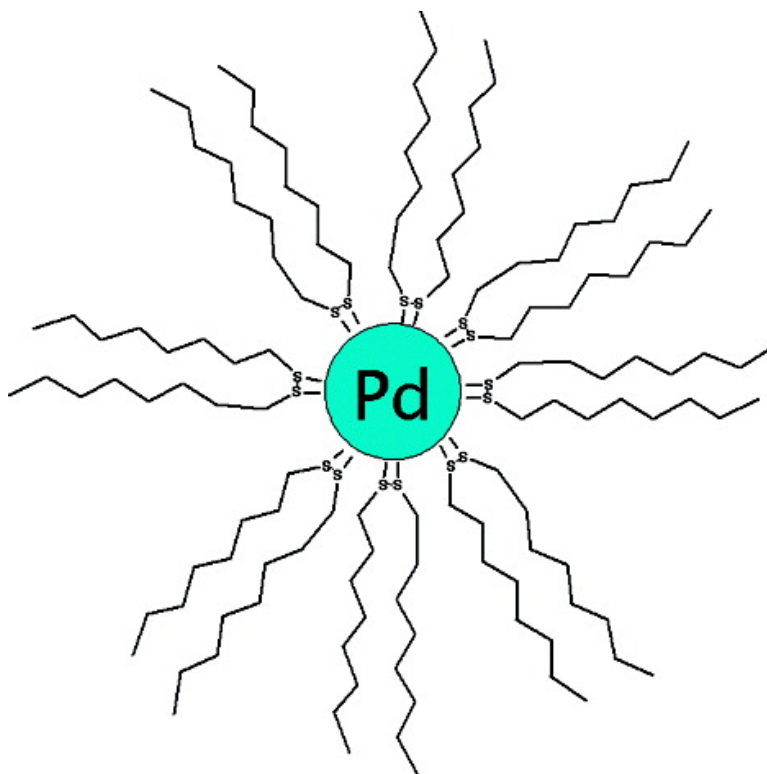Article

C NMR and Infrared Evidence of a Dioctyl–Disulfide Structure on Octanethiol-Protected Palladium Nanoparticle Surfaces

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^{13}C NMR and Infrared Evidence of a Dioctyl−Disulfide Structure on Octanethiol-Protected Palladium Nanoparticle Surfaces

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Abstract: On $^{13}C_1$-labeled octanethiol-protected 2.7 nm Pd nanoparticle surfaces, it has been observed that the $^{13}C_1$ NMR of the α-carbon shows a peak centered around 38 ppm (with respect to tetramethylsilane (TMS)), which virtually coincides with that of the α-carbons in a dioctyl−disulfide molecule (39.3 ppm), and the corresponding $^{13}C_1$ spin−spin relaxation becomes nonexponential. In addition, the infrared spectrum of the same sample shows that the ligands have a 100% gauche conformation, which is also consistent with a dioctyl−disulfide arrangement. By comparing with data obtained on $^{13}C_1$-labeled octanethiol-protected 2.8 nm Au nanoparticles, we propose that a dioctyl−disulfide structure of the ligands is formed on the octanethiol-protected Pd nanoparticle surface, in contrast to the thiolate structure proposed on the Au nanoparticles. In addition, CO adsorption experiments show no sign of a PdS layer formed on the Pd nanoparticle surface. Furthermore, data taken over a period of more than 1 year show that the Pd nanoparticles are rather stable in organic solvents (for instance benzene), although slow degradation does happen and oxygen seems to play an important role in accelerating the degradation.

Introduction

For the most intensively studied archetypal systems of self-assembled monolayers (SAMs)[1] of alkanethiols on metal (specifically gold) single crystal or the corresponding nanoparticle (NP) surfaces, the prevailing experimental observations consistently suggest an alkanethiolate structure with a dominant trans conformation.[1−4] So far, few dialkyl−disulfide structures have been observed. The best-known example is probably the one published by Fenter et al. a decade ago in which grazing X-ray diffraction data have suggested the existence of a dialkyl−disulfide structure on a Au(111) surface.[5] Most interestingly, Whitesides, Nuzzo, and their co-workers have recently proposed an unusual palladium sulfide (PdS) interlayer sandwiched between the alkanethiol SAM and the Pd surfaces with a dominant (111) facet.[6] A similar PdS interlayer structure has been inferred by extended X-ray absorption fine structure (EXAFS)[7] and X-ray photoelectron spectroscopy (XPS)[8] for alkanethiols adsorbed on *preformed* Pd NP surfaces. On the other hand, for Pd NPs synthesized in the presence of alkanethi-

