Preparation of Organic Solutions or Solid Films of Small Particles of Ruthenium, Palladium, and Platinum from Organometallic Precursors in the Presence of Cellulose Derivatives

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Received October 30, 1992. Revised Manuscript Received December 31, 1992

Reaction of Ru(cod)(cot) with hydrogen in the presence of nitrocellulose (NC) or cellulose acetate (CA) at 20 °C yields colloidal ruthenium solutions containing particles of 10, 15, and 20 Å, respectively, and showing a low dispersity for concentrations in Ru of 2, 5, and 10 wt % (NC) or particles of average size 15, 20, and 25 Å for concentrations in Ru of 2, 5, and 10 wt % (CA). No change in particle size is observed upon reaction with CO in NC whereas agglomeration occurs in CA. The infrared spectra of CO adsorbed on Ru colloids have been recorded. Whatever the stabilizing polymer, two bands were observed. A band at 2030 cm^{-1} has been assigned to the stretching vibration of CO linearly adsorbed on the Ru surface. A low-frequency band at 1965 cm^{-1} has been assigned to bridging CO. The relative intensities of these two bands were found to vary with particle size. Reaction of $M(dba)_2$ (M = Pd, Pt; dba = dibenzylidene acetone) under CO in the presence of NC or AC leads to colloidal solutions containing small metal particles (respectively 35 Å for Pd in NC or CA, 12 Å for Pt in NC, 15 Å for Pt in CA independent of metal/polymer concentration). The presence of coordinated CO was observed in all cases. At maximum coverage, palladium colloids showed 3-fold and 2-fold bridging CO respectively at 1950 and 1890 cm^{-1}; platinum colloids showed both bridging and terminal CO at 1880 and 2050 cm^{-1}.

Introduction

Small metal particles in solution display fascinating chemical and physical properties which explain the continuing interest shown in these systems. Recent developments in this field involve the study of quantum size effects such as the recently observed pressure dependance of the surface plasmon absorption spectra of silver and gold colloids[1] or use for enhancement of nonlinear optical properties of polymers.[2]

One major goal of colloid research is the preparation of catalytically active solutions;[3-10] use of these solutions for reactions such as photoreduction of CO_2 to methane[6] in aqueous solution, hydrogenation of alkenes in biphasic or organic media,[7,8] and hydrosilylation of alkenes in organic solutions[10] have been described in recent reports. In the last case a careful analysis of the reaction mechanism demonstrated that the originally proposed homogeneous reaction involved the presence of platinum colloids as active species.

Another aspect of this chemistry which is attracting increasing interest is the study by simple spectroscopic methods of the coordination chemistry of the metal surfaces.[11] These studies can give information on the surface chemistry of small molecules (for example observation by infrared[11,12] and NMR[11b,c] spectroscopy of CO adsorption on palladium and ruthenium colloids, observation of terminal, bridging, and possibly triply bridging carbonyl groups) and also on the metallic nature of the particle itself (^{13}C NMR evidence has been reported for

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a strong Knight shift for ^{13}CO adsorbed on 25- and 75-Å colloidal palladium particles).[11b]

These experiments which have shown size-dependent properties clearly give evidence for the importance of selective preparation of these particles, i.e., control of the monodispersity and of the size of the particles. As far as the synthesis of these particles are concerned, the two main methods employed are either the Faraday method[13] or its modifications, i.e., reduction of a metal salt by an inorganic or organic reducing agent, in most cases in water solution,[1,2,6–10,12–19] or metal atom evaporation[3–5,11,20] on frozen organic solutions and/or polymers. These two methods can lead to monodisperse colloidal solutions but do not allow a clear control of particle size.

A third method is the use of organometallic precursors in organic solutions. This method should display several advantages such as a wide range of the temperature of decomposition (which can occur below room temperature), the use of a variety of supporting polymers or ligands to stabilize the metal particles, and variation of the solvents and concentrations used. Furthermore, decomposition of appropriately chosen organometallics induced by a reducing gas (e.g., H_2 or CO) does not lead to any byproducts containing halogens, boron, phosphorus, or other main-group elements which could create problems in both catalysis or subsequent metal deposition (microelectronic applications).

