JOURNAL OF CATALYSIS **129**, 530–539 (1991)

Surface Chemistry on Transition Metal Colloids—An Infrared and NMR Study of Carbon Monoxide Adsorption on Colloidal Platinum

JOHN S. BRADLEY, JOHN M. MILLAR, ERNESTINE W. HILL, AND SUTINDER BEHAL

Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey

Received November 15, 1990; revised January 24, 1991

Highly dispersed (<10 Å) platinum has been prepared in colloidal solution by condensing platinum vapor into a solution of triisobutylaluminoxane in methylcyclohexane. Carbon monoxide, adsorbed in a linear mode on the surface of the colloidal metal, has been characterized by infrared spectroscopy and ^{13}C NMR. The chemical shift of the adsorbed CO is 192 ppm, and the absence of a Knight shift is interpreted in terms of a pseudomolecular description of the highly dispersed platinum particles, which are not large enough to exhibit metallic properties. The CO covered colloid is converted by hydrolysis into the molecular platinum carbonyl anion clusters $[Pt_3(CO)_6]_n^{2-}$, n = 3,4. © 1991 Academic Press, Inc.

INTRODUCTION

A continuing theme in cluster chemistry is the analogy drawn between clusters and metal surfaces in the context of catalysis. An extensive variety of cluster structures and ligand conformations is known for organometallic clusters, and these have in some instances provided good structural models for surface-adsorbed species on metals. Attempts have been made to extend this analogy, both to link the reactivity of organic ligands bound to multiple sites in organometallic cluster molecules to the reactivity of organic species on metal surfaces, and to attempt to use molecular clusters in solution as homogeneous catalysts of unique activity and selectivity. Neither has met with uniform success. We have adopted an alternative approach to the relationship between surface chemistry and molecular catalysis in solution by starting from metals in their catalytically active *colloidal* form, and attempting to bring the techniques of synthetic organometallic cluster chemistry to the study of the colloidal metal particles.

To this end, and as we reported previously (*1*, *2*), we are engaged in an investigation of the chemical, catalytic, and spectroscopic properties of highly dispersed colloidal metals in organic solutions. The preparation of metal colloids and their use in catalysis is almost as old as the study of catalysis itself (*3*), and the efficiency of these colloidal metals as catalysts is well established. Indeed their high activity in a number of catalytic processes has been a constant complicating factor in the investigation of homogeneously catalyzed reactions, where the adventitious presence of even a minute fraction of the catalytic metal in colloidal form can provide sufficient activity to outperform a respectable homogeneous catalyst (*4*).

Our goal is to describe the chemistry of colloidal metals in terms of the concepts and techniques of molecular cluster chemistry—the coordination of ligands to the surface of the colloids and the spectroscopic analysis of ligand reactions in the "coordination sphere" of the colloids—and to develop a surface organometallic chemistry of colloidal metals. To this end we have developed a route to the synthesis of transition metal organosols in which the metal particle size approaches that found in some of the larger molecular clusters, and in this paper we describe the synthesis and properties of stable organic solutions of highly dispersed platinum in which the metal particles are

0021-9517/91 $3.00

extremely small (<8 Å). The colloidal clusters are sufficiently small that they fall below the size range usually associated with the onset of metallic properties, and this enables solution spectroscopic techniques, such as liquid-phase high-resolution NMR, to be applied to the study of small molecules adsorbed at surface sites on the colloid particles. We interpret the results in terms of analogies between molecular organometallic cluster chemistry and surface chemistry.

EXPERIMENTAL

The platinum colloid solutions were prepared by the general method we previously reported (*1*) for the preparation of stable colloidal transition metals in non-polar organic solvents, by condensing vapors of the metal into a solution of a poly(alkylaluminoxane), $(RAlO)_n$, at low temperature in a modified rotary metal vapor synthesis reactor (Torrovap Industries, Toronto, Canada) (*5*). Poly(isobutylaluminoxane) (*6*) was prepared by the careful addition of one equivalent of water to 100 mmol triisobutylaluminum (1 *M* toluene solution, Aldrich), evaporation of the solvent, and dissolution of the residual gummy solid into 500 ml methylcyclohexane (previously dried over molten sodium and distilled under nitrogen). The aluminoxane solution was thoroughly degassed and introduced into the 12-liter flask of the rotary metal vapor synthesis reactor. After cooling to $-120°C$ the flask was evacuated to ca. 2×10^{-5} Torr, rotated at ca. 200 rpm, and platinum vapor, generated by electron beam evaporation of the molten metal, was contacted with the solution. In a typical preparation under these conditions 1–200 mg/h of platinum could be evaporated into the liquid phase in our apparatus. After an appropriate time the furnace was cooled and the flask allowed to warm to room temperature. The deep brown liquid was transferred under helium by cannula to a Schlenk tube, and any bulk metal suspended in the liquid product was removed by passage through a 0.2-μm Teflon filter. The colloidal platinum solution was stored under helium. All subsequent manipulations were performed by standard anaerobic handling techniques under argon or helium atmospheres. Analysis of the colloid solution was performed by the Analytical Sciences Laboratory of Exxon Research and Engineering Company by inductively coupled plasma spectroscopy, and revealed that 28% of the total platinum evaporated had dissolved in the polymer solution during evaporation of the metal. Treatment of the platinum colloid solution with a stream of nitrogen, which had been saturated with water vapor, resulted in rapid hydrolysis of the stabilizing aluminoxane polymer and the precipitation of aluminum oxide hydroxide $Al(O)(OH)(H_2O)$, containing elemental platinum. Analysis of this precipitate gave a Pt/Al ratio that was consistent with the results obtained by ICP. Typically we prepare solutions containing 0.5–1.0 g platinum in 500 ml methylcyclohexane stabilized with 50–100 mmol poly(isobutylaluminoxane).