ols from the very beginning, no such interlayer structure has been reported.[9−12] Instead, the available XPS[11] data suggest that it is in an all Pd^0 state. However, Murray and co-workers did observe a much higher alkanethiol content in alkanethiol-protected Pd than Au NPs and speculated that the protecting layer includes a Pd(II) thiolate ring and/or chain structures.[12] In this paper, we report new ^{13}C nuclear magnetic resonance (NMR) and infrared (IR) evidence that strongly suggests the formation of a dioctyl−disulfide structure on the octanethiol-protected Pd NP surface, as compared to that obtained on octanethiol-protected Au NPs that have similar particle size. In addition, CO adsorption shows that no PdS layer is formed on the surface of the Pd NPs investigated in this paper. Furthermore, a rather good long-term stability of the Pd NPs is confirmed by data taken over a period of more than 1 year. However, slow degradation does happen, and oxygen appears to play an important role in accelerating the degradation.

Experimental Section

Synthesis of NPs. Our synthesis of octanethiol-protected Pd (and Au) NPs followed the conventional two-phase procedure[13] utilizing tetra-*n*-octylammonium bromide (TOAB, 98%, Aldrich) as a phase-transfer reagent. All aqueous solutions were prepared with water purified

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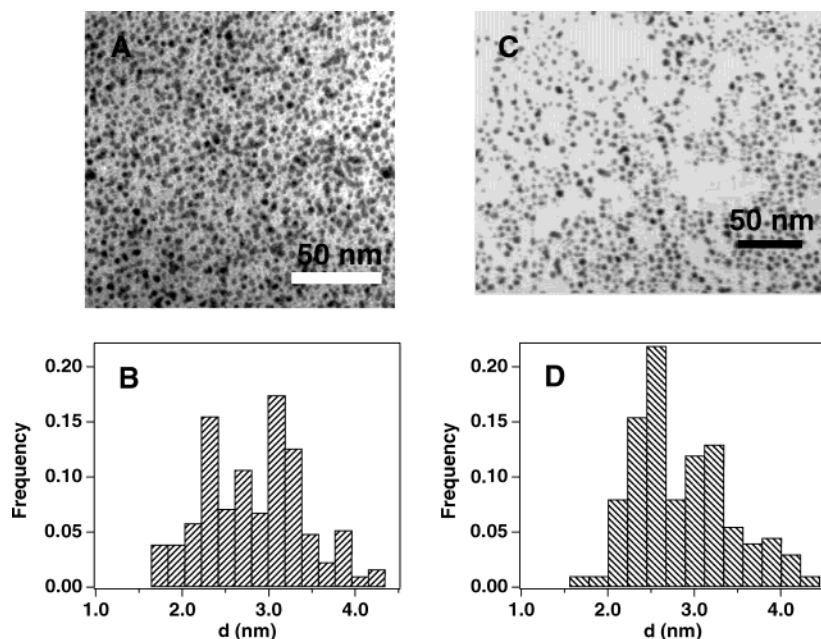
Figure 1. TEM pictures and size distribution histograms for the Pd (A and B) and Au (C and D) NPs.

by a Millipore Milli-Q Gradient A-10 system to 18.2 MΩ. For Pd, 20 mM $PdCl_2$ (99.9%, Strem) in 0.5 M HCl (Fisher) and 25 mM of TOAB (in 2 times excess) in toluene were shaken vigorously, resulting in a complete phase transfer of the Pd ions. For Au, 34 mM hydrogen tetrachloroaurate hydrate (99.9985%, Strem) in Milli-Q water was mixed with 47 mM TOAB (in 1.5 times excess) in toluene under vigorous stirring that also results in a complete phase transfer of the $AuCl_4^-$ into the organic phase. $^{13}C_1$-labeled $C_8H_{17}SH$ (Isotech, Miamisburg OH) was added to the separated organic phase according to a Pd/thiol ratio of 2:1 and a Au/thiol ratio of 5:1. Then a 10 times excess of 0.5 M $NaBH_4$ (99.995%, Aldrich) was poured into the mixtures under vigorous stirring, and dark brown Pd and Au colloids were instantaneously formed. Multiple cycles of filtering, rotary evaporation, and redissolving of the separated Pd and Au colloids gave the final dark brown product whose purity was checked by routine ^1H and ^{13}C NMR. Parts A−D of Figure 1 show the transmission electron microscopic (TEM) images of the samples so prepared and the corresponding size distribution histograms. Average particle sizes of 2.7 ± 0.6 and 2.8 ± 0.6 nm were obtained for Pd and Au, respectively.

