Accepted Manuscript

Fluoro-tagged osmium and iridium nanoparticles in oxidation reactions

Lynay Santacruz, Silvia Donnici, Albert Granados, Alexandr Shafir, Adelina Vallribera

PII: S0040-4020(18)31246-8

DOI: 10.1016/j.tet.2018.10.040

Reference: TET 29873

To appear in: Tetrahedron

Received Date: 12 July 2018

Revised Date: 15 October 2018

Accepted Date: 16 October 2018

Please cite this article as: Santacruz L, Donnici S, Granados A, Shafir A, Vallribera A, Fluorotagged osmium and iridium nanoparticles in oxidation reactions, *Tetrahedron* (2018), doi: https:// doi.org/10.1016/j.tet.2018.10.040.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Graphical Abstract

To create your abstract, type over the instructions in the template box below. Fonts or abstract dimensions should not be changed or altered.





Tetrahedron journal homepage: www.elsevier.com



Fluoro-tagged osmium and iridium nanoparticles in oxidation reactions

Lynay Santacruz,^{a,b} Silvia Donnici,^a Albert Granados,^{a,c} Alexandr Shafir^{a*} and Adelina Vallribera,^{a,c*}

^a Department of Chemistry, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193 Barcelona, Spain. ^bDepartment of Chemistry, Universidad de Nariño, sede Torobajo, Pasto, Colombia. ^cCentro de Innovación en Química Avanzada (ORFEO-CINQA)

ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

Keywords: metallic nanoparticles osmium iridium sol-gel oxidation process

ABSTRACT

Osmium and iridium metal nanoparticles were supported on a fluorous organicinorganic hybrid material prepared by the sol-gel process. Moreover, we also found that the thermolysis of the $Ir_4(CO)_{12}$ cluster in simply diphenylether also gave Ir(0)nanoparticles. All the materials were studied as catalysts in oxidation processes. Fluoro-tagged iridium nanoparticles were particularly active in aerobic oxidation processes, whereby the catalytic activity could be greatly enhanced through a simple pre-activation procedure. With this material, benzylic alcohols could be oxidized under O_2 balloon in the absence of a basic additive; the oxidative stopped selectively to the corresponding benzaldehyde. Promisingly, the same reaction conditions were used in a benzylic CH oxidation of xanthene.

2009 Elsevier Ltd. All rights reserved.

1. Introduction

Metal nanoparticles (M NPs) have been the subject of intensive study due to their important size-dependent functional attributes. Several approaches are used for the preparation of M NPs, with some of the most common consisting in chemical and electrochemical reduction or thermal decomposition of a metal salt, metal vapour deposition, as well as photolysis and sonochemical decomposition of metal complexes or salts. The most used method is the chemical reduction of a metal salt in the presence of a suitable stabilizer employed to prevent cluster overagglomeration and the formation of bulk metal. At the time of our group's entry into this field, the heavily fluorinated compounds did not seem suitable as stabilizers for metallic nanoparticles. Since then, we and other groups have designed and used different type of stabilizers containing polyfluorinated chains. Among them we want to emphasize the employment of triblock-type fluoroalkylated oligomers ($[R_{F}-(M)_{n}-R_{F}], R_{F}$: perfluorinated chain), which aggregate in aqueous or organic media, and were shown to stabilize Au, Cu, Fe NPs.¹ The use of perfluorinated amphiphiles (HS-R_F-PEG) for the preparation of water soluble Au NPs,² as well as the study of dendrimers perfluorinated shells containing (from perfluorinated alkenethiols) to encapsulate Ag NPs in perfluorinated solvents have also been described.³ Moreover, the group of Zhu reported the use of fluorous-tagged molecules for the construction of Au NPs assemblies into superstructures using previously stabilized Au NPs by the protein wheat germ aggutinin (WGA-Au NPs).⁴ The Cai's group described the use of a fluorous pyrrolidine imide as stabilizer of palladium nanoparticles.⁵ In addition, structured semifluorinated polymer ionic liquids form fluorous compartiments, that have been used for the preparation of Au and Ag NPs.⁶ More recently, the spontaneous self-organization of dissimilar ligands (hydrogenated (H-) and fluorinated (F-)) on the surface of gold nanoparticles was studied by ¹⁹F NMR experiments and multiscale molecular simulations.⁷

