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Stabilizing structure of tertiary amine-protected rhodium colloid dispersions in chloroform†

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Tertiary amine-protected rhodium colloids have been prepared in chloroform by phase transfer of a rhodium(III) salt from an aqueous to the organic phase followed by reduction with hydrogen. The rhodium colloid dispersions, thus prepared, present a narrow size distribution and are stable. The structure of the protecting amine molecules on the surface of the colloids was investigated by NMR spectroscopy, transmission electron microscopy (TEM), and hydrodynamic radius measurements according to the Taylor dispersion method. Carbon-13 NMR spectroscopy can provide some information on the conformation of the amine molecules on the surface. The size of the entire colloid including the amine layer surrounding the metal surface, obtained by the Taylor dispersion method, is considered to be fairly consistent with the size of the naked metal particles obtained by TEM and the size of the adsorbed layer, and thus supports the conformational information.

Nanoscopic metal colloids and colloids are now a hot research topic.[1] However, to prepare metal colloid homogeneous dispersions, usually an aqueous or an aqueous/organic solvent system is employed and there are only a few examples of metal colloid homogeneous organosol dispersions. The metal colloid organosols are important for the application of metal colloid particles as effective catalysts in organic reactions.

For example, reverse micelles[2,3] have been used for the preparation of metal colloid organosols. Aqueous drops containing metal salt precursors can be highly dispersed in an organic phase by surfactant molecules forming reverse micelles. The metal salts are then reduced by reducing agents, resulting in metal colloid organosol dispersions. The reverse micelle system can provide small and uniform metal colloids, because the amount of metal salt precursors needed to form one colloid particle can be controlled by the volume of the small water droplets in the reverse micelles.

The protection of hydrophobic colloids in solution to prevent particle aggregation by soluble polymers or surfactants has been discussed[4] since the era of Faraday,[5] mainly from the viewpoint of steric stabilization or electrostatic stabilization if the protecting agent has electrical charges. Recently, the protecting agents surrounding the colloid surface have been considered to play not only the role of preventing aggregation but also providing the metal cluster with valuable functions.[6] Therefore, the structure of such reagents becomes much more important. However, this has not been investigated in detail until now.

Many physical techniques have been employed to probe the structure and dynamics of organic molecules on solid surfaces, *e.g.* Raman,[7] IR[8] and NMR spectroscopy.[9] Especially, ^{13}C NMR techniques are useful to obtain conformational information about adsorbed organic molecules from their chemical shifts,[10] peak intensities, and relaxation times.[11]

In the present study, the protecting structure of tertiary amines on the surface of nanoscopic metal colloids in an organic solvent was investigated. These rhodium colloid particles can be used as an effective catalyst for stereoselective hydrogenation of aromatic compounds such as dibenzo-18-crown-6 (6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecine) to *cis*,*cis*-dicyclohexano-18-crown-6[12,13] or other aromatic compounds.[14] To investigate the conformational structure of the amine molecules, ^{13}C NMR chemical shifts, relaxation times and J_{CH} coupling constants were obtained.

The estimation of Stokes' radii on the basis of the diffusion coefficient measured by the Taylor dispersion method[15,16] is also proposed here in order to determine the size of the entire amine-protected rhodium colloids. Its combination with transmission electron microscopy (TEM) measurements, providing the size of the naked metal particles, gives the thickness of the protective amine layer (Fig. 1).

Experimental

Materials

The tertiary amines, tri-*n*-pentylamine, tri-*n*-octylamine, tri-*n*-decylamine and tri-*n*-dodecylamine were obtained from Aldrich or Tokyo Kasei Co., Ltd. and used as received except trioctylamine which was first distilled. No impurity was revealed by the ^{1}H and ^{13}C NMR spectra of any of these amines. Chloroform used as the solvent for the metal colloids was obtained from Aldrich or Nakarai Tesque, and $CDCl_3$ (Aldrich or SDS) was used as the solvent for NMR measurements. Rhodium(III) chloride (Aldrich, Alfa, Nakarai Tesque or Kosoh Chemical, GR grade) was used as a precursor salt for the rhodium colloid particles. Water used for their preparation was purified by a ELGA water purification system. Hydrochloric acid was obtained from Prolabo.

