Supplementary Information.

Unexpected, Spontaneous and Selective Formation of Colloidal Pt_3Sn Nanoparticles at Room Temperature using Organometallic Pt and Sn Complexes.

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Experimental procedures.

I. General Information.

The colloidal solution of Pt_3Sn particles and the Pt $(dba)_2$ complex[1] were prepared under Argon atmosphere, using freshly distilled and degassed solvents.
THF was distilled on NaK with benzophenone under Argon.
Dibenzylideneacetone (dba), potassium tetrachloroplatinate salt (K_2PtCl_4-97%), were purchased from Aldrich and used as received.

Elemental Analysis Elemental analyses were performed at the "Laboratoire de Synthèse et d'Electrosynthèse Organométallique", UMR 5188 CNRS, Dijon, France and at the "Service Central d'Analyses" of the CNRS in Vernaison, France.

Transmission Electron Microscopy (TEM).
For micrographs of Pt nanoparticles colloids:
1) Conventional TEM micrographs were performed at the "Centre Technologique des Microstructures", UCBL, Villeurbanne, France, using a Philips 120 CX electron microscope. The acceleration voltage was 120 kV. The samples were prepared by dispersing a drop of the ethanol suspension of a ground sample on a Cu grid covered by a carbon film.
2) High Resolution TEM micrographs were performed at the "Institut de Recherche sur la Catalyse et l'Environnement de Lyon" (IRCELyon), CNRS, Villeurbanne, France on a Jeol 2010 Transmission Electron Microscope. The acceleration voltage was 200 kV.

Wide-Angle X-ray Diffraction
The data collection for the wide-angle X-ray scattering was performed using a Bruker D8 Advance diffractometer (33 kV & 45 mA) with CuKα radiation (λ = 0.154 nm) in the "Centre de diffractometrie H. Longchambon", UCBL, Lyon, France. The diffraction patterns were collected in the 2θ angle range [0.5°-100.0°] at a scanning rate of 0.1°/min. The size of the Pt crystallite was obtained with the Scherrer formula.

[1] Prepared according to the protocol published by: Moseley, K.; Maitlis, P. M. *Chem. Comm.* **1971**, 1604-1605.

Infra red spectroscopy

Infrared spectra were recorded on a Nicolet 550-FT spectrometer by using a custom infrared cell equipped with CaF_2 windows, allowing in situ studies. Typically, 16 scans were accumulated for each spectrum (resolution of 4 cm^{-1}).

Mössbauer spectroscopy

^{119}Sn Mössbauer spectra were recorded in transmission geometry in the constant acceleration mode, using equipment supplied by Ortec and Wissel. Low temperature spectra were recorded by placing the sample in a helium flow cryostat. The nominal activity of the $Ba^{119m}SnO_3$ source was 10 mCi. The velocity scale was calibrated by means of a room temperature spectrum of α-Fe recorded with a 57Co(Rh) source. The hyperfine parameters δ (isomer shift) and ΔEq (quadrupolar splitting) were determined by fitting Lorentzian lines to the experimental data by using the ISO programme. Isomer shifts of samples studied in the present work are given with respect to the room temperature spectrum of $BaSnO_3$. The error in the determination of the hyperfine parameters is ± 0.06 mm/s.

II preparation:

Representative preparation of the colloidal solution of Pt_3Sn nanoparticles using 1 equiv. of trialkyltinhydride :

100 mg of $Pt(dba)_2$[1] (0.15 mmol) were introduced into a batch reactor and treated under vacuum during 30 min at room temperature before dissolution in 90 mL of THF. 10 mL of THF containing 43.7 mg (0.15 mmol) of trialkyltinhydride were subsequently added at room temperature. The resulting solution was pressurized with 3 bars of dihydrogen under stirring overnight. The colloidal suspension was purified by solvent evacuation to dryness. After solvent evaporation, washings with pentane were achieved: 50 ml of pentane were introduced in the schenk-tube containing the particles residue. After 10 min at room temperature under stirring, the stirring was stopped and the bottom of the schlenk tube was put into liquid N_2 for a further 15 min order to precipitate the colloid. When the colloid had precipitated, the supernatant was removed and this operation was repeated three times.