Our work in this field began with the preparation of Pd NPs using discrete polyfluorinated compounds as stabilizers. Thus, in a 2002 publication, M. Moreno-Mañas et al. reported that several simple organofluorine species were efficient in preventing Pd nanoparticles agglomeration.8 We later discovered that certain 15-membered olefinic macrocycles bearing three fluorous chains were also good stabilizers for Pd NPs.9 Further development of the concept, however, required the design of new stabilizers, which would be easier to prepare. We envisaged that the features that could enhance the stabilizing effects should be: (i) presence of long polyfluorinated chains; (ii) the sterical bulk, and (iii) presence of potentially coordinating donor atoms. Based on these criteria, we prepared some star-shaped fluorous aromatic sulfurs.¹⁰ We demonstrated that, despite that heavily fluorinated compounds are not expected to be the best constituents for protecting shields due to the very small attractive interactions

toward other materials and among themselves, they stabilize M Nps. Then, we considered adapting such materials for use in heterogeneous catalysis. In particular, we were intrigued by the idea of immobilizing these M NPs on fluorours silica gel by taking of the possible fluorous-fluorous interactions. In a subsequent study, the catalyst recycling was performed with the nanoparticles contained within a fluorous silica and using the Mizoroki-Heck coupling between iodobenzene and methyl acrylate as the model system.¹¹ The supported catalyst was reused 14 consecutive cycles without loss of activity with the catalyst recovered each time via centrifugation. Control experiments, by ¹⁹F NMR, of the crude mixture after filtration of the catalyst were also carried to assess whether leaching of the palladium fluorous stabilizer could take place. In an effort to create a more robust catalyst, we envisioned the synthesis of an hybrid material with the stabilizer linked covalently to the silica gel matrix, 1. The idea, in fact, was not completely new, given prior work by Bannwarth et al on the adsorption of palladium(II) complexes containing perfluoro-phosphine ligands on FSG.¹² We essayed fluorous material 1 as stabilizer for metal nanoparticles (Pd, Ru, Rh) with excellent results (Scheme 1; a, b and c). The Pd@1 resulted a valuable tool for facilitating the recovery and reuse of the expensive metal in palladium catalyzed cross-coupling reactions that were carried out under aerobic and phosphine free conditions as Mizoroki-Heck,¹³ Sonogashira¹⁴ and Suzuki-Miyaura.¹⁵ The catalytic properties of **Rh@1** and **Ru@1** were

Miyaura.¹⁵ The catalytic properties of $\mathbf{Rh}@1$ and $\mathbf{Ru}@1$ were tested in the hydrogenation of arenes, a process of high industrial interest.¹⁶ We found that $\mathbf{Rh}@1$ catalyzes the quantitative hydrogenation of aromatic compounds such as benzene, toluene, styrene, phenol and pyridine at mild conditions, whereas $\mathbf{Rh}@1$ was less active.¹⁷

Herein, we report our recent results on the synthesis and characterization of fluoro-tagged iridium and less common osmium nanoparticles using material **1** as stabilizer (Scheme 1) and its uses as catalysts in oxidation reactions.



Scheme 1. Preparation of materials **M@1**: **a-c** illustrate previous results, while **d** and **e** show new work.

2. Results and discussion

The full details on the synthesis of the stabilizer **1** have already been described by our group elsewhere.^{13a} Briefly, the synthesis of **1**, took advantage of a controlled stepwise nucleophilic aromatic substitution to the 2,4,6-trichloro-1,3,5triazine core. Specifically, selective substitution of two out of three chlorine atoms of cyanuric chloride, **2**, with the thiol $F_{17}C_8CH_2CH_2SH$ could be achieved at 0 °C. The remaining chlorine atom was replaced with the commercially available bifunctional sylilated amine linker (Scheme 2), affording the target tri-substituted **4** in 97% yield. As we described earlier, initial attempts to carry out the co-gelification of **4** with Si(OEt)₄ (15 equiv) in a standard water-methanol mixture under NH_4F catalysis proved unsuccessful, as did the tests employing the formic acid as both solvent and catalyst. However, very efficient sol-gel formation was achieved using a trifluoroacetic acid-based approach described by Sharp *et al.*,¹⁸ affording the homogeneous material **1** (Scheme 2, Figure 1) after a 5 days ageing period; the incorporation of the fluorous stabilizer was confirmed by elemental analysis (0.441 mmol of ligand per g of **1**).^{13a}

Material 1 was subsequently applied as a stabilizer to the synthesis of osmium nanoparticles. Previously, the formation of such nanoparticles has been promoted by diverse types of including chemical entities. the ionic liquid butyl(methyl)imidazolium tetrafluoroborate,19 the 4-(2hydroxyethyl)-1-piperazineethanesulfonic acid²⁰ or by cetyl trimethyl ammonium bromide.²¹ Several groups also reported the preparation of Os(0) nanoclusters supported on carbon nanotubes,²² zeolite,²³ silica,²⁴ and on graphene.²⁵ We found that Os@1 nanoparticles could be easily prepared by the reduction of OsCl₃³H₂O in THF using LiEt₃BH (superhydride) at room temperature for 2 hours (Scheme 1, d). The new nanoparticles were found to be uniformly small and disperse, with a $Ø_{mean} = 1.3 \pm 0.2$ nm as determined by TEM (Figure 2a). The electron diffraction rings obtained for this material were indexed to the (101), (102), (110) and (201) crystallographic planes of the hexagonal close-packed structure (see SI). Similarly, the power X-ray diffraction (pXRD) measurements showed the pattern expected for the metallic hexagonal osmium ($2\theta = 43.5^{\circ}$, corresponding to the metal (101) plane (see SI). Multiplex spectra corresponding to F1s, Os4f and Si2p were obtained through XPS studies of a sample of Os@1 (see SI).



