Synthesis of Thiol-capped Gold Nanoparticles with Organometallic Reagents as a New Class of Reducing Agent

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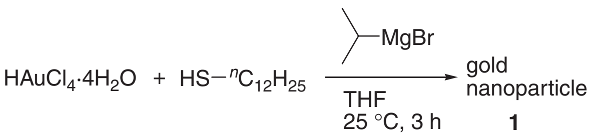
The reaction of chloroauric(III) acid and dodecanethiol with THF solution of 2-propylmagnesium bromide furnishes thiol-capped gold nanoparticles. The obtained nanoparticles are spherical and exhibit average diameter of 5.5 ± 0.61 nm. Synthesis of the nanoparticles are also carried out by using other Grignard reagents and organometallic reagents.

Gold nanoparticles (AuNPs) have attracted considerable attention in conjunction with applications to catalysis, nonlinear optics, and biological sensing due to characteristic magnetic, electronic, and optical properties.[1]

AuNPs have been generally produced by the reduction of a gold salt in the presence of a capping agent which brings about stability and functionality to the nanoparticle.[2] A variety of metal hydrides such as sodium borohydride,[3] lithium borohydride,[4] superhydride ($LiBHEt_3$),[5] borane–amine complex,[6] and silanes[7] are used to obtain AuNPs. However, little has been studied on the synthesis of AuNP using organometallic reagents which bear a metal–carbon bond.[8] Herein, we describe that alkyl organometallic reagent serves as a reducing agent for the synthesis of thiol-capped AuNPs.

We first examined the reaction with 2-propylmagnesium bromide, which is a Grignard reagent widely used in organic synthesis.[9] Synthesis of AuNP was carried out as follows: A solution of $HAuCl_4 \cdot 4H_2O$ (0.1 mmol) and 1-dodecanethiol (0.1 mmol) in 10 mL of THF was vigorously stirred for 3 h at 25 °C under a nitrogen atmosphere. To the resulting solution, excess THF solution (0.78 M) of 2-propylmagnesium bromide (1.0 mmol, 1.28 mL) was added dropwise over a period of 30 s at 25 °C. The color of the solution turned yellow to dark purple which indicates characteristic surface plasmon resonance of AuNP.[10] After stirring for 3 h at 25 °C, ethanol was added to the solution to precipitate AuNP, which was centrifuged to isolate the thiol-capped AuNP (**1**, 18.3 mg) as a dark brown powder (eq 1). The obtained **1** was found to be dispersible in organic solvents such as THF or $CHCl_3$ suggesting that aggregation did not occur during the isolation procedure.



$$HAuCl_4 \cdot 4H_2O + HS{-}{}^{n}C_{12}H_{25} \xrightarrow[\text{THF, 25 °C, 3 h}]{\text{(CH}_3\text{)}_2\text{CH}{-}\text{MgBr}} \text{gold nanoparticle } \mathbf{1} \quad (1)$$

TEM image of the obtained AuNP shows that nanoparticles are spherical with an average diameter of 5.5 ± 0.61 nm (Figure 1). The ^{1}H NMR spectrum of AuNP exhibited signals assigned as CH_3– and –CH_2– of dodecanethiol, indicating that the 2-propyl group of the Grignard reagent was not incorporated into the capping agent of AuNP.

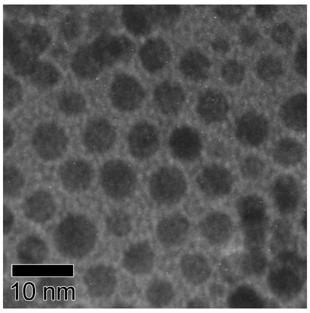


Figure 1. TEM image of AuNP **1**.

