15-Membered triolefinic macrocycles as stabilizers of palladium(0) nanoparticles†

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15-Membered triolefinic macrocycles form complexes with palladium(0). However, metal nanoparticles are formed instead of discrete complexes if substituents provided with the ability to stabilize nanoparticles are incorporated into the structure of the macrocycle. Ancillary substituents include fluorous and polyoxyethylenated chains. The role of initial organometallic coordination in the early steps of nanoparticle formation is underlined.

Introduction

The 15-membered triolefinic macrocycles **1** (Fig. 1) form stable palladium(0) and platinum(0) complexes **2**[1] and are reminiscent of the cyclic butadiene trimers, the 12-membered cyclododeca-1,5,9-trienes **3**, which coordinate nickel(0).[2] Coordination of one metal atom in macrocycles **1** takes place by the three olefinic double bonds, the nitrogen atoms of sulfonamides being devoid of coordinating ability. Macrocycles **1** can be prepared from *trans*-1,4-dibromobutene and aromatic sulfonamides. Since many sulfonamides or their related sulfonyl chlorides are commercially available, the properties of compounds **1**—solubility, crystallinity, electrochemical properties—can be tailored varying the aromatic ring.[1] Moreover, macrocycles **1** or their palladium complexes have found use in heterogeneous catalysis when anchored to a mesostructured silica,[3] and as liquid crystals.[4] The 15-membered cyclic triacetylenes related to **1** also coordinate palladium(0) and cycloisomerize to hexasubstituted benzenes under metal catalysis.[5] In summary, a vast array of properties can be conferred to macrocycles **1** depending on the nature of the substituents in the aromatic ring, while maintaining the coordinating ability.

Some time ago we found in a truly serendipitous manner that heavily fluorinated ketone **4** (Fig. 1) stabilized palladium nanoparticles.[6] Other fluorous compounds, even fluorinated hydrocarbons, stabilize nanoparticles of palladium,[6b,c] gold[6d,7] or metal oxides.[8] Stabilization of nanoparticles is customarily divided into three categories:[9,10] (i) electrostatic stabilization by cationic and anionic surfactants; (ii) steric stabilization by compounds possessing a functional group endowed with high affinity for metals: thiols, sulfides, amines and phosphines; and (iii) entrapment: in polymers (*e.g.* polyvinylpyrrolidone), cyclodextrins, or dendrimers, although electrostatic stabilization also operates with polymers.[11] In all cases the protecting agents ought to interact in an attractive manner with the surface of the metal.

Ketone **4** is a fluorous analogue of dibenzylideneacetone, dba, (H instead of C_8F_{17}), the ligand of palladium in the family of stable complexes $Pd_2(dba)_3 \cdot L$ (L = solvent or dibenzylideneacetone). When we attempted to reproduce the preparation of $Pd_2(dba)_3 \cdot L$ with ketone **4**, we obtained palladium nanoparticles instead of the expected discrete complex.[6a,b]

We thought that the different outcome of the reactions—discrete complex from dba and nanoparticles from **4**—was due to the fluorinated chains. This poses the intellectual problem of understanding the reason for the difference. Since then, we felt that initial coordination of an initial metal atom was helpful for the formation of nanoparticles albeit not necessarily, since also other non-coordinating fluorous compounds do stabilize nanoparticles.[6,7] Although kinetic work on the growing of nanoparticles has been published,[11,12] little is known on the process of binding together the first few metal atoms, *e.g.* less than ten.[13]

Coordinating macrocycles **1** fulfil the requirements to test our idea that initial coordination of the metal with the double bonds promoted the formation of nanoparticles if appropriate stabilizing groups were bound to the aromatic rings. We have chosen macrocycles bearing long fluorinated chains, which could provide more examples of the curious stabilizing effect of these chains and macrocycles having polyoxyethylenated chains because stabilization of palladium nanoparticles by ligands containing polyoxyethylenated chains has

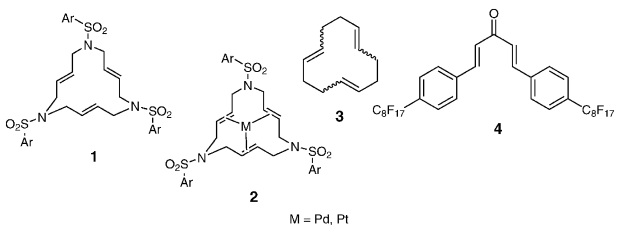

Fig. 1 Structures of macrocycle **1** and other pertinent compounds.

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† Electronic supplementary information (ESI) available: Full experimental details on the preparation of macrocycles **5**, **11** and **12**. ^1H and ^{13}C NMR of **11** and **17**, ESI-MS of **11**, MALDI-TOF MS of **17**. High Resolution Transmission Electron Microscopy (HRTEM) and Electron Diffraction (ED) of nanoparticles of Entries 2, 4–13. p-XRD of **7** and nanoparticles of Entry 9. See DOI: 10.1039/b608673j

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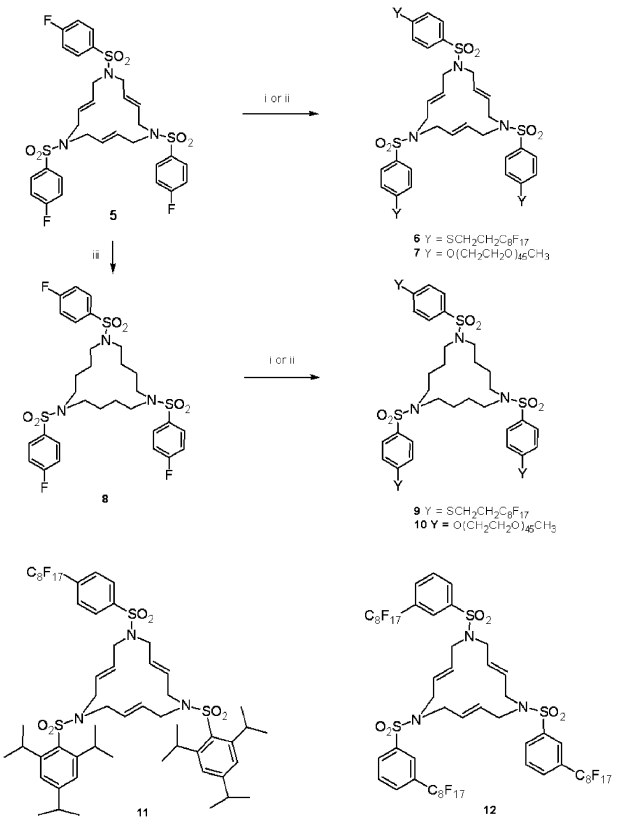
precedents.[14] Moreover, hydrogenation of the three double bonds of products of type **1** give another series of macrocycles which obviously cannot form metal complexes of type **2**. Consequently, hydrogenated macrocycles should be less effective towards formation of nanoparticles.

The most used method for the formation of palladium(0) nanoparticles involves reduction of a palladium(II) salt by an appropiate reducing agent in the presence of a stabilizer.[9] However, in a preliminary work aimed at the preparation of macrocyclic palladium complexes **2** using our standard methodology,[1] which involved the use of $Pd(dba)_2$ as a palladium(0) source, we had observed the formation of black solids containing metal nanoparticles when fluorous or polyoxyethylenated chains were present in the macrocycle.

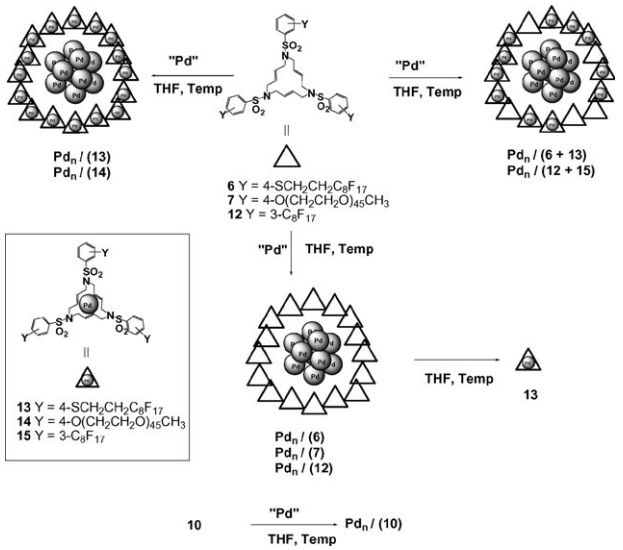
Therefore, we decided to explore further this new method for the preparation of palladium(0) nanoparticles and to determine the role of initial organometallic coordination in the formation of palladium nanoparticles using a new type of stabilizing macrocyclic compound possessing the above mentioned polyfluorinated and polyoxyethylenated chains.