Nuclear Magnetic Resonance and Infrared Spectroscopy. All NMR measurements reported here were carried out at room temperature on a "home-assembled" 400 MHz spectrometer equipped with an Oxford active-shielded 9.395 T widebore superconducting magnet and a Tecmag Libra acquisition system. The NMR samples consisted of the concentrated C_6D_6 solution of Pd and Au NPs flame-sealed into 10 mm × 25 mm glass ampules. A Hahn spin−echo pulse sequence ($\pi/2 - \tau_0 - \pi - \tau_0 -$ acquisition) with 16-phase cycling was used for data acquisition. The $\pi/2$ pulse = 6 μs and τ_0 = 50 μs. The chemical shift of C_6D_6 (128.39 ppm with respect to TMS) was used as the internal secondary reference. The T_1's were measured by conventional inversion−recovery method and the T_2's by monitoring the spectral amplitude as a function of τ_0 in the Hahn echo sequence. The across-the-spectrum relaxation values were obtained by reading the variations in signal amplitude at a given spectral position. All repetition times were set to $5T_1$.

IR spectra were recorded in transmission mode using a Bruker Vector 22 IR spectrometer with a spectral resolution of 2 cm^{-1} and 126 scans. The IR samples were prepared by grinding ca. 1 mg Pd or Au NPs together with KBr and then pressing it into a wafer. All the resulting data were background-subtracted and treated with baseline correction and smoothing.
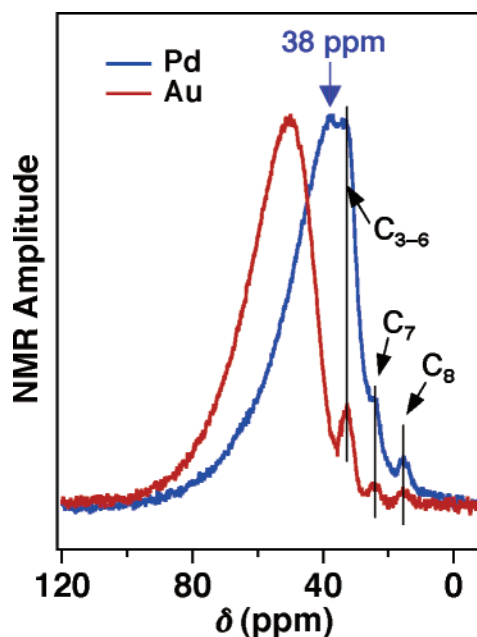
Figure 2. $^{13}C_1$ NMR spectra of $^{13}C_1$-labeled octanethiol-protected Pd (blue) and Au (red) NPs.

Results and Discussion

$^{13}C_1$ NMR Shifts and Relaxations. We compare in Figure 2 the $^{13}C_1$ NMR spectrum of Pd NPs (blue) with that of Au NPs (red). The spectrum of the Au NPs was previously published[14] and is reproduced here for comparison. The vertical lines at 15, 24, and 33 ppm indicate the positions of the ^{13}C NMR peaks from C_3 to C_8 along the octane chain.[15] As expected, they appear at the same positions for both samples. However, the $^{13}C_1$ positions are noticeably different: 38 ppm for Pd NPs but 50 ppm for Au NPs, although their particle