Transmission electron microscopic examination of the colloids was performed on films cast by evaporation of the solvent from a drop of the colloid solution placed on a 3-mm microscope grid. The grid was transferred to the microscope (Phillips EM 420 ST) with exclusion of air. Microscopic examination was performed at 100 kV and low beam current to minimize beam damage. Examination of precipitated solid samples was performed on sonicated samples dispersed in a hydrocarbon diluent, supported on a lacy Formvar coated 3-mm copper grid.

Reaction of the colloidal platinum with ^{12}CO and ^{13}CO (Isotec, 99.1 at.% ^{13}C) was performed by addition of the gas to a rapidly stirred solution of the colloid at 1 atm. and room temperature. Gas uptake was apparently complete within less than a minute as judged by infrared spectroscopy on the solution.

Infrared spectra was recorded in methylcyclohexane solution in standard 0.1-mm pathlength CaF_2 window solution cells (fitted with Teflon stopcocks to preserve the solutions from ambient moisture) on a Perkin–Elmer 783 spectrometer. ^{13}C NMR spectra were recorded at 75 MHz on liquid samples containing ca. 1 wt% metal in standard 10-mm NMR tubes, sealed under argon or ^{13}CO, using a standard Bruker 10-mm high-resolution liquids probe on a commercial Bruker MSL-300 spectrometer. ^{195}Pt spectra were recorded at 64.1 MHz on the same instrument in a similar manner. ^{195}Pt chemical shifts were referenced to H_2PtCl_6 by defining the resonance frequency of a saturated aqueous solution of H_2PtCl_6 as 6300 ppm (*7*).

Catalytic hydrogenation of acenaphthylene was performed at 25°C under a total pressure of 1 atm on a gas uptake manifold. The olefin was dissolved in the colloidal catalyst solution in methylcyclohexane in a Schlenk flask, the solution frozen, and the flask evacuated. After the solution was warmed to 25°C in a thermostatted bath, hydrogen was added to a total pressure of 1 atm. Rapid stirring was continued throughout gas uptake measurement.

RESULTS AND DISCUSSION

The Preparation and Characterization of the Colloid

The use of metal vapors, co-condensed with organic vapors, to prepare colloidal metals in non-aqueous media was first reported in 1927, some 50 years before the recent wave of activity in metal vapor chemistry (*8*). More recently, variations of this technique have been employed by Wada and Ichikawa (*9*) and by Kimura and Bandow (*10*) to prepare organosols of a number of main group and transition metals. Andrews and Ozin (*11, 12*) have recently reported a spectroscopic and kinetic study of the clustering of metal atoms after condensation from the vapor phase into organic media.

The use of metal vapors in the preparation of metal colloids has also been reported by Klabunde and co-workers (*13*), who have used organic polymers as stabilizing agents. We have chosen the oligomeric aluminoxanes as stabilizing agents with a view to synthesizing colloids with a *reactive* organometallic polymer coating, to allow for subsequent chemical manipulation of the colloidal metal in a manner compatible with applications in catalysis and the synthesis of novel oxide-based materials. In the colloidal solutions prepared here, the polymeric aluminoxane successfully fulfills the typical role of a polymer stabilizer in colloid chemistry, associating with the surface of the colloidal particles and preventing aggregation. Poly(isobutylaluminoxane) (*6*) has proved to be particularly suitable for our purposes in its compatibility with the experimental conditions imposed by our use of the metal vapor technique (*14*). In order to bring the agglomerating metal atoms into contact with the stabilizing polymer the reaction medium must remain fluid and the polymer must remain in solution during the preparation. However, in order to generate the atomic metal vapor at a useful rate, the metal must be heated to a temperature at which its vapor pressure is ca. 1–10 μm. Of course the liquid phase must be simultaneously cooled to the point at which the vapor pressure of the solvent is at or below this value, and the dissolved polymer must remain in solution at this temperature. Poly(isobutylaluminoxane) is highly soluble in the solvent we generally use for these preparations (methylcyclohexane) at the low temperatures (−120°C) needed to maintain an adequately low vapor pressure for metal evaporation.

