

New Ru Nanoparticles Stabilized by Organosilane Fragments

K. Pelzer,^{†,‡} B. Laleu,[†] F. Lefebvre,[†] K. Philippot,[‡] B. Chaudret,[‡]
J. P. Candy,^{*,†} and J. M. Basset^{*,†}

LCOMS, UMR CNRS-CPE 9986, 43 bd du 11 novembre 1918, 69616 Villeurbanne, France,
and LCC, UPR CNRS 8241, 205 rte de Narbonne, 31077 Toulouse, France

Received June 8, 2004. Revised Manuscript Received September 2, 2004

The decomposition of the organometallic ruthenium precursor [Ru(COD)(COT)] (COD = 1,5-cyclooctadiene; COT = 1,3,5-cyclooctatriene) in mild conditions (193 K, 3 bar H₂) in *n*-pentane leads, in the presence of octylsilane (H₃SiC₈H₁₇) as stabilizer (ligand), to the formation of nanoparticles of about 2.3 nm in diameter with a narrow size distribution as demonstrated by TEM observations. Infrared spectroscopy shows that all the $\nu(\text{Si-H})$ bands disappeared and that some alkyl fragments remain grafted on the metallic surface. Both liquid and solid state ¹³C CP-MAS NMR could be successfully applied to characterize alkylsilane fragments grafted on the ruthenium nanoparticles' surface. Similar results were obtained by the two techniques. Although the signal corresponding to the carbons in α position was missing and the signal corresponding to the carbon in β position was strongly lowered, the signals corresponding to the other carbons were clearly identified. This may be the result of both the lack of surface homogeneity and the weak "knight shift" of ruthenium. To our knowledge, it is the first time that ruthenium nanoparticles stabilized by surface-grafted alkylsilane fragments are synthesized and fully characterized by electron microscopy as well as solid state ¹³C MAS NMR.

Introduction

A large variety of organometallic compounds react quite easily with the surface of reduced supported or unsupported metal particles. This observation has been at the origin of a field of chemistry named surface organo-metallic chemistry on metals (SOMS/M).¹ SOMS/M was mostly used to prepare new kinds of catalytic materials at the border between heterogeneous and homogeneous catalysts. For example, tetraalkyl tin, SnR₄ (R = Me, Et, Bu, tBu, Np, cyhex, etc.) reacts at room temperature under hydrogen with the surface of metallic particles (Pt, Rh, Ni, Ru, etc.)^{2–6} leading to alkane evolution and formation of grafted organometallic fragments on the surface of the "host" metal. Grafted organometallic fragments on the surface of metallic particles have been evidenced by EXAFS^{3,4} and Mössbauer,⁷ but, to our knowledge, no study by tech-

niques easily available to molecular chemistry such as solid-state NMR was reported. However, this NMR technique is expected to demonstrate the presence of the ligand on the surface of the particles but could also give an idea of the energetics and the dynamics of the ligand's coordination. Since the presence of a support (silica, alumina, etc.) could render difficult the observation of the ligand, the use of unsupported metallic particles was preferred.

Another approach to this fascinating field is to graft an organic ligand at the surface of the particles. The use of organic ligands as stabilizers for the synthesis of metal nanoparticles has been considerably developed in the past few years.^{8–12} The presence of ligands coordinated at the surface prevents the particles from coalescing and allows their self-assembly onto various surfaces. Organic molecules such as amines,¹¹ thiols,^{13,14} or

* To whom correspondence should be addressed. E-mail: candy@cpe.fr.

[†] LCOMS, UMR CNRS-CPE.

[‡] LCC, UPR CNRS.

(1) Candy, J. P.; Didillon, B.; Smith, E. L.; Shay, T. B.; Basset, J. M. *J. Mol. Catal.* **1994**, *86*, 179.

(2) Candy, J. P.; Ferretti, O. A.; Mabilon, G.; Bournonville, J. P.; El Mansour, A.; Basset, J. M.; Martino, G. *J. Catal.* **1988**, *112*, 210.

(3) Humblot, F.; Didillon, B.; Le Peltier, F.; Candy, J. P.; Corker, J.; Clause, O.; Bayard, F.; Basset, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 137.