Results and discussion

Thus, we prepared **6**, **7**, **11** and **12** (Scheme 1) as candidates for nanoparticle stabilization. We synthesized also hydrogenated macrocycles **9** and **10** (Scheme 1), which should not form

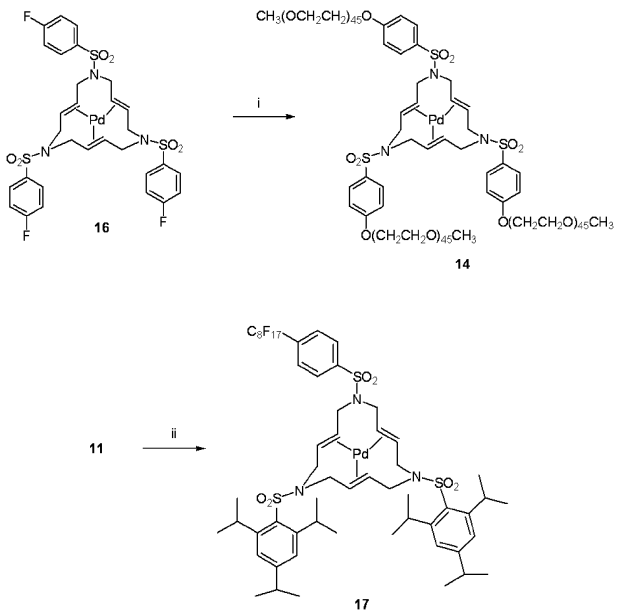


Scheme 1 Preparation of macrocycles; reagents and conditions. (i) To obtain **6** and **9**: $HSCH_2CH_2C_8F_{17}$, Cs_2CO_3, *n*-BuNCl, THF, room temperature. (ii) To obtain **7** and **10**: $HO(CH_2CH_2O)_{45}CH_3$, NaH, THF, room temperature. (iii) Pd–C 10%, $PtO_2 \cdot H_2O$, THF, room temperature.



Scheme 2 Preparation of palladium(0) nanoparticles. See Table 1 and the Experimental section.

nanoparticles. For the sake of clarity in the schematic presentation of results, we summarize the synthesis of the different macrocycles in Scheme 1, the experiments leading to palladium nanoparticles in Scheme 2 and the obtaining of palladium(0) macrocyclic triolefinic complexes in Scheme 3. Pivotal compound **5**[15] and its conversion into fluorous macrocycle **6**[16] have been reported elsewhere. We have now introduced a significant improvement in the preparation of macrocycles of type **1** in general and **5** in particular: *trans*-1,4-dichloro-2-butene is used instead of the corresponding dibromo compound. In one step of the synthesis a large excess of dihalogenobutene is required and elimination of the low-boiling dichlorobutene is much easier than elimination of



Scheme 3 Preparation of macrocyclic palladium(0) complexes. Reagents and conditions: (i) PEG-2000 monomethyl ether, NaH, THF, room temperature; (ii) $Pd(dba)_2$ or $Pd(PPh_3)_4$, refluxing THF.

dibromobutene. The new preparation of **5** is fully described in the Supplementary Information.† Compound **6** was prepared by nucleophilic aromatic substitution of fluoride with 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol. The same type of reaction performed with polyethylene glycol 2000 (PEG 2000) monomethyl ether afforded **7**. Compounds **9** and **10**, devoid of olefinic coordinating ability, were prepared in two steps consisting of catalytic hydrogenation of **5** into **8** followed by S_NAr-type reaction[16] with 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol or polyethylene glycol 2000 (PEG 2000) monomethyl ether to afford **9** and **10**, respectively. Macrocycles **11** and **12** (Scheme 1) were prepared by standard methods.†

As we have mentioned before, macrocycles having many different substituents in the arenesulfonyl moiety form discrete stable palladium(0) complexes when treated with sources of palladium(0) such as $Pd_2(dba)_3 \cdot L$ or $Pd(PPh_3)_4$.[1,17] In contrast, macrocycles **6**, **7** and **12** —but not **11**—afforded directly metal nanoparticles by the same treatment (Scheme 2, Table 1). The nanoparticles prepared in our work are frequently stabilized by macrocycles possessing already a coordinated central palladium atom, in other words, the stabilizing shield is made of complexes **13** or **14**; these materials are denoted as **Pd_n/(13)** or **Pd_n/(14)**. But other metal nanoparticles were surrounded by free macrocycles and denoted as **Pd_n/(6)**, **Pd_n/(7)** and **Pd_n/(12)**. In the first situation two types of palladium atoms are present in the material, some atoms form the nanoparticles, whereas some others are coordinated to the macrocycles in the protecting shield. We have also found that under some conditions palladium(0) nanoparticles were stabilized by both free macrocycles and their palladium(0) complexes, such as in the case of **Pd_n/(6 + 13)** and **Pd_n/(12 + 15)** (see Scheme 2). NMR spectra distinguish very well free macrocycles from their palladium(0) complexes since free macrocycles present signals for the olefinic protons and carbons at δ *ca.* 5.50–5.80 and *ca.* 124 ppm, whereas in palladium complexes strong upfield shifts are observed, up to δ 2.5–4.40—depending on the proton considered—and 78–83 ppm, respectively (see the Experimental section and Supplementary Information†). The complexity of the NMR spectra of palladium(0) complexes of macrocycles **1** stems from the generation of chirality on the olefinic carbon atoms upon complexation. This is better understood if the palladacyclopropane formulation is adopted. Depending on which face of the olefin coordinates, the chirality will be *R,S* or *S,R* in the former olefinic carbon atoms. Since the three olefins do not give rise to identical chirality on coordination, this produces non-equilibrating isomers when two aryl groups are identical and the third is different. This problem has been thoroughly discussed.[17b]

When fluorous macrocycle **6** was treated with $Pd(dba)_2$ in refluxing THF nanoparticles containing complex **13** in the stabilizing shield were formed (Entries 1–3, Table 1). This behaviour is in sharp contrast to the general behaviour of macrocycles **1** that afford stable palladium(0) complexes of type **2** without problems.[1,17] Nanoparticles of Entries 1 and 2 presented signals in ^{1}H-NMR for the olefinic protons only at δ *ca.* 2.84, 3.76, 4.02, indicating clearly the presence of a palladium atom coordinated to the three olefins of the macrocycle. Free macrocycle **6** is present up to 30% in the stabilizing

Table 1 Palladium nanoparticles[a] stabilized by macrocycles and complexes

Entry	Notation of nanoparticles	Pd source	Temperature	Time	Initial molar ratio[b]	Molar ratio in nanoparticles	Weight% of Pd[c]	Yield[d] (%)	ϕ/nm	Atoms per particle[e]
1[f]	**Pd_n/(13)**	$Pd(dba)_2$	Reflux	3 + 2 days[g]	Pd : **6** = 2.4	Pd : **13** = 1.0[h]	10.20	70	3.9	2.1×10^3
2[f]	**Pd_n/(13)**	$Pd(dba)_2$	Reflux	3 + 2 days[g]	Pd : **6** = 2.4	Pd : **13** = 0.4[h]	6.8	58	2.9	8.7×10^2
3	**Pd_n/(6 + 13)**	$Pd(dba)_2$	Reflux	3 days[i]	Pd : **6** = 2.4	30% of **6** and 70% of **13**[j]	3.47	32	2.9	8.7×10^2
4	**Pd_n/(6)**	$Pd(dba)_2$	140 °C[k]	22 h[l]	Pd : **6** = 2.4	—[l]	—[l]	—[l]	4.9	4.1×10^3
5	**Pd_n/(12 + 15)**	$Pd(dba)_2$	Reflux	2 + 3 days[g]	Pd : **12** = 5.0	93% of **15** and 7% of **12**[j]	23	76	4.6	3.5×10^3
6	**Pd_n/(12 + 15)**	$Pd(PPh_3)_4$	Rt	14 + 24 + 72 h[g]	Pd : **12** = 2.7	92% of **15** and 8% of **12**[j]	—[l]	—[l]	3.8	1.9×10^3
7	**Pd_n/(12)**	$Pd(dba)_2$	140 °C[k]	14 h	Pd : **12** = 2.4	—[l]	—[l]	—[l]	5.3	5.2×10^3
8	**Pd_n/(14)**[m]	$Pd(dba)_2$	Reflux	24 h	Pd : **7**[i] = 2.3	Pd:**14** = 1.34[h]	1.78	46	4.8	3.9×10^3
9	**Pd_n/(7)**	$Pd(dba)_2$	140 °C[k]	24 h	Pd : **7**[i] = 2.3	Pd:**7** = 0.31[h]	0.48	11	5.6	6.2×10^3
10	**Pd_n/(7)**	$Pd(dba)_2$	Reflux[n]	1 + 6 + 4 days[g]	Pd : **7** = 2.3	Pd:**7** = 2.4[h]	3.25	61	5.3	5.2×10^3
11	**Pd_n/(14)**[m]	$Pd(PPh_3)_4$	Rt	24 + 24 h[g]	Pd : **7** = 2.0	Pd:**14** = 1.4[h]	1.48	36	5.5	5.7×10^3
12	**Pd_n/(14)**[m]	$Pd(dba)_2$	Rt	17 h	Pd : **7**[i] = 2.1	Pd:**14** = 1.1[h]	1.16	23	3.4	1.3×10^3
13	**Pd_n/(10)**	$Pd(dba)_2$	Reflux	18 h	Pd : **10** = 2.3	—[l]	0.33	8	4.0	2.2×10^3

