Investigation of the surface chemistry of phosphine- stabilized ruthenium nanoparticles – An advanced solid-state NMR study

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S 0: Synthesis of RuPTA NPs (**1**) and RuPPh$_3$ NPs (**2**).

*RuPTA NPs (**1**)*

Nanoparticles stabilized with PTA were prepared in a way similar to recently published works.[1,2] In a typical procedure 100 mg of [Ru(COD)(COT)] (0.317 mmol) were introduced in a Fisher-Porter bottle (FB) and dissolved in 100 ml of desoxygenated THF under argon. The resulting yellow solution was cooled down with an acetone/ethanol freezing bath and 40 mg of PTA (0.254 mmol; 0.8 eq./Ru) dissolved in 100 ml THF were added. After the FB had returned to room temperature, it was pressurized with 3 bar of hydrogen gas. The reaction mixture was heated to 50°C and stirred for 16 h. THF was evaporated to a volume of 10 ml and 100 ml of pentane were added to induce the precipitation of the NPs. The brown precipitate was isolated by filtration and dried in vacuum, giving rise to RuPTA NPs (36 mg; **1**) as a dark brown powder.

Mean diameter (TEM): 1.3±0.2 nm

Elementary analyses: 41.6 wt% Ru, 9.4 wt% P

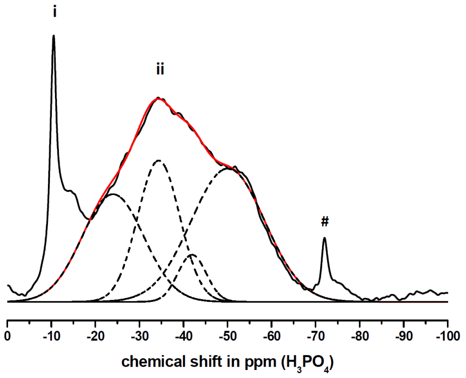
RuPPh$_3$ NPs (2)

In a typical procedure 202 mg of Ru(COT)COD (0.64 mmol) were introduced in a FB under argon and dissolved in 120 ml of desoxygenated THF. The resulting yellow solution was cooled down with an acetone/ethanol freezing bath. 34 mg of PPh$_3$ (0.13 mmol; 0.2 eq/Ru) previously dried under vacuum, were dissolved in 40 ml of THF. The ligand solution was then transferred through a cannula in the FB and THF was completed to 180 ml of reaction mixture. After the FB had returned to room temperature, it was pressurized with 3 bar of hydrogen gas. The reaction mixture was stirred vigorously for 16 h at room temperature yielding a dark brown solution. THF was evaporated to a volume of 10 ml and 80 ml of pentane were added to induce the precipitation of the NPs. After filtration and washings with pentane (2x 40 ml), the solid was dried under vacuum over night giving rise to $RuPPh_3$ NPs (54 mg; **2**) as a dark brown powder.

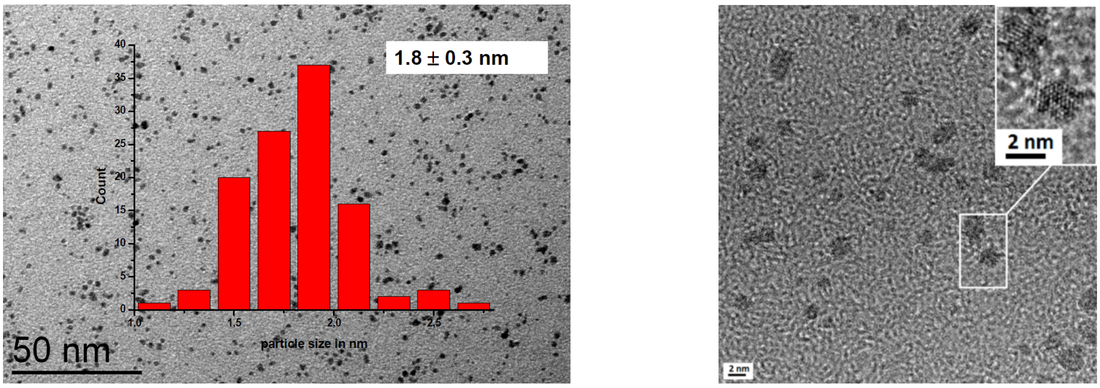
Mean diameter (TEM): 1.8 ± 0.3 nm

Elementary analyses: 61.3 wt% Ru, 4.13 wt% P;

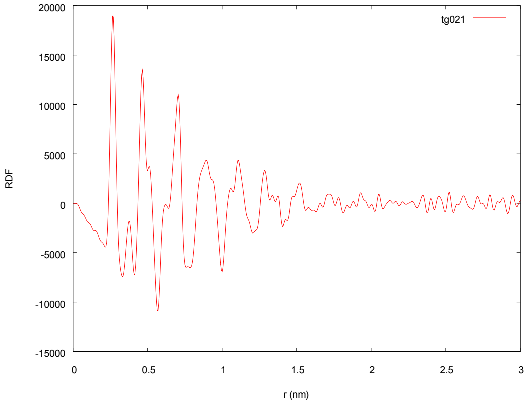
S 1: ^{31}P CP MAS spectrum at 10 kHz spinning of RuPTA NPs after adsorption of CO: Deconvolution of component **ii** into 4 single signals.