The aluminoxane-stabilized colloidal platinum prepared by metal vapor deposition in this manner is extremely highly dispersed. Attempts to image directly the metal particles by transmission electron miscroscopy on a film cast from the colloid solution onto a carbon-coated copper grid film failed to reveal any detectable metal clusters until sufficient beam damage had occurred to cause the platinum clusters to grow to greater than 8 Å in diameter. Although this is not a satisfactory determination of the dispersion of the metal clusters as prepared, it is interesting to note that the upper limit of 8 Å which it sets for the particle size places these metal particles in a size range

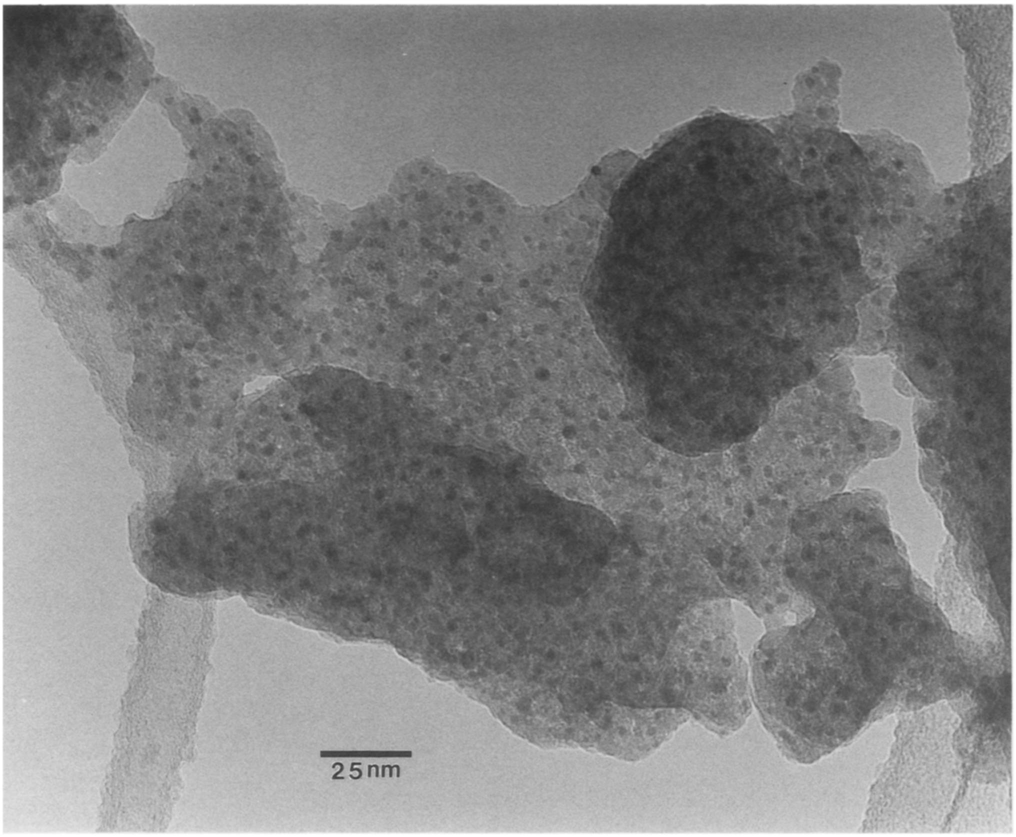

FIG. 1. Transmission electron micrograph of platinum particles in $Al(O)(OH)H_2O$, prepared by the hydrolysis of the isobutylaluminoxane-stabilized platinum colloid.

comparable to the core sizes of some of the larger molecular carbonyl clusters. The colloid is stable at room temperature indefinitely, no bulk metal deposition being apparent after 1 year in a sealed ampoule.

When a stream of nitrogen saturated with water vapor was passed through the aluminoxane-stabilized platinum colloid the organoaluminum oligomer is rapidly hydrolyzed and precipitates as $Al(O)(OH)H_2O$. The resulting dark gray precipitate contains platinum particles of ca. 15–25 Å in diameter, as shown in Fig. 1, with some particles discernable down to the resolution limit of ca. 8 Å.

The platinum particles have grown from their original size of less than 8 Å during the hydrolysis of the aluminoxane, presumably as a consequence of the loss of steric stabilization afforded by the oligomer in solution. However, it is evident from Fig. 1 that although the colloidal metal particles are no longer stabilized at their original level of dispersion during hydrolysis, bulk metal formation has not occurred. The metal particles entrained in the precipitated $Al(O)(OH)H_2O$ are quite discrete, and there is no agglomeration to microcrystalline metal.