Amine-protected rhodium colloids

Preparation. For the preparation of tertiary amine-protected nanoscopic rhodium colloids in an organic solvent, a phase-transfer and hydrogen-reduction method was used.[12,13] A

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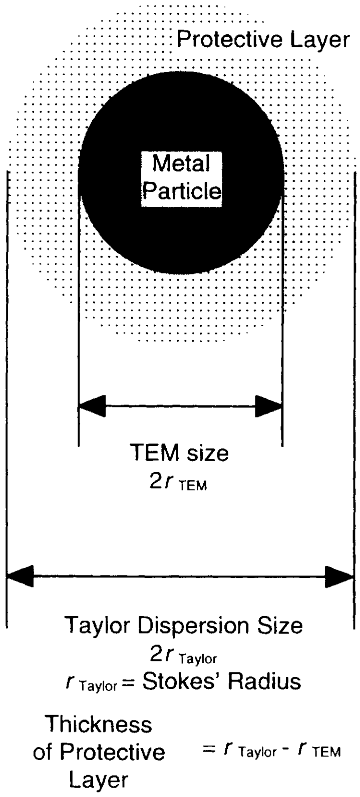

Fig. 1 Principle of the determination of the protective layer thickness of a tertiary amine-protected rhodium colloid particle by combination of the Taylor dispersion method and TEM

carefully cleaned Pyrex tube or flask without any defects was filled with an aqueous solution of rhodium(III) chloride and a solution of a protective amine at designed concentrations in chloroform. The samples for Stokes' radius measurements were prepared with $CHCl_3$ (25 cm^3), and those for NMR study with $CDCl_3$ (4 cm^3). It is assumed that no isotope effect is likely to occur within the scope of our study. The non-miscible mixed solutions were stirred vigorously whereupon the orange-red $RhCl_3$ was transferred from the aqueous to the organic phase. Then, hydrogen at atmospheric pressure was introduced and the solution was stirred continuously and vigorously for some hours or 1 d at ambient temperature. A colour change from orange-red to brown-black was used to monitor the reduction of the rhodium(III) salt and the formation of rhodium colloid particles. The time required to obtain a black suspension gives an estimate of the reduction rate.

Characterization. Transmission electron microscopy observations of the samples analysed by the Taylor method were made with a Hitachi model H-7000 microscope operated at 100 kV with a magnification between 50 000 and 100 000 to determine the size of the naked metal particles. The sample studied by ^{13}C NMR spectroscopy was also examined on a JEOL 100CX microscope at a magnification of 160 000. In both cases a drop of the colloidal suspension was deposited on a copper grid coated with a thin carbon layer. For each sample, the diameters of a large number of rhodium particles were determined from enlarged photoimages in order to obtain a size distribution with good statistics.

NMR measurements. The ^{13}C NMR measurements were performed at 25 MHz on a Bruker AC-100 superconductive Fourier-transform spectrometer using field/frequency lock on the $CDCl_3$ in the samples at 26–27 °C. Chemical shift measurements were made under conditions of broad-band ^1H decoupling. The J_{CH} coupling constants were measured at 75 MHz on a Bruker superconductive Fourier-transform spectrometer. Samples were normally placed in tubes of 5 mm outside diameter. Chemical shifts were referred to $SiMe_4$ as internal or external reference. Some samples were measured twice for confirmation.

Diffusion coefficient measurements. The Taylor dispersion method was used; the sample injected is dispersed in a tube as the result of a combination of convection and molecular diffusion. By choosing suitable values of the flow rate, tube radius and length, in accord with Taylor's criteria, a Gaussian distribution of concentration is attained, and the diffusion coefficient, D, can be calculated from equation (1) where r is the

$$D = \frac{r^2 t \ln 2}{3W^2} = \frac{0.2310\, r^2 t}{W^2} \qquad (1)$$

radius of the tube, t the residence time of the solute, and W the width at half-height of the peak detected. The Stokes' radius (R) can be calculated from the diffusion coefficient as in equation (2) where T is the absolute temperature, k is Boltzmann's

$$R = kT/6\pi\eta D \qquad (2)$$

constant, and η is the viscosity of the solvent containing the amine, measured also in this study with an Ubbelohde-type viscometer.

A small amount of a solution (typically 20 μl) was injected into a solvent flowing through a capillary tube (0.5 mm internal diameter × 50 m).[17] The eluent solvent, chloroform containing the same concentration of the amine, was delivered by a Waters model 510 HPLC pump (at a typical speed of 0.02 cm^3 min^{-1}). The concentration profile of the rhodium colloids was detected from the absorption at 500 or 600 nm using a spectrophotometric detector for HPLC (Waters model 490). The temperature was kept at 25 ± 0.02 °C.