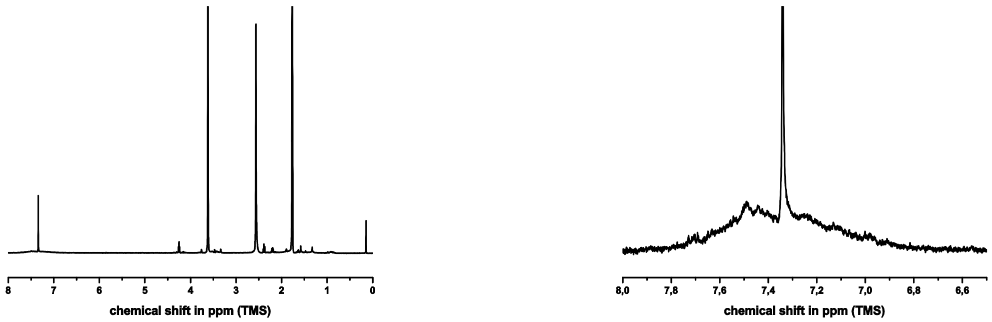
S 2: TEM and HRTEM pictures of $RuPPh_3$ NPs show well dispersed particles with a mean size diameter of 1.8 nm.



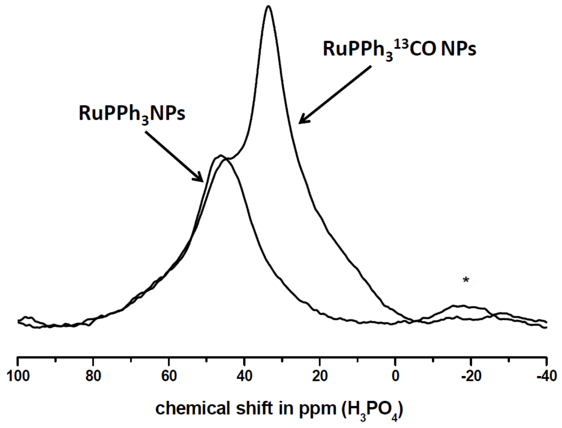
<u>S 3:</u> WAXS measurements of $RuPPh_3$: From the RDF function a bonding distance Ru-Ru in the metal core of 2.68 Å can be derived. The coherence length is between 1.8 and 2 nm.



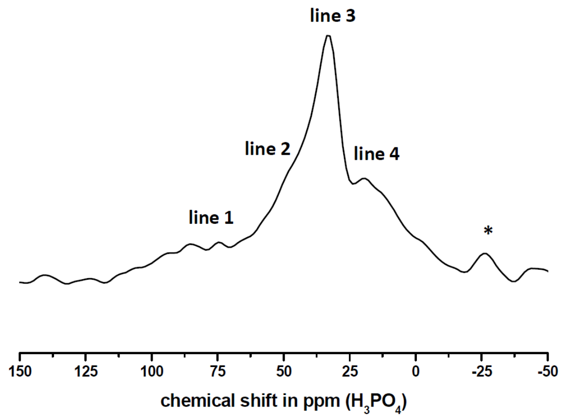
<u>S 4:</u> ^1H NMR of $RuPPh_3$ NPs in THF-d_8: The broad signal between 7 and 7.8 ppm refer to strongly bound PPh_3 at the Ru metal core. Signals at 1.77 ppm, 3.62 ppm and 2.6 ppm assign to THF and water respectively. Other small signals refer to some impurities.



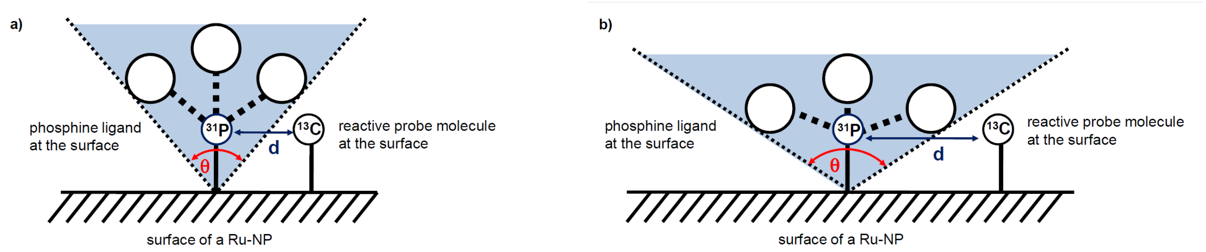
<u>S 5:</u> ^{31}P CP MAS spectra of $RuPPh_3$ NPs and $RuPPh_3{}^{13}CO$ NPs at 10 kHz spinning.



S 6: ^{31}P CP MAS spectrum of $RuPPh_3{}^{13}CO$ NPs at 10 kHz spinning calculated from the sum of FIDs of the REDOR reference signals. The lineshape of this spectrum illustrate more distinctive that minimum 4 signals are required to reflect the lineshape in a properly way.



S 7: Illustration of the dependence of the distance d between the ^{31}P nucleus of the phosphine ligand and the ^{13}C nucleus of the reactive probe molecule on the cone angle θ of the ligand: (a) small cone angle and (b) large cone angle.



The Tolman cone angle θ describes the size of ligands. It was defined by Tolman in 1970 for phosphine ligands in nickel complexes as angle formed with the metal at the vertex and the hydrogen atoms at the perimeter of the ligand cone.[3] This definition can be also transferred to other metals as for example ruthenium, yielding smaller or larger cone angles depending on the bond length between phosphorous and metal.
In Fig. S7 a schematically illustration of the dependence of the distance d between ^{31}P of the phosphine ligand and ^{13}C of the reactive probe molecule on the cone angle θ of the ligand is given, which shows that with increasing cone angle θ the distance d between the ^{13}C nucleus of the reactive probe molecule and the ^{31}P nucleus of the phosphine ligand should increase since the ^{13}C nucleus can be not located within the ligand cone.

References

[1] P.-J. Debouttière, V. Martinez, K. Philippot and B. Chaudret, *Dalton Trans.*, 2009, 10172-10174.

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[3] C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2956-2965.