A few reports describing the use of organometallics (mainly acetates) as precursors to colloidal solutions have been published[11,21,22] including a particularly interesting approach by Schrock et al. in which phase separated organic/organometallic diblock copolymer films were reduced to give well-dispersed polymer supported metal particles.[23] We have reported recently the preparation of ruthenium and palladium colloids in the presence of poly(vinylpyrrolidone) (PVP) by decomposition of zerovalent organometallic derivatives.[11c]

Finally, metal particles dispersed in adhesive films could be valuable precursors for metal coating and laser writing.[24] In this case, the absence of main-group element contaminants is crucial. We looked therefore for a polymer which could both stabilize metal particles in solution and also be easily deposited on various surfaces. Cellulose derivatives and particularly nitrocellulose, which is used industrially in varnishes and paints, seemed particularly attractive.

We describe in this paper the preparation of colloids of Ru, Pd, and Pt in the presence of cellulose derivatives, the study of some factors influencing the particle size, the characterization of the particles by TEM and their reactivity with carbon monoxide.

Experimental Section

General Methods. All operations were carried out using standard Schlenk tube techniques under inert atmosphere (Ar, N_2). THF was purified by distillation over sodium benzophenone; dichloromethane was distilled from P_2O_5 under nitrogen atmosphere immediately before use.

The general method employed in colloid synthesis involved the arrested precipitation of metal from a solution of a molecular complex precursor in the presence of a polymer stabilizer.

The colloid solutions were characterized by transmission electron microscopy (TEM) on films cast from the colloid solutions. Samples were prepared by placing a drop of the colloidal metal solution, appropriately diluted, on a 2,3-mm copper support grid placed on a disc of adsorbent paper to remove excess solution. Microscopic examination of samples was carried out using a JEM 200 CX-T electron microscope operating at 200 keV.

Films were prepared by slow evaporation of the solvent either in air in a watch glass or in a slow stream of argon in a Schlenk tube. The films are adhesive on glass and alumina but can be removed using a standard spatula.

Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrophotometer using soild films prepared as above. Substraction of reference films prepared in the absence of CO from those of carbonylated colloids gave clean spectra of adsorbed CO (see Figures 2, 4, 5, and 7).

Materials. Ru(cod)(cot),[25] $Pt(dba)_2$,[26] and $Pd(dba)_2$[27] were prepared via literature procedures.

Preparation of Nitrocellulose Stabilized Ruthenium Colloids:[28] To a solution of nitrocellulose (500 mg) in tetrahydrofuran (30 mL) was added 150 mg of Ru(cod)(cot). (Ru/polymer is 10 wt %). A similar procedure was used for 2 wt % and 5 wt % Ru by using respectively 32 and 78 mg of Ru(cod)(cot) for 500 mg of nitrocellulose dissolved in 30 mL of THF.

Hydrogen was bubbled through the solution at 25 °C until the color turned from yellow to orange brown, indicating decomposition of the precursor to the colloidal metal state.

The time necessary for this reduction varied with the metal/polymer ratio, requiring 90, 60, and 30 min, for 2, 5, and 10 wt % samples respectively.

The average diameters of the ruthenium particles in the nitrocellulose were 10, 15, and 20 Å corresponding respectively to the 2, 5, and 10 wt % samples.

No precipitation of metal was observed during the hydrogenation. The colloidal solutions could be kept for several months under a nitrogen atmosphere. Homogeneous air-stable films are obtained upon evaporation of the solvent to dryness but cannot be dissolved again with the original solvent to yield the colloidal dispersion.

Preparation of Cellulose Acetate Stabilized Ruthenium Colloids. Ruthenium colloids in cellulose acetate were prepared using the procedure described above, using cellulose acetate in

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place of nitrocellulose. The Ru/cellulose acetate ratios used were 2, 5, and 10 wt %.

Preparation of Palladium Colloids. (*a*) *In nitrocellulose*: To a solution of a polymer stabilizer (500 mg) in 20 mL of tetrahydrofuran, was added a solution of $Pd(dba)_2$ (54 mg) in the same solvent (10 mL), giving a Pd/polymer ratio = 2 wt %. A stream of hydrogen, saturated with THF was passed through the solution at 25 °C until the color turned from purple to brown, indicating decomposition of the precursor to colloidal metal state.[29] Reaction times varied from 1 h to several hours. When carbon monoxide was used as the reducing gas, colloid formation was almost instantaneous, being complete in less than 1 min. The same procedure using 135 mg of $Pd(dba)_2$ and 500 mg of nitrocellulose yielded a 5 wt % palladium colloid. The colloidal particles describe above were found by TEM to have a 35-Å diameter. No Pd/polymer ratio effect on particle size was observed in this case.