(4) Lesage, P.; Clause, O.; Moral, P.; Didillon, B.; Candy, J. P.; Basset, J. M. *J. Catal.* **1995**, *155*, 238.

(5) Agnelli, M.; Louessard, P.; El Mansour, A.; Candy, J. P.; Bournonville, J. P.; Basset, J. M. *Catal. Today* **1989**, *6*, 63.

(6) Louessard, P.; Candy, J. P.; Bournonville, J. P.; Basset, J. M. In *Structure and Reactivity of Surfaces*; Morterra, C., Cecchina, A., Costa, G., Eds.; Elsevier: Amsterdam, 1989; Vol. 48, p 591.

(7) Millet, J. M.; Toyir, J.; Didillon, B.; Candy, J. P.; Nédéz, C.; Basset, J. M. *Hyperfine Interact.* **1997**, *108*, 477.

(8) Dassenoy, F.; Philippot, K.; Amiens, C.; Casanove, M. J.; Chaudret, B. *New J. Chem.* **1998**, *22*, 703.

(9) Badia, A.; Gao, W.; Singh, S.; Demers, L.; Cuccia, L.; Reven, L. *Langmuir* **1996**, *12*, 1262.

(10) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989.

(11) Pan, C.; Pelzer, K.; Philippot, K.; Chaudret, B.; Dassenoy, F.; Lecante, P. M.; Casanove, J. J. *Am. Chem. Soc.* **2001**, *123*, 7584.

(12) Rodriguez, A.; Amiens, C.; Chaudret, B.; Casanove, M. J.; Lecante, P.; Bradley, J. S. *Chem. Mater.* **1996**, *8*, 1978.

(13) Hosteler, M. J.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1994**, *116*, 11608.

(14) Terrill, R. H.; Postlethwaite, T. A.; Chen, C.-H.; Poon, C.-D.; Terzis, A.; Chen, A.; Hutchinson, J. E.; Clark, M. R.; Wignall, G.; Londono, J. D.; Superfine, R.; Falvo, M.; Johnson, C. S.; Samulski, E. T.; Murray, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 12537.

alcohol¹⁵ were used as stabilizers and for these systems. ¹³C and ¹H NMR in the liquid^{8,9,11} or in the solid state⁹ were successfully used to characterize the grafted ligands. It was therefore of interest to combine the expertise in both fields to have a better understanding of the structure, mobility, and reactivity of surface organometallic fragments, using solid-state NMR.

We have been interested in ruthenium, which is a metal of catalytic interest and a precursor for semiconducting oxides but for which the literature remains very limited. Moreover, this metal is known to present a small "Knight shift".¹⁶ It has been shown that the decomposition of the ruthenium precursor Ru(COD)-(COT), (COD = 1,5-cyclooctadiene; COT = 1,3,5-cyclooctatriene) could be carried out in mild conditions (room temperature, 1–3 bar H₂) in THF to yield nanoparticles of ruthenium.¹⁷ Tetraalkyltin complexes were widely used as reactant,^{2–6} but, since the Si–C bond is stronger than the Sn–C bond toward hydrogenolysis, silanes have been considered as better candidates to keep the organometallic fragments at the surface of Ru particles, and we will apply the SOMS/M route¹ to the H_xSiR_{4–x}/Ru–H system.

Experimental Section

Reactants and Solvents. The solvents were used immediately after drying and distillation (over calcium hydride for methanol, on benzophenone for THF, on sodium for toluene, and on sodium/potassium for pentane) under argon.

The alumina used for filtration of Ru(COD)(COT) in pentane was standardized 90 alumina from Merck (activity 2–3 according Brockmann).

The reactants were COD (99% from Aldrich), RuCl₃·3H₂O (from Strem Chemicals), Zn powder (from Aldrich), and octylsilane (from ABCR).

