Synthesis and Spectroscopic Properties of a Novel Class of Copper Particles stabilized by Triphenylphosphine

Dominique de Caro, Hans Wally, Catherine Amiens and Bruno Chaudret*

Laboratoire de Chimie de Coordination du CNRS, UPR 8241, liée par convention à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205, route de Narbonne, 31 077 Toulouse Cedex, France

The reaction of $(C_5H_5)Cu(Bu^tNC)$ with CO (1 or 3 atm) in the presence of sub-stoichiometric amounts of PPh_3 leads to phosphine stabilized copper particles of *ca.* 20 Å showing a narrow size distribution; $^{31}P\{^1H\}$ NMR studies demonstrate both the fluxionality of the phosphine ligands and the absence of the Knight shift on these particles whereas UV–VIS spectroscopy indicates an important modification of the absorption bands of these compounds compared to non complexed copper particles of similar size.

The synthesis of metal particles in organic solutions (metal colloids) is attracting an ever-growing interest because of the properties of the new nanosize materials formed which find applications both in catalysis and various aspects of material science.[1–5] Several groups have recently shown that organometallic precursors can be used to prepare such particles under very mild conditions without contamination.[2] In most cases the particles are sterically protected by polymers but recently the preparation of nanosize metal particles protected by classical ligands has been described. Hence, Schmid[3] and Moiseev[4] prepared particles of several noble metals by partial reduction of metal salts in the presence of ligands such as PPh_3 or phenanthroline. These particles contain chloro or oxo groups on their surface which remains therefore oxidized. We have developed a different approach based on the decomposition of a zerovalent organometallic precursor by a reactive gas in the presence of PPh_3.[2b] This allowed us to prepare palladium and platinum particles with a defined size controlled by the reaction conditions, a narrow size distribution and a good stability. The synthesis of similar copper species seemed much more challenging. Copper colloids have been obtained by several authors by reduction of copper salts in the presence of polymers or micelles but large size distributions are usually observed.[5] We describe in this communication the preparation of copper particles stabilized by PPh_3 from the new organometallic precursor $(C_5H_5)Cu(Bu^tNC)$[6] and the spectroscopic properties of these new species.

The reaction of $(C_5H_5)Cu(Bu^tNC)$ with sub-stoichiometric amounts of PPh_3 (PPh_3 : Cu = 0.45–0.85) under CO in THF leads to metal particles of a mean diameter near 20 Å (see Table 1). The particles can be isolated and purified by washing with pentane.† They are stable in the solid state under argon at −18 °C and can be redissolved unchanged. The mechanism of the decomposition of the organometallic precursor has been precedently discussed and involves the formation of fulvalene.[6] The particles were first characterized by transmission electron microscopy (TEM) which indicated a relatively narrow size distribution (see Fig. 1). The electron diffraction pattern revealed the fcc structure of the copper particles with lattice parameters close to those of bulk copper. The size distribution is comparable or more narrow than those previously reported in polymers or micelles.[5] Neither the phosphine : Cu ratio nor the conditions of the decomposition (temperature, pressure) have a large influence on the particles size but they influence the degree of agglomeration of the particles (see Table 1). For example, for the same phosphine : Cu ratio (0.8) the particles are agglomerated if the reaction is carried out at 70 °C or by bubbling CO in a solution of $(C_5H_5)Cu(Bu^tNC)$ whereas they are dispersed if the reaction occurs at room temperature under 3 atm CO.

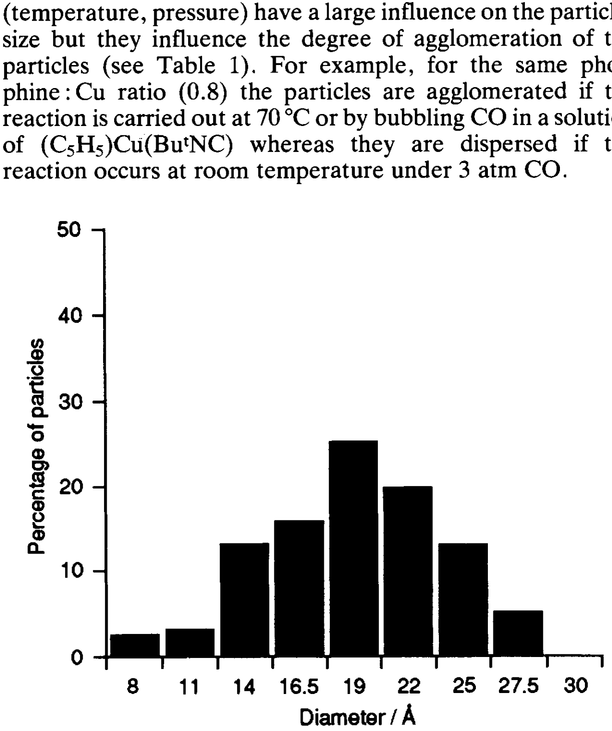

Fig. 1 Histograms showing the size distribution for copper particles (for a molar ratio P : Cu equal to 0.45, decomposition under 3 atm CO at 20 °C)

Table 1

Molar ratio P : Cu	Experimental conditions	Mean diameter/Å	Agglomerates	^{31}P NMR at 188 K (ppm/H_3PO_4 85% in D_2O)	UV-VIS/ nm
0.80	20 °C, 3 atm CO, 5 days	20.0	No	28, 6, 3.5 and −3[a] 32 and −3[b]	640 (v.br) 550 (br) 410 (sh)
0.45	20 °C, 3 atm CO, 5 days	22.0	No	28, 6, 3.5 and −3[a]	640 (v.br) 550 (v.br) 400 (sh)
0.85	20 °C, bubbling CO, 6 h	19.0	Yes	28, 6 and −3[a]	650 (v.br) 470 (br) 370 (sh)
0.80	70 °C, 3 atm CO, 20 min	19.5	Yes	28, 6 and −3[a]	590 (v.br) 470 (br)

[a] Crude product in CD_2Cl_2 {signal at 28 ppm attributed to phosphines on copper particles, at 6 ppm to $(C_5H_5)Cu(PPh_3)$, at −3 ppm to free triphenylphosphine and at 3.5 ppm to an unidentified species}. [b] Purified product in a 1 : 1 mixture of THF–C_7D_8 at 172 K.