(*b*) *In cellulose acetate*: The same procedure was used to obtain palladium particles but only using CO reduction. H_2 reduction was very slow and led to extensive precipitation of metal. It was impossible to determine the particle size in this case. In contrast, with CO reduction the palladium particle size was 35 Å irrespectively of Pd/polymer ratio.

Preparation of Platinum Colloids. Using $Pt(dba)_2$ and either NC or CA, the procedure used was exactly the same as that used for $Pd[dba]_2$.[30] Pt/polymer ratios used were 2 and 5 wt % [53 mg and 133 mg of $Pt(dba)_2$ for 250 mg of polymer corresponding respectively to 2 and 5 wt % ratio]. CO reduction was used to prepare platinum particles. Under H_2, we observed metallic precipitation at all metal/polymer ratios, so no particle size could be determined. For CO reduction, the particle size was found to be 10 Å in the presence of NC and 15 Å in the presence of AC.

Results

The two supporting polymers we considered were cellulose acetate (CA) and tetranitrocellulose (N.C., Parlodion). Both polymers are soluble in organic solvents such as THF (CA, NC), methanol (NC), and acetone (NC), which are compatible with organometallic compounds.

Ruthenium Colloids. *Preparation.* The decomposition of Ru(cod)(cot) was carried out at room temperature in THF in the presence of hydrogen slowly bubbled through the solution.[28] In the absence of polymer rapid precipitation of metallic powder is observed.

The preparation of the colloid was performed at a fixed polymer/solvent concentration but at variable metal/polymer ratios. The latter varied from 2 to 10 wt %. The rate of decomposition reaction increased with increasing metal concentration; thus decomposition was complete after 90, 60, and 30 min for concentrations of 2, 5, and 10 wt %. The reaction is probably autocatalytic and similar to the hydrogenation of $Pt(cod)_2$ to metallic platinum previously studied in detail.[31] In all cases, stable colloidal solutions were obtained with colours varying from orange (2 wt %) to deep brown (10 wt %).

Characterization. The ruthenium colloids prepared by the techniques described above were characterized by TEM. Regardless of metal/polymer concentration, the size distribution is very narrow. An example of the shape and dispersity of the particles is given on Figure 1. Within the limits of error of the method, TEM gave particle sizes of 10, 15, and 20 Å for metal/polymer concentrations of 2, 5, and 10 wt %, respectively. At higher concentrations up to 20 wt %, stable colloidal solutions were obtained, but the particle size was not determined.

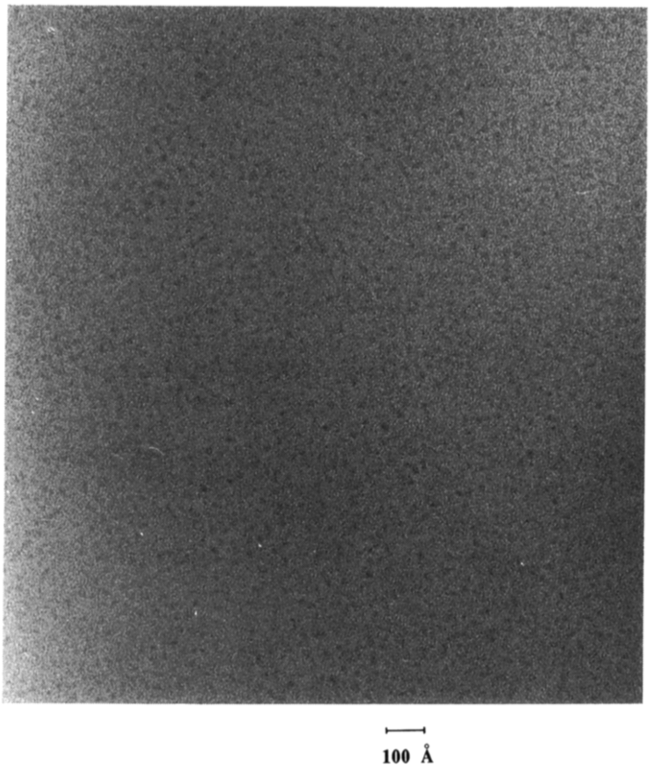

Figure 1. Electron micrograph of ruthenium colloids in nitrocellulose (2 wt %, 12 Å).