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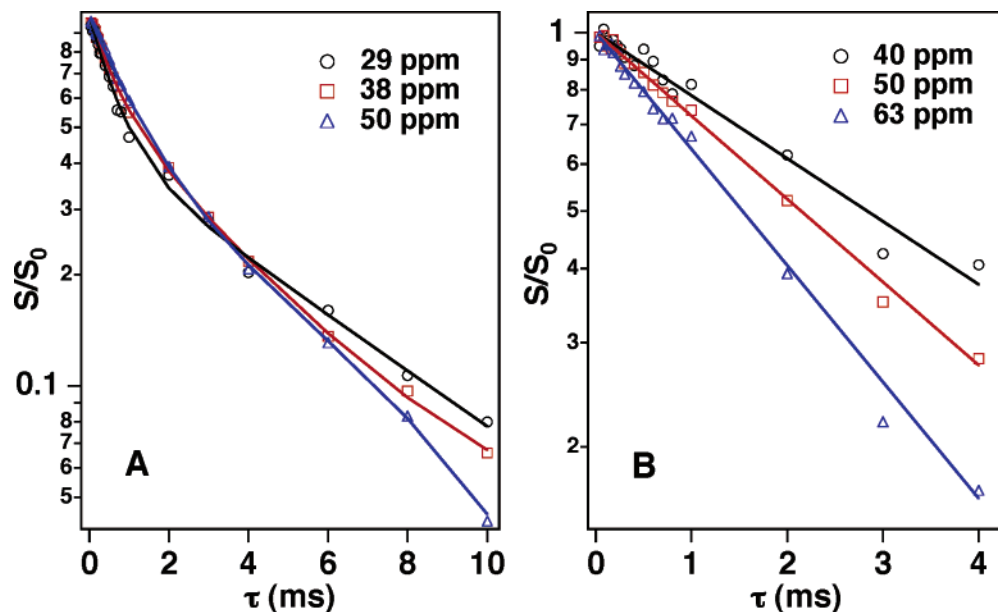
Figure 3. Representative $^{13}C_1$ spin−spin relaxation curves across the spectra for the Pd (A) and Au (B) NPs.

sizes are virtually the same. Compared to the $^{13}C_1$ NMR chemical shift of a free octanethiol at 24.7 ppm,[16] binding to the Pd NPs only causes a 13 ppm shift toward high frequency, which is 12 ppm less than when bound to the Au NPs. It is generally accepted that alkanethiols form a thiolate structure when self-assembled on a single crystal or nanoparticle Au surface.[2] Since hydrogen has a higher electronegativity than Au, charge withdrawing from the C_1 location is unlikely to be the cause of the deshielding observed when the octanethiol is bound to the Au surface. We think the deshielding is most likely caused by either the back-donation from the metal to the bound ligand, which would increase the population of low-lying molecular LUMOs (lowest unoccupied molecular orbitals), or by the spillover of conducting electrons (or both) and, therefore, an increase of the paramagnetic contribution to the NMR shift. Now, if the same thiolate structure is also formed on the Pd nanoparticle surface, then an even larger deshielding would be expected since Pd is usually much more able to back-donate electrons to the ligand than Au does. Indeed, available experimental evidence (vide infra) strongly suggests this is the case. Thus, a deshielding of 12 ppm less for Pd NPs than for Au NPs is somewhat surprising.

Interestingly, the peak position of the $^{13}C_1$ NMR spectrum of the $^{13}C_1$-labeled octanethiol-protected Pd NPs, 38 ppm, coincides with that of the α-carbons in a dioctyl−disulfide molecule (39.3 ppm).[16] This coincidence leads us to propose that a dioctyl−disulfide structure may be formed on the Pd NP surface. An immediate consequence of the formation of such a structure is that it will significantly modify local motions, e.g., reduce substantially the rotational freedom and local chemical environment as seen by the $^{13}C_1$. It, therefore, will influence the relaxation behaviors accordingly, for nuclear spin relaxations are highly sensitive to changes in the local motions. Indeed, the $^{13}C_1$ spin−spin relaxation of the Pd NPs behaves qualitatively different from that of the Au NPs, as shown in Figure 3. Parts A and B of Figure 3 present three representative relaxation curves at different spectral positions for Pd and Au NPs. As

(16) *KnowItAll Informatics System 3.0*; Bio-Rad Labortories, Inc., 2001−2003.

can be clearly seen, the spin−spin lattice relaxation is not a single-exponential for the Pd NPs (the solid curves in Figure 3B are ad hoc biexponential fits to the data, i.e., $S(\tau)/S_0 = \alpha \exp(-2\tau/T_2^{slow}) + (1 - \alpha) \exp(-2\tau/T_2^{fast})$, where α is the fraction of the slow component), while it is a single-exponential for the Au NPs. It is also less variant for the former than for the latter NPs. More detailed data are shown in Figure 4A. On the other hand, the $^{13}C_1$ spin−lattice relaxation of the Pd NPs is a single-exponential, whose across-the-spectrum values are compared with those of the Au NPs in Figure 4B. Although the spin−lattice relaxation is slightly slower for the Pd than for the Au NPs, they are overall very similar, indicating that the $^{13}C_1$ spin−lattice relaxation of the octanethiols on the Pd NPs is still dominated by the random tumbling of the particles.[14]