Synthesis of Ru(COD)(COT). The first preparation of Ru(COD)(COT) by Grignard reduction of [RuCl₂(COD)]_n in the presence of 1,3,5-cyclooctatriene under UV irradiation was reported by Müller and Fischer,^{18,19} but resulted in poor yield. Pertici and Vitulli²⁰ reported an easier preparation from ruthenium chloride hydrate, zinc powder, and the less expensive COD, all of which are readily available. Cycloocta-1,5-diene (8.8 g, 81 mmol) and zinc dust (3.5 g) were added to a solution of RuCl₃·3H₂O in 30 mL of methanol. The mixture was heated under reflux with magnetic stirring for 3 h and then filtered. The resulting brown solution was evaporated in a vacuum until the residue was completely dry. Extractions with distilled pentane (3 × 20 mL) gave a yellow-brown solution which was filtered through a column of alumina (20 cm). The volume of solvent was reduced to 5 mL and the yellow solution was cooled to 243 K for 24–48 h to give yellow crystals of Ru(COD)(COT) (0.28 g, 70%), M = 316 (mass spectrometry), C₁₆H₂₂Ru. Ru(COD)(COT) is a yellow crystalline solid which is atmospheric oxygen sensitive and must be stored for a prolonged period of time under argon at 273 K. Elemental analysis (C = 60.5%; H = 6.7%; Ru = 30.9%) is in good accordance with the expected values (C = 61%; H = 7%; Ru = 32%). Liquid ¹H NMR (300 MHz, C₆D₆) δ = 5.19 (dd, 2H), 4.70 (m, 2H), 3.77 (m, 2H), 2.92 (m, 4H), 2.25 (m, 8H), 1.68 (m, 2H), 0.83 (m, 2H) and ¹³C NMR (75 MHz, C₆D₆) δ = 101.5 (CH), 99.4 (CH), 76.6 (CH), 65–75 (large) (CH), 37.0 (CH₂),

31.7 (CH₂) results were identical with the data previously reported in the literature.²¹

Ruthenium Particles Stabilized by Octylsilanes. Ru(COD)(COT) (0.32 mmol; 100 mg) was introduced into a glass reactor and treated under vacuum during 30 min at room temperature before dissolution in 90 mL of pentane. Octylsilane (0.32 mmol; 45.8 mg) in 10 mL of pentane was added at 193 K. The resulting solution was pressurized with 3 bar of dihydrogen and the temperature was slowly raised to room temperature under strong stirring. After 8 h of reaction, a dark brown solution was formed from which a black powder could be obtained after depressurization, concentration of the solution, and addition of cold pentane under argon. The precipitate was removed by filtration, purified by several wash cycles with pentane, and dried under argon.

Elemental Analysis. Elemental analyses were performed at the Laboratoire de Synthèse et Electrosynthèse Organométalliques, UMR 5188 CNRS, Dijon, France. The sample was taken under argon and the elemental analyses were done without contact with air.

NMR Spectroscopy. Liquid-phase NMR spectra were obtained at room temperature in deuterated THF or benzene on a Bruker AC300 spectrometer. The chemical shifts are expressed in ppm (singlet = s, doublet = d, doublet of doublet = dd, and multiplet = m). ¹³C and ²⁹Si Solid-state NMR spectra were obtained on a Bruker DRX 300 spectrometer (Bruker CP 4 mm probehead, rotor 4 mm in ZrO₂, rotation frequency of the sample 10 kHz). All solids studied here were kept under argon. They were prepared in a Schlenk tube and transferred into the rotor in a glovebox under argon.

Infrared Spectroscopy. The infrared spectrometer was a FTIR apparatus Nicolet 550. The dry solid was mixed with KBr and compressed into a disk before acquisition of infrared spectra.

Electron Microscopy (TEM). Conventional transmission electron microscopy was performed at the Institut de Recherches sur la Catalyse, CNRS, Villeurbanne, France, using a JEOL 100 CX electron microscope to establish particle size distributions.

Wide-Angle X-ray Scattering. The data collection for the wide-angle X-ray scattering was performed at the Centre d'Elaboration des Matériaux et Etudes Structurales, UPR 8011, CNRS, Toulouse, France. Time for data collection was typically 20 h for a set of 457 measurements collected at room temperature in the range 0° < θ < 65°. The data were reduced to extract the structure-related component of WAXS, the so-called reduced intensity function, normalized to a number of atoms corresponding to the size of the particle, and then Fourier transformed to allow for radial distribution function (RDF) analysis.