The aluminoxane associates with the metal particles in a manner as yet undetermined (it seems probable that the inorganic –O–Al–O skeleton would interact with the metal) but it is not so firmly bound over the entire cluster that the surface is rendered inert. The colloidal clusters in solution are active catalysts in a probe reaction, the hydrogenation of acenaphthylene to acenaphthene. The hydrogenation experiments, (which were carried out under less than ideal conditions in which mass transport limitations were rate determining), were performed simply to demonstrate that some fraction of the surface of the colloid particles was available for catalysis, and no attempt was made to measure specific rates. Thus the polymer, while conferring stability on the colloid particles with respect to agglomeration to bulk metal, does not do so with the prohibitive consequences for catalytic activity which usually accompany ligand stabilization of molecular transition metal clusters. The catalytic properties of colloidal platinum and of other transition metal colloids stabilized with poly(isobutylaluminoxane) are under investigation and will be described separately.

The remarkably small size of the colloidal platinum particles makes them excellent candidates for an investigation of metallic and molecular properties, both chemical and physical, of small metal clusters. In this light, and from the perspective of the organometallic cluster chemist, it is of interest to investigate further the coordination (or surface) chemistry of transition metal colloids with a view to making more detailed comparisons with both heterogeneous supported metals and molecular organometallic clusters.

Reaction with Carbon Monoxide—Infrared Studies

Carbon monoxide was passed through the solution for several minutes. The infrared spectrum of the solution, shown in Fig. 2, revealed that CO was absorbed quickly, with no further change in intensity of the carbonyl stretching band observed after the initial spectrum was recorded 1 min after exposure of the solution to CO.

FIG. 2. Infrared absorbance of CO on isobutylaluminoxane-stabilized platinum colloid in methylcyclohexane solution.

The infrared band at 2035 cm^{-1} corresponds to the expected absorption for linear (terminal) carbonyls, and falls in the lower range of the frequencies reported for CO on platinum in a number of systems (*15*). The profile of the band resembles that found for CO on platinum surfaces and crystallites, and contrasts with the relatively sharp bands characteristic of molecular cluster carbonyls. It is not possible to draw any precise conclusions on the nature of the carbonylated colloidal platinum particles from simple frequency considerations. It is known that the stretching frequency for surface-adsorbed CO is markedly affected by a number of factors, the relative importance of each being often a matter of debate. For example, early work of Eischens and Pliskin (*16*) showed a coverage dependency for the frequency of the vibrational absorption of CO on silica-supported platinum in which the linear CO stretching mode frequency varied from 2040 cm^{-1} at low coverage to 2067 cm^{-1} at high coverage, and Crossley and King (*17*) reported a similar shift of 2063 cm^{-1} to ca. 2100 cm^{-1} for CO on a {111}-oriented polycrystalline film, a phenomenon ascribed to vibrational coupling between adsorbed CO molecules (*18*).

Metal particle size and the structure of the adsorption site also have an effect on stretching frequencies for adsorbed CO. In the relatively loosely defined environment present at the CO adsorption site on a dissolved colloidal metal particle it is difficult to correlate vibrational frequencies with a specific factor. For example a report has recently appeared on the infrared absorptions of CO on *aqueous* platinum colloids in which a broad absorption due to linear adsorbed CO shifted from 2066 to 2045 cm^{-1} over several hours *(19)*. It is, however, interesting to compare the infrared data for CO on colloidal platinum with that available for molecular platinum carbonyl clusters in a similar size range. Ichikawa has reported the infrared spectra of the anionic molecular platinum carbonyl clusters $[Pt_3(CO)_6]_n^{2-}$ (n = 2,3,4,5), on silica and γ-alumina *(20b)*. In that study, the CO stretching absorptions of the adsorbed clusters were shifted slightly to lower frequency from those observed for the pure clusters in solution. For example the terminal CO stretching frequencies for the dissolved and supported (γ-alumina) clusters are 2055 (2040) cm^{-1} (n = 5), 2040 (2025) cm^{-1} (n = 4), 2030 (2005) cm^{-1} (n = 3), and 1995 (1970) cm^{-1} (n = 2). However, both for the clusters in solution and those adsorbed on alumina the CO stretches form a clear progression to lower frequency as the size of the cluster decreases, as shown in Fig. 3. Since it is known that these CO stretching frequencies are size dependent for this entire family of clusters (n = 1–6) *(20a)* it is tempting in our study to ascribe an approximate size to the colloid particles on the basis of the observed stretching frequency of adsorbed CO. For example, $[Pt_{12}(CO)_{24}]^{2-}$ on γ-alumina has a terminal CO stretching absorption at 2025 cm^{-1}, and in solution at 2040 cm^{-1}; the corresponding values for $[Pt_9(CO)_{18}]^{2-}$ are 2005 and 2030 cm^{-1}. In the absence of other data on which to assign a size range to the colloids, and bearing in mind the upper limit of ca. 8 Å set by TEM (see above) we suggest that the infrared absorption for CO adsorbed on the colloidal platinum is consistent with the presence of clusters of less than 20 metal atoms.