Blank Experiments :

c.a. 50mg (0.15 mmol) of trialkyltinhydride were introduced, at room temperature and under argon, into a batch reactor containing 100 mL of THF. The resulting solution was pressurized with 3 bars of dihydrogen under stirring overnight. After evacuation of H_2, the solution was concentrated (to 10 mL)

and analysed by TEM (by dispersion of a droplet on a Cu grid) and by IR spectroscopy (using infrared cell equipped with CaF_2 windows).

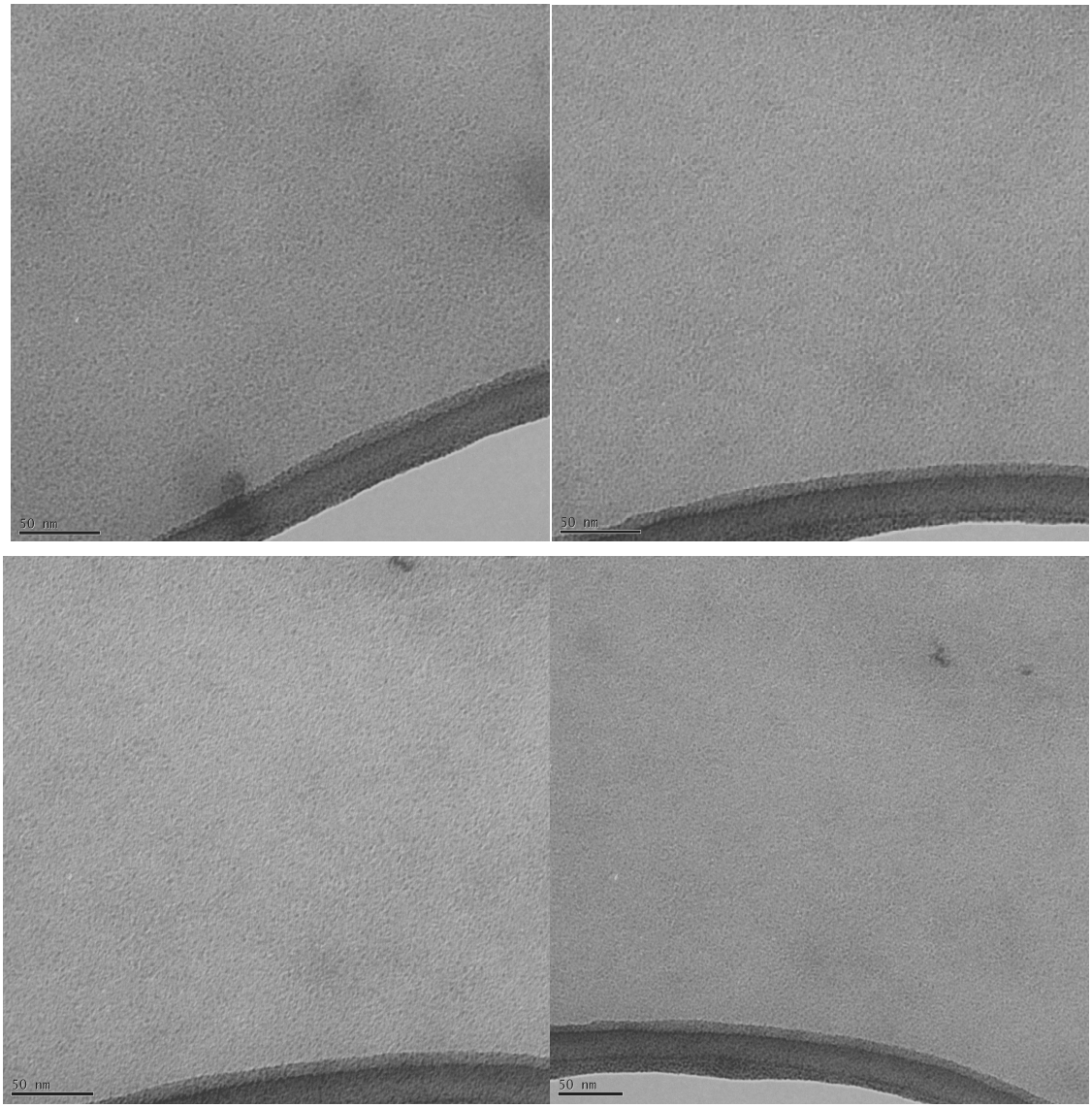

Figure S1. TEM pictures od the blank solution after one night under H_2

Noteworthy, the darker spots do not correspond to Sn particles and they are also present on "naked" grids and correspond to defaults in the Carbon film on the grid.