[a] In all cases face-centred cube palladium(0) was determined by electron diffraction (see text). [b] For the sake of clarity moles of Pd have been calculated as if the precursor was $Pd(dba)_2$ or $Pd(PPh_3)_4$. [c] Total palladium (in metallic core + in surrounding complexes when applicable) determined by elemental analyses. [d] Total palladium in nanoparticle/initial palladium. [e] Determined as $(V_{nano}/V_{atom}) \times 0.74$ (space occupation). [f] For different working up in entries 1 and 2 see Experimental. [g] The total amount of Pd was added in several portions. [h] Calculated from elemental analyses. [i] All palladium was added at once. [j] Molar ratio of stabilizers by ^{1}H NMR. [k] Closed reactor. [l] Not determined. [m] See text for explanation about the nature of stabilizing complex. [n] Accidentally, in a certain moment during the last 4 days at reflux the solvent was evaporated to dryness.

shield of nanoparticles of Entry 3 as evidenced by a signal at $\delta = 5.62$. When more severe conditions were adopted (heating at 140 °C in a closed reactor for about one day, Entry 4), the nanoparticulated material showed only the presence of macrocycle **6** as a stabilizing agent.

A sample of complex **13** (see the structure in Scheme 2) could be obtained when the black solution from the reaction of macrocycle **6** with $Pd(dba)_2$ in refluxing THF was directly chromatographed through silica gel. The chromatography decomposes the nanoparticulated material, the non-coordinated palladium being retained on top of the column.

Nanoparticles of Entries 1 (Fig. 2) and 3 (Fig. 3) are of good quality, small and disperse. Once more fluorous compounds stabilize small nanoparticles. HRTEM permits the observation of details of the particles. Nanoparticles of Entry 2 (Supplementary Information†) are more agglomerated although in general are well defined.

Compound **11** (Scheme 1) did not form nanoparticles, probably the fluorine loading was insufficient. Instead, complex **17** (see Scheme 3 for the preparation of macrocyclic palladium complexes) was isolated without problems when it was treated with $Pd(dba)_2$ or $Pd(PPh_3)_4$ in refluxing THF.

In other words, macrocycle **11** exhibits the standard coordination ability characteristic of this family of 15-membered macrocycles.[17]

In contrast, macrocycle **12** (Scheme 1) has enough fluorous character to stabilize nanoparticles and direct formation of nanoparticulated material was found upon treatment with a palladium(0) source, whereas isolation of complex **15** was not possible (see **Pd_n/(12 + 15)** and **Pd_n/(12)** in Scheme 2 and Table 1). Thus, in the experiment performed with **12** and $Pd(dba)_2$ in refluxing THF, the stabilizing shield was made of a 93 : 7 mixture of complex **15** (olefinic signals at δ = *ca.* 2.81, 3.80, 4.06) and free ligand **12** ($\delta = 5.64$) (Entry 5). The

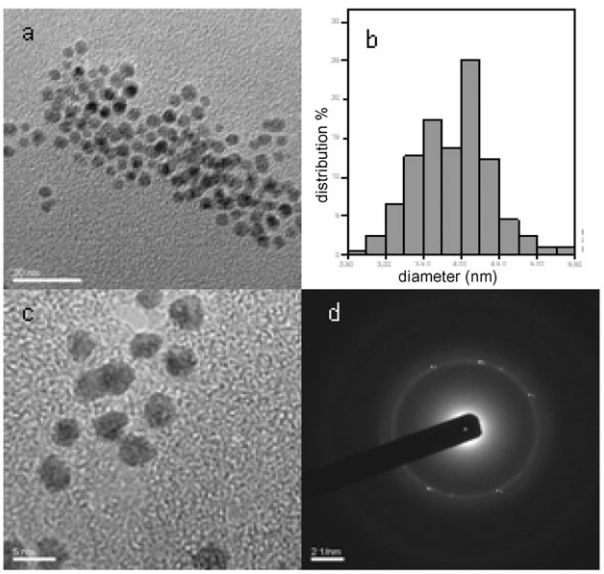


Fig. 2 Nanoparticles **Pd_n/(13)** of Entry 1 (Table 1). (a) TEM image (scale bar = 20 nm); (b) size distribution (average 3.93 ± 0.50 nm); (c) HRTEM (scale bar = 5 nm); (d) electron diffraction (0.23 nm between Pd layers).

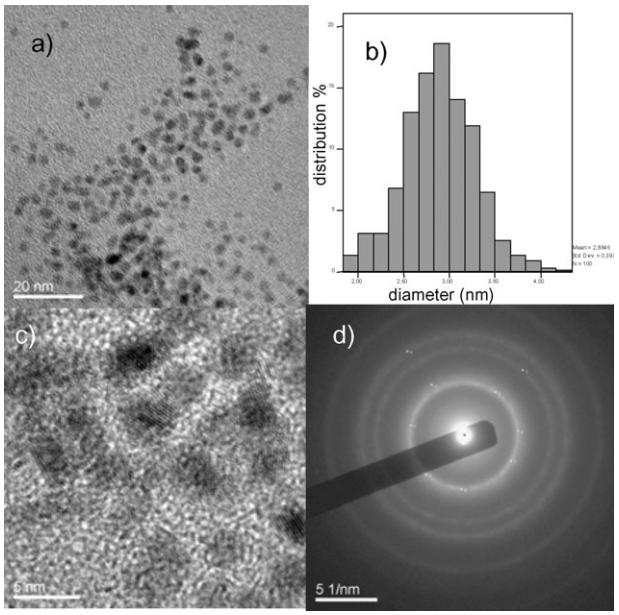


Fig. 3 Nanoparticles **Pd_n/(6 + 13)** of Entry 3. (a) TEM image (scale bar = 20 nm); (b) size distribution (average 2.94 ± 0.39 nm); (c) HRTEM (scale bar = 5 nm); (d) electron diffraction (0.23 nm between Pd layers).

nanoparticles presented a certain tendency to agglomerate. Similar results were obtained when fluorous macrocycle **12** was treated with $Pd(PPh_3)_4$ at room temperature for several days (Entry 6). In contrast, when **12** was reacted with $Pd(dba)_2$ at higher temperature (140 °C in a closed reactor) only the free macrocycle **12** was observed by NMR in the stabilizing shield (Entry 7).

Fluorous compound **9** (Scheme 1), devoid of coordinating ability, does not form nanoparticles under the same experimental conditions used for the triolefinic fluorous macrocycle **6**. This reinforces our hypothesis: the initial coordination of a first palladium atom is a favourable factor for nanoparticle formation.

Polyoxyethylenated triolefinic macrocycle **7** (Scheme 1) is also a good stabilizer of palladium(0) nanoparticles. Thus, when **7** was treated with $Pd(dba)_2$ in refluxing THF, nanoparticles **Pd_n/(14)** were formed featuring complex **14** in the stabilizing shield (Entry 8). Similar results were found by treatment of **7** with $Pd(PPh_3)_4$ or $Pd(dba)_2$ in THF at room temperature (Entries 11 and 12 of Table 1). But if the temperature is raised to 140 °C in a closed reactor or if the solvent is permitted to dry (*ca.* 110 °C of bath temperature), the palladium coordinated with the olefins is lost and **Pd_n/(7)** material is formed with macrocycle **7** as stabilizer (Entries 9 and 10 of Table 1).