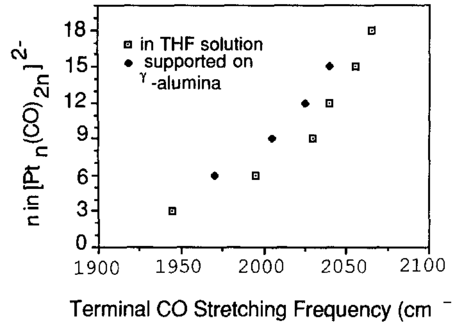

FIG. 3. Particle size dependency of linear C=O stretching mode for (a) supported $[Pt_n(CO)_{2n}]^{2-}$ clusters on γ-alumina, (b) $[Pt_n(CO)_{2n}]^{2-}$ in solution (Ref. *(21)*).

When the original colloidal platinum solution is hydrolyzed prior to addition of CO, the gray precipitate produced contains particles of platinum (see Fig. 1), as described above. Addition of CO to the precipitate causes a perceptible change in color of the solid to dark red-green, with infrared absorptions at 2040 and 1825 cm^{-1} (Fig. 4(b)). These absorptions fall in the range reported *(20)* for the terminal and bridging CO stretching modes in the platinum carbonyl clusters $[Pt_3(CO)_6]_n^{2-}$, and in fact the molecular cluster $[Pt_9(CO)_{18}]^{2-}$ is isolated by extraction of the solid with tetraethylammonium bromide in methanol. The residual solid precipitate retains a varying fraction of the platinum, between 60 and 80%. The yields of the molecular cluster are enhanced by reversing the procedure as follows. Carbon monoxide was passed through a solution of colloidal platinum, prepared as above, containing ca. 1 wt% Pt. Infrared spectroscopy of the carbonylated colloid solution showed an absorption at 2035 cm^{-1}, as described above (Fig. 2). The aluminoxane in the carbonylated colloid solution was hydrolyzed by passing through it a water-saturated stream of nitrogen, yielding a dark solid with a strong infrared band at 2039

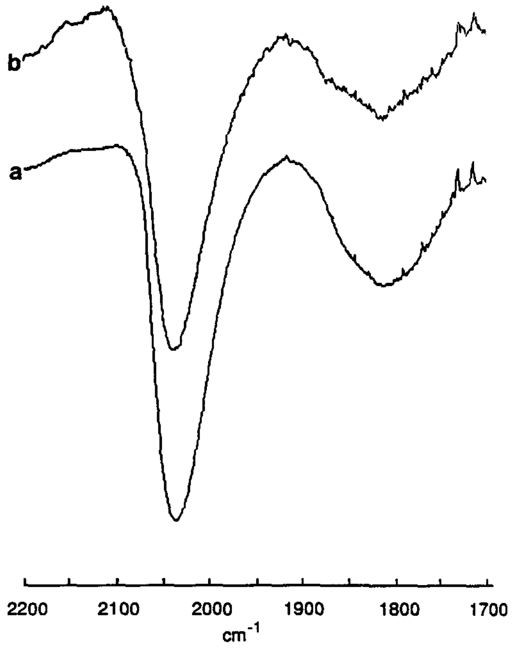

FIG. 4. Infrared spectra of (a) platinum colloid, after (i) addition of CO (see Fig. 2) and (ii) precipitation by hydrolysis of aluminoxane; (b) platinum colloid, after (i) precipitation by hydrolysis and (ii) addition of CO.

cm^{-1} and a weaker broadband at ca. 1830 cm^{-1}, as shown in Fig. 4(a). After collection by filtration and drying under reduced pressure, the solid was dispersed in a solution of tetraethylammonium bromide in methanol. After stirring for several minutes the solution was dark red, with infrared absorptions centered at 2040 and 1840 cm^{-1} and, after filtration from the pale gray solid residue and reduction in volume of the filtrate under reduced pressure, a black crystalline material was isolated. This compound was characterized as $(ET_4N)_2[Pt_9(CO)_{18}]$ by comparison with an authentic sample, prepared by literature methods (*20*), of its infrared spectrum (2028(s), 1854(sh), 1839(m), 1809(w) cm^{-1} in tetrahydrofuran solution; reported for $[Pt_9(CO)_{19}]^{2-}$, 2030(s), 1855(sh), 1840(m), 1810(w) cm^{-1},) and its ^{195}Pt NMR spectrum (*21*) (see Fig. 5). Comparison of the platinum concentration in the precipitate obtained by hydrolysis of the as-prepared colloidal platinum solution with that in the residue after extraction of the carbonyl cluster revealed that 50–60% of the platinum in the original colloid had been converted to the molecular cluster.