When a stream of CO was passed through a solution of colloidal ruthenium stabilised by NC, IR spectroscopy showed two absorptions in the 2050–1950-cm^{-1} region, as shown in Figure 2. The main feature of the spectra is the band localised at 1968 cm^{-1}. This frequency value is not typical of CO adsorption on ruthenium metal surfaces.[32] We assign this band at 1968 cm^{-1} to a CO molecule adsorbed in a bridging mode, Ru(CO)Ru, as we previously reported in the case of ruthenium colllids stabilised in PVP.[11] The high-frequency band at 2030 cm^{-1} is assigned to a CO molecule adsorbed in a linear mode on ruthenium surfaces.

CO adsorption was found to be complete within 4 h. The band intensity increased with the amount of CO added, but no band shift was observed. This relatively slow reaction suggests a competition between the NO_2 group of the NC and the CO in solution, for the coordination to the ruthenium surface colloids. The size of the particles was found to be unaffected by the coordination of CO and remained 10, 15, and 20 Å for colloids at 2, 5, and 10 wt %, respectively.

As shown in Figure 2, the ratio of linear CO to bridging CO decreases as the metal particle size increases. In a previous publication, CO adsorption mode on Pd was studied extensively.[11b] In that case, for very small particles, CO is adsorbed in a predominantly linear fashion, whereas the bridging mode was predominant when the particles size was bigger. It is difficult to use this variation of intensity for an estimation of particle size since the bridging mode has never been visualised before by IR spectroscopy in the case of ruthenium particles dispersed on solid

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(29) Precedent for formation of Pd metal from $Pd(dba)_2$.[26] See also: Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065. For reactions of $Pd(dba)_2$ with H_2 or CO see ref 11c,d.

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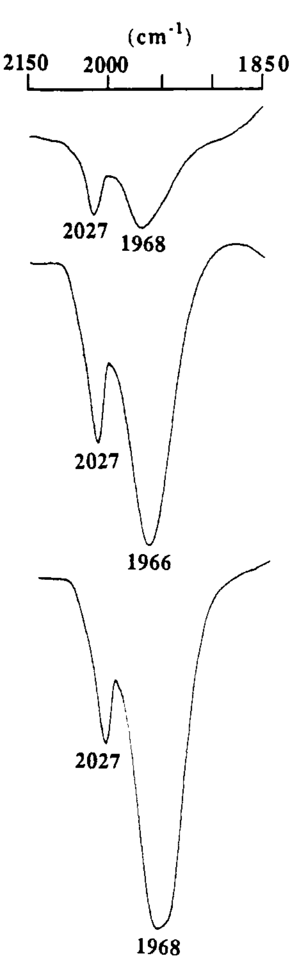

Figure 2. Infrared spectra of carbon monoxide on 10-, 15-, and 20-Å ruthenium colloids in nitrocellulose.

supports.[32-34] Nevertheless, this clear effect could be similar to that of palladium particles stabilized in PVP.

The correlation between particle size and the initial concentrations of the solutions is clear and interesting; this can give the opportunity to prepare particles of desired sizes in the range 10–20 Å. It is also worth mentioning that stable films containing up to 20 wt % of ruthenium can be prepared and deposited on glass, alumina, or iron and thus used as precursors in the field of microelectronics for laser writing.

Decomposition of Ru(cod)(cot) can be achieved under the same conditions in the presence of cellulose acetate. In this case too, stable brown colloidal solutions are obtained which can be deposited as films. The rate of decomposition observed is much higher than for NC (20 min for the 2 wt % sample, 10 min for the others). Colloidal solutions were found to be stable with ruthenium/polymer loadings of up to 10 wt %. Decomposition was attempted with a sample containing 15 wt % ruthenium, but in that case metal precipitation was observed.