There are two possible reasons for the nonexponential $^{13}C_1$ spin−spin relaxation observed in the Pd NPs, and both can be rationalized as a result of the dioctyl−disulfide formation. The first is the motional hindrances caused by the dioctyl−disulfide formation that generates large anisotropy in the local motions which cannot be totally averaged out by the particle tumbling on the NMR time scale. Thus, the $^{13}C_1$ spin−spin relaxation sees an inhomogeneously distributed autocorrelation behavior that causes a nonexponential relaxation in the Pd NPs. The other possibility is simply that the formation of the dioctyl−disulfide structure generates two nonequivalent $^{13}C_1$ sites which have different spin−spin relaxation rates, yet whose spectra largely overlap. Indeed, the average fraction of the slowly relaxing component across the spectrum is α = 0.52 ± 0.06, strongly suggesting a half−half partition.

Gauche vs Trans S−C IR Stretching. If the adsorbed octanethiols do form a dioctyl−disulfide structure on the Pd NP surface, then a dominant gauche conformation of the S−C bonds is expected.[5] This is, in fact, the case observed by IR measurements, as presented in Figure 5. Two spectral regions of a typical IR spectrum are shown: from 500 to 800 cm^{-1} for the S−^{13}C (A) and from 2800 to 3100 cm^{-1} for the methylene/methyl (B) stretching frequencies. The red and blue spectra are for the thiols on the Au and the Pd NPs, respectively. According
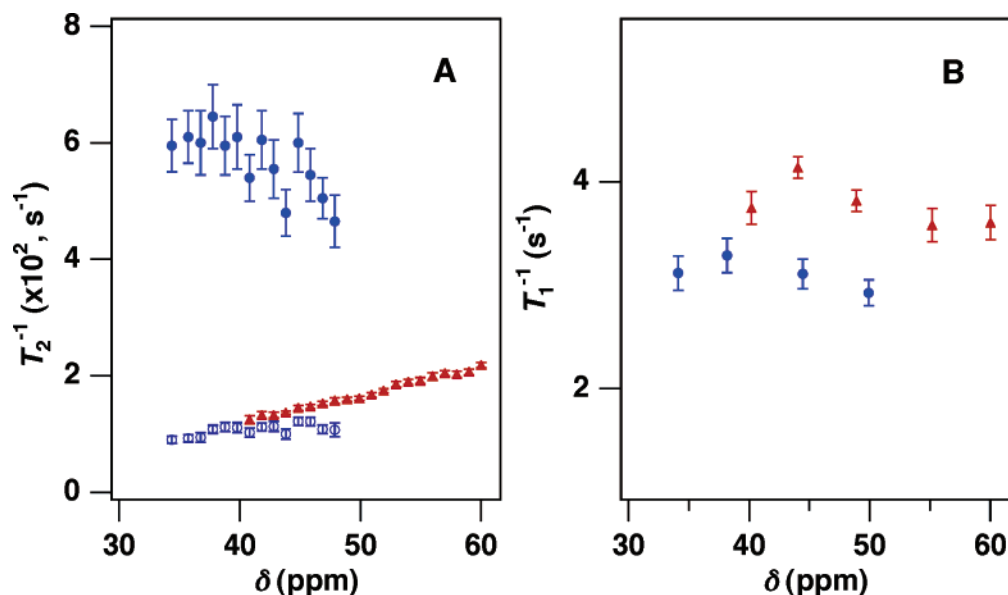
Figure 4. Across-the-spectrum $^{13}C_1$ spin−spin (A) and spin−lattice (B) relaxation data for the Pd (blue circles) and Au (red triangles) NPs. The blue solid and open circles in A are, respectively, the fast and slow components for Pd NPs.
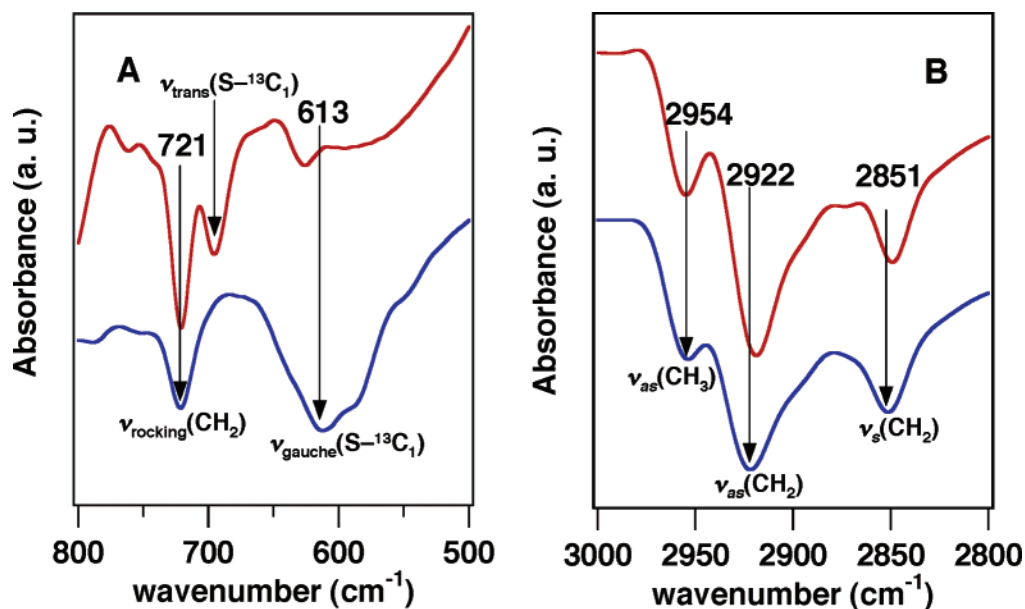