Results and Discussion

Formation of rhodium colloid particles protected by tertiary amines

Upon vigorous stirring at room temperature the red-orange colour of the aqueous phase moved to the chloroform phase. When the phase-transfer agent is a quaternary ammonium salt, Sasson *et al.*[18] have shown that the extraction of rhodium ions proceeds *via* the formation of an ion pair $RhCl_4(OH_2)_2^-$, $^+NR_4$. In the present case, since the aqueous solutions of rhodium chloride are acidic, the tertiary amines dissolved in the organic phase could be protonated at the interphase boundary and a similar extraction mechanism be involved in the extraction of the rhodium(III) species. After the extraction of rhodium(III) species into chloroform, hydrogen was introduced into the flask or tube at atmospheric pressure at room temperature, and the rhodium(III) ions were reduced to form nanoscopic rhodium colloids protected by the tertiary amines (Fig. 2). For the reduction of the rhodium(III) salt, the higher the amine concentration of amine the longer it takes. This means that the dissociation of the ion pair is required for the reduction of the rhodium(III) species, which can be written as in equation (3). The amount of 'free' rhodium(III) species is always

$$RhCl_4(OH_2)_2^-,{}^+HNR_3 \rightleftharpoons [RhCl_4(OH_2)_2]^- + {}^+HNR_3 \qquad (3)$$

very low in the organic solvent and a higher concentration of amine, which is protonated in the course of the reduction by the hydrochloric acid released, displaces equilibrium (3) even further to the left. This could explain the increase of the reduction time with the amount of amine introduced.

Even when the concentration of rhodium(III) ions is high

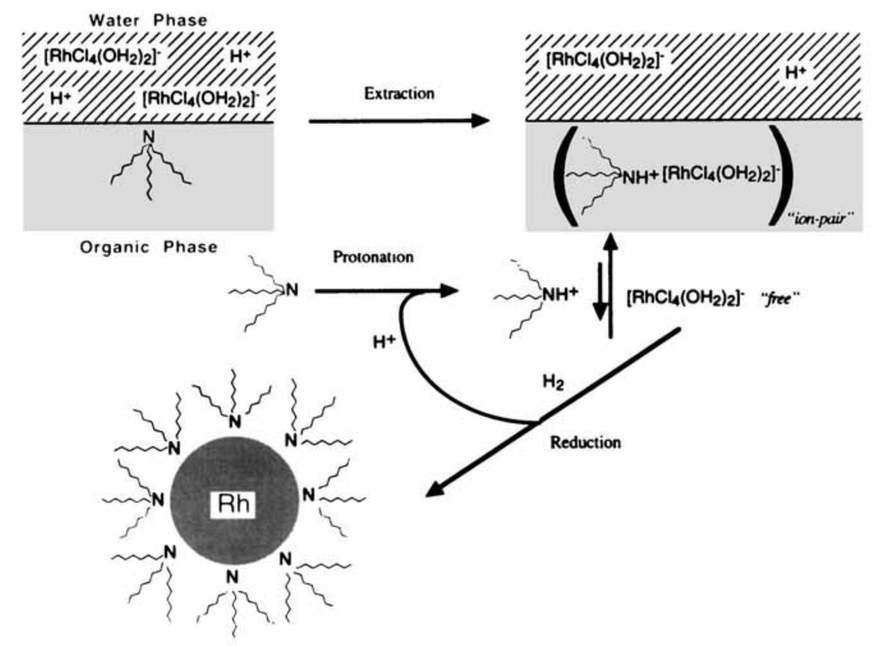

Fig. 2 Schematic illustration of the formation of tertiary amine-protected rhodium colloids in an organic solvent

(maximum 2.5×10^{-2} mol dm^{-3}), the reduction can proceed mildly without any formation of flocculates provided that the amount of amine introduced to extract the rhodium(III) ions is sufficient. A similar situation has been reported in the case of gold colloid formation with tetrachloroauric(IV) acid, $HAuCl_4$, and cationic surfactants.[19]

TEM characterization

Fig. 3 shows representative TEM micrographs and corresponding histograms giving the particle size distributions of the rhodium colloids. In the case of the samples for the present Taylor dispersion method (total quantity of precursor chloroform solution 25 cm^3) the particles have very narrow size distributions with average diameters of *ca.* 1.6 nm. However, when the quantity of sample is very small as in the NMR experiments (total 4.0 cm^3), the dispersions seem to be less stable than those prepared on a larger scale. The rhodium particles are rather larger in this case. However, the size distribution of the NMR samples is still narrow enough even when the average diameter is *ca.* 4.0 nm. This uniformity of the particle size allows us to discuss the protective structure of the amines in relation to the average diameter of the rhodium colloids.

^{13}C NMR measurements

All peaks in the ^{13}C NMR spectra of $N(C_5H_{11})_3$ and $N(C_8H_{17})_3$ were resolved but some of the carbons of $N(C_{10}H_{21})_3$ and $N(C_{12}H_{25})_3$ could not be separately detected with the present instrument. However, 25 MHz measurements were enough to discuss the conformation of the amines on the surface of the rhodium colloids. The peaks were assigned on the basis of the literature[20] and the present relaxation-time measurements. Table 1 summarizes the ^{13}C chemical shifts.