Scheme 2. Preparation of fluorinated organic-inorganic hybrid material **1**



Figure 1. Images: a) gel 1 after ageing (5 days); b) gel 1 isolated; c) material 1 after drying.

As part of the same study, the formation of iridium nanoparticles was investigated. It is important to note that most of the reported syntheses of Ir NPs involve the reduction of an iridium salt by the appropriate reducing agent in the presence of the stabilizer. Following this approach, Ir NPs have been prepared using a variety of iridium precursors, most commonly $IrCl_3 \cdot H_2O^{26}$ and $H_2IrCl_6 \cdot H_2O^{27}$ Another suitable method is the so-called "organometallic approach" starting with the Ir olefin complexes as for example $[Ir(cod)Cl]_2$,²⁸ Ir(cod)(meCp),²⁹ $[Ir(OMe)(cod)]_2^{30}$ and $Ir(cod)(acac)^{31}$. In what could be considered a variation on the latter approach, the synthesis of iridium nanoparticles was also performed *via* the thermolysis of

the tetrairidium dodecacarbonyl cluster ($Ir_4(CO)_{12}$) in a high- \bigwedge batches of the Ir@1 materials following the same conditions.

boiling ionic liquid.³¹ Given the unsatisfactory results obtained in the preparation of **Ir@1** with previously assayed methodologies, the latter thermolysis method drew our attention. For these tests, the diphenyl ether was chosen as a reaction medium, given its boiling point of 259 °C, which we hoped would be sufficient for the decarbonylative thermolysis of the Ir carbonyl clusters. In a typical experiment, the Ir₄(CO)₁₂ cluster was first dissolved under nitrogen atmosphere in diphenyl ether (DPE) (heating at 90 °C for 1.5 hours to improve solubility). Then, the stabilizer 1 was added and the solution was heated up to 210 °C for 29 hours (Scheme 1, e). The decomposition of the cluster was followed by IR spectroscopy, with the gradual decrease in the intensity of a carbonyl absorption band at 2058 cm⁻¹, until its full disappearance, which was used as a sign that the reaction had reached completion. The procedure afforded a dark material containing Ir nanoparticles with $Ø_{mean} = 0.5-1.4$ nm. The protocol was repeated multiple times, affording reproducibly batches of nanoparticles with Ir content between 14.6-22.7 % w (Figure 2b, Table 1). X-ray powder diffractometry revealed the presence of fcc Ir(0) with the presence of a peak at $2\theta = 40.6^{\circ}$ corresponding to the metal (111) plane. Elemental analysis (17.7 % Ir and 42.5% of C), IR spectrum and solid ¹³C NMR of the batch corresponding to entry 7 of Table 1, confirmed the presence of the hybrid organic-inorganic matrix. Based on the % Ir content, the yield of this sample of Ir@1 (entry 1, Table 1) was calculated to be 93%. Multiplex spectra corresponding to F1s, Ir4f, Si2p, C1s were obtained through XPS studies of a sample of Ir@1. The new material presented a surface area of 14.5 m^2/g (BET) and was found to be stable for over four months according to the TEM images.

a) HRTEM image of Os@1:



As has been mentioned, the method was highly reliable for the preparation of the Ir NPs (Table 1). Less reproducible results were obtained in the case of Os NPs.

During the course of the preparation of the Ir NPs via the thermolysis of the $Ir_4(CO)_{12}$ cluster, we were surprised to find that Ir NPs were formed even in the absence of a fluorous stabilizer, i. e. simply by heating $Ir_4(CO)_{12}$ in Ph₂O. The reaction produced nanoparticles with a mean particle size of 0.5-1.3 nm Table 1. Reproducibility results in the synthesis of different

Entry	Ir % w/w ^a	Average particle size (nm)
1	14.6	1.1 ± 0.2
2	22.7	0.5 ± 0.2
3	16.0	1.1 ± 0.2
4	17.0	1.2 ± 0.3
5	20.1	0.9 ± 0.2
6	20.1	0.8 ± 0.2
7	17.7	1.0 ± 0.2
8	15.8	1.4 ± 0.4

^aMolar relation of metal to stabilizer 1 (1:1) in all the cases

(Figure 3); the pXRD analysis confirmed, once again, the presence of the fcc Ir(0) phase. Given an apparent lack of a stabilizing additive, we went on to further probe the nanoparticle composition. The material was found to contain 23 % w in Ir (ICP analysis), with the rest consisting of organic matter, attributed as stemming from the Ph2O used during the synthesis (Scheme 3). Indeed, the solid state ¹³C CP-MAS NMR spectrum of this material, which we denote as Ir@DPE, contained signals which could be matched to those present in the ¹³C NMR spectrum of pure Ph₂O (Figure 3). We are currently unsure of the mode by which diphenylether could stabilize a metal nanoparticle, given that, beyond the weakly donating oxygen, the Ph₂O lacks any feature typically associated with an effective nanoparticle stabilizer. We speculate that the stabilization might involve an activation of the aromatic CH group ortho to the oxygen; in that respect, we note the formation of small amounts of dibenzofuran observed in the GC-MS trace of the mother liquor of the reaction mixture. Even in the experiments with 1 as support and stabilizer of Ir Nps (using Ph2O as solvent), incorporation of Ph₂O was observed by solid state ¹³C CP-MAS NMR spectrum of material Ir@1 (see SI). The new material presented a surface area of 7.0 m^2/g (BET).