Figure 5. IR spectra for the Pd (blue) and Au (red) NPs: (A) S−C and (B) methylene and methyl stretching regions.

to the assignments proposed in the literature for thiols on Au surfaces,[3,4,17] the bands for $\nu_{stretch}(S-^{12}C)_{trans}$ and $\nu_{stretch}(S-^{12}C)_{gauche}$ stretching should appear at 721 and 642 cm^{-1}, with the former overlapping with that of the more intensive methylene rocking (P$_1$) band[3]. With $^{13}C_1$ labeling, as is the case here, both are expected to show a red shift. Of particular importance is that such a red shift would enable a resolution of the $\nu_{stretch}(S-^{13}C)_{trans}$ from the $\nu_{rocking}(CH_2)$ band. This is indeed being observed in the red spectrum, Figure 5A, for the octanethiols on the Au NPs: $\nu_{stretch}(S-^{13}C)_{trans} = 696$ cm^{-1}, well-separated from $\nu_{rocking}(CH_2) = 721$ cm^{-1}. A tiny band appears at 627 cm^{-1} which can be assigned to the $\nu_{stretch}(S-^{13}C)_{gauche}$. In the 2800−3100 cm^{-1} spectral range (Figure 5B), we observed $\nu_s(CH_2) = 2849$ cm^{-1}, $\nu_{as}(CH_2) = 2919$ cm^{-1}, and $\nu_{as}(CH_3) = 2955$ cm^{-1},

which are in excellent agreement with the literature values.[3] Altogether, the IR data confirm that the octanethiols on the Au NP surface have a thiolate structure and a dominant trans conformation.

It is, however, an entirely different story for the octanethiols on the Pd NPs, as shown by the blue spectrum in Figure 5A. Although a band appears at 721 cm^{-1}, which can be assigned to the methylene rocking (P$_1$) band, there is no band around 696 cm^{-1}, as expected for the $\nu_{stretch}(S-^{13}C)_{trans}$ band. Instead, a rather broad peak appears at 613 cm^{-1}, which can be reasonably assigned to the $\nu(S-^{13}C)_{gauche}$ band. That is, within the uncertainty of the experiments, all the octanethiols on the Pd NPs surface take a gauche conformation which is in agreement with a dioctyl−disulfide structure. The methylene and methyl stretching frequencies (Figure 5B) are $\nu_s(CH_2) = 2851$ cm^{-1}, $\nu_{as}(CH_2) = 2922$ cm^{-1}, and $\nu_{as}(CH_3) = 2954$ cm^{-1},

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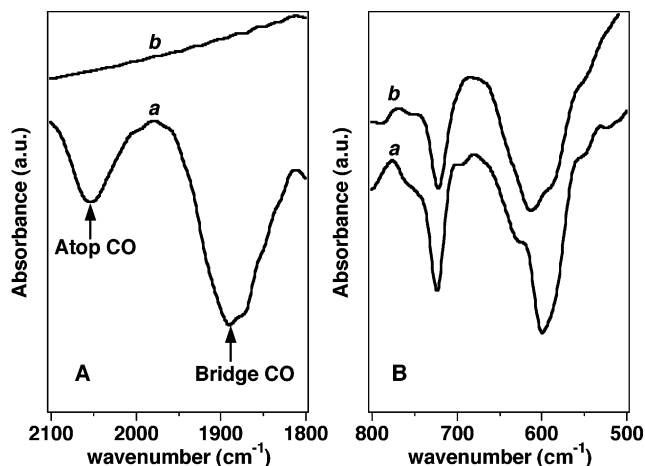
Figure 6. IR spectra for the Pd NPs with (a) and without (b) CO bubbling: (A) C—O and (B) S—C stretching regions.