Thus, for both fluorous and polyoxyethylenated macrocycles the effect of the temperature on the outcome of the process appears to be the same: nanoparticles are formed in refluxing THF and even at room temperature, the corresponding macrocyclic palladium(0) complex being the only or the major stabilizer present in the protecting shield in these cases. At higher temperatures (140 °C) the palladium coordinated to the olefins is lost and the stabilizing shield of the nanoparticles is formed by the free triolefinic macrocycle. Thus, the initially

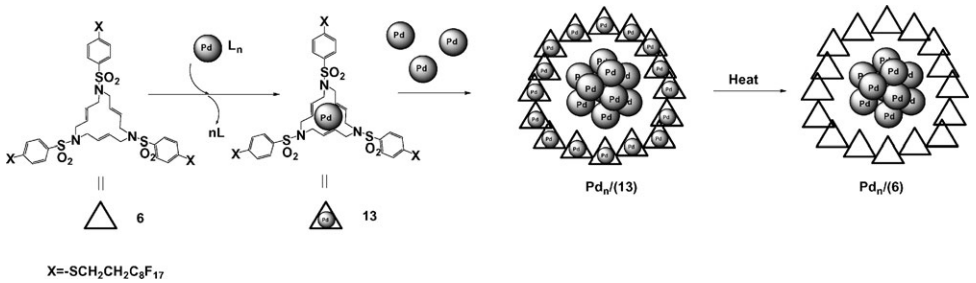


Fig. 4 Sequence of events in the formation of nanoparticles **Pd$_n$/(6)** and **Pd$_n$/(13)**.

coordinated palladium atoms form metal nanoparticles upon heating, although partial decomposition to black palladium cannot be ruled out, which should be eliminated by filtration through Celite or PTFE filter (see Experimental). Fig. 4 describes a sequence of steps compatible with these observations.

When a THF solution of fluorous macrocyclic complex **13** was heated overnight at 140 °C in a sealed tube, a grey solid containing nanoparticles stabilized by the corresponding free ligand, **Pd$_n$/(6)**, was obtained (Scheme 2). This fact seems to confirm in this case the sequence of events described in Fig. 4, the formation of nanoparticles from the palladium(0) complex and then the loss of the coordinated palladium due to the high temperature.

Pure macrocyclic polyoxyethylenated palladium complex **14** is not available under the usual conditions, because nanoparticles **Pd$_n$/(14)** are formed as we have mentioned before. Alternatively, compound **14** has been obtained by an S_NAr-type reaction of complex **16**[18] with PEG-2000 monomethyl ether in THF at room temperature in the presence of sodium hydride (Scheme 3).

In contrast with the behaviour of fluorous macrocyclic complex **13**, polyoxyethylenated macrocyclic complex **14** resulted to be more stable and no decomplexation and no nanoparticle formation was observed after the heating for one day of a THF solution of **14** at 140 °C. After addition of $Pd(dba)_2$ to this solution and further heating at 140 °C for about 30 h, partial decomplexation was observed by ^{1}H NMR (70% of **14**, 30% of **7**), but no nanoparticles were detected by HRTEM. Therefore, for triolefinic macrocycles bearing polyoxyethylenated chains the sequence of events seems to be different from that in the fluorous macrocycles and probably the initial coordination to the three carbon–carbon double bonds of the triolefinic core is not the first step in the process of nanoparticle formation. This thermal stability was intriguing us after the observation of nanoparticles in Entries 8–10 of Table 1. For this reason, we monitored by ^{1}H NMR the reaction of **14** and $Pd(dba)_2$ (molar ratio 1 : 2.2) in THF at 140 °C in a sealed tube. After 20 min signals corresponding to coordinated olefins at 4.60 (dd) were present, together with a signal at 5.55 (apparent d) corresponding to free olefins. Similar results were obtained after 3 h and after 5 h. After 20 h of reaction the signal at 4.6 ppm corresponding to the coordinated olefins was still present, together with a broad singlet at 5.59 (corresponding to free olefins of macrocycle **7**), which was of higher intensity than another broad singlet at 5.52 ppm. The presence of a residual signal of free olefins at *ca.* 5.5 ppm had been observed in the **Pd$_n$/(14)** nanoparticles. In contrast, this signal is absent in the complex **14** formed from complex **16** (Scheme 3). We presume that the complex stabilizing the palladium nanoparticles in Entries 8, 11 and 12 of Table 1 is not **14**, but a related complex in which the olefins are partially decomplexed and probably the polyoxyethylenated chain acts as a coordinating agent. This would explain the unexpected thermal stability of **14** and that formation of nanoparticles is not observed by thermal treatment of this complex.

Moreover, we tested the behaviour of the polyoxyethylenated compound **10** (Scheme 1), devoid of a triolefinic coordinating core. We found that it was able to form palladium(0) nanoparticles, **Pd$_n$/(10)**, by reaction with $Pd(dba)_2$ in refluxing THF, although the content of metal is low (Entry 13 of Table 1). This is in sharp contrast with the behaviour of fluorous compound **9**. The coordinating ability of the oxygen atoms present in the polyoxyethylenated chains should be the reason for such a difference. In the polyoxyethylenated macrocycles the triolefinic core is thus not essential for nanoparticle formation.

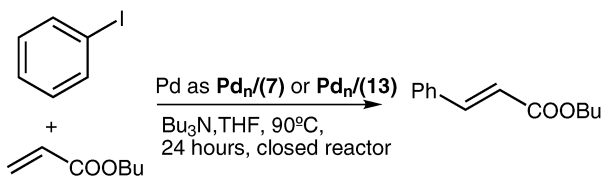
In all cases where nanoparticles were formed, electron diffraction of the samples showed the characteristic pattern of face-centred cubic palladium(0) with the average d-spacing values given in the electronic Supplementary Information.†

In our previous studies of formation of metal nanoparticles (Pd, Au)[6c,d] with fluorinated stabilizers, powder X-ray diffraction provided us with significant information. Solid fluorinated stabilizers showed well-defined diffractograms in the low angle range 2–20 of the 2θ scale, which indicated a degree of order that was basically preserved in the nanoparticles, which presented diffractograms showing similar ordered structures. This observation made us to postulate a mechanism of stabilization based on the entrapment of the palladium and gold nanoparticles within the fluorinated compound. In this work, we have also performed the powder X-ray diffraction of polyoxyethylenated triolefinic macrocycle **7** and the nanoparticles **Pd$_n$/(7)** of Entry 9 of Table 1 (See Supplementary Information†). Compound **7** exhibits diffraction peaks indicating a long-range ordered structure and the same crystalline phases of this polyoxyethylenated compound exist in the related nanoparticle sample **Pd$_n$/(7)**. Therefore, we assume a similar mechanism of stabilization for the fluorous and the polyoxyethylenated macrocycles described in this work, which should be an entrapment of the palladium(0) nanoparticles within the solid framework of the mentioned compounds. Long-range ordered structures for compounds bearing

polyoxyethylenated[19] and fluorinated chains[6c,d,20] have been previously reported. These ordered structures provided by these type of chains must be in the origin of the competitive formation of nanoparticles when palladium(0) complexation with the macrocycles **6**, **7** and **12** is tested. The ^{1}H NMR spectra allows us to know the nature of the stabilizing species (free macrocycle or macrocyclic complex) present in the solid nanomaterial and in solution. While an entrapment stabilization mechanism is postulated for the solid material, the kind of interaction acting in solution remains unclear.