Measurement of the particle size by TEM indicates, as in the case of NC, a dependance of the particle size upon the initial ruthenium concentration of the solution. Thus the sizes of the particles were found to be around 15, 20, and 25 Å for initial concentrations of ruthenium of 2, 5, and 10 wt %. However, as shown on the histograms of Figure 3, the particles in this case show a much wider distribution in sizes. For example, in the case of the 10 wt % sample the sizes vary between 10 and 40 Å.

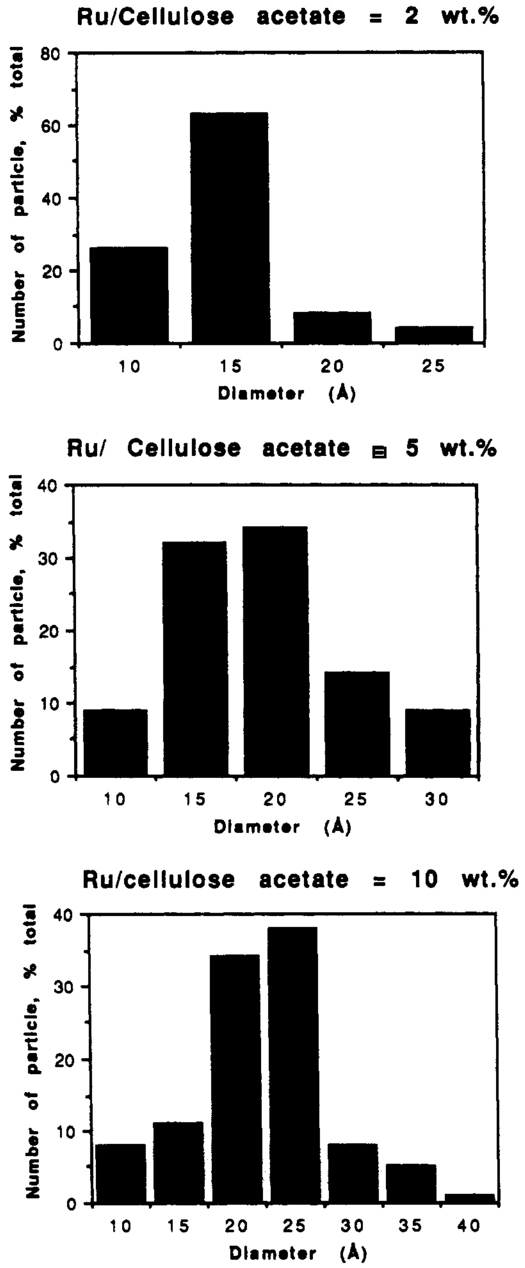

Figure 3. Dispersity of particle size in ruthenium colloids prepared in cellulose acetate at 2, 5, and 10 wt %.

It is also possible in this case to react the small particles with carbon monoxide. We observe by TEM agglomeration of the particles as well as an increase in their sizes. The infrared spectra nevertheless show a size dependance (see Figure 4). It is noteworthy that for a given mean size of the particles, the intensity of the terminal CO stretch is much higher in the case of the colloids in NC. This might reflect a change in the morphology of the particles or a preferred coordination of NC to the sites accomodating linear CO groups, possibly edge sites.

In summary, changing NC for CA leads to an increase in the rate of decomposition, to an increase of the particle sizes, to an increase of the size distribution, to a lower stability against precipitation at high ruthenium concentration, and to modification and agglomeration of the particles under CO. All these effects reflect the poorer stabilizing ability of CA compared to NC. The reason for

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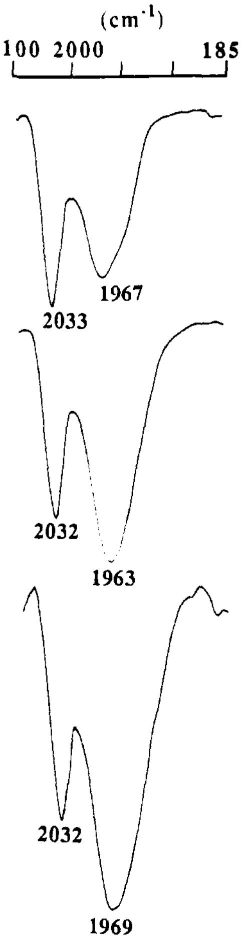

Figure 4. Infrared spectra of carbon monoxide on ruthenium colloids in cellulose acetate, at 2, 5, and 10 wt %.

this is probably the presence in NC of four polar nitro groups which can strongly coordinate to the metal surface but which may also slow down the intrinsic motions of the polymers and thus prevent agglomeration of the particles.