Fig. 4 shows the ^{13}C chemical shift changes ($\Delta\delta$) of $N(C_8H_{17})_3$ with rhodium colloids at various concentrations, equation (4) where δ_{free} indicates the shift of free $N(C_8H_{17})_3$

$$\Delta\delta = \delta_{free} - \delta_{Rh} \qquad (4)$$

and δ_{Rh} indicates that of the amine in a rhodium colloid dispersion; upfield shifts are shown as positive $\Delta\delta$. The ^{13}C NMR peaks of all carbons are shifted upfield in the rhodium colloid dispersions. However, during the preparation, in the solution, HCl is produced and this protonates the amine molecules, as shown in equations (5) and (6). This amine

$$RhCl_3 + \tfrac{3}{2}H_2 \longrightarrow Rh + 3HCl \qquad (5)$$

$$HCl + {:}N[(CH_2)_nCH_3]_3 \xrightarrow{\text{Protonation}} Cl^- + H{:}\overset{+}{N}[(CH_2)_nCH_3]_3 \qquad (6)$$

protonation can also cause the upfield chemical shifts. The chemical shift changes of $N(C_8H_{17})_3$ in the presence of HCl at a concentration three times that of $RhCl_3$ have been measured and are also presented in Fig. 4. It can be seen that the changes due to protonation are always smaller than those observed in the presence of rhodium colloids. Thus, this protonation cannot account for all the changes observed and some conformational changes of the amines in the presence of rhodium colloids are likely.

Among the carbons of the alkyl chains of $N(C_8H_{17})_3$, C^2 shows the largest chemical shift change, then C^1 and C^3–C^8 show smaller changes. The large difference observed for C^1 and C^2 can be explained by the following two effects. (1) These excess upfield shifts are caused by the γ effect, which gives some indication of the conformation of long alkyl chains. The extent of shielding of a carbon atom depends on the relative population of *trans* and *gauche* conformers where the *gauche* conformation gives rise to an upfield shift. For example, surfactant molecules show an upfield shift at concentrations below their critical micelle concentrations because their hydrophobic alkyl part should have a large population of carbon atoms in a *gauche* conformation.[21] These large upfield shifts clearly reflect a large population of the *cis* conformation for the pairs C^1–C^4 and C^2–C^5. (2) The second effect is a co-ordination interaction between a surface rhodium atom and an amine nitrogen. The nitrogen lone pairs of the amine molecules can interact with the surface of the rhodium colloid, resulting in downfield shifts in the ^{13}C NMR spectra, especially for C^1. This should be the reason why the shift of C^1 is smaller than that of C^2. This co-ordination is not strong since the dynamic exchange between free and co-ordinated amine resulted in only one set of amine peaks in the spectra.

To confirm the generality of the chemical shift changes, we have studied some other amine-protected rhodium colloids prepared by the same method. Fig. 5 shows the typical chemical shift changes of the tertiary amines in the presence of rhodium