Metal nanoparticles in general and palladium nanoparticles in particular, have found application in catalysis due to their high specific surface.[9p] We have described fluorous biphasic systems that permitted recovery and reutilization of palladium nanoparticles as catalysts in Suzuki cross-coupling and in Mizoroki–Heck reactions.[6a] Now, we have tested two batches of nanoparticles stabilized by macrocycles featuring different stabilizing chains. Our experiments are not biphasic; however, the catalytic material was recovered in a different manner and reutilized. Thus, nanoparticles **Pd$_n$/(13)** of Entry 2 catalyzed the Mizoroki–Heck reaction of iodobenzene with *n*-butyl acrylate (Scheme 4). Excellent conversions of iodobenzene were secured in six consecutive runs using the recovered sample of nanoparticulated material from the previous run. Recovery was achieved by evaporation of the mixture and extraction of all reaction products with cold acetonitrile. The insoluble nanoparticles were used in the following reaction. Butyl cinnamate was isolated in 94% yield in the third run. The loss of activity of the catalytic material was evident in the sixth run. The recovered material from the fifth run was examined by HRTEM showing particles of about 100 nm. Whereas this size is considered in the limit of the nanometric scale, agglomeration of the original catalyst was evident, which can explain the loss of activity. On the other hand the recovered catalytic material was **Pd$_n$/(6)** (^{1}H-NMR monitoring) or in other words, free macrocycle **6** was the only stabilizing compound around the metal nanoparticles.

Nanoparticles **Pd$_n$/(7)** of Entry 10 containing 3.25% of metal were tested also in the Mizoroki–Heck reaction of iodobenzene with *n*-butyl acrylate (Scheme 4). Excellent conversions of iodobenzene were secured in five consecutive runs using the same sample of nanoparticulated material, the reaction time being the same in all runs (24 h). Butyl cinnamate was isolated in 79% yield in the first run. However, reactions with 4-bromoacetophenone failed. Recovery of the catalytic material was achieved by addition of diethyl ether followed by centrifugation and separation of the organic layer. The insoluble nanoparticles were introduced in the following reaction.



Conversions for **Pd$_n$/(13)**
Run 1: 97% (at 7 hours)
Run 2: 99%
Run 3: 99% (94% isolated)
Run 4: 99%
Run 5: 99%
Run 6: 90% (95% at 38 h)

Conversions for **Pd/7**
Run 1: 97% (79% isolated)
Run 2: 94%
Run 3: 88%
Run 4: 84%
Run 5: 86%

Scheme 4 Heck reaction catalyzed by **Pd$_n$/(13)** (Entry 2) and **Pd$_n$/(7)** nanoparticles (Entry 10).

Conclusions

15-Membered triolefinic macrocycles **1** are organometallic coordinating agents through the olefinic bonds.[17] This standard behavior is modified if substituents that stabilize nanoparticles (fluorous chains and polyoxyethylenated chains) are introduced in the aromatic sulfonamide moieties of the macrocycles. In such cases nanoparticles between 2.9 and 5.6 nm of diameter are formed. Therefore, we formulate this hypothesis: nanoparticle formation is favoured if the stabilizing molecule has the ability to coordinate an initial metal atom. This ability is secured in the fluorous macrocycles by the triolefinic core. In the polyoxyethylenated macrocycles these chains contain coordinating oxygen atoms, the triolefinic core being non-essential for nanoparticle formation. However higher content of palladium(0) in the nanoparticulated material have been found when the triolefinic macrocycle is present.

In general, smaller size nanoparticles are obtained when fluorous macrocycles are used as stabilizing agents. The way of addition of the palladium(0) source or the amount of metal added have small effect on the size of the nanoparticles.

Our method of forming nanoparticles is different from other methods currently used that are based on: (i) the reduction of a high valence metal salt in the presence of the stabilizer; (ii) the hydrogenation of an unsaturated ligand in a metal(0) complex; or (iii) vapour metal deposition. Our method, here described, is based in the interchange of ligand between a discrete complex ($Pd(dba)_2$ or $Pd(PPh_3)_4$) and macrocycles of type **1**. Indeed macrocycles **1** are better ligands than dba and therefore, transfer of the initial palladium atom to the macrocycle is favoured.[1] In the case of $Pd(PPh_3)_4$, triphenylphosphine is a better ligand than macrocycles **1**.[1] However, transfer of metal to the macrocycle is favoured by oxidation of the phosphine to its oxide, a process difficult to avoid even by working under an inert atmosphere.

Two of these new nanoparticuled materials have been tested as catalyst or precatalyst of a Mizoroki–Heck reaction in homogeneous media, being easily recovered and reused. Several cycles have been performed and small variations in their catalytic activity have been observed. These phosphine-free palladium catalysts offer the advantage of superior stability in the face of oxidation. Phosphines are readily oxidized to the corresponding phosphine oxides, which can prevent the easy recovery and recycling of the catalyst. Further experiments will be done in the future in order to study more deeply the catalytic activity of these new materials.

Experimental

General methods and materials

Elemental analyses for C, H, N, S and Pd are the average of two determinations. IR spectra were determined by the Attenuated Total Reflectance (ATR) mode.

HRTEM analyses were performed in the Servei de Microscópia of the Universitat Autónoma de Barcelona, in a Hitachi H-7000 model at 100 kV and in a JEOL JEM-2010 model at 200 kV.

The HRTEM measurements were made by sonication of the nanoparticulate material in hot THF for about ten minutes; then one drop of the finely divided suspension was placed on a specially produced structureless carbon support film having a thickness of 4–6 nm and dried before observation.

p-XRD measurements were carried out on a Siemens D5000 diffractometer with an area detector operating under Cu Kα (1.5406 Å) radiation, at the Laboratori de Cristal.lografia i Raigs X at the Institut de Ciència de Materials de Barcelona.

Compounds **5**[15], **6**[16] and **17**[18] have been previously reported. The preparation of macrocycles **11** and **12** is described in the Supplementary Information.† HRTEM and electron diffraction images for materials of Entries 2 and 4–13 of Table 1 and p-XRD of **7** and nanoparticles of Entry 9 of Table 1 are available as Supplementary Information.†

Syntheses of macrocycles

(*E*,*E*,*E*)-1,6,11-Tris[4-(methoxy(polyoxyethylene)phenylsulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene, 7. A solution of PEG-2000 monomethyl ether (1.820 g, *ca.* 0.91 mmol) in THF (5 mL) was added under inert atmosphere over a stirred suspension of sodium hydride (59 mg of 60% suspension in mineral oil, 1.47 mmol) in THF (1 mL). The mixture was stirred for 10 min and then a solution of macrocycle **5** (200 mg, 0.29 mmol) in anhydrous THF (10 mL) was added dropwise. The stirring was continued for one day. The solvent was evaporated and chloroform was added. The suspension was filtered through a wool pad and the chloroform was evaporated to afford a brown solid that was washed with hexane to afford 1.6 g (*ca.* 82%) of macrocycle **7** contaminated with PEG-2000 monomethyl ether; IR: 2885, 2859, 1591, 1337, 1149, 1106, 1056, 955, 840 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 3.34 (s, 9H), 3.50–3.69 (broad absorption, *ca.* 522 H), 3.85–3.91 (m, 12H), 4.16 (t, J = *ca.* 4.4 Hz, 6H), 5.54 (br s, 6H), 6.97 (d, J = 8.8 Hz, 6H), 7.66 (d, J = 8.7 Hz, 6H); MALDI-TOF MS: m/z 5982 (40 × 3 CH_2CH_2O units) to 7348 (50 × 3 CH_2CH_2O units) separated by 44 Da [M + Na^+], the more intense peak occurs at 6728 (45 × 3 CH_2CH_2O units).

1,6,11-Tris[4-fluorophenylsulfonyl]-1,6,11-triazacyclopentadecane, 8. A stirred mixture of macrocycle **5** (519 mg, 0.76 mmol), 10% Pd–C (24 mg) and platinum(IV) oxide monohydrate (43 mg) in THF (15 mL) was hydrogenated at atmospheric pressure for 2 h (^{1}H NMR monitoring). The mixture was filtered through Celite that was washed with more THF (3 × 15 mL). The solvent was evaporated and the white solid residue was washed with pentane (30 mL) and dried to afford 486 mg (93%) of **8**, mp 191–193 °C; IR (ATR) 2954, 2867, 1590, 1492, 1334, 1156, 1092, 841, 692 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.72 (br s, 12H), 3.07 (br s, 12H), 7.20 (apparent t, J = 8.6 Hz, 6H), 7.79 (dd, J = 9 and 5 Hz, 6H); ^{13}C-NMR ($CDCl_3$, 62.5 Mz): δ = 27.2, 50.5, 116.7, (d, J = 22.9 Hz), 130.2 (d, J = 9.5 Hz), 134.8 (d, J = 3.8 Hz), 165. 4 (d, J = 253 Hz); Anal. calcd for $C_{30}H_{36}F_3N_3O_6S_3$: C, 52.39; H, 5.28; F, 8.29; N, 6.11; S, 13.99; found: C, 52.17; H, 5.08; N, 6.01; S, 13.89.