Palladium Colloids. *Preparation.* The decomposition of the precursor $Pd(dba)_2$ (dba = dibenzylidene acetone) was achieved in THF at metal/polymer concentrations of 2, 5, and 8 wt %. In contrast to the case of ruthenium, the nature of the polymer (NC or CA) has little influence on either the decomposition reaction or the nature of the resulting colloids. Thus decomposition of $Pd(dba)_2$ was found to be very rapid under carbon monoxide. Whatever the supporting polymer, an apparently homogeneous black suspension forms immediately and no further effect was found if CO was bubbled through the solution for more than 1 min. In contrast, the decomposition under dihydrogen is slow (ca. 1 h) and some metal precipitation, especially in the case of CA, is observed together with formation of a black colloidal solution. In NC the decomposition time under dihydrogen is shorter when the metal concentration is higher, as for ruthenium, and probably also implies an autocatalytic process.

Characterization. The mean particle sizes measured by TEM are 35 Å in the case of decomposition under CO, regardless of the metal percentage and nature of the supporting polymer. In the case of decomposition under H_2, 35-Å particles are also observed in NC but agglomerated. Agglomeration is too severe in CA to allow determination of particle size.

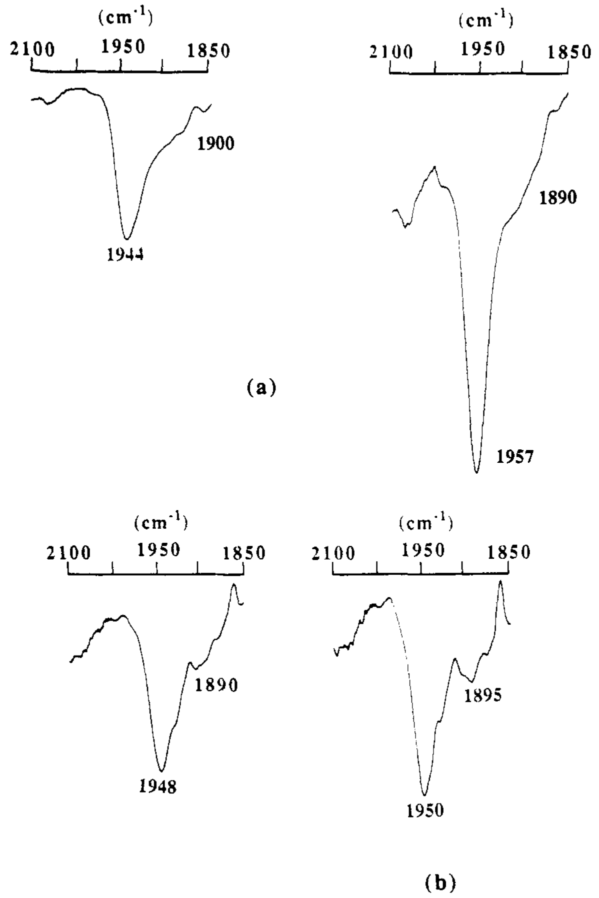

Figure 5. Infrared spectra of carbon monoxide on palladium colloids at 2 and 5 wt % (a) in CA and (b) in NC.

IR spectra of CO adsorbed on Pd colloids stabilized in cellulose derivatives show two bands at ~1950 and ~1895 cm^{-1} (see Figure 5). By comparison with published data concerning carbon monoxide adsorbed on supported metal particles, it is possible to assign these two bands to doubly and triply bridged CO groups.[32] We do not observe any absorption corresponding to a linear mode of coordination of carbon monoxide. Palladium PVP colloids of similar size[11c] adsorb CO in both terminal and bridging modes, in contrast to the present system. Furthermore, in the Pd/PVP case, the triply bonded mode of coordination is primarily detected at low carbon monoxide coverage of the palladium surface. In the present case however, exposure to CO was continued until no further change in the IR spectra was observed, at which point all accessible coordination sites were presumably covered with CO. These observations strongly suggest the coordination of functional groups of the cellulose polymer, presumably the nitro donors, specifically to the linear sites in NC stabilized palladium colloids.

