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Rapid Phosphine Exchange on 1.5-nm Gold Nanoparticles

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Triphenylphosphine-cappped, 1.5-nm gold nanoparticles "$Au_{101}(PPh_3)_{21}Cl_5$" prepared following Hutchison's procedure (Weare, W. W.; Reed, S. M.; Warner, M. G.; Hutchison, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 12890) undergo rapid exchange of capping ligand phosphine with dissociated and added phosphine in dichloromethane solvent at 298 K. Remarkably, while the ^1H NMR spectrum resonances of the attached phosphine are broad, characteristic of a range of incompletely averaged environments, the ^{31}P NMR spectrum (observable only at 213 K and below) exhibits a single, narrow resonance indicating that all of the phosphorus atoms are magnetically equivalent.

Gold nanoparticles are being intensely investigated because of their size-dependent catalytic, photophysical, and electronic properties and their potential applications in sensors and electronics.[1] While the bulk of the recent work has utilized thiolate capping ligands to stabilize the gold clusters against agglomerization to bulk metal,[2] the phosphine-capped series,[3] e.g., $Au_9(PPh_3)_8(CN)_3$, $Au_{11}(PPh_3)_8Cl_3$, $Au_{55}(PPh_3)_{12}Cl_6$,[4,5] etc.,[4] originally of interest as stains for electron microscopy of biological samples,[6,7] has received renewed attention. Clusters of this series have been proposed as starting materials for preparation of thiolate-capped clusters,[8,9] their conductance properties have been studied,[5] and they have been utilized as contacts in conductance measurements of thiolate self-assembled monolayers.[10] The lability of phosphines in solutions of $Au_{55}(PPh_3)_{12}Cl_6$ [11−13] has long been recognized.[11] Here we describe evidence for rapid exchange of free and bound triphenylphosphine on 1.5-nm "$Au_{101}(PPh_3)_{21}Cl_5$" nanoparticles. This lability has significant implications for syntheses[8,9] involving these clusters and for design and interpretation of physical studies of these clusters dissolved in or in contact[10] with solution (as in attached to a surface that is immersed in a solution). It is noteworthy that thiolate-capped gold clusters undergo replacement reactions on the time scale of days.[14,15]

We note that small Au_n clusters even up to $n = 39$, $[(Ph_3P)_{14}Au_{39}Cl_6]Cl_2$,[16] are molecular in nature as established by single crystal diffraction. However, "$Au_{55}(PPh_3)_{12}Cl_6$", once believed to have a unique molecular formula, has been shown to be polydisperse,[12] and "$Au_{101}(PPh_3)_{21}Cl_5$" is as well.[8]

No ^{31}P signal can be detected for room temperature solutions of "$Au_{101}(PPh_3)_{21}Cl_5$". (This is in contrast to the Au_{55} species for which a peak is observed at δ 32;[17] in that case, addition of free PPh_3 results in an averaged, shifted resonance.[11]) Addition of "$Au_{101}(PPh_3)_{21}Cl_5$" to a solution of PPh_3 results in broadening its ^{31}P resonance and shifting of this peak downfield with increasing amount of gold cluster added as is shown in Figure 1.

The broadening and shifting shown in Figure 1 are consistent with exchange of phosphine between two magnetically inequivalent sites, and the fact that the broadening increases with the amount of cluster added indicates that the exchange is in the "slow exchange" regime.[18] Several possible explanations for these observations must be considered. First, Hutchison has attributed the narrower δ 7.5 resonance in the ^1H NMR spectrum to $Au(PPh_3)Cl$ impurity.[9] Qualitatively, at least, addition of this impurity can account