Scheme 3. Formation of Ir NPs via thermolysis of $Ir_4(CO)_{12}$ in Ph_2O .



Figure 3. HRTEM image of **Ir@DPE**; ¹³C CP-MAS NMR of **Ir@DPE** (green) *vs* the ¹³C NMR of Ph₂O (brown).

ACCEPTED

In the process of exploring the chemical reactivity of the newly prepared Os and Ir NPs, we tested their ability to promote the aerobic oxidation of alcohols.



Scheme 4. Aerobic metal-catalyzed oxidation of benzyl alcohols

Thus, we proceeded to test the Os- and Ir-based materials in the aerobic oxidation of the benzylic alcohol. Regarding the former, indeed, S. Özkar et al.³² have demonstrated that zeolite-Y-based Os Nps could be successfully employed in the aerobic oxidation of alcohols under mild conditions (2 mol% Os, 80 °C and 1 atm of O₂). In this protocol, however, the recycling studies with this material showed the loss of activity in the second run. Herein we describe the use of fluoro-tagged osmium nanoparticles Os@1 as active catalysts in aerobic oxidation of benzyl alcohol, 5a, to benzaldehyde, 6a (Scheme 4). The experiments were conducted using a Fischer-Porter vessel in toluene under O₂ at 80 °C and in the absence of any added base. A control experiment in the absence of catalyst and at 0.5 atm O₂ overpressure only led to traces of benzaldehyde (entry 1, Table 2). In contrast, moderate yields of 6a were achieved using 1 mol% Os at 0.5-2.5 atm of oxygen (entries 2-3, Table 2). Some improvement in yield could be achieved by raising the temperature and the amount of catalyst loaded, leading to an 87% yield of 6a (entries 4-5, Table 2). However, the recycling of the catalyst showed a substantial loss of activity in the second run (down to 38%, entry 5). Next, same oxidation process was tested using the Ir@1 material as catalyst. During preliminary tests, we noticed that benzaldehyde was obtained only in a moderate 50-60% yield even after two days at 100 °C in toluene and under a balloon of O_2 (entry 6, Table 2). Suspecting that the low catalytic activity might be due to the presence of absorbed species on the surface of a nanoparticle (such as residual CO), we introduced a pre-activation step, whereby the Ir@1 material was subjected to heating prior to a catalytic run. Such catalyst reactivation is not uncommon (including preheating of a M NPs under H₂).³ Indeed, pre-heating the catalyst to 135 °C proved effective, with the subsequent aerobic oxidation of benzyl alcohol (1.33 mol% Ir, a balloon of O₂) affording excellent yields of benzaldehyde after 23 h (entries 7-8, Table 2); inferior results were achived using Ir@1 activated at 200 °C (entries 9-10). In fact, a 2 hours pre-heating to 135 °C proved sufficient, as represented by the 96% yield recorded in entry 7 of Table 2. An analysis by TEM of nanoparticles pre-heated at 135 °C indicated the presence of well dispersed spherical nanoparticles of an average diameter among 0.5-1.3 nm. No agglomeration was observed. It should also be noted that the optimized reaction could be conducted using less solvent (at 3M), leading to a 97% of the target aldehyde 6a (entry 11, Table 2). Two additional primary benzyl alcohols were also selectively oxidized to the aldehydes under the optimized conditions (entries 14 and 15, Table 2). The oxidation of 5b (pmethyl) and 5c (p-NO₂) gave the aldehydes in 89 and 98 % yield respectively (entries 12 and 13, Table 2). The oxidation of 5a and 5b was also tested using the material Ir@DPE obtained previously via thermolysis of $Ir_4(CO)_{12}$ in diphenyl ether. Once again, pre-heating the nanoparticles to 135 °C proved beneficial for the catalytic activity. Under the optimized conditions the

corresponding aldehydes **6a** and **6b** were obtained in 85% and 90%, respectively (entries 14-15, Table 2 and Scheme 4), indicating that, at least for these substrates, **Ir@1** was a more effective catalyst than **Ir@DPE**.

The recycling of the Ir NPs proved difficult, given that both Ir@1 and Ir@DPE are very fine powders difficult to filter or centrifuge. After five centrifugation cycles we were able to recover Ir@DPE, and this catalyst, once pre-heated, was as effective as in the first run (entry 15, Table 7). No agglomeration of nanoparticles was observed after the first run and the average particle size was found to be 0.5-1.3 nm (by TEM). While supporting the concept, obviously, the recycling procedure was not operationally practical.