Platinum Colloids. *Preparation.* The case of platinum is very similar to that of palladium; thus, bubbling CO through a solution of $Pt(dba)_2$ in THF in the presence of NC or AC causes an immediate colour change from crimson red to yellow brown.[30] The decomposition is complete after 2 min; colloidal solutions containing up to 5 wt % metal could be prepared in this way, metal deposition being observed at higher concentrations. If the decomposition is carried out under hydrogen, the reduction is slow and metal precipitation is observed.

Characterization. The particles were characterised by TEM. Little or no size dependance upon the initial metal concentration was found in this case. In nitrocellulose the particles had a mean diameter of 10 Å, and in cellulose

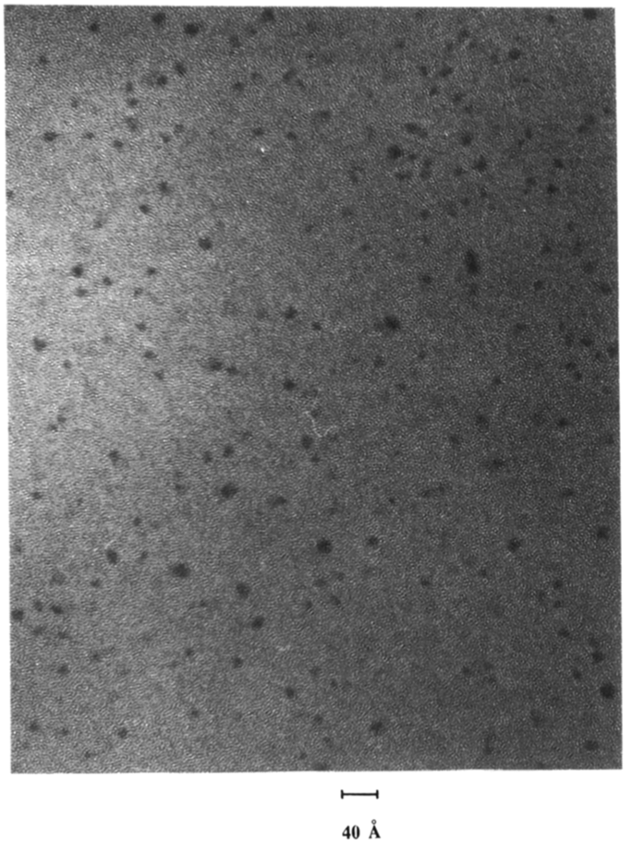

Figure 6. Electron micrograph of platinum colloids in cellulose acetate (2 wt %, 15 Å).

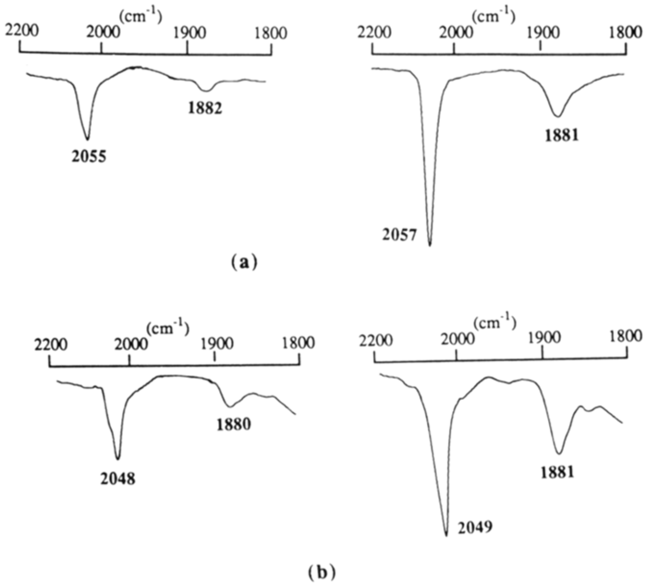

Figure 7. Infrared spectra of platinum colloids prepared in NC (a) or CA (b) at 2 and 5 wt %.

acetate a mean diameter of 15 Å as shown in Figure 6. Estimation of the size of the particles prepared under H_2 was precluded in all cases (2 wt %, 5 wt % in NC, AC) by severe agglomeration of the particles.