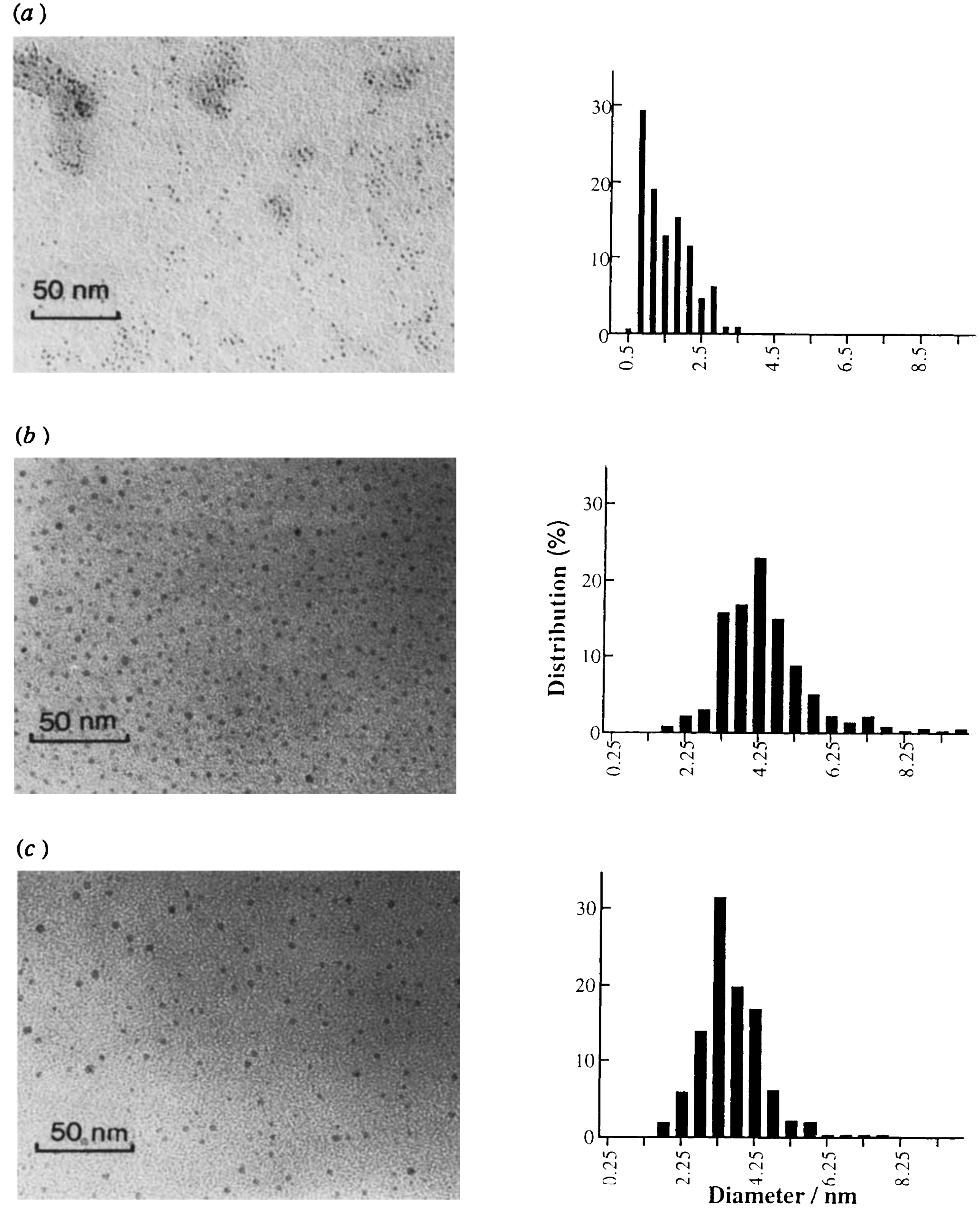

Fig. 3 Transmission electron microscope photographs and particle size-distribution histograms of tertiary amine-protected rhodium colloids: (*a*) $[N(C_5H_{11})_3] = 4.4 \times 10^{-2}$ mol dm^{-3}, $[Rh] = 2.2 \times 10^{-2}$ mol dm^{-3}, $[N(C_5H_{11})_3]/[Rh] = 20$; (*b*) $[N(C_8H_{17})_3] = 0.23$ mol dm^{-3}, $[Rh] = 2.3 \times 10^{-2}$ mol dm^{-3}, $[N(C_8H_{17})_3]/[Rh] = 10$; (*c*) $[N(C_8H_{17})_3] = 0.41$ mol dm^{-3}, $[Rh] = 2.05 \times 10^{-2}$ mol dm^{-3}, $[N(C_8H_{17})_3]/[Rh] = 20$

colloids. This figure clearly shows that the tertiary amines with various alkyl chain lengths should be adsorbed in the same fashion on the surface of the nanoscopic rhodium colloids. Especially, C^1 and C^2 always exhibit the largest upward chemical shift changes, which indicate that the pairs C^1–C^4 and C^2–C^5 have a large population of the *cis* conformation.

The spin–lattice relaxation time (T_1) of the ^{13}C NMR reflects the mobility of a carbon atom. The value should be smaller when the atom has some interaction with other molecules or atoms and is less mobile. Therefore, the T_1 values of the amine molecules were measured in the presence or not of rhodium in order to investigate the behaviour of the carbon atoms on the surface of the rhodium particles. Fig. 6 shows the T_1 changes between $N(C_8H_{17})_3$ in $CDCl_3$ and a $N(C_8H_{17})_3$-protected rhodium colloid dispersion in $CDCl_3$, *i.e.* the ratios of T_1 (amine-protected Rh)/T_1 (free amine) *vs.* carbon position. In

Table 1 The ^{13}C NMR chemical shifts of the tertiary amines used for rhodium colloid preparation in chloroform *

Carbon atom number	Amine $N(C_5H_{11})_3$	$N(C_8H_{17})_3$	$N(C_{10}H_{21})_3$	$N(C_{12}H_{25})_3$
1	54.25	54.29	54.28	54.29
2	26.72	27.07	27.04	27.08
3	29.91	27.73	27.72	27.75
4	22.70	29.66	29.71	29.45
5	14.11	29.38	29.68	29.74
6		31.92	29.64	29.74
7		22.72	29.37	29.74
8		14.14	31.94	29.74
9			22.71	29.74
10			14.13	32.01
11				22.76
12				14.15
c/mol dm^{-3}	2.33	2.25	2.21	2.16

* Measurement conditions: 25 MHz, 26–27 °C, SiMe$_4$ as reference.