The Ir NPs were also tested in the aerobic benzylic oxidation of xanthene. The reaction proved somewhat sluggish, and, as seen in the oxidation of alcohols, the catalytic activity of Ir@1was superior to that of Ir@DPE (Scheme 5). Thus, after approx. 1 week at 100 °C under a balloon of O₂ the use of Ir@1 (1.3 mol% Ir) led to a quantitative formation of the target 8; only 64% of 6 was obtained using Ir@DPE.



Scheme 5. Ir NPs catalyzed aerobic CH oxidation of xanthene

As conclusion, fluoro-tagged Os and Ir NPs have been prepared, demonstrating once more, the ability of fluorous hybrid organic-inorganic silica to support and stabilize metal NPS. In adittion, thermolysis of the $Ir_4(CO)_{12}$ in diphenyl ether gave Ir(0)Nps. We have shown that Os and Ir NPs could catalyze aerobic oxidation of benzyl alcohols. Particularly effective was found to be the iridium nanoparticles Ir@1, whereby the catalytic activity could be greatly enhanced through a simple pre-activation procedure. With this material, benzylic alcohols could be oxidized under O₂ balloon in the absence of a basic additive; the oxidation stopped selectively at the corresponding benzaldehyde. Promisingly, the same reaction conditions were used in a benzylic CH oxidation of xanthene. The presence of the fluorous stabilizer 1 was found to be crucial for the catalytic activity, with inferior catalytic performance achieved using material Ir@DPE lacking this stabilizer.

 Table 2. Tested conditions of Os and Ir NPs as catalysts in aerobic oxidation of benzyl alcohols via Scheme 4

 Entry
 Alcohol
 M NPs cat
 Mol % cat
 Pre Pressure
 T (°C)
 T (h)
 Yield (%)

			activation		- (-)	- ()	11010 (70)
5a	-	-	-	0.5 atm	80	20	3
5a	Os@1	1	No	0.5 atm	80	20	63
5a	Os@1	1	No	2.5 atm	80	20	75
5a	Os@1	1	No	2.5 atm	100	15	84
5a	Os@1	2	No	2.5 atm	100	15	87/38
5a	Ir@1	1.3	No	O2 balloon	100	23	61
5a	Ir@1	1.3	135 °C/2h	O2 balloon	100	23	96
5a	Ir@1	1.3	135 °C/22h	O2 balloon	100	23	91
5a	Ir@1	1.3	200 °C/2h	O ₂ balloon	100	23	86
5a	Ir@1	1.3	200 °C/22h	O ₂ balloon	100	23	59
5a	Ir@1	1.3	135 °C/2h	O ₂ balloon	100	23	97
5b	Ir@1	1.3	135 °C/2h	O ₂ balloon	100	12	89
5c	Ir@1	1.3	135 °C/2h	O ₂ balloon	100	74	98
5a	Ir@DPE	1.3	135 °C/2h	O ₂ balloon	100	23	85
5b	Ir@DPE	1.3	135 °C/2h	O ₂ balloon	100	12	90/90
	5a 5a 5a 5a 5a 5a 5a 5a 5a 5a 5a 5a 5b 5c 5a 5b	5a Os@1 5a Os@1 5a Os@1 5a Os@1 5a Os@1 5a Os@1 5a Ir@1 5b Ir@1 5c Ir@1 5a Ir@1 5b Ir@1 5a Ir@1	5a Os@1 1 5a Os@1 1 5a Os@1 1 5a Os@1 1 5a Os@1 2 5a Os@1 2 5a Os@1 1.3 5a Ir@1 1.3 5b Ir@1 1.3 5a Ir@1 1.3 5b Ir@1 1.3 5a Ir@0PE 1.3	5a - - - 5a Os@1 1 No 5a Os@1 1 No 5a Os@1 1 No 5a Os@1 1 No 5a Os@1 2 No 5a Os@1 2 No 5a Ir@1 1.3 135 °C/2h 5a Ir@1 1.3 200 °C/22h 5a Ir@1 1.3 200 °C/2h 5a Ir@1 1.3 135 °C/2h 5a Ir@1 1.3 135 °C/2h 5a Ir@1 1.3 135 °C/2h 5b Ir@1 1.3 135 °C/2h 5b Ir@1 1.3 135 °C/2h 5a Ir@1 1.3 135 °C/2h 5b Ir@1DPE 1.3 135 °C/2h	5a - - - 0.5 atm 5a Os@1 1 No 0.5 atm 5a Os@1 1 No 2.5 atm 5a Os@1 1 No 2.5 atm 5a Os@1 2 No 2.5 atm 5a Os@1 1 No 0.2 balloon 5a Ir@1 1.3 135 °C/2h O2 balloon 5a Ir@1 1.3 200 °C/2h O2 balloon 5a Ir@1 1.3 200 °C/2h O2 balloon 5a Ir@1 1.3 135 °C/2h O2 balloon 5a Ir@1 1.3 135 °C/2h O2 balloon 5b Ir@1 1.3 135 °C/2h O2 balloon 5b Ir@1 1.3 135 °C/2h O2 balloon 5b Ir@DPE 1.3 135 °C/2h O2 ball	5a - - - 0.5 atm 80 5a Os@1 1 No 0.5 atm 80 5a Os@1 1 No 2.5 atm 80 5a Os@1 1 No 2.5 atm 80 5a Os@1 1 No 2.5 atm 100 5a Os@1 2 No 2.5 atm 100 5a Os@1 2 No 2.5 atm 100 5a Os@1 2 No 2.5 atm 100 5a Ir@1 1.3 No O ₂ balloon 100 5a Ir@1 1.3 135 °C/2h O ₂ balloon 100 5a Ir@1 1.3 200 °C/2th O ₂ balloon 100 5a Ir@1 1.3 135 °C/2th O ₂ balloon 100 5a Ir@1 1.3 135 °C/2th O ₂ balloon 100 5b Ir@1 1.3 135 °C/2th O ₂ balloon 100 5b Ir@0PE 1.3 135 °C/	5a - - 0.5 atm 80 20 5a Os@1 1 No 0.5 atm 80 20 5a Os@1 1 No 2.5 atm 80 20 5a Os@1 1 No 2.5 atm 80 20 5a Os@1 1 No 2.5 atm 100 15 5a Os@1 2 No 2.5 atm 100 15 5a Os@1 2 No 2.5 atm 100 15 5a Ir@1 1.3 No O ₂ balloon 100 23 5a Ir@1 1.3 135 °C/2h O ₂ balloon 100 23 5a Ir@1 1.3 200 °C/2h O ₂ balloon 100 23 5a Ir@1 1.3 135 °C/2h O ₂ balloon 100 23 5a Ir@1 1.3 135 °C/2h O ₂ balloon 100 23 5b Ir@1 1.3 135 °C/2h O ₂ balloon 100 12 <t< td=""></t<>