1,6,11-Tris[4-(*1H*,*1H*,*2H*,*2H*-perfluorodecylthio)phenylsulfonyl]-1,6,11-triazacyclopentadecane, 9. Anhydrous cesium carbonate (1.5 g, 4.6 mmol), was warmed up at 50 °C in vacuum (*ca.* 1 mmHg) for 30 min. After cooling under an argon atmosphere THF (5 mL) and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (0.75 mL, 2.5 mmol) were added. Then, a solution of **8** (360 mg, 0.054 mmol) and tetrabutylammonium chloride (25 mg, 0.086 mmol) in THF (6 mL) was added *via* cannula with stirring under an inert atmosphere. The dark-orange mixture was stirred overnight at room temperature. The solvent was eliminated by means of a nitrogen stream. The residue was washed by a solvent system made of perfluorooctanes (FC-77) (20 mL), ethyl acetate (20 mL) and water (15 mL) with vigorous stirring for 1 h. The washed solid was filtered and recrystallized from THF and finally washed again with more FC-77 to afford 808 mg (74%) of **9** as a white powder, mp 164–186 °C. IR (ATR): 1333, 1201, 1149 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.71 (br s, 12 H), 2.34–2.60 (m, 6H), 3.08 (br s, 12H), 3.18–3.27 (m, 6H), 7.38 (d, J = 8.6 Hz, 6H), 7.70 (d, J = 8.8 Hz, 6H). Anal. calcd for $C_{60}H_{48}F_{51}N_3O_6S_6$: C, 34.84; H, 2.34; N, 2.03, S, 9.30; found: C, 34.73; H, 2.08; N, 1.93; S, 9.49.

1,6,11-Tris[4-methoxy(polyoxyethylene)phenylsulfonyl]1,6-11-triazacyclopentadecane, 10. A solution of PEG-2000 monomethyl ether (3.5 g, *ca.* 1.75 mmol) in anhydrous THF (10 mL) was added under an inert atmosphere over a stirred suspension of sodium hydride (113 mg of 60% suspension in mineral oil, 2.82 mmol) in THF (2 mL). The mixture was stirred for 10 min and then a solution of macrocycle **8** (388 mg, 0.56 mmol) in THF (20 mL) was added dropwise. The mixture was stirred overnight. An excess of NaH was added in two portions (2 × 56 mg, 1.41 mmol) in order to complete the reaction during the next two days. After filtration, the solvent was evaporated to afford a brown solid that was washed with hexane to afford a pink solid of **10** (3.80 g, 98%). IR: 2879, 1593, 1466, 1341, 1101 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.69 (s, 12H), 3.02 (s, 12H), 3.38 (s, 12H), 3.56–3.64 (m, 578H), 3.87–3.90 (m, 12H), 4.18 (m, 6H), 6.99 (d, J = 8.5 Hz, 6H), 7.7 (d, J = 9.0 Hz, 6H); MALDI-TOF MS: m/z 5900 (39 × 3 CH_2CH_2O units) to 7440 (50, 51, 51 CH_2CH_2O units) separated by 44 Da [M + Na^+], the more intense peak occurs at 6561 (44 × 3 CH_2CH_2O units).

Preparation of palladium(0) nanoparticles

Nanoparticles Pdn/(13) (Entry 1). A solution of $Pd(dba)_2$ (89 mg, 0.154 mmol) in THF (10 mL) was added *via* syringe with stirring under an inert atmosphere into a boiling solution of (*E*,*E*,*E*)-1,6,11-tris[4-(1*H*,1*H*,2*H*,2*H*-perfluorodecylthio)-phenylsulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene, **6** (205 mg, 0.097 mmol) in THF (70 mL). The mixture was refluxed with stirring. After three days more $Pd(dba)_2$ (47 mg, 0.082 mmol) in THF (4 mL) was added. The mixture was heated to reflux for two more days. The black solution was then filtered first through Celite and then through a pad of PTFE of 0.2 μm of filter pore. The filtrate was completely evaporated with a stream of nitrogen to afford 330 mg of a black solid containing dba and traces of **6** (^{1}H-NMR monitoring) and palladium nanoparticles (HRTEM monitoring). The solid (200 mg) was digested for two days with chloroform

(14 mL). The suspension was filtered through PTFE of 0.2 μm of filter pore and the solid was washed with cold chloroform (3 × 2 mL) and dried to afford 112 mg (70% yield) of black **Pd_n/(13)**. The IR and ^{1}H-NMR spectra were identical with those of complex 13 (*vide infra*). Anal. calcd for $C_{60}H_{42}F_{51}N_3O_6S_6Pd_2$ (**$Pd_1$13$_1$**): C, 31.67; H, 1.86; N, 1.85; S, 8.46; F, 42,59; Pd, 9.36; found: C, 31.12; H, 1.63; N, 1.81; S; 8.74; F, 42.81; Pd 10.2 ± 0.2 (ICP analysis).

Nanoparticles Pd_n/(13) (Entry 2). The same procedure as for Entry 1 but different working up were followed. After the five reaction days the solution was filtered through the PTFE filter. The filtrate was concentrated to 20 mL and left two days at −20 °C. The resulting black precipitate was filtered and washed with cold THF (2 × 5 mL) to afford 239 mg of nanoparticles (58%). Anal. found: C, 33.45; H, 1.81; N, 1.96; S, 9.37; Pd, 6.8.

Nanoparticles Pd_n/(6 + 13) (Entry 3). The same procedure as for Entry 2, but $Pd(dba)_2$ was added in one portion and the reaction time was three days. The yield was 32%. Anal. found: Pd, 3.47.

Nanoparticles Pd_n/(6) (Entry 4). A mixture of macrocycle **6** (103 mg, 0.049 mmol), $Pd(dba)_2$ (65 mg, 0.12 mmol) and THF (30 mL) was heated 22 h at 140 °C in a closed reactor. The solid was filtrated through Celite and the filtrate was evaporated. The solid was washed several times with cold THF in order to eliminate dba. Grey nanoparticles of composition **Pd_n/ (6)** were obtained (49 mg). IR and ^{1}H-NMR spectra were identical with that of **6**.

Nanoparticles Pd_n/(12 + 15) (Entry 5). A mixture of **12** (0.11 g, 0.056 mmol) and $Pd(dba)_2$ (0.051 g, 0.089 mmol) in THF (6 mL) was refluxed for two days. NMR monitoring indicated that some free **12** remained. Then more $Pd(dba)_2$ (0.11 g, 0.19 mmol) was added and the mixture was refluxed three more days. The formed black solid was filtered and washed with THF and chloroform till total elimination of dba to afford 0.099 g of brown nanoparticles of composition **Pd_n/(12** (7%) + **15** (93%)**)** (76%); decomp. at 179–185 °C; IR(ATR): 1201, 1152 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.6–1.9 (m, 4H), 2.81 (t, J = 11.5 Hz, 2H), 3.10 (d, J = 8.0 Hz, 1H), 3.11 (d, J = 6.2 Hz, 1H), 3.70–3.86 (m, 3H), 4.06 (t, J = 10.6 Hz, 2H), 4.69 (d, J = 14.1 Hz, 3H), 4.86 (d, J = 8.4 Hz, 2H), 7.70 (t, J = 8.0 Hz, 3H), 7.81 (d, J = 8.0 Hz, 3H), 8.00–8.10 (m, 6H), traces of free **12** (*ca.* 7%) were detected by a broad singlet at δ = 5.64. Anal. found: C, 28.60; H, 6.14; N, 1.78; S, 1.19; Pd 23.0.

Nanoparticles Pd_n/(12 + 15) (Entry 6). A mixture of **12** (50 mg, 0.027 mmol) and $Pd(PPh_3)_4$ (34 mg, 0.029 mmol) in THF (5 mL) was stirred at room temperature overnight. Monitoring by ^{1}H-NMR revealed that not all the macrocycle was complexed. Then, more $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) was added and the new mixture was stirred for 24 h more. Then, more $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) was added and the mixture was stirred for 3 more days. The black mixture was filtered through a filter of polytetrafluoroethylene (PTFE) of 0.2 μm of pore. The filtrate was evaporated and the solid washed with pentane and dried to afford 50 mg of brown nanoparticles of composition **Pd_n/(12** (8%) + **15** (92%)**)**.