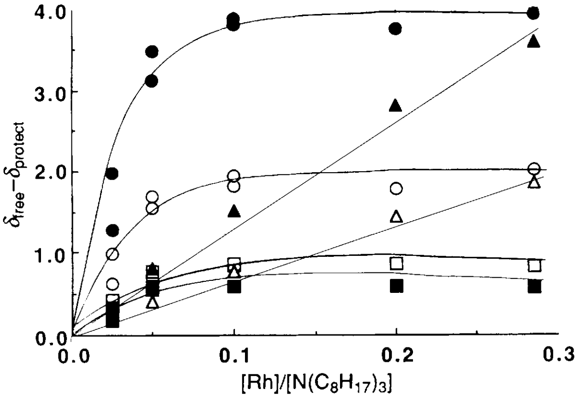

Fig. 4 The ^{13}C chemical shift changes (Δδ) of tri-*n*-octylamine *vs.* $[N(C_8H_{17})_3]/[Rh]$ molar ratio ($[Rh] = 2.5 \times 10^{-2}$ mol dm^{-3} and $[N(C_8H_{17})_3] = 1–8.75 \times 10^{-3}$ mol dm^{-3}, thus $[Rh]/[N(C_8H_{17})_3]$ varying from 0.025 to 0.285): (○) C^1, (●) C^2, (□) C^3, (■) C^4. The ^{13}C chemical shift change observed for carbons C^1 (△) and C^2 (▲) in the presence of HCl, *i.e.* such as $[H^+] = 3[N(C_8H_{17})_3]$ (without Rh), is also shown. All changes refer to the same concentration

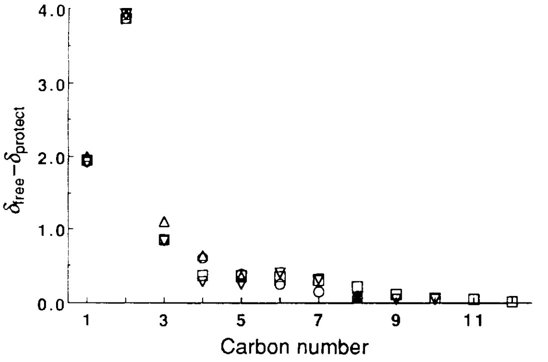

Fig. 5 The ^{13}C chemical shift changes (Δδ) of the different amines *vs.* carbon atom position. [amine]/[Rh] = 20. Amines: △, $N(C_5H_{11})_3$; ○, $N(C_8H_{17})_3$; ▽, $N(C_{10}H_{21})_3$; □, $N(C_{12}H_{25})_3$

the presence of rhodium colloid, the T_1 values are smaller, especially for C^1 and C^2. These relaxation time changes, which means that the mobility of the alkyl carbons decreases, can be explained by an interaction between the surface of the rhodium colloid and the alkyl chain carbons. The mobility of the carbons located far from the surface (C^6–C^8) does not change much with the colloid protection.

The J_{CH} coupling constants of free (partially protonated) and rhodium-colloid-protecting $N(C_8H_{17})_3$ and carbons were also obtained by 75 MHz ^{13}C NMR spectroscopy. In Fig. 7 the differences in coupling constants of the carbons between free and colloid-protecting $N(C_8H_{17})_3$ are shown. The three carbon atoms closest to the amine nitrogen (C^1–C^3) present considerable increases of their J_{CH} coupling constants. These increases should be interpreted in terms of the fact that these three carbon atoms are located near to the rhodium colloid surface. The rhodium atom should have some effect on the carbon resonances but there is no direct bonding between it and these carbon atoms, because no coupling by rhodium was found in the ^{13}C NMR spectra of the tertiary amine-protected rhodium colloids.

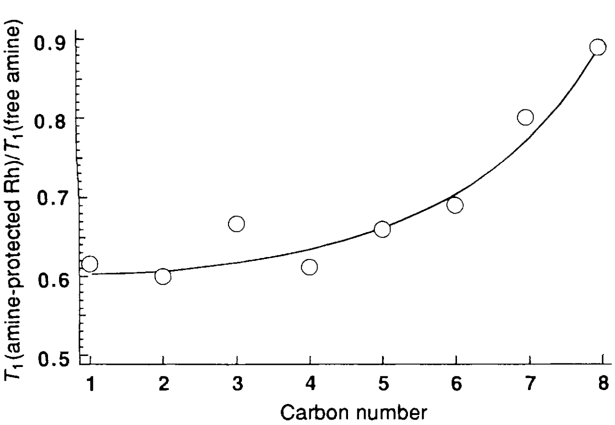

Fig. 6 The ratios of the spin–lattice relaxation time (T_1) of $N(C_8H_{17})_3$ in CDCl$_3$ and of $N(C_8H_{17})_3$-protected rhodium colloid dispersion in CDCl$_3$. $[N(C_8H_{17})_3] = 0.41$ mol dm^{-3}, $[N(C_8H_{17})_3]/[Rh] = 20$