Synthesis of the AuNP with several kinds of Grignard reagents was examined in a similar manner. The results are summarized in Table 1. It was found that the formation of the AuNP was dependent on the reaction temperature. No nanoparticle was obtained when 2-propylmagnesium bromide was added at 0 °C. The reaction at 10 °C afforded purple solution suggesting the nanoparticle formation; however, the obtained solid was not completely dispersible in organic solvents resulting in partial aggregation of the nanoparticles. Though the reaction at 40 °C gave nanoparticle of a smaller particle, dispersity was found to be inferior to that prepared at 25 °C. Treatment with *t*-butylmagnesium chloride, which is a more sterically hindered reagent than 2-propylmagnesium bromide, similarly afforded particles of 8.1 ± 0.78 nm. The reaction with sterically less hindered Grignard reagent such as ethylmagnesium chloride also proceeded to give nanoparticles with an average diameter of 3.9 ± 0.80 nm. However, no particles were obtained when phenylmagnesium bromide and methylmagnesium iodide were employed. The nanoparticle size obtained was found to be similar to the case with metal hydrides such as sodium borohydride, superhydride, and borane–amine complex, etc.

Table 1. Synthesis of Au nanoparticles with Grignard reagents[a]

RMgX	Temp/°C	Time/h	Yield/mg	Size/nm
^{i}PrMgBr	0	4	0	—
	10	10	19.0	—[b]
	25	3	18.3	5.5 ± 0.61
	40	6	18.2	3.0 ± 0.59
^{t}BuMgCl	25	6	12.6	8.1 ± 0.78
CH_3CH_2MgBr	25	6	18.1	3.9 ± 0.80
PhMgBr	25	3	0	—
CH_3MgI	25	3	0	—

[a]The reaction was carried out with $HAuCl_4 \cdot 4H_2O$ (0.1 mmol), 1-dodecanethiol (0.1 mmol), and THF solution of Grignard reagent (1.0 mmol) in 10 mL of THF. [b]Partial aggregation of the nanoparticle.

Table 2. Synthesis of Au nanoparticles with various organometallic reagents[a]

Organometallic reagent	Temp/°C	Yield/mg	Size/nm
^{n}BuLi	−78 to 25	16.6	2.9 ± 0.40
Et_2Zn	25	6.8	2.4 ± 0.36
$^{i}Bu_3Al$	25	8.3	4.9 ± 0.67
$EtAlCl_2$	0	0	—

[a] The reaction was carried out with $HAuCl_4 \cdot 4H_2O$ (0.1 mmol), 1-dodecanethiol (0.1 mmol), and hexane solution of organometallic reagent (1.0 mmol) in 10 mL of THF for 3 h.

It is well known that alkyl Grignard reagents release the hydrogen atom at the β-position to the metal, which serves as a surrogate reagent of metal hydride and have been employed as a reducing agent for carbonyl and related compounds in organic synthesis.[9] Accordingly, we consider that several Grignard reagents also serve as a reducing agent in the gold nanoparticle synthesis. Indeed, the attempted nanoparticle synthesis with MeMgX or PhMgX, which did not possess a β-hydrogen atom, resulted in no reaction.

Encouraged by the results of Grignard reagents, we examined the synthesis of thiol-capped AuNP with other main group alkyl organometallic reagents as shown in Table 2. The reaction of *n*-butyllithium afforded nanoparticles in a reasonable yield, and the particle size was found to be 2.9 ± 0.40 nm. Treatment of diethylzinc and triisobutylaluminum also gave AuNPs, although removal of the metal residue by filtration was required during the isolation. On the other hand, addition of ethylaluminum dichloride, which is recognized as a class of Lewis acid, was found to be ineffective.

In summary, we demonstrated the synthesis of thiol-capped gold nanoparticles from $HAuCl_4 \cdot 4H_2O$ and long-chained alkanethiol with alkyl organometallic reagents. Grignard reagents serve as a ubiquitous reagent in organic synthesis that is readily available in laboratory scale. Treatment of organolithium, -zinc, and -aluminum reagents were also found to be effective for the synthesis of AuNP. These results suggest that several common organometallic reagents are available as a facile reducing agent for AuNP synthesis. Further studies on the nanoparticles bearing a functional group on the capped thiol moiety will be carried out, in which organometallic reagent would be a method of choice concerning the tolerance of functional groups.[11]

This work was partially supported by a Grant-in-Aid for Scientific Research for Exploratory Research, by Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors thank Professor Yasukiyo Ueda for valuable suggestion on TEM analyses.

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