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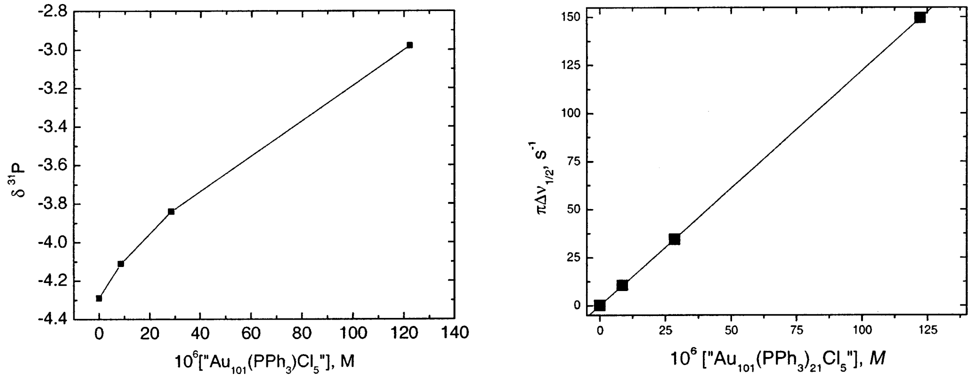

Figure 1. Behavior of the ^{31}P resonance of 0.1 M PPh_3 as a function of the concentration of gold cluster added at 298 K. The peak shifts to higher field (left, line segments added to guide the eye) and broadens (right). The fit (solid line) to the peak widths (radians s^{-1}) vs concentration plot yields a slope of 1.22×10^6 M^{-1} s^{-1} and intercept of -0.12 s^{-1}.

for the shifting of the PPh_3 resonance since mononuclear gold(I) complexes undergo rapid exchange with phosphines in solution except at very low temperature.[19] However, the exchange of PPh_3 with $Au(PPh_3)Cl$ is in the fast exchange limit[11] and so should produce narrowing, not broadening, of the ^{31}P resonance of PPh_3. Thus, the exchange implicated by the data in Figure 1 is caused by the gold cluster. Since the room temperature ^{31}P resonance is too broad to observe in the absence of added PPh_3, it is reasonable to attribute the process to the exchange of bound and dissociated ligand formed as in eq 1.

$$Au_{101}(PPh_3)_{21}Cl_5 \rightleftharpoons Au_{101}(PPh_3)_{20}Cl_5 + PPh_3 \qquad (1)$$

Equation 1 is presumably shifted to the left at low temperature since no (≤30%) dissociated phosphine is observed in the low temperature spectrum (Figure S4, Supporting Information).

The data reported in Figure 1 pertain to the lifetime of free triphenylphosphine in the presence of the gold cluster and thus to the forward (k_f) exchange process indicated in eq 2.

$$^{*}P_aPh_3 + Au_{101}(P_bPh_3)(PPh_3)_{20}Cl_5 \rightleftharpoons P_aPh_3 + Au_{101}(^{*}P_bPh_3)\,(PPh_3)_{20}Cl_5 \quad k_f, k_r \;(2)$$

Thus, the lifetime of free PPh_3 in the presence of the gold cluster ranges from 100 to 6 ms in the cluster concentration range examined here. Line-width simulations are consistent with this exchange being the process responsible for our failure to observe the cluster-bound phosphine in the absence of added phosphine above 253 K.

Observations of ^{31}P NMR and substitutional lability of phosphine-substituted Au(I) complexes and Au_n clusters at room temperature are summarized in Table 1. In thiolate capped self-assembled monolayers (SAMs) and nanoparticles (e.g., 2.5-nm particles), there is evidence that the ligated surface sites might be regarded as Au(I),[20] in contrast to Au(0) at the interior of the nanoparticle. Then, the reactivity of mononuclear Au(I) compounds might be examined as a model for the substitutional behavior of these surface gold sites. Gold(I) phosphine complexes undergo rapid substitution, exhibiting a propensity for associative processes. Of the small clusters, the Au_{11} species undergo slow substitution,[9,21] in contrast to Au_9 and Au_8 clusters.[22] With Au_9L_{10}, rapid exchange of the two phosphines attached to the central Au atom is observed.[23] The reactions of $Au_9L_8^{3+}$ ($L = PPh_3$) with L, SCN^-, and Cl^- to yield $Au_8L_8^{2+}$, $Au_{11}L_8(SCN)_2^+$, and $Au_{11}L_8Cl_2^+$ have been elucidated through ^{31}P NMR and other studies.[24] Larger, but intermediate-size, Au_{32-36} is reported to undergo phosphine replacement with a half-life of 1−2 min (6.6 mM $Au_{34}L_{10}(CN)_8^{n-}$, 0.09 M L′).[25] As noted above, the Au_{55} phosphine exchange rates lie in the microsecond regime, while the Au_{101} rates lie in the millisecond region.