which are blue-shifted compared with those for the Au NPs. This is consistent with the expectation that the gauche conformation of the S—C bonds will result in a less ordered crystalline carbon chain structure.

Surface Composition. As mentioned in the Introduction, an unusual palladium—palladium sulfide (PdS)—thiols interlayer structure has been proposed for alkanethiol SAM on the Pd surfaces with a dominant (111) facet.[6] To verify if this could also be the case for our Pd NPs, we used CO adsorption as a qualitative probe. The idea is quite simple: Since a Pd—S bond (~70 kcal/mol)[18] is much stronger than a Pd—CO bond (~45 kcal/mol),[19] CO would not be able to displace the S bound to the Pd surface in the form of a sulfide. This is why the S is one of the strongest poisons for catalytic transition metal surfaces in general and Pd surfaces in particular.[20] Therefore, CO would either not be able to absorb on a Pd NP coated with a PdS layer or, if adsorption does happen, it would have very different IR stretching frequencies as compared to COs on a normal Pd surface.

For the IR measurement, a toluene solution of the Pd NPs was bubbled by gaseous CO for about 20 min and then drop-cast onto a KBr wafer which was subject to IR measurements. The IR spectrum so obtained is presented in Figure 6 (spectrum a). Also shown in Figure 6 (spectrum b) is the IR spectrum of the Pd NPs that have not been subject to CO bubbling. The appearance of a dominant bridge-bound CO band at 1889 cm^{-1} with a minor atop-bound CO band at 2050 cm^{-1} (Figure 6A), which are characteristic for CO adsorbed on small Pd NPs having a particle size of ca. 2.5 nm,[21] demonstrates quite clearly that the presence of a PdS layer on the Pd NP surface is highly unlikely, if not at all impossible. Equally important is the observation, as shown in Figure 6B, that the adsorption of CO does not alter the gauche conformation of the S—C bonds. Notice that the CO adsorption cannot exclude the possible presence of adsorbed oxygen on the Pd surface because CO can eliminate adsorbed oxygen via a reaction CO + O$_{ads}$ →

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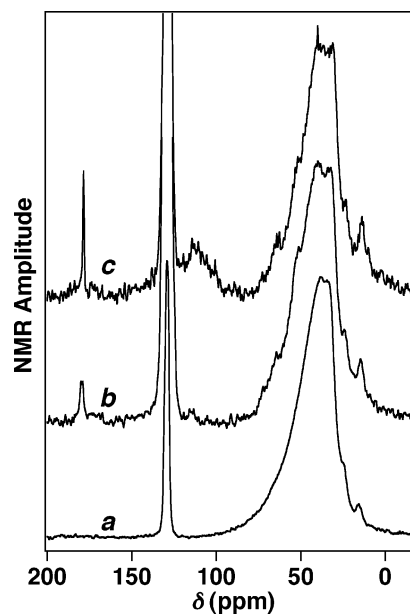
Figure 7. $^{13}C_1$ NMR spectra taken (a) 2 days after the Pd NPs were made, (b) 400 days after the Pd NPs were made during which the sample was sealed in a glass ampule, and (c) 34 days after spectrum b during which the sample was exposed to air. The spectra were normalized by setting the signal amplitude at 38 ppm to 1. See the text for detailed discussions.

CO$_2$. However, the results do strongly suggest that it seems unlikely that the possible presence of adsorbed oxygen, if any, could be the reason for the gauche conformation of the S—C bonds since the CO adsorption does not alter it at all.