3. Experimental section

3.1. General methods

HR-TEM analyses were performed in the "Servei de Microscòpia" of the Universitat Autònoma de Barcelona, in a JEOL JEM-2010 model at 200 kV. Os and Ir analyses were performed in the "Servei d'Anàlisi Química" (SAQ) at the Universitat Autònoma de Barcelona.

3.2. General preparative methods

3.2.1. Preparation of material 1: Trifluoroacetic acid (1.8 mL) was added to a vial containing the fluorinated monomer 2 (300 mg, 0.24 mmol) and Si(OEt)₄ (767 mg, 3.61 mmol, 15.1 eq). The mixture was stirred manually to assure homogeneity and was left undisturbed at room temperature. After 2 h, gelation was observed. After a 5-day ageing period, the resulting gel was crushed to a fine powder and was washed successively three times with each of the following solvents: CH₂Cl₂, water, EtOH, and, finally, Et₂O. The product was dried overnight in a vacuum oven at 80 °C affording 500 mg of a light-orange solid. Anal. Found (in two separate analyses): C, 14.02 and 14.29; H, 1.27 and 1.30; N, 2.47 and 2.46.

3.2.2. Fluoro-tagged osmium nanoparticles Os@1: A 25 mL round-bottom flask was charged with material 1 (63 mg) and anhydrous THF (10 mL) under nitrogen atmosphere. OsCl₃.3H₂O (16 mg, 0.5 mmol) was added under vigorous stirring and then a solution of LiB(C₂H₅)H (7 mL, 1M in THF) was slowly added. The resulting mixture was left stirring during 2 hours. The solid was centrifugated and then washed with EtOH, water, and acetone successively. A black solid was obtained. Osmium content: 11 %. Average particle diameter: 1.3 ± 0.2 nm (based on TEM). XRD: 43.5° (20).

3.2.3. Fluoro-tagged iridium nanoparticles Ir@1: A 25 mL round-bottom flask was charged with $Ir_4(CO)_{12}$ (100 mg, 0.09 mmol) and diphenylether (5 mL). The mixture was left stirring at 90 °C for 1.5 h. Then material **1** (110 mg) was added to the flask, and the resulting mixture was heated to 210 °C for 29 h. The

precipitate was filtered of and was washed with toluene to afford 360 mg Ir@1 (93% yield). Analysis found: 17.7 % Ir; 42.5 % C. Average particle diameter: 0.5-1.4 nm (based on TEM). XRD: 40.6° (20). BET: 14.50 m²/g.