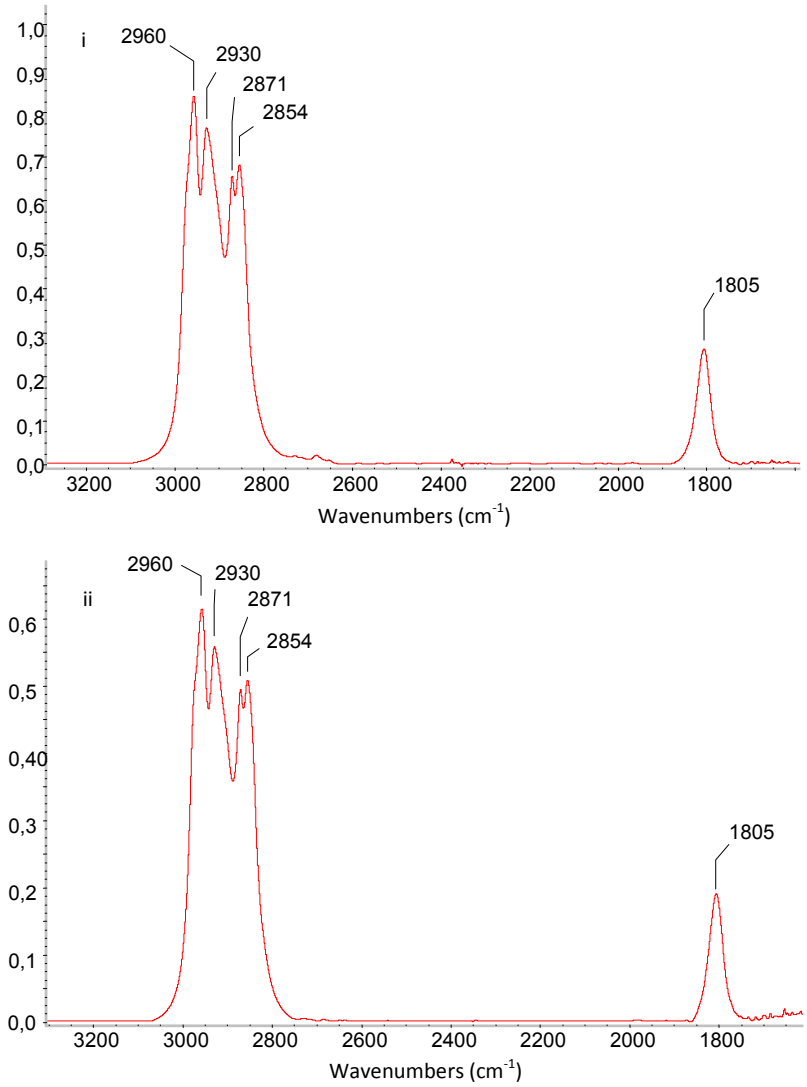

Figure S1. I.R. spectra of i) the concentrated THF solution just after introduction of the Sn precursor and ii) the concentrated THF solution containing the Sn precursor after one night under H_2

III Characteristics of the Pt_3Sn colloids:

Table S1. EDX measurements on the Pt_3Sn nanoparticles prepared using 1.0 equivalent of tin precursor

dparticles (nm)	d spot (nm)	Pt atomic (%)	Sn atomic (%)	Sn/Pt
3.5	2	3.82	2.01	0.55
4	2	2.33	1.31	0.56
2	2	1.77	1.18	0.66
2.5	2	3.49	1.97	0.56
2	2	3.73	2.00	0.53
4 particles	10	1.64	0.91	0.55
10 particles	50	1.78	0.84	0.47

Table S2. Comparison of the theoretical (JCPDS) and the experimental cristallographic data obtained by TEM diffraction on two different Pt_3Sn particles prepared using 1.0 equivalent of tin precursor.

	Experimental	Theoretical Pt_3Sn alloy	Experimental	Theoretical Pt_3Sn alloy
D(h k l)	0.229 (1 1 1) 0.141 (2 0 0) 0.233 (1 1 -1)	0.231 (1 1 1) 0.141 (2 0 0) 0.231(1 1 -1)	0.230 (-1 1 1) 0.226 (1 1 1) 0.200 (2 0 0)	0.231 (-1 1 1) 0.231 (1 1 1) 0.200 (2 0 0)
Angle (°)	0 33.95 68.23	0 35.26 70.52	0 69.38 123.37	0 70.53 125.26