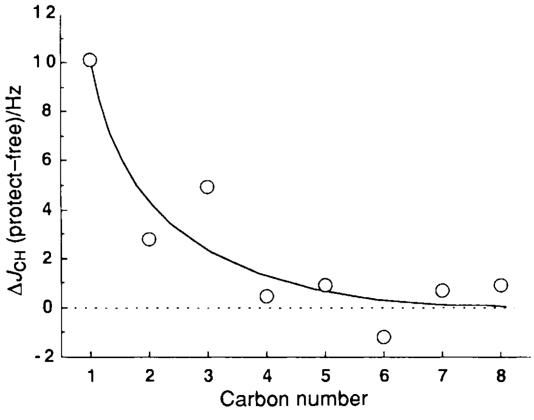

Fig. 7 The difference in J_{CH} coupling constants between $N(C_8H_{17})_3$ in CDCl$_3$ (partially protonated) and $N(C_8H_{17})_3$-protected rhodium colloid dispersion in CDCl$_3$. $[N(C_8H_{17})_3] = 0.41$ mol dm^{-3}, $[N(C_8H_{17})_3]/[Rh] = 20$

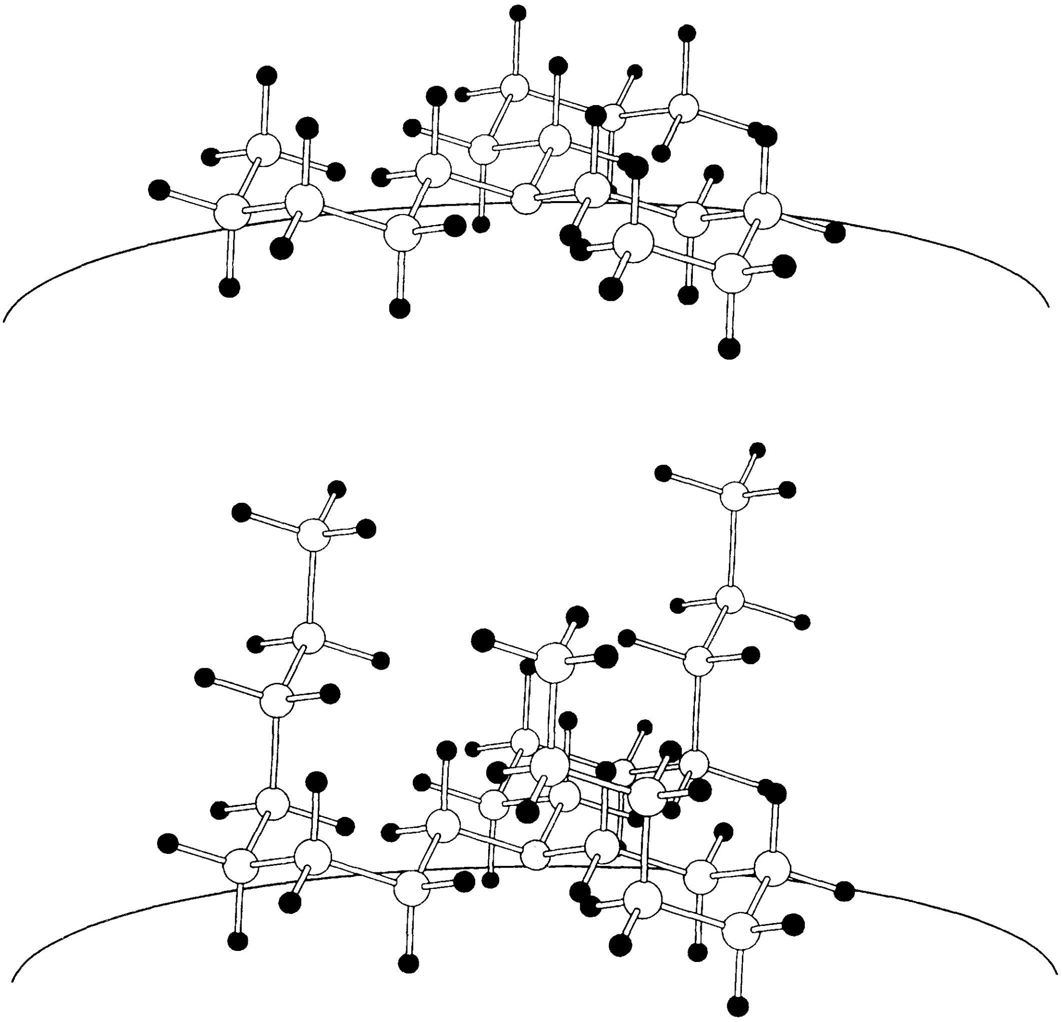

Fig. 8 Proposed model of $N(C_5H_{11})_3$- (top) and $N(C_8H_{17})_3$- (bottom) protected rhodium colloid particles