The infrared spectra of the colloids prepared under CO showed two bands at 2056 and 1882 cm^{-1} (2 wt % NC) and 2057 and 1878 cm^{-1} (5 wt % NC) corresponding to terminal and bridging CO stretches (Figure 7). The intensity of the terminal CO stretch is much larger than that of the bridging absorption and is in agreement with the results described by Sheppard and Nguyen[32] in the case of platinum particles dispersed on solids supports. Similar values were found for colloids prepared in cellulose acetate (respectively 2050 and 1881 cm^{-1} for 2 wt % solutions and 2049 and 1879 cm^{-1} for wt 5 wt % solutions). No influence of the initial metal concentration on the IR spectra of adsorbed carbon monoxide was found for a given polymer, possibly as a result of the similarity in sizes of the colloidal platinum particles. Changing NC for CA leads to a net increase of the absorption ratio between bands corresponding to bridging CO and bands corresponding to linear CO. This phenomenon could at least partly result from the increase in size of the colloids in CA compared to those in NC as in the previously discussed Pd case although no such correlation has been proved to date for Pt.

Discussion

This study demonstrates the selective preparation at room temperature of colloidal solutions of narrow size distribution for various metals using organometallic precursors and cellulose derivatives as stabilizing agents.

One of the goals of this research is the preparation of stable uniform polymer films containing highly dispersed metals, for potential application in microelectronics. The colloidal metal solutions we have prepared with cellulose polymers as stabilizing agents can be easily cast into films by evaporation of THF solutions onto glass substrates. These adhesive films, which can be kept in air and daylight for months without decomposition, were in fact used, as described above, for infrared analysis and for deposition onto alumina and silicon. Preliminary experiments of laser writing have been carried out and shown to yield metal or metal oxide wires according to the reaction conditions. The properties of these films and of others containing different metals, will be described separately.[35]

Another objective of our work was to study factors influencing the size of the particles. We find that both the support and the initial metal content of the solutions have an influence on the size of the particles in the case of ruthenium, little influence in the case of platinum, no influence in the case of palladium. Furthermore we find under hydrogen homogeneous dispersion of the ruthenium particles in the supporting polymer, whereas the metal particles are agglomerated in the case of palladium and platinum.

The exact phenomena which control the particle sizes are unknown but a few qualitative trends can be proposed. Thus the control of particle sizes in the case of ruthenium must be related to a strong interaction between the metal and the supporting polymer, in other words to a possible ligation of ruthenium by the oxygenated function of the polymer. In the case of palladium, in the absence of CO, agglomeration occurs extensively whereas under CO it is probably CO itself which controls the size of the particles, the polymer being only present as a protecting superstructure. These effects can probably be related to the harder nature of ruthenium and to a metal oxygen coordination bond energy vs metal–metal bond energy more favorable in the case of ruthenium than in the case of palladium.

This is further exemplified by the difference between ruthenium colloids in cellulose acetate and nitrocellulose. In the first case the smaller number of coordination sites and the poorer ligand properties of hydroxy and acetate groups compared to the nitro ones probably explain the

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(35) Bourée, J. E.; Tonneau, D. Unpublished results.

observed increase in both size dispersion and particle sizes. The effect of particle size increase as a function of initial metal concentration in our opinion is also related to the coordination affinity of the metal which prevents or slow the migration of the metal particles on the polymer.

Conclusion

In conclusion we report in this paper the preparation of new colloidal particles of ruthenium, palladium, and platinum. From a fundamental point of view this study demonstrates that the size of the particle can be controlled by matching the coordination properties of a polymer and the nature of the metal. These particles are stable in solution and can be used both for catalysis applications (they were found to be active for classical hydrogenation reactions which will be reported in a further paper) and also for deposition as adhesive precursor films.

Acknowledgment. We thank M. Saur for technical assistance, Johnson Matthey for a generous loan of $RuCl_3{\cdot}3H_2O$, and CNRS for support.