Results and Discussion

Elemental analysis of the dried solid obtained after 8 h of reaction of Ru(COD)(COT) with dihydrogen in the presence of octylsilane, H₃Si(*n*-C8) (Si/Ru = 1), at 193 K in *n*-pentane solution (see Experimental section) gave 68.6% (w/w) Ru and 10.4% (w/w) Si, (Si/Ru = 0.55) for metals, 24.4% for C (C/Si = 5.4), and 5.1% for H₂ (H/C = 2.5). These values indicate that about 0.55 silicon atoms per ruthenium atom are grafted on the metal surface and about 0.7 octyl chains remain bonded per silicon atom.

The TEM picture (Figure 1) shows that isolated small metallic nanoparticles were obtained.

The distribution of the metallic particle diameters obtained by observation of more than 200 particles from 5 TEM pictures is reported in Figure 2. The average

(15) Peltzer, K.; Vidoni, O.; Philippot, K.; Chaudret, B.; Collière, V. *Adv. Funct. Mater.* **2003**, *13*, 118.

(16) Riley, C. C. A.; Jonsen, P.; Meehan, P.; Frost, J. C.; Packer, K. *J. Catal. Today* **1991**, *9*, 121.

(17) Duteil, A.; Queau, R.; Chaudret, B.; Mazel, R.; Roucau, C.; Bradley, J. S. *Chem. Mater.* **1993**, *5*, 341.

(18) Müller, J.; Fischer, E. O. *J. Organomet. Chem.* **1966**, *6*, 275.

(19) Müller, J.; Fischer, E. O. *Chem. Ber.* **1963**, *96*, 3217.

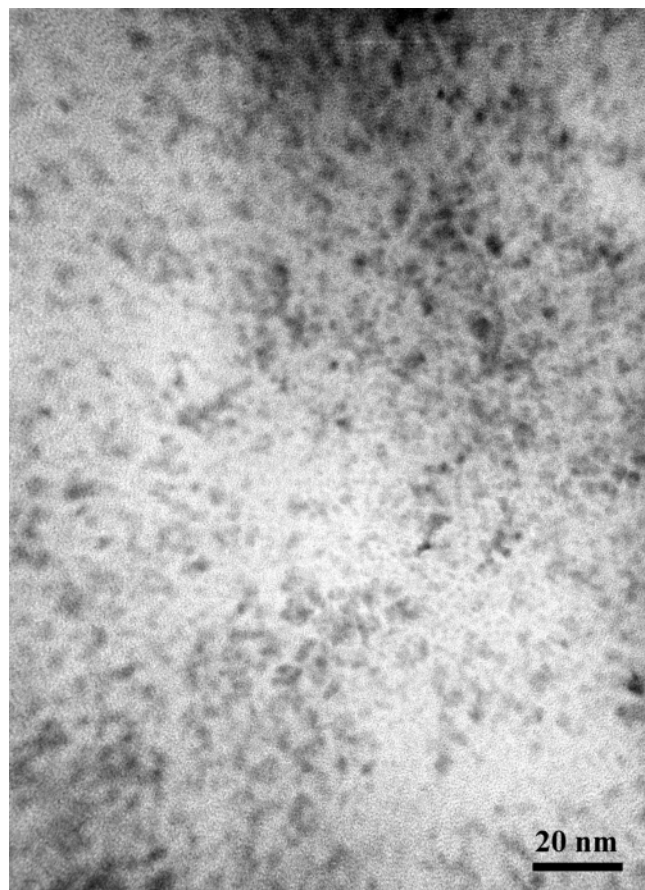
(20) Pertici, P.; Vitulli, G. *Inorg. Synth.* **1983**, *22*, 178.

(21) Vidoni, O.; Philippot, K.; Amiens, C.; Chaudret, B.; Balmes, O.; Malm, J.-O.; Bovin, J.-O.; Senocq, F.; Casanove, M.-J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 3736.