Table 2 Stokes' radii of the tertiary amine-protected rhodium colloids in chloroform obtained by Taylor dispersion *

Amine	[Amine]/mol dm^{-3}	Stokes' radius/nm
$N(C_5H_{11})_3$	0.44	0.8
$N(C_8H_{17})_3$	0.41	1.1
$N(C_{10}H_{21})_3$	0.39	1.3
$N(C_{12}H_{25})_3$	0.38	2.0

* [Amine]/[Rh] = 20; radius of naked particle ≈0.8 nm.

Similar conformational changes were reported in a surface-enhanced Raman spectroscopy (SERS) investigation of silver colloids stabilized by (hexadecyl)trimethylammonium bromide.[22] The enhancement of the Raman spectra by the surface of the silver colloid was found not only for the peaks due to the ionic head group, $^+NMe_3$, but also for those of other parts of the alkyl group, *i.e.* $CH_2CH_2CH_2N^+$.

Diffusion coefficient and Stokes' radius measurement

The determination of the size of the entire amine-protected rhodium colloids is important in order to know the structure of the protecting amine molecules on the surface of the colloids. The combination of scanning tunnelling microscopy (STM) and high-resolution TEM has been proposed recently to determine the entire size of surfactant-protected noble metal particles and the thickness of the protective layer of surfactant molecules surrounding the particle surface.[23] However, the samples studied by STM were dried and the conformation of the protecting molecules could have been modified.

The size of the naked metal particles can be obtained by TEM measurement of the rhodium colloid dispersions. Therefore, we can derive the thickness of the protective layer of amines surrounding the metal colloid particles from a measurement of the hydrodynamic Stokes' radius of the amine-protected colloids (Fig. 1). For this purpose, we used a physicochemical method, called Taylor dispersion,[15–17,24] to obtain the Stokes' radii of amine-protected rhodium colloids from their diffusion coefficients. One of the great advantages of this method is that the entire particle size can be directly measured in solution, where the amine molecules on the surface of the colloid particles rapidly exchange with those in solution. In addition, it should be possible to measure the entire particle size under catalytic conditions, for example at higher temperature or in the presence of a substrate.

In Table 2 the Stokes' radii of the tertiary amine-protected rhodium colloids are collected. The average colloid radii obtained by TEM for the samples analysed by the Taylor dispersion method were about 0.8 nm. In comparison, the Stokes' radii obtained here were considerably smaller than expected, *i.e.* than the sum of the radius of the naked metal particle and the chain length of the tertiary amine. Although further experiments should be done, for example with different concentrations of colloids or amines, these results clearly indicate that the protecting amine molecules do not have an expanded structure with a *trans* conformation of their alkyl chains, but a folded structure on the surface of the rhodium colloids, *i.e.* a *cis* conformation of the alkyl chains. Despite the fact that the sizes of the naked particles of the samples used for Taylor dispersion measurements are smaller than those of the samples for the NMR measurements, the protecting structure of both types of particles should be very similar.

Protecting model

The measurements described above allow us to present a model of the protection by the tertiary amines on the surface of the rhodium colloids (Fig. 8). As indicated by the ^{13}C NMR spectra, atoms C^1 and C^2 of the tertiary amines that we investigated have large populations of the *cis* conformation on the surface of the rhodium colloid particles. Assuming that the three alkyl chains of the tertiary amines have the same structure, one C^2 should be located near to the surface without folding the chain vertically to the colloid particle surface (all the three C^2 carbons cannot be located like this).

A similar model was proposed for non-ionic surfactant-protected platinum colloids in water, also as a result of ^{13}C NMR investigations.[25] In this case the platinum colloids are protected by hydrophobic interaction between the metal surface and the alkyl chain (hydrophobic part) of the non-ionic surfactant, and by expansion of the ethylene glycol chain (hydrophilic part) of the surfactant. Silver organosols protected by a cationic surfactant also exhibit a similar protecting model, as evidenced by SERS, and discussed above.[22] Another similar model was proposed for cationic surfactant-protected platinum colloids,[26] which also involve a hydrophobic interaction between the surface of the colloids and the surfactant alkyl chain. This interaction deforms the micelle structure of the cationic surfactants.

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