Table 1. ^{31}P NMR Data and/or Exchange Rate Behavior (at 298 K unless Otherwise Noted)

compd/cluster	δ ^{31}P	exchange characteristics
$Au(PPh_3)Cl$	33.7[a] (CD_2Cl_2)[b]	fast exchange limit with added PPh_3 [a]
$Au_{11}(PPh_3)_7(SCN)_3$	51.9 (CD_2Cl_2)[c]	hours[f]
"$Au_{34}L_{10}(CN)_8^{n-}$"	not reported	1−2 min[d]
"$Au_{55}(PPh_3)_{12}Cl_6$"	32 ± 0.5 (CD_2Cl_2)[e]	$\tau(PPh_3) = 3 \pm 0.5$ μs[a]
"$Au_{101}(PPh_3)_{21}Cl_5$"	42.7 (CD_2Cl_2, 213 K)[b]	$\tau(PPh_3) \ll 0.1$ s[b] at 298 K

[a] Schmid, G. *Struct. Bonding* **1985**, *62*, 51−85. Solvent and reference were not stated. [b] This study. $\tau(PPh_3)$ is a function of the cluster concentration (Figure 1). [c] Vollenbroek, F. A.; Bour, J. J.; Trooster, J. M.; Van der Velden, J. W. A. *J. Chem. Soc., Chem. Commun.* **1978**, 907−909. Reported originally as −ca. 50 ppm relative to trimethyl phosphate (cf. Vollenbroek, F. A.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 137−141). With the current sign convention, these are ca. +50 vs trimethyl phosphate. δ ^{31}P for trimethyl phosphate = +2.0 vs 85% H_3PO_4 [30] was used to obtain the values listed here. [d] In the presence of 6.6 mM Au_{34}, 0.09 M L′. Jahn, W. *Z. Naturforsch.* **2001**, *56b*, 728−734. [e] Schmid, G. *Inorg. Synth.* **1990**, *27*, 214−217. [f] Vollenbroek, F. A.; Van den Berg, J. P.; Van der Velden, J. W. A.; Bour, J. J. *Inorg. Chem.* **1980**, *19*, 2685−2688.

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Finally, we draw attention to the contrast between the ^1H and ^{31}P NMR spectra of these clusters. As noted by Hutchison,[8] the proton NMR spectrum of Au_{101} exhibits very broad peaks as have been observed for alkanethiolates bound to gold nanoparticles.[2,26] These broad signals have been attributed to the heterogeneity of sites presented by the nanoparticle surface and to the slow rotation (as for proteins and other macromolecules) in solution. Consistent with the latter dependence on T_2, line width was found to increase with particle size.[27,28]

In striking contrast to the range of capping ligand environments indicated by the ^1H NMR spectra, the Au_{11}, Au_{55}, and Au_{101} clusters each exhibit a single phosphine resonance, despite the fact that PPh_3 must be bound to chemically inequivalent sites in all three. Discussed by Schmid[11] for the larger clusters, rapid motion of the phosphine along the particle surface was invoked. In the case of the small clusters, no evidence of such dynamic behavior was found, although facile, fluxional motions of the metal skeleton have been considered as a source of the phenomenon.[29] In mixed PPh_3, PR_3 clusters, the $^{31}P-^{31}P$ coupling through the gold cluster was considered to provide the mechanism for inducing magnetic equivalence of the different sites.[21] Evidently, the gold cluster core provides a mechanism for producing magnetic equivalence of the phosphorus atoms in these clusters.

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Supporting Information Available: Experimental details, transmission electron micrograph, and UV−vis, ^1H NMR, and ^{31}P NMR spectra of the 1.5 nm gold nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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