The isolation of the Pt_9 cluster emphasizes the high reactivity of clusters of metal atoms in this highly dispersed state. The identity of the cluster isolated is probably more a reflection of the stability of the $[Pt_3(CO)_6]_n^{2-}$ family of clusters than a clue to the precise particle size or structure of the colloidal metal clusters. Indeed in other ostensibly similar experiments on the hydrolysis of the carbonylated platinum colloid we have extracted $[Pt_{12}(CO)_{24}]^{2-}$, another cluster in this family, mixed with $[Pt_9(CO)_{18}]^{2-}$. Clusters in this family have recently been reported in the reaction of Pt^{2+} in basic zeolites with CO (*22*).

Reaction with Carbon Monoxide—NMR Studies

In the solid state, magic-angle spinning and other magnetic resonance techniques

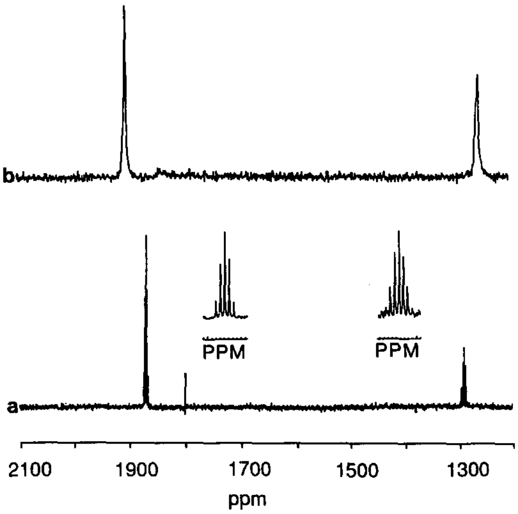

FIG. 5. 64.1 MHz ^{195}Pt NMR spectrum of (a) $[Pt_9(CO)_{18}]^{2-}$ (b) $[Pt_{12}(CO)_{24}]^{2-}$ (36,000 acquisitions, 1-s recycle delay) (see Ref. (*22*) for similar data on samples prepared by literature methods).

have made accessible chemically significant NMR data from hitherto intractable systems, including the observation of surface and bulk resonances for supported metals (*23*) and chemical shift and relaxation time data for adsorbed molecules on metal surfaces (*23, 24*).

In the case of the colloidal solutions studied here, the fact that the metal particles are so small suggested that high-resolution *liquid phase* NMR might successfully be applied to the study of adsorbed molecules. In molecular systems, of course, the presence of colloidal metal in an ostensibly homogeneous sample can utterly destroy any prospect of obtaining the high-resolution spectra characteristic of liquid samples. However, if we restrict our expectations to the acquisition of data at higher resolution than that easily available from *solid* samples, what would otherwise be unacceptably broad resonances from a molecular spectroscopic perspective would become acceptably sharp for samples containing colloidal metals, and we have reported separately (*2*) the successful observation of ^{13}C resonances with linewidths of 20 ppm for carbon monoxide adsorbed on colloidal palladium (~20-Å particles). In the case of the platinum colloids there is the added prospect that since ^{195}Pt (30% natural abundance) has a nuclear spin of $\frac{1}{2}$, the metal colloid particle itself is potentially amenable to study by NMR. Molecular platinum clusters with metal core sizes in the 5-to 10-Å range give well-resolved ^{195}Pt resonances (*21*), as can be seen from the ^{195}Pt NMR spectra of molecular platinum carbonyl clusters in the size range we propose for the colloid particles and which we have extracted from the colloid solutions after treatment with CO and hydrolysis (see above), shown in Fig. 5. ^{195}Pt NMR has also been successfully applied by Slichter and co-workers (*23*) and by Bucher *et al.* (*25*) to the study of supported platinum particles larger than those in our solutions. However, we have been unsuccessful in attempts to observe the ^{195}Pt resonances due to colloidal platinum in the high-resolution liquid mode. A possible explanation for this failure can be found in the observation of Bucher *et al.* (*25*) that the linewidth observed for surface platinum atom resonances in supported platinum catalysts is dependent on dispersion, the smaller particles having the wider resonances. This is attributed to the greater inhomogeneity of the surface of the smaller particles which have a higher concentration of discontinuities (edges, vertices, etc.), whereas the larger particles have a preponderance of atoms in regular planes. In the colloidal solutions under study here the particles are extremely small, with the result that virtually all the platinum atoms are surface atoms. The particles are of unknown but presumably irregular structure, and thus would represent an extreme case of inhomogeneity among the atomic sites. ^{195}Pt chemical shifts over a wide range (*7*), and for a system in which a range of environments is present, such as the colloidal platinum solution, an extremely broad resonance is to be expected.