Pd NP Stability. It has been observed previously that alkanethiol-protected Pd NPs are not as stable as alkanethiol-protected Au NPs.[10,12,22] In particular, the degradation process is significantly accelerated in the presence of the reaction media in which the Pd NPs were synthesized[10,12] and/or in the presence of extra free thiols,[22] presumably leading to some yet unidentified Pd(II) thiol complexes as the final products.[12,22] To see if such Pd complexes could be the reason for the proposed dioctyl—disulfide structure, we carried out a long-term $^{13}C_1$ NMR study. In Figure 7, three $^{13}C_1$ NMR spectra of the Pd NPs recorded at different times are presented, which are normalized by setting the signal amplitude at 38 ppm to 1. Spectrum a was taken 2 days after the sample was prepared, and spectrum b was taken after 400 days during which the sample had been sealed in a glass ampule. After spectrum b was taken, the sealed ampule was opened to air. Half of the sample was recollected for TEM and IR measurements. The other half of the sample was left in a glass tube for recording spectrum c, which was taken 34 days after the sample was exposed to air. The variation in signal-over-noise ratio is due to different numbers of acquisition scans and sample quantities. The peak at 128.39 ppm is from C$_6$D$_6$. However, C$_6$D$_6$/C$_6$H$_6$ was used for spectrum a, resulting in a reduction of the peak amplitude. Notice that the sample preparation and the subsequent flame-sealing were carried out in ambience and no special precautions were taken to exclude air.

A couple of important observations can be made from the data presented in Figure 7. First, for all cases, the dominant peak is still the one at 38 ppm that has been assigned to the

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dioctyl−disulfide structure on the Pd NP surface, indicating that the majority of the sample does not change. This is consistent with the observations in which the TEM and IR taken on the sample exposed to air after 400 days show no qualitative changes in terms of the particle size and the S−C stretching bands. This means that the results we have observed are clearly not due to the degradation of the sample. Second, however, new ^{13}C NMR peaks do appear in spectra b and c, which are indicative of a degradation process, although very slow. Most interesting is the narrow peak at 179 ppm that we tentatively assign to $^{13}C_1$ of the alkane chains in some detached product generated during the degradation. Its substantial increase in amplitude after 34 days of exposure to air clearly indicates that oxygen may play an important role in the degradation of alkanethiol-protected Pd NPs.

In spectrum c, another narrow peak appears at 39.5 ppm. Coincidently, the $^{13}C_\alpha$ chemical shift of a free dioctyl−disulfide molecule is 39.3 ppm. Such a coincidence points to the presence of free dioctyl−disulfide molecules in the solution which may directly come from the disulfide on the Pd NP surface. It is not clear at this moment why it is below the detection limit in spectrum b. Since it appears after the sample was exposed to air, oxygen may again play a role here. We also think that, purely based on sensitivity considerations, the shoulders at 50 and 63 ppm and the hump at 110 ppm in spectra b and c are all from the labeled $^{13}C_1$ contained in other products generated during the degradation. Although we refrain from any specific assignment of these new peaks for the lack of information, we would like to point out the fact that they are all more deshielded than 38 ppm, the shift value found for octanethiols on the Pd NP surface. It is highly likely that one of the products is some sort of Pd(II) thiolate. Thus, it is reasonable to conjecture that a thiolate structure on the Pd surface would at least have a $^{13}C_1$ shift of 50 ppm, again supporting the assignment of the 38 ppm peak to the dioctyl−disulfide structure. The appearance of these new peaks indicates that the degradation of the Pd NPs does happen slowly, even in normal organic solvent, and is apparently a complicated multipath process.

Conclusions

In summary, we have reported new $^{13}C_1$ NMR and IR evidence that is consistent with the formation of a dioctyl−disulfide structure on an octanethiol-protected Pd NP surface. CO adsorption experiments demonstrate that the formation of a PdS layer is highly unlikely on the surface of the Pd NPs studied here. Concerns on the long-term stability of the Pd NPs were investigated with data taken over a period of more than 1 year, which show clearly that the Pd NPs are rather stable, although slow degradation does happen and oxygen seems to accelerate the degradation process. In addition, the appearance of multiple new $^{13}C_1$ NMR peaks from the degradation products indicates that the degradation is a complicated multipath process.

Because of a much shorter sulfur−sulfur distance, a dialkyl−disulfide structure could allow a denser packing of SAMs on metal surfaces than a simple alkanethiolate structure does. Therefore, higher alkanethiol coverage, i.e., higher sulfur content, could be expected.

One important question that needs to be addressed in the future, in particular theoretical research, is why the $^{13}C_1$ NMR shift of a dioctyl−disulfide on a Pd surface appears almost at the same place as a free dioctyl−disulfide molecule. A possible explanation is that a saturated sulfur−sulfur bond might significantly reduce the influence from the metal surface.