Nanoparticles Pd_n/(12) (Entry 7). A mixture of macrocycle **12** (50 mg, 0.027 mmol), $Pd(dba)_2$ (36 mg, 0.064 mmol) and THF (1 mL) was heated overnight at 140 °C in a closed reactor. Half of the solvent was evaporated and 5 mL of pentane were added. The mixture was stirred for 10 min and the solid was filtered and washed twice more with a mixture of THF : pentane (0.5 : 5 mL) in order to remove the last traces of dba. The black solid was dried and 42 mg of nanoparticles of composition **Pd_n/(12)** were obtained. IR and ^{1}H-NMR spectra were identical with that of **12**.

Nanoparticles Pd_n/(14) (Entry 8). A mixture of macrocycle **7** containing PEG-OMe (300 mg, <0.045 mmol), $Pd(dba)_2$ (57 mg, 0.104 mmol) and THF (2.3 mL) was refluxed for one day. Then the mixture was filtered through Celite using THF as eluent. The solvent was evaporated to afford a black solid that was washed with hexane and dissolved in water. The aqueous solution was partitioned again with hexane to remove the last traces of dba. The water was finally evaporated at reduced pressure and the resulting solid was washed once again with hexane to afford 283 mg of nanoparticles of composition **Pd_n/(14)** (46% yield with respect to Pd); Anal. found: C, 52.12; H, 8.53; N, 0.54; S, 1.11; Pd 1.78 ± 0.04.

Nanoparticles Pd_n/(7) (Entry 9). A mixture of macrocycle **7** containing PEG-OMe (300 mg, <0.045 mmol), $Pd(dba)_2$ (57 mg, 0.104 mmol) and THF (1.0 mL) was heated at 140 °C in a closed reactor for one day. Then the mixture was filtered through Celite using THF as eluent. The solvent was evaporated to afford a black oil that was washed with hexane and dissolved in water. The aqueous solution was partitioned again with hexane to remove the last traces of dba. The water was finally evaporated at reduced pressure and the resulting black oil was washed with hexane to afford 253 mg of solid nanoparticles of composition **Pd/7** (11% yield with respect to Pd). IR and ^{1}H-NMR spectra were identical with that of **7**; Anal. found: C, 52.80; H, 8.71; N, 0.68; S, 1.23; Pd 0.48 ± 0.05.

Nanoparticles Pd_n/(7) (Entry 10). A mixture of macrocycle **7** containing PEG-OMe (1.3 g, <0.20 mmol), $Pd(dba)_2$ (147 mg, 0.25 mmol) and THF (1.0 mL) was refluxed for one day. Then more $Pd(dba)_2$ (57 mg, 0.10 mmol) was added and refluxed for 6 days. More $Pd(dba)_2$ (57 mg, 0.10 mmol) was added and the mixture was left to reflux for a long weekend of 4 days. In the meantime, accidentally, the solvent was evaporated. The crude mixture was filtered through Celite using THF as eluent. The solvent was evaporated to afford a black oil, which was washed with hexane to eliminate dba. A black solid was obtained of composition **Pd_n/(7)** (906 mg, 61% yield with respect to Pd). IR and ^{1}H-NMR spectra were identical with that of **7**; Anal. found: C, 52.84; H, 8.58; N, 0.57; S, 1.15; Pd 3.25 ± 0.06.

Nanoparticles Pd_n/(14) (Entry 11). A mixture of **7** (200 mg, <0.030 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.030 mmol) in THF (5 mL) was stirred at room temperature for 24 h. Monitoring by ^{1}H-NMR revealed that not all the macrocycle was complexed. Then, more $Pd(PPh_3)_4$ (35 mg, 0.030 mmol) was added and the

new mixture was stirred for 24 h more. The solvent was evaporated, the residual solid was dissolved in THF (1.5 mL) and precipitated with pentane (10 mL). The supernatant liquid was eliminated *via* cannula and the process was performed up to five times in order to eliminate all the triphenylphosphine oxide. The solution was filtrated through Celite using THF as eluent and the solvent was evaporated to afford brown nanoparticles of composition **Pd_n/(14)** (157 mg, 36% yield with respecto to Pd). MALDI-TOF: m/z = 1332–2699 $[PEG\text{-}OMe + Na]^+$, 3919–4974 [disubstituted macrocycle-Pd + Na]$^+$ and 5891–7384 [**14** + Na]$^+$. Anal. found: C, 54.21; H, 8.56; N, 0.45; S, 0.83; Pd 1.48 ± 0.06.

Nanoparticles Pd_n/(14) (Entry 12). A mixture of **7** (300 mg, <0.045 mmol), $Pd(dba)_2$ (56 mg, 0.095 mmol) in THF (2.3 mL) was stirred overnight at room temperature. Then 5 mL of THF were added and the mixture was filtered through Celite using THF as eluent. The solvent was evaporated to afford a black solid, which was dissolved in water (*ca.* 30 mL) and filtered to eliminate $Pd(dba)_2$ and dba. The filtrate was evaporated, the residue was dissolved in CH_2Cl_2 and the resulting solution dried with anhydrous Na_2SO_4. Then the mixture was filtered and the solvent was evaporated to afford brown nanoparticles of composition **Pd_n/(14)** (200 mg, 23% yield with respect to Pd). Anal. found: C, 52.62; H, 8.98; N, 0.48; S, 0.83; Pd 1.16 ± 0.03.

Nanoparticles Pd_n/(10) (Entry 13). A mixture of **10** (300 mg, <0.045 mmol) and $Pd(dba)_2$ (57 mg, 0.104 mmol) in THF (2.3 mL) was refluxed overnight. Then 5 mL of THF were added and the mixture was filtered through Celite using THF as eluent (*ca.* 80 mL). The solvent was evaporated to afford a brown solid that was dissolved in water and the solution filtered. The water was evaporated and the solid obtained was dissolved in CH_2Cl_2. The new solution was dried with anhydrous Na_2SO_4, filtered and the solvent was evaporated to afford clear brown solid nanoparticles of composition **Pd_n/(10)** (281 mg, 8% yield with respect to Pd). IR and ^{1}H-NMR spectra were identical with that of **10**. Anal. found: Pd 0.33 ± 0.007.

Preparation of palladium(0) complexes

(*E,E,E*)-1,6,11-Tris[4-(1*H*,1*H*,2*H*,2*H*-perfluorodecylthio)phenylsulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene palladium(0), 13. A solution of $Pd(dba)_2$ (138 mg, 0.234 mmol) in THF (15 mL) was added *via* syringe and with stirring into a solution of (*E,E,E*)-1,6,11-tris[4-(1*H*,1*H*,2*H*,2*H*-perfluorodecylthio) phenylsulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene, **6** (318 mg, 0.15 mmol) in THF (115 mL) heated at 60 °C. The mixture was heated at 60 °C with stirring. After three days more $Pd(dba)_2$ (77 mg, 0.127 mmol) in THF (10 mL) was added. The mixture was heated at 60 °C for two more days. The black solution was then filtered while hot through a filter of polytetrafluoroethylene (PTFE) of 0.2 μm pore. The filtrate was concentrated to 20 mL and left for two days at −20 °C in the freezer. The black solid was isolated by filtering, washed with cold THF (2 × 5 mL) and flash-chromatographed through silica gel with hot THF (drying pistol over the column) as eluent to afford a white solid that was digested with pentane (2 × 25 mL) to afford 146 mg of **13** (48% yield), mp 187–196 °C; IR (ATR): 1337, 1242, 1203, 1166, 1142 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.65–1.85 (m, 4H), 2.35–2.6 (m, 6H), 2.85 (br t, J = 15.2 Hz, 2H), 3.05–3.11 (m, 2H), 3.15–3.25 (m, 6H), 3.76–3.80 (m, 2H), 4.02 (broad t, J = 14 Hz, 4H), 4.65 (br d, J = 6.8 Hz, 4H), 4.79 (d, J = 13.3, Hz 2H), 7.34 (m, 6H), 7.69 (d, J = 8.4 Hz, 4H), 7.76 d, J = 8.4 Hz, 2H). MALDI-TOF: m/z 2168.184 (M + 1)$^+$, 2190.163 (M + Na)$^+$, 2206.123 (M + K)$^+$. Anal. calcd for $C_{60}H_{42}F_{51}N_3O_6PdS_6$: C, 33.23; H, 1.95; N, 1.94; S, 8.87; found: C, 33.69; H, 1.66; N, 1.92; S, 9.24.