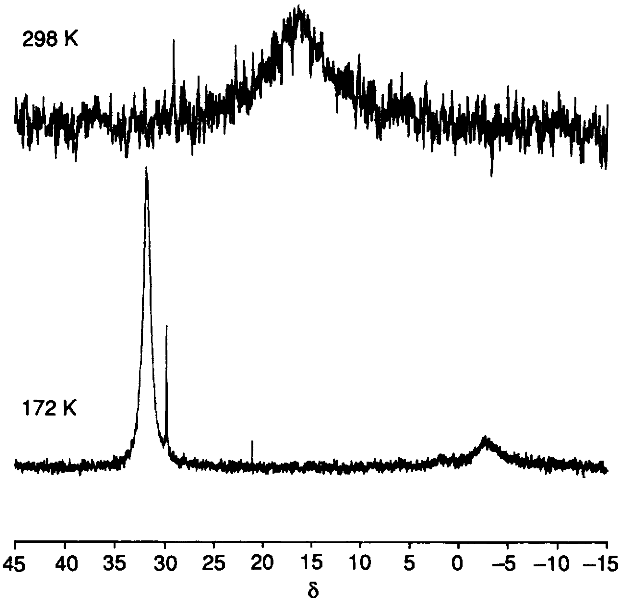

Fig. 2 $^{31}P\{^1H\}$ NMR spectra of purified copper particles linked PPh_3 (copper colloids with P : Cu = 0.80 obtained by decomposition under 3 atm CO at room temp., the spectrum has been recorded in a 1:1 mixture of THF–C_7D_8 at 101.256 MHz)

We obtained no evidence by IR spectroscopy for the presence of CO adsorbed on these particles but a band at 2170 cm^{-1} is present on spectra of a sample purified by washing several times with pentane to eliminate excess Bu^{t}NC and unreacted $(C_5H_5)Cu(Bu^tNC)$. This result is consistent with the presence of Bu^{t}NC coordinated to the copper surface.

The UV–VIS spectra in solution in THF for well dispersed copper particles consist of three absorptions, a very broad weak one at 640 nm, a broad weak one at 550 nm and a shoulder at *ca.* 400 nm. The band near 550 nm could be attributed to plasmon resonance commonly observed between 580 and 550 nm for sterically protected copper colloids.[5] The other bands have an unknown origin but do not arise from free PPh_3 or $(C_5H_5)Cu(PPh_3)$, which show no absorption in this region. When the particles are agglomerated, the spectra only show two signals at longer wavelengths (see Table 1).

The $^{31}P\{^1H\}$ NMR spectra of the particles were recorded at 101.256 MHz in CD_2Cl_2. They show, whatever the method of preparation and phosphine : copper ratio, a very broad peak at room temperature centred on δ 10 to 20. Cooling the sample down to 188 K leads to a decoalescence and the appearance of four new peaks at δ 28 (major one), 6, 3.5 and −3 respectively attributed to PPh_3 on metal particles, $(C_5H_5)Cu(PPh_3)$, a very minor unknown species and free PPh_3. Purifying the sample by washing with pentane leads to the observation of only one peak at δ 28 (in CD_2Cl_2) or δ 32 at 172 K (in THF–C_7D_8; see Fig. 2). Addition of extra PPh_3 does not lead at room temperature to the appearance of a new peak but rather to the shift of the mean broad peak to high field therefore confirming the presence of an intermolecular exchange of phosphines. Two important conclusions can be drawn from these experiments. First, we can identify a single peak corresponding to our metal particles. The peak is relatively broad ($\omega_{1/2}$ = 80 Hz at 172 K) which could reflect the presence of a small size distribution in agreement with the TEM observations. Secondly, the existence of an intermolecular exchange at room temperature allows us to demonstrate, by comparing the position of the room temperature peak to those of the peaks observed at low temperature, that we observe all the phosphorus present in solution whether coordinated or not. In other terms, there is no Knightshift for the phosphorus atoms coordinated to 20 Å copper particles which contain *ca.* 300 atoms of a metal exhibiting a paramagnetic ground state.[7] This result is unexpected but can be related to the UV–VIS ones which suggest an important modification of the electronic properties of the surface.

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† All reactions were carried out under an Ar atmosphere using the classical Schlenk technique, typically as follows: a Fischer–Porter bottle was charged with 30 mg of triphenylphosphine and 30 mg of $(C_5H_5)Cu(Bu^tNC)$ (for a mol ratio P:Cu equal to 0.80). The two solids were dissolved into 10 ml of freshly distilled and degassed THF and the resulting solution was submitted to 3 atm CO for 5 days under vigorous stirring during which time the solution changed from colourless to yellow–brown.

The copper particles were isolated by evaporating the solvent and purified by washing the solid three times with 5 ml distilled pentane.

TEM experiments were carried out on purified copper particles in a very diluted solution in THF. $^{31}P\{^1H\}$ NMR spectra were recorded on a crude sample in 0.7 ml CD_2Cl_2 or on purified copper particles in 0.7 ml of a 1:1 mixture of THF–C_7D_8 (the deuterated solvents were previously degassed under vacuum after freezing in liquid nitrogen).

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