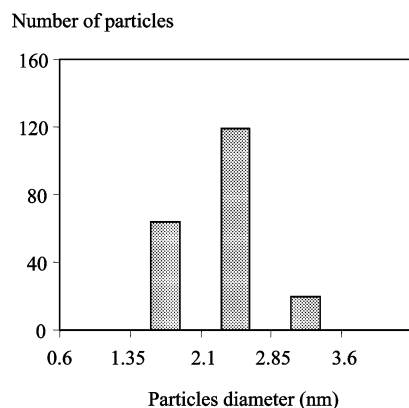
Table 1. ^{13}C NMR Chemical Shift (ppm) of Free Octylsilane and Ruthenium Particles Stabilized by Octylsilane Ligands in Deuterated Benzene or in the Solid State

carbon	α	β	$-\text{C}^*\text{H}_2-$	$-\text{C}^*\text{H}_2-\text{CH}_3$	$-\text{C}^*\text{H}_3$
free ligand, liquid NMR	6.2	26.8	32.9–29.7	23.1	14.4
Ru stabilized liquid NMR	non obs.	27.0	32.4–29.7	23.2	14.4
Ru stabilized solid NMR	non obs.	27.3	32.6–29.9	23.2	14.3

metallic particle diameter is close to 2.3 nm with a relatively narrow size distribution.

**Figure 1.** Electron microscopy (TEM) of the ruthenium nanoparticles covered by octylsilane fragments.

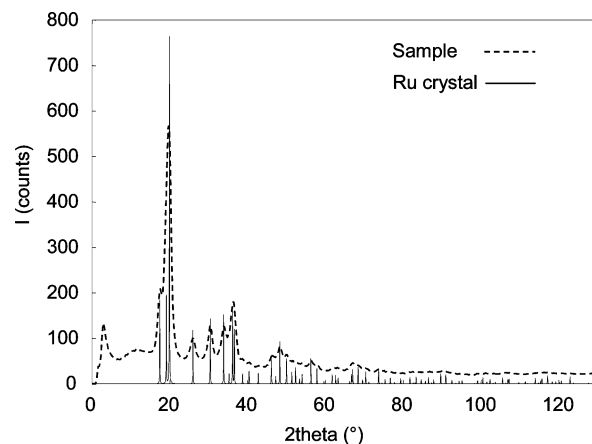
The structure of the particles has been determined by WAXS analysis (Figure 3). It can be observed that

**Figure 2.** Metallic particle diameter distribution.

the peaks are thin and in exact accordance with those expected for the hcp structure of crystalline ruthenium. The coherent length is of about 4 nm, revealing a larger

size than that determined by TEM. This could be due to agglomeration of some particles.

According to Van Hardevel and Hartog,²² a ruthenium particle of 2.3 nm in diameter, with a cubooctahedral shape, contains 586 Ru atoms, among which 272 are surface atoms, (Ru_s), yielding a dispersion (number of surface metal atoms per total number of metal atom) for this particle of about 0.46. Knowing that the number

**Figure 3.** WAXS measurements of Ru nanoparticles stabilized with silane fragments.

of silicon atoms per ruthenium atom determined by elemental analysis is 0.55 Si/Ru and that there are 0.7 octyl chain remaining per silicon atom, the stoichiometry of the surface complexes is, on average, $\text{Ru}_s[\text{Si}(\text{n-C8})_{0.7}]_{1.2}$.

We can then reasonably conclude that ruthenium particles covered with chemically bonded organosilane were prepared. According to Nuzzo et al.,¹³ primary organosilanes (RSiH_3) react on transition metal surfaces Pt(111) to give surface-bound silyl group ($\text{RSi}\equiv$), as demonstrated by reflection-absorption infrared spectroscopy. These species seem to be stable in the range 110–300 K. In our case, we can expect that the $(\text{n-C8})\text{-Si}\equiv$ fragments were grafted onto the metallic surface.

Infrared spectroscopy of the nanoparticles (embedded in KBr) and of pure octylsilane are reported in Figure 4. In the range $2600\text{--}3200\text{ cm}^{-1}$, the same characteristic bands of CH_3 and CH_2 groups are observed. No bands in the range $2050\text{--}2250\text{ cm}^{-1}$ can be observed for the colloids (a), while the $\nu(\text{Si-H})$ band at 2150 cm^{-1} can be observed for free octylsilane (b). This result is in accordance with the results of Nuzzo et al.¹³ who did not observe the $\nu(\text{Si-H})$ band with the complexes obtained from reaction of RSiH_3 on Pt(111). These results appear in agreement with the formation of a surface-bound silyl group $[\equiv\text{Si}(\text{n-C8})_{0.7}]$ probably linked to several surface ruthenium atoms.

The solution-state ^{13}C NMR spectra of the octylsilane is given in Figure 5a. The various peaks are attributed (Table 1) in agreement with the literature data.⁹

(22) Van Hardevel, R.; Hartog, F. *Surf. Sci.* **1969**, *15*, 189.

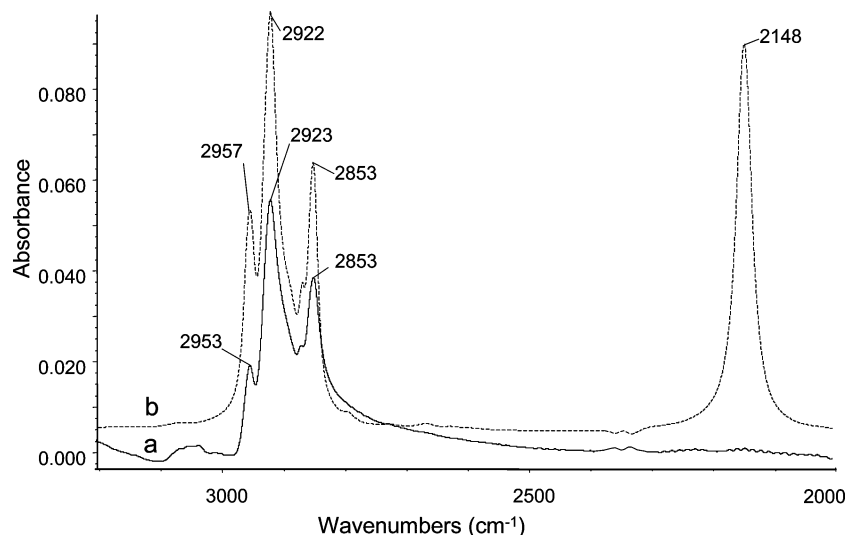


Figure 4. Infrared spectroscopy of (a) dry powder of ruthenium nanoparticles covered by octylsilane fragments in KBr and (b) pure octylsilane.

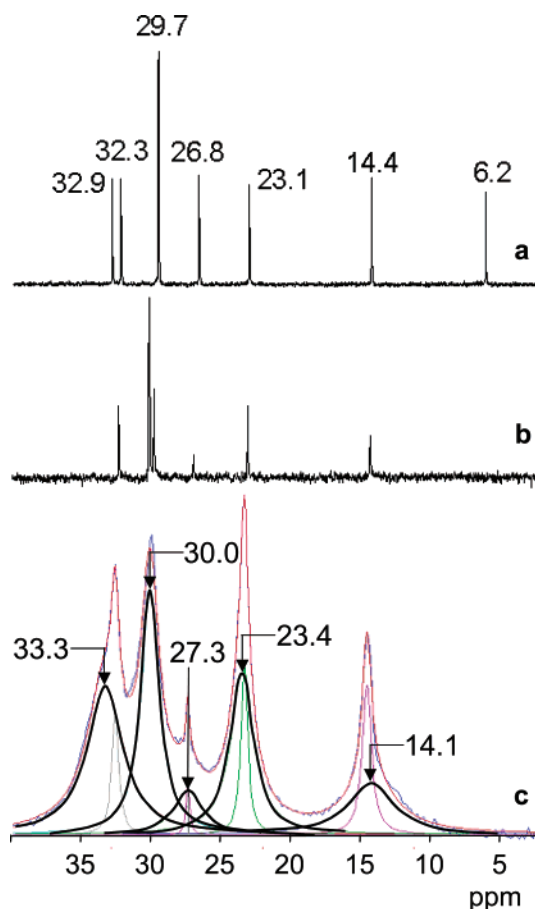


Figure 5. Liquid ^{13}C NMR spectra of free octylsilane (a) and ruthenium particles stabilized by octylsilane ligands (b) in deuterated benzene. Solid state ^{13}C NMR of ruthenium particles stabilized by octylsilane ligands (c).

The solution-state ^{13}C NMR spectra of the colloids stabilized by grafted octylsilane (Figure 5b and Table 1) show features similar to those of the particles stabilized by hexadecylamine as described previously by some of us.¹¹ First of all, some peaks corresponding to the carbon atoms of the alkyl chain of the grafted silane can be observed. When observing the spectra in more detail, it is evident that some peaks of the starting

ligand are missing or are smaller. For example, the peak attributed to the carbon in α position (6.2 ppm) is missing, while the peaks attributed to the carbon in β (26.8 ppm) or to the methyl group (14.4 ppm) are less intense.

The solid-state ^{13}C NMR spectrum (Figure 4c and Table 1) shows interesting features. First of all, it is well-resolved and presents numerous peaks between 10 and 35 ppm. The high signal-to-noise ratio allows a reliable deconvolution, showing the presence of two families of peaks depending on their line widths (the very sharp peak at 27.3 ppm is an artifact corresponding to the irradiation frequency). Three sharp peaks are seen at 14.4, 23.2, and 32.6 ppm. These three peaks can be attributed to pentane (used for the synthesis) remaining in the sample. The other peaks at 14.1, 23.4, 27.3, 30.0, and 33.3 ppm can be attributed to the octyl chain of the silane ligand. The signal at 14.1 ppm, which is relatively broad (line width 300 Hz), can be attributed to the methyl group, while the signal at 27.3 ppm (line width ca. 200 Hz) corresponds to the carbon in β position. Similar to solution NMR investigations, the signal corresponding to the carbon in α position, and expected at ca. 7 ppm, is missing.

The solid-state ^{29}Si NMR spectrum shows no signal, even after acquisition during one week on a 500 MHz spectrometer. This result indicates that dimerization of silyl groups does not occur.

The most important feature of these results is that for both solid and liquid state ^{13}C NMR of the powder, the signals attributed to carbon in α position is missing and the peaks attributed to the carbon in β (26.8 ppm) or to the methyl group (14.4 ppm) are less intense. These results are very similar to those obtained by some of us for ruthenium nanoparticles stabilized by alkyamines.¹¹ It must be noticed that when octadecylsilane is grafted on a titania surface,²³ the solid-state ^{13}C NMR spectrum shows similar features, except that the peak attributed to the carbon in α position is clearly observed (5.0 ppm). Disappearance and weakening of the signals associated with a carbon in α position when polysilsesquioxanes

(23) Shafi, K. V. P. M.; Ulman, A.; Yan, X.; Yang, N.-L.; Himmelhaus, M.; Grunze, M. *Langmuir* **2001**, *17*, 1726.

are formed were previously described,²⁴ but in these cases, ²⁹Si CP MAS NMR shows sharp signals in the -50 to -80 ppm region. These results suggest that the octylsilane fragment is grafted on the ruthenium surface and that oligomeric (RSi)_n species are not formed.

The X-ray data, as well as the relatively good agreement between the number of grafted octylsilanes and the number of surface ruthenium atoms, suggests that the octylsilanes fragments are at the periphery of the particles. The fact that the ratio Si/C is 5.4 instead of 8 suggests that part of the Si(*n*-C8) fragments have been hydrogenolysed during the synthesis.

Conclusion

It has been demonstrated that ruthenium nanoparticles of about 2–3 nm in diameter can be obtained

using octylsilane as ligand. These nanometallic particles were characterized by elemental analysis, TEM, WAXS, IR spectroscopy, and solid ¹³C NMR. The catalytic properties of these ruthenium nanoparticles will be investigated. Solid state CP-MAS NMR can be successfully applied to characterize alkylsilane fragments grafted on the surface of ruthenium nanoparticles. This technique will now be applied to silica-supported ruthenium catalysts.

Acknowledgment. We greatly thank the German Academic Exchange Service (DAAD) for giving a post-doctoral grant to Ms. K. Pelzer, Mr. M. Aouine from IRC (CNRS, Villeurbanne, France) for electron microscopy pictures, and Dr. P. Lecante from CEMES (CNRS, Toulouse, France) for WAXS analysis.

(24) Bronstein, L. M.; Linton, C. N.; Karlinsey, R.; Ashcraft, E.; Stein, B. S.; Svergun, D. I.; Kozin, M.; Khotina, I. A.; Spontak, R. J.; Werner-Zwanziger, U.; Zwanziger, J. W. *Langmuir* **2003**, *19*, 7071.