3.2.4. Iridium nanoparticles stabilized by diphenyl ether Ir@DPE: A 25 mL round-bottom flask was charged with Ir₄(CO)₁₂ (100 mg, 0.09 mmol) and diphenyl ether (5 mL). The mixture was left stirring first at 90 °C for 24 h and then heated to 210 °C for 29 h. The precipitate was isolated by filtration and was washed with toluene to afford 280 mg of Ir@DPE (91% yield). Analysis found: 22.7 % Ir; 45.4 % C. Average particle diameter: 0.5-1.3 nm (based on TEM). XRD: 40.6° (20). BET: 6.90 m²/g

3.2.5. Typical procedure for oxidation of alcohols with Os@1: A mixture of benzyl alcohol (208 µL, 218 mg, 2 mmol) and Os@1 (60 mg, 2%) in toluene (10 mL) was charged on a Fischer-Porter reactor. We purged three times (pressurizing/ depressurizing cycles) with oxygen and then left at 2.5 atm for 15 h at 100 °C. Upon cooling to room temperature, the reaction mixture was filtered through celite using CH₂Cl₂ and dried to give the benzaldehyde (182 mg, 87 % yield).

3.2.6. Typical procedure for oxidation of alcohols with Ir@1 or Ir@DPE: Ir@1 was activated by heating at 135°C during 2 hours. Then, a mixture of benzyl alcohol (310 μ L, 323 mg, 3 mmol) and preactivated Ir@1 (46 mg, 1.3 mol%) in toluene (1 mL) was charged into a reactor tube. We purged three times (pressurizing/ depressurizing cycles) with oxygen and left for 23 h at 100 °C under an oxygen atmosphere (balloon). Upon cooling to room temperature, the reaction mixture was filtered through celite using CH₂Cl₂ and dried to give the benzaldehyde (305 mg, 97 % yield).

Acknowledgments

We are thankful for financial support from Spain's MICINN (Grants CTQ2014-53662-P and CTQ2017-86936-P) and MEC (CTQ2016-81797-REDC). The DURSI-Generalitat de Cataluña (2017-SGR465) is also acknowledged.

Tetrahedron

References and notes

- 1. Sawada, H. Prog. Polym. Sci. 2007, 32, 509-533.
- Gentillini, C.; Evangelista, F.; Rudolf, P.; Franchi, P.; Lucarini, M.; Pasquato, L. J. Am. Chem. Soc. 2008, 130, 15676-15682.
- 3. Garcia-Bennabé, A.; Krämer, M.; Olàh, B.; Haag, R. Chem. Eur. J. 2004, 10, 2822-2830.
- 4. Lu, Z.; Zhou, X.; Hu, S.; Shu, X.; Tian, Y.; Zhu, J. J. Phys. Chem. C 2010, 114, 13546-13550.
- (a) Wan, L.; Cai, C. *Catal. Lett.* 2011, *141*, 839-843. (b) Wan, L.; Cai, C. *Transition Met. Cat.* 2011, *36*, 747-750. (c) Wan, L.; Cai, C. *Catal. Commun.* 2012, 105-108.
- 6. Schadt, K.; Kerscher, B.; Thomann, R.; Muelhaupt, R. Macrmolecules **2013**, *46*, 4799-4804.
- Sologan, M.; Marson, D.; Polizzi, S.; Pengo, P. Boccardo, S.; Pricl, S. Posocco, P.; Pasquato, L. ACS Nano 2016, 10, 9316-9325.
- Moreno-Mañas, M.; Pleixats, R.; Villarroya, S. Chem. Commun. 2002, 60-61.
- Serra-Muns, A.; Soler, R.; Badetti, E.; de Mendoza, P.; Moreno-Mañas, M.; Pleixats, R. Sebastián, R. M.; Vallribera, A. New J. Chem. 2006, 30, 1584-1594.
- Niembro, S.; Vallribera, A.; Moreno-Mañas, M. New J. Chem. 2008, 32, 94-98.
- Bernini, R.; Cacchi, S.; Fabrizi, G.; Forte, G.; Niembro, S.; Petrucci, F.; Pleixats, R. Prastaro, A.; Sebastián; R. M.; Soler, R.; Tristany, M.; Vallribera, A. Org Lett. 2008, 10, 561-564. Synfacts 2008, 5, 0550-0550.
- (a) Tzschucke, C. C.; Markert, C.; Glatz, H.; Bannwarth, W. Angew. Chem. Int. Ed. 2002, 41, 4500-4503. (b) Tzschucke, C. C.; Bannwarth, W. Helv. Chim. Acta 2004, 87, 2882-2889.
- (a) Niembro, S.; Shafir, A.; Vallribera, A.; Alibés, R. Org. Lett.
 2008, 10, 3215-3218. Synfacts 2008, 11, 1228. (b) Boffi, A.; Cacchi, S.; Ceci, P.; Cirilli, R.; Fabrizi, G.; Prastaro, A.; Niembro, S.; Shafir, A.; Vallribera, A ChemCatChem 2011, 3, 347-353.
- Bernini, R.; Cacchi, S.; Fabrizi, G.; Forte, G.; Petrucci, F.; Prastaro, A.; Niembro, S.; Shafir, A. Vallribera, A. Org. Biomol. Chem. 2009, 7, 2270-2273.
- (a) Bernini, R.; Cacchi, S.; Fabrizi, G.; Forte, G.; Petrucci, F.; Prastaro, A.; Niembro, S.; Shafir, A. Vallribera, A. *Green Chem.* **2010**, *12*, 150-158. (b) Wang, L.; Cai, C. J. Mol. Catal. A: Chem **2009**, *306*, 97-101.
- Metin, O.; Alp, N. A.; Akbayrak, S.; Bicer, A.; Gultekin, M. S.; Ozkar, S.; Bozkaya, U. *Green Chemistry* 2012, *14*, 1488-1492.
- Niembro, S.; Donnici, S. Shafir, A.; Vallribera, A.; Buil, M. L.; Esteruelas, M. A.; Larramona, C. New J. Chem. 2013, 37, 278-282.
- Michalczyk, M. J.; Sharp, K. G.; Stewart, C. W. Fluoropolymer nanocomposites. United States Patent 5726247, 1998.
- Kraemer, J.; Redel, E.; Thomann, R.; Janiak, C. Organometallics 2008, 27, 1976-1978.
- So, M.-H.; Ho, C.-M.; Chen, R.; Che, C.-M Chem-Asian J. 2010, 5, 1322-1331.

Phys. 2014, *16*, 22723-22734.
Sarlak, N.; Karimi, M. U.S. Pat. Appl. Pub. (2011) US20110124040 A1 20110526.

CCEPTED MAN 21S Ede, SPR.; Nithiyanantham, U.; Kundu, S. Phys. Chem. Chem.

- (a) Zahmakiran, M.; Akbayrak, S.; Kodaira, T.; Özkar, S. Dalton Trans. 2010, 39, 7521-7527; (b) Metin, O.; Alp, N. A.; Akbayrak, S.; Bicer, A.; Gultekin, M. S.; Ozkar, S.; Bozkaya, U. Green Chemistry 2012, 14, 1488-1492.
- Low, J. E.; Foelske-Schmitz, A.; Krumeich, F.; Worle, M.; Baudouin, D.; Rascon, F.; Coperet, C. *Dalton Trans.* 2013, 42, 12620-12625.
- Bramhaiah, K.; Pandey, I.; Singh, V. N.; Kavitha, C.; John, N. S. J. Nanopart. Res. 2018, 20, 1-13.
- (a) Mévellec, V.; Roucoux, A.; Ramorez, E.; Philippot, K; Chaudret, B. Adv. Synth. Catal. 2004, 346, 72-76; (b) Park, S.; Kwon, M. S.; Kang, K. Y.; Lee, J. S.; Park, J. Adv. Synth. Catal. 2007, 349, 2039-2047; (c) Kundu, S.; Liang, H. J. Colloid. Interf. Sci. 2011, 354, 597-606; (d) Kobayashi, H.; Yamauchi, M.; Kitagawa, H. J. Am. Chem. Soc. 2012, 134, 6893-6895; (e) Gao, L.; Kojima, K.; Nagashima, H. Tetrahedron 2015, 71, 6414-6423; (f) An, B.; Zeng, L.; Jia, M.; Li, Z.; Lin, Z.; Song, Y.; Zhou, Y. Cheng, J.; Wang, C.; Lin, W. J. Am. Chem. Soc. 2017, 139, 17747-17750; (g) Lettenmeier, P.; Majchel, J.; Wang, L.; Saveleva, V. A.; Zafeiratos, S.; Savinova, E. R.; Gallet, J.-J.; Bournel, F.; Gago A. S.; Friedrich, K. A. Chem. Sci. 2018, 9, 3570-3579.
- (a) Yee, C. K.; Jordan, R.; Ulman, A.; White, H.; King, A.; Rafailovic M.; Sokolov, J. *Langmuir* **1999**, *15*, 3486-3491; (b) Zhang, Y.; Zhang, H.; Zhang, Y.; Ma, Y. Zhong, H.; Ma, H. *Chem Commun.* **2009**, 6589-6591.
- Fonseca, G. S.; Umpierre, A. P.; Fichner P. F. P.; Teixeira S. R.; Dupont J. Chem. Eur. J. 2003, 9, 3263-3269.
- 29. Zahmakiran, M. Dalton Trans., 2012, 41, 12690-12696.
- Cano, I.; Tschan, M. J.-L.; Martinez-Prieto, L. M.; Phillipot, K.; Chaudret, B.; van Leeuwen, P.W.N.M. *Catal. Sci. Technol. Catal. Sci. Technol.* 2016, *6*, 3758-3766.
- 31. Rueping, M.; Koenigs, R. M.; Borrmann, R.; Zoller, J.; Weirich, T. E.; Mayer, *J. Chem. Mater.* **2011**, *23*, 2008-2010.
- Zahmakiran, M.; Akbayrak, S.; Kodaira, T.; Özkar, S. Dalton Trans. 2010, 39, 7521-7527.
- 33. Yoshida, A.; Mori, Y.; Ikeda, T.; Azemoto, K.; Naito, S. *Catal. Today* **2013**, *203*, 153-157.

Supplementary Material

Click here to remove instruction text...