***E,E,E*-1,6,11-Tris[4-(methoxy(polyoxyethylene)phenylsulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene palladium(0), 14.** A solution of PEG-2000 monomethyl ether (393 mg, 0.197 mmol) in 4 mL of THF was added under inert atmosphere over a stirred suspension of sodium hydride (13 mg of 60% suspension in mineral oil, 0.32 mmol) in THF (0.5 mL). The mixture was stirred for 10 min and then a solution of palladium(0) complex **16** (50 mg, 0.063 mmol) in THF (4 mL) was added dropwise. The mixture was stirred overnight. An excess of NaH (13 mg, 0.317 mmol) was added in order to complete the reaction during the next day. After filtration, the solvent was evaporated to afford a white solid that was washed with hexane to afford 390 mg (89%) of **14**. IR: 2880, 1593, 1465, 1341, 1102 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 3.38 (s, 17H), 3.64 (m, 670H), 4.14 (m, 6H), 4.62 (d, J = 13 Hz, 3H), 4.76 (d, J = 12.5 Hz, 1H), 6.96 (d, J = 8.2 Hz, 6H), 7.67 (d, J = 8.5 Hz, 4H), 7.74 (d, J = 7.2 Hz, 2H). MALDI-TOF MS: m/z 6175 (40, 40, 41 CH_2CH_2O units) to 7454 (50 × 3 CH_2CH_2O units) separated by 44 Da [M + Na$^+$], the more intense peak occurs at 6706 (44, 44, 45 CH_2CH_2O units).

1,6-Bis-[2,4,6-(triisopropyl)phenylsulfonyl]-11-[4-(perfluorooctyl) phenylsulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene palladium (0), 17 (mixture of two isomers). A mixture of macrocycle **11** (0.11 g, 0.084 mmol) and freshly prepared tetrakis(triphenylphosphine)palladium(0) (0.116 g, 0.100 mmol) in THF (30 mL) in a Schlenk tube was refluxed for 20 h. The crude was filtered through Celite and the solvent was evaporated to afford an oil that upon digestion with hexane gave 0.052 g (40%) of complexes **17**, mp 145–148 °C; IR(ATR) 1246, 1216, 1151 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz, see Supplementary Information†): δ = 1.24 (br s, 36H), multiplets for 24H at 1.6–2.2, 2.80–2.96, 2.88, 3.22, 3.73–3.94, 4.0–4.25, 4.45–4.85, 7.17 (s, 4H), 7.74 (d, J = 8.5 Hz, 2H), 7.85–8.05 (two doublets of relative intensity *ca.* 1 : 3, J = 8.3 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 62.5 MHz): δ = 23.5, 24.8, 29.2, 29.6, 29.7, 34.2, nine peaks assigned to the methylenic ring carbon atoms at 43.8, 45.4, 46.4, 47.7, 47.9, 48.4, 49.1, 49.8, 51.0, nine peaks assigned to the olefinic carbons of both isomers at 78.0, 78.3, 79.2, 79.4, 79.9, 80.0, 82.3, 83.9, 84.5, aromatic carbons at 123.7, 126.9, 127.1, 127.7–127.8 (br signal), 129.8 (t, J = 22 Hz), 130.5, 130.8, 130.9, 130.9, 132.8 (t, J = 24 Hz), 142.2, 142.8, 151.0, 151.2, 152.9, 153.0, 153.0; MALDI-TOF MS: m/z = 1403.8 [M]$^+$, 1425.8 [M + Na]$^+$, 1441.8 [M + K]$^+$.

An alternative preparation was accomplished with excess $Pd(dba)_2$ in refluxing THF under analogous conditions of Entry 1 of Table 1. In contrast with the behaviour of fluorous macrocycle **6**, this compound **11** did not give nanoparticles, but only the triolefinic palladium complex **17**.

Thermal treatment of palladium(0) complexes

Formation of nanoparticles Pd_n/(6) by thermal treatment of the macrocyclic triolefinic complex 13. Palladium complex **13** (49 mg, 0.023 mmol) in 17 mL of THF was heated overnight at 140 °C. The hot mixture was filtered through a filter of polytetrafluoroethylene (PTFE) of 0.2 μm of pore and the filtrate was evaporated. A grey solid was obtained (45 mg), corresponding to nanoparticles of composition **Pd_n/(6)**. IR and ^{1}H-NMR spectra were identical with that of **6**.

Behaviour of complex 14 when heated in the absence and in the presence of $Pd(dba)_2$. (a) A solution of **14** (106 mg, <0.016 mmol) in THF (2 mL) was placed in a sealed tube and heated at 100 °C overnight, no change being observed by ^{1}H NMR. The solution was heated at 140 °C overnight and then at 175 °C for one more night. The complex **14** was recovered unchanged according to the ^{1}H NMR spectrum.

(b) A mixture of **14** (100 mg, <0.015 mmol) and $Pd(dba)_2$ (7 mg, 0.019 mmol) in THF (2 mL) was heated overnight at 140 °C (sealed tube). The crude mixture was diluted in THF and filtered through Celite. The solvent was evaporated and the resulting solid was taken in water and filtered. The evaporation of water gave a yellow solid corresponding to complex **14** contaminated with the free macrocycle **7** (70 : 30 by ^{1}H NMR). Nanoparticles were not observed by TEM.

(c) A mixture of **14** (150 mg, <0.022 mmol) and $Pd(dba)_2$ (28 mg, 0.049 mmol) in THF (0.5 mL) was heated at 140 °C in a sealed tube and the following observations were made by ^{1}H NMR: after 20 min of reaction signals corresponding to coordinated olefins at 4.60 (dd) were present, together with a signal at 5.55 (apparent d) corresponding to free olefins. Similar results were obtained after 3 h and after 5 h. After 20 h of reaction the signal at 4.6 ppm corresponding to the coordinated olefins was present, together with a broad singlet at 5.59 (corresponding to free olefins of macrocycle **7**), which was of higher intensity than another broad singlet at 5.52 ppm.

Catalytic activity of palladium(0) nanoparticles

Preparation of *n*-butyl cinnamate under catalysis by Pd_n/(13) of Entry 2 and recovery of the catalytic material (Run 3). A mixture of iodobenzene (0.7 mL, 6.3 mmol), butyl acrylate (1.3 mL, 8.9 mmol), tributylamine (1.8 mL, 7.6 mmol), **Pd_n/(13)** (Entry 2) (21 mg, 0.013 mmol of Pd, 0.2 molar%) and THF (10 mL) was heated at 90 °C in a closed reactor for 24 h. The solvent was removed with a nitrogen stream and the residue was extracted with cold acetonitrile filtering through a cannula. The residual black solid was used in the fourth run. The acetonitrile solution was evaporated and the residue was purified by column chromatography on silica gel with hexanes–ethyl acetate (95 : 5) as eluent, to afford *n*-butyl cinnamate (1.2 g, 94%) as an oil (99% purity by gas chromatography): IR 2966, 2867, 1710, 1637, 1172 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 0.97 (t, J = 7.4 Hz, 3H), 1.44 (m, 2H), 1.70 (m, 2H), 4.21 (t, J = 6.6 Hz, 2H), 6.44 (d, J = 16.0 Hz, 1H), 7.38 (m, 3H), 7.53 (m, 2H), 7.69 (d, J = 16.0 Hz, 1H).

Preparation of *n*-butyl cinnamate under catalysis by Pd_n/(7) of Entry 10 and recovery of the catalytic material. A mixture of iodobenzene (0.06 mL, 0.5 mmol), butyl acrylate (0.10 mL, 0.7 mmol), tributylamine (0.14 mL, 0.6 mmol), **Pd_n/(7)** of Entry 10 (15 mg, 0.0046 mmol of Pd, 3.25 molar %) and THF (1 mL) was heated at 90 °C (oil bath) in a closed reactor for 24 h. After cooling diethyl ether (1 mL) was added, the mixture was centrifuged and the supernatant organic solution was separated. A second centrifugation was performed after addition of more diethyl ether (2–3 mL). The combined ethereal solutions were washed with diluted aqueous HCl and with water, dried (sodium sulfate) and evaporated. The obtained oil was purified by column chromatography through silica gel using hexanes–ethyl acetate (95 : 5) as eluent to afford *n*-butyl cinnamate (74 mg, 79%) as a colourless oil with the same spectroscopic characteristics as above.

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