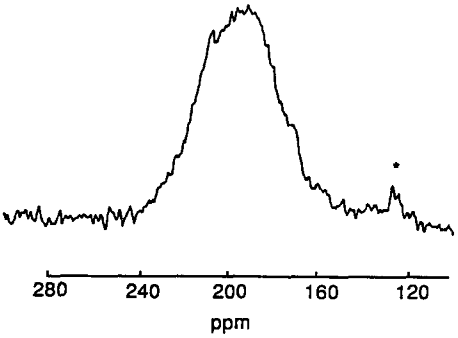

FIG. 6. 75 MHz ^{13}C NMR spectrum of ^{13}CO adsorbed on isobutylaluminoxane stabilized platinum colloid. (36,000 acquisitions, 1.5-s recycle delay (T_1 measured by inversion recovery = 0.44 s).

We applied high-resolution ^{13}C NMR to solutions containing ca. 1 wt% platinum which had been saturated by exposure to 99% ^{13}CO at 1 atm, as shown in Fig. 6. The ^{13}C chemical shift of the CO resonance (ca.

194 ppm) is shifted slightly downfield from that of free CO dissolved in a solution of isobutylaluminoxane in the same solvent (184 ppm). The resonance has a half-width of ca. 50 ppm at 298°C, significantly broader than that observed for the analogous palladium colloid (20 ppm), and shows no marked asymmetry at 298°C. We are currently performing variable temperature experiments in order to reveal any kinetic effects, that would cause motional averaging of CO molecules in bridging and terminal sites, as we previously observed for the analogous palladium system (*2*). The broad CO resonance extends well into the chemical shift range associated with bridging carbonyls in molecular platinum carbonyl clusters, but we doubt that any of the intensity of the resonance in this region is due to bridging CO since infrared spectroscopy shows an absence of CO in twofold bridging sites. The broader resonance observed for CO on colloidal platinum (<8 Å) in comparison to the analogous palladium system (ca. 18 Å) is consistent with the suggestion that the smaller platinum particles present a more inhomogeneous surface to the adsorbed carbon monoxide than do the larger palladium particles. That the broad resonance might be caused by the failure of the system to tumble rapidly enough to average the chemical shift to its isotropic value, or by ^{13}C dipolar interactions, can be ruled out by a hole-burning experiment (*2*, *26*) in which saturation of the resonance in a narrow frequency range results in a "hole" in the resonance. If the linewidth of the adsorbed CO resonance was due to restricted motion of the colloid particle in solution, then as the particle reoriented, the resonance of any individual carbon would sweep out the range of chemical shifts corresponding to the observed linewidth. This would result in a broadening of the saturation "hole" with time and a time constant for recovery of the saturated spins which reflected the correlation time for reorientation of the system. In the absence of such an effect the hole recovers without broadening and with a time constant of T_1, the spin–lattice relaxation time, and this is what we observe in the present case.

It is interesting to compare the chemical shift of CO on colloidal platinum in our system (194 ppm) with that found for coordinated CO in molecular platinum carbonyl clusters and with CO adsorbed on supported platinum. The mean shift for bridging and terminal carbonyls in $[Pt_{19}(C)_{22}]^{4-}$ is 198.7 ppm (*27*), a value quite characteristic for a third-row metal cluster carbonyl. For CO on Pt/γ-Al_2O_3 (76% dispersion, ca. 16 Å as a sphere) a shift of 360 ppm has been observed (*28*), and the downfield shift of more than 250 ppm with respect to CO is attributed to a Knight shift mechanism involving coupling to the conduction electrons in the platinum particle which is thus exhibiting metallic properties. The chemical shift of 194 ppm for CO on the sub-nanometer colloid is thus consistent with the particles being below the size at which metallic properties begin to manifest themselves, and we may thus consider them in this sense *pseudomolecular*. It is, of course, of interest to monitor the size dependency of the ^{13}C chemical shift of adsorbed CO in this system and in other colloidal metal solutions. Details of these experiments and of the NMR experiments in general will be reported separately.

CONCLUSIONS

Colloidal platinum clusters less than 10 Å in diameter have been prepared in methylcyclohexane solution in the presence of isobutylaluminoxane. Solutions of these subnanometer platinum particles rapidly adsorb carbon monoxide. Infrared and high-resolution liquid-phase NMR spectroscopic analysis suggests an overlap with both the properties of adsorbed CO on metal surfaces and the behavior of molecular carbonyl clusters. The clusters are of a size below that required for the onset of metallic properties, as revealed by the absence of a Knight shift for adsorbed carbon monoxide. Molecular carbonyl clusters have been synthesized using colloidal clusters in a similar size range. Colloidal metal particles in non-polar solvents thus provide interesting models for investigating the adsorbed state of small molecules on catalyst surfaces, and our study suggests that they may be especially appropriate as a bridge between homogeneous and heterogeneous catalysts.

