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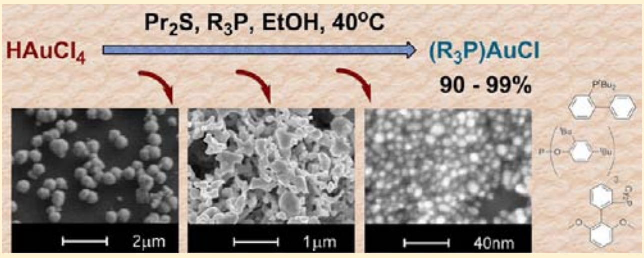
Efficient General Procedure To Access a Diversity of Gold(0) Particles and Gold(I) Phosphine Complexes from a Simple $HAuCl_4$ Source. Localization of Homogeneous/Heterogeneous System's Interface and Field-Emission Scanning Electron Microscopy Study

Sergey S. Zalesskiy, Alexander E. Sedykh, Alexey S. Kashin, and Valentine P. Ananikov*

Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow 119991, Russia

S *Supporting Information*

ABSTRACT: Soluble gold precatalysts, aimed for homogeneous catalysis, under certain conditions may form nanoparticles, which dramatically change the mechanism and initiate different chemistry. The present study addresses the question of designing gold catalysts, taking into account possible interconversions and contamination at the homogeneous/heterogeneous system's interface. It was revealed that accurate localization of boundary experimental conditions for formation of molecular gold complexes in solution versus nucleation and growth of gold particles opens new opportunities for well-known gold chemistry. Within the developed concept, a series of practical procedures was created for efficient synthesis of soluble gold complexes with various phosphine ligands $(R_3P)AuCl$ (90−99% yield) and for preparation of different types of gold materials. The effect of the ligand on the particles growth in solution has been observed and characterized with high-resolution field-emission scanning electron microscopy (FE-SEM) study. Two unique types of nanostructured gold materials were prepared: hierarchical agglomerates and gold mirror composed of ultrafine smoothly shaped particles.



1. INTRODUCTION

In recent decades, gold-catalyzed reactions have widely spread over the field of organic chemistry.[1−6] Numerous examples of gold-catalyzed reactions include nucleophilic additions, cyclizations, oxidative couplings, multiple bond activation processes, hydrogenations, and other fascinating transformations.[1−12] These examples show that gold catalysis tends to succeed in the utmost direction of the organic synthesis. Moreover, it is a common practice now to utilize a cascade of gold-catalyzed cyclizations to yield complex frameworks of natural compounds in one step instead of step-by-step buildup of polycyclic skeleton.[1−13]

Interestingly, despite the high activity of the catalyst and tolerance to a wide range of functional groups, gold-catalyzed reactions proved to be very sensitive to the minor changes in the catalyst structure. Selected examples show that even small changes in the ligand, counterion, additives, or conditions can direct the reaction to a completely different route.[1−5]

A series of recent studies have shown that fundamentally different reactions and mechanisms are accessible using soluble gold complexes and gold nanoparticles.[14,15] Heterogeneous pathways can contribute in distinct ways to activity and/or selectivity of gold-catalyzed transformations, including alternative pathways due to decomposition of common gold salts used as catalyst precursors toward nanoparticles.[14,16] Ongoing research on transition-metal-mediated transformations has emerged the problem of identity of the active form of the catalyst in view of possible interconversion of soluble complexes and nanoparticles in the catalyst precursor and in the catalytic system in solution.[17,18] An excellent example of the gold-catalyzed transformation through the involvement of heterogeneous and homogeneous pathways and the control of leaching was published.[19] The important mechanistic tools for in situ reduction of gold catalysts[20] and for the proof of homogeneous pathway with EXAFS/XANES measurements have been successfully demonstrated.[21] A valuable insight in the gas-phase ion chemistry suggested a more detailed look at the gold clusters, where a particularly strong ligand effect may be observed.[22]

So far, numerous factors have pointed out that successful implementation and development of gold catalysis in organic synthesis requires an extensive set of various gold precatalysts for rapid screening. Nowadays, these should include not only soluble complexes, but also nanoparticles of various sizes and shapes.

Widely used starting materials to prepare soluble complexes represent gold(I) stabilized by a weak-coordinated ligand, such as Me_2S (**1**), thiodiglycol (tdg; **2**), or tetrahydrothiophene (tht; **3**) (Scheme 1). However, all three of these precatalysts have noticeable drawbacks. Preparation of $(Me_2S)AuCl$ and (tht)-AuCl involves handling of dimethylsulfide and tetrahydrothio-

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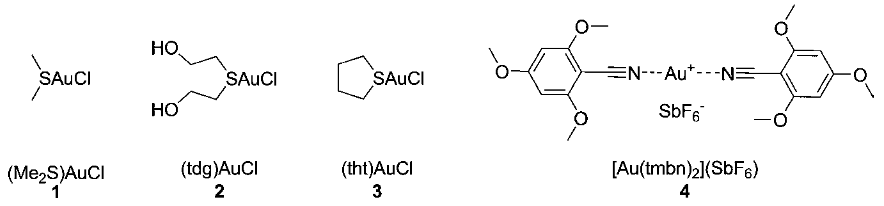
Scheme 1. Commonly Used Au(I) Complex Precursors



phene, both having very strong odor (in fact, even used as odorants for LPG and natural gas).[23] Apart from this, $(Me_2S)AuCl$ was reported to be light- and air-sensitive with a limited storage period.[24,25] The complex of gold(I) with thiodiglycole has limited stability, and therefore it has to be used without isolation. Thiodiglycole itself belongs to Schedule 2 of the Chemical Weapons Convention as a restricted compound, and routine laboratory usage of thiodiglycole is limited in some countries.[26] A recent example to prepare a multipurpose precatalyst was demonstrated by the synthesis of gold–nitrile complex bis(2,4,6-trimethoxybenzonitrile)gold hexafluoroantimonate (**4**; Scheme 1), and the application for generation of soluble gold species was shown.[27]

Another challenging task for the "all-from-one" catalyst kit is efficient generation of nanostructured gold particles. Several excellent reviews cover the preparation and application of nanoparticles in details.[14] However, the preparation of nanosized gold catalyst with required particles size and shape is not a trivial task. The majority of studies still use specific physical or physicochemical procedures to control the morphology of the nanoparticles during the synthesis. Particularly, it is often necessary to use stabilizers to prepare gold nanoparticles (citrate-capped, etc.).[28] However, the stabilizers have to be removed from the surface of the nanoparticle for catalytic applications.

Thus, an important direction for the improvement of currently available catalyst preparation procedures is to avoid impractical intermediate derivatives (**1**–**3**) and to get the necessary insight into the nature of gold species. The protocols developed for the synthesis of soluble complexes were not extended for nanoparticles, although uncontrolled formation of the nanoparticles cannot be anticipated and recalls for possible contamination. Vice versa, the procedures for the preparation of nanoparticles were not proven to be compatible with those developed for soluble complexes. An important aim is to prepare gold nanoparticles directly suitable for catalytic applications without the need of intermediate stabilizers.

In the present study, we describe a simple approach to access well-established gold(I) complexes and a diversity of gold(0) particles with varying size and shape. The synthesis of the complexes and nanoparticles was performed in high yields starting from the same $HAuCl_4$ source as an easily available gold salt. A fascinating advantage of the developed approach is governed by sequential procedure to access gold products of different nature. We have chosen simple and well-known reagents to mediate formation of gold complexes and particles. The usage of these reagents was proven in gold chemistry, and here we describe the systematic study focused on detailed characterization of soluble complexes and particles as well as addressing the question of possible contamination at the homogeneous/heterogeneous interface.

2. RESULTS AND DISCUSSION

2.1. Preparation of Gold Particles by Reduction of $HAuCl_4$ with $N_2H_4 \cdot 2HCl$, $NaBH_4$, and Hydroquinone. In the first step, we identified what gold complexes or nanoparticles can be obtained by reduction of $HAuCl_4$ using a set of well-known reducing agents, $N_2H_4 \cdot 2HCl$, $NaBH_4$, and hydroquinone. The milestone study of Schmid and co-workers has demonstrated that Au_{55} clusters can be readily formed by reduction of Au(III) salt with B_2H_6.[29] Formation of large metal clusters is an important prerequisite for the homogeneous (soluble mononuclear molecular species) and heterogeneous (insoluble metal particles) system's boundary in solution.[30]

Reduction of $HAuCl_4$ in solution is known to proceed smoothly, and, in the absence of a stabilizer, it results in the formation of insoluble precipitate. In the case of sodium borohydride, the reaction at room temperature was completed immediately and yielded a black precipitate without a noticeable amount of metal mirror on the walls of the reaction vessel.[31] Field-emission scanning electron microscopy (FE-SEM) study showed that the precipitate consisted of nonuniformly shaped particles in a 100–400 nm size with the individual particles arranged in a well-developed porous network (Figure 1A and B).

Reduction with hydrazine dihydrochloride was completed in 5 min after addition of the reductant (somewhat slower as compared to $NaBH_4$ reduction) and resulted in the formation of a clear colorless solution with dark brown precipitate and gold mirror on the walls of the tube. Both the precipitate and the mirror were subject to FE-SEM analysis and showed almost the same morphology and particle size (Figure 1C and D). The particles on the glass surface (mirror) were spherically shaped and were not aggregated with boundaries between separate particles clearly visible. The particles from precipitate had the same size distribution and shape, but due to more dense packing formed an agglomerated structure (Figure 1C). The diameter of the particles in both cases was about 300–700 nm.

At first sight, the reaction of $HAuCl_4$ with hydroquinone proceeded very similar to that with $N_2H_4 \cdot 2HCl$, but the amount of the formed gold mirror was significantly lower. The mirror consisted of loosely arranged metal particles (Figure 1F): the major fraction consisted of the particles of nearly spherical shape, and a smaller fraction consisted of rods and polygonal-shaped particles. However, FE-SEM analysis of the precipitate revealed a surprisingly complex 3D structure (Figure 1E). The bigger particles (about 1.5 μm in size) were arranged in a complex agglomerated porous three-dimensional framework. As shown in the high magnification image, each of the particles in turn had a highly developed surface with multiple spikes, ledges, and pits (Figure 2). Such hierarchy of particles was previously described for lanthanide salts,[32] CdS,[33] and Ni–Al binary systems;[34] however, to the best of our knowledge, the formation of such a framework for gold materials based on a simple preparation procedure has not been described. These

