *J. Chem. Soc. Dalton Trans.* (1996) 783.
- [15] T. Sato, D. Brown, B.F.G. Johnson, *J. Chem. Soc. Chem. Commun.* (1997) 1007.
- [16] S. Gomez, K. Philippot, V. Colliere, B. Chaudret, F. Senocq, P. Lecante, *J. Chem. Soc. Chem. Commun.* (2000) 1945.
- [17] R.H. Terrill, T.A. Postlethwaite, C.-H. Chen, C.-D. Poon, A. Terzis, A. Chen, J.E. Hutchison, M.R. Clark, G. Wignall, J.D. Londono, R. Superfine, M. Falvo, C.S. Johnson Jr., E.T. Samulski, R.W. Murray, *J. Am. Chem. Soc.* 117 (1995) 12537.
- [18] A. Wei, *Chem. Commun.* (2006) 1581; P. Leyton, S. Sanchez-Cortez, J.V. Garcia-Ramos, C. Domingo, M. Campos-Valette, C. Saitz, R.E. Clavijo, *J. Phys. Chem. B* 108 (2004) 17484; T.R. Tshikhudo, D. Demuru, Z. Wang, M. Brust, A. Secchi, A. Arduini, A. Pochini, *Angew. Chem. Int. Ed.* 44 (2005) 2913; A. Arduini, D. Demuru, A. Pochini, A. Secchi, *Chem. Commun.* (2005) 645.
- [19] A. Casnati, R. Ferdani, A. Pochini, R. Ungarol, *J. Org. Chem.* 62 (1997) 6236; P.C. Leverd, V. Huc, S. Palacin, M. Nierlich, *J. Inclusion Phenom. Macrocyclic Chem.* 36 (3) (2000) 259–266.
- [20] C. Pan, K. Pelzer, K. Philippot, B. Chaudret, F. Dassenoy, P. Lecante, M.-J. Casanove, *J. Am. Chem. Soc.* 123 (2001) 7584–7593.
- [21] R.A. Dalla Betta, *J. Phys. Chem.* 79 (23) (1975) 2519.
- [22] K. Christmann, *Surf. Sci. Rep.* 9 (1998) 1.
- [23] K. Pelzer, K. Philippot, B. Chaudret, *Z. Phys. Chem.* 217 (12) (2003) 1539–1547.
- [24] T. Pery, K. Pelzer, G. Buntkowsky, K. Philippot, H.-H. Limbach, B. Chaudret, *Chem. Phys. Chem.* 6 (4) (2005) 605–607; K. Christmann, *Mol. Phys.* 66 (1998) 1; J. Kubota, K. Aika, *J. Chem. Soc. Chem. Commun.* (1992) 6