Note added in proof. After the submission of this paper we became aware of a report of the successful observation of a ^{195}Pt resonance in the NMR of an aqueous platinum colloid. No particle size was measured for the colloid, which was estimated at ca. 20 Å from its method of preparation. Newmark, R. D., Fleischmann, M., Pons, B. S., *J. Electroanal. Chem. Interfacial Electrochem.* **255,** 325 (1988).

REFERENCES

1. Bradley, J. S., Hill, E. W., Leonowicz, M. E., and Witzke, H., *J. Mol. Catal.* **41,** 59 (1987).
2. Bradley, J. S., Millar, J., Hill, E. W., and Melchior, M., *J. Chem. Soc. Chem. Commun.* 705 (1990).
3. See for example Bredig, R., Muller, R., and Berneck, B., *Z. Phys. Chem.* **31,** 2258 (1899).
4. Lewis, L. N., and Lewis, N., *J. Am. Chem. Soc.* **108,** 7228 (1986).
5. Ozin, G. A., Andrews, M. P., Francis, C. G., Huber, F. X., and Molnar, K., *Inorg. Chem.* **29,** 1068 (1990).
6. Manyik, R. M., Walker, W. E., and Wilson, T. P., *J. Catal.* **47,** 197 (1977).
7. Carter, G. C., Bennet, L. H., and Kahan, D. J., Metallic shifts in NMR, *in* "Progress in Material Science" (B. Chalmers *et al.*, Ed.), Vol. 20. Pergamon, Elmsford, NY, 1977.
8. Roginsky, S., and Shalnikoff, A., *Kolloid Z.* **43,** 67 (1926).
9. Wada, N., and Ichikawa, M., *Japan. J. Appl. Phys.* **15,** 755 (1976).
10. Kimura, K., and Bandow, S., *Bull. Chem. Soc. Japan* **56,** 3578 (1983).
11. Andrews, M. P., and Ozin, G., *J. Phys. Chem.* **90,** 2922 (1986).
12. Andrews, M. P., and Ozin, G., *J. Phys. Chem.* **90,** 2929 (1986).
13. Klabunde, K. J., Habdas, J., and Cárdenas-Triviño, G., *Chem. Materials* **1,** 481 (1989) and references therein.
14. See Blackborow, J. R., and Young, D., "Metal Vapor Synthesis in Organometallic Chemistry," Springer-Verlag, New York, 1979.
15. Sheppard, N., and Nguyen, T. T., *in* "Advances in Infrared and Raman Spectroscopy" (R. J. Clarke, and R. E. Hester, Eds.), Vol. 5, pp. 106. Wiley, New York, 1978.
16. Eischens, R. P., and Pliskin, W. A., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, and V. I. Komarewsky, Eds.), Vol. 10, p. 1, Academic Press, New York, 1958.
17. Crossley, A., and King, D. A., *Surf. Sci.* **68,** 528 (1977).
18. Hammaker, R. A., Francis, S. A., and Eischens, R. P., *Spectrochim Acta* **21,** 1295 (1965).
19. Mucalo, M. R., and Cooney, R. P., *J. Chem. Soc. Chem. Commun.*, 94 (1989).
20a. Longoni, G., and Chini, P., *J. Am. Chem. Soc.* **98,** 7225 (1976).
20b. Ichikawa, M., *Chem. Lett.* **335** (1986).
21. Brown, C., Heaton, B. T., Towl, D. C., Chini, P., Fumagalli, A., and Longoni, G., *J. Organomet. Chem.* **181,** 233 (1979).
22. De Mallmann, A., and Barthomeuf, D., *Catal. Lett.*, **5,** 293 (1990).
23. Slichter, C. P., *Ann. Rev. Phys. Chem.* **37,** 25 (1986); and references therein.
24. (a) Duncan, T. M., and Root, T. W., *J. Phys. Chem.* **92,** 4426 (1988); (b) Duncan, T. M., Zilm, K. W., Hamilton, D. M., and Root, T. W., *J. Phys. Chem.* **93,** 2583 (1989).
25. Bucher, J. P., Buttet, J., van der Klink, J. J., Graetzel, M., Newson, E., and Truong, T. B., *J. Mol. Catal.* **43,** 213 (1987).
26. Duncan, T. M., Root, T. W., and Thayer, A. M., *Phys. Rev. Lett.* **63,** 62 (1989).
27. Washecheck, D. M., Wucherer, E. J., Dahl, L. F., Cerriotti, A., Longoni, G., Manassero, M., Sansoni, M., and Chini, P., *J. Am. Chem. Soc.* **101,** 6110 (1979).
28. Rudaz, S. L., Ansermet, J. P., Wang, P. K., Slichter, C. P., and Sinfelt, J. H., *Phys. Rev. Lett.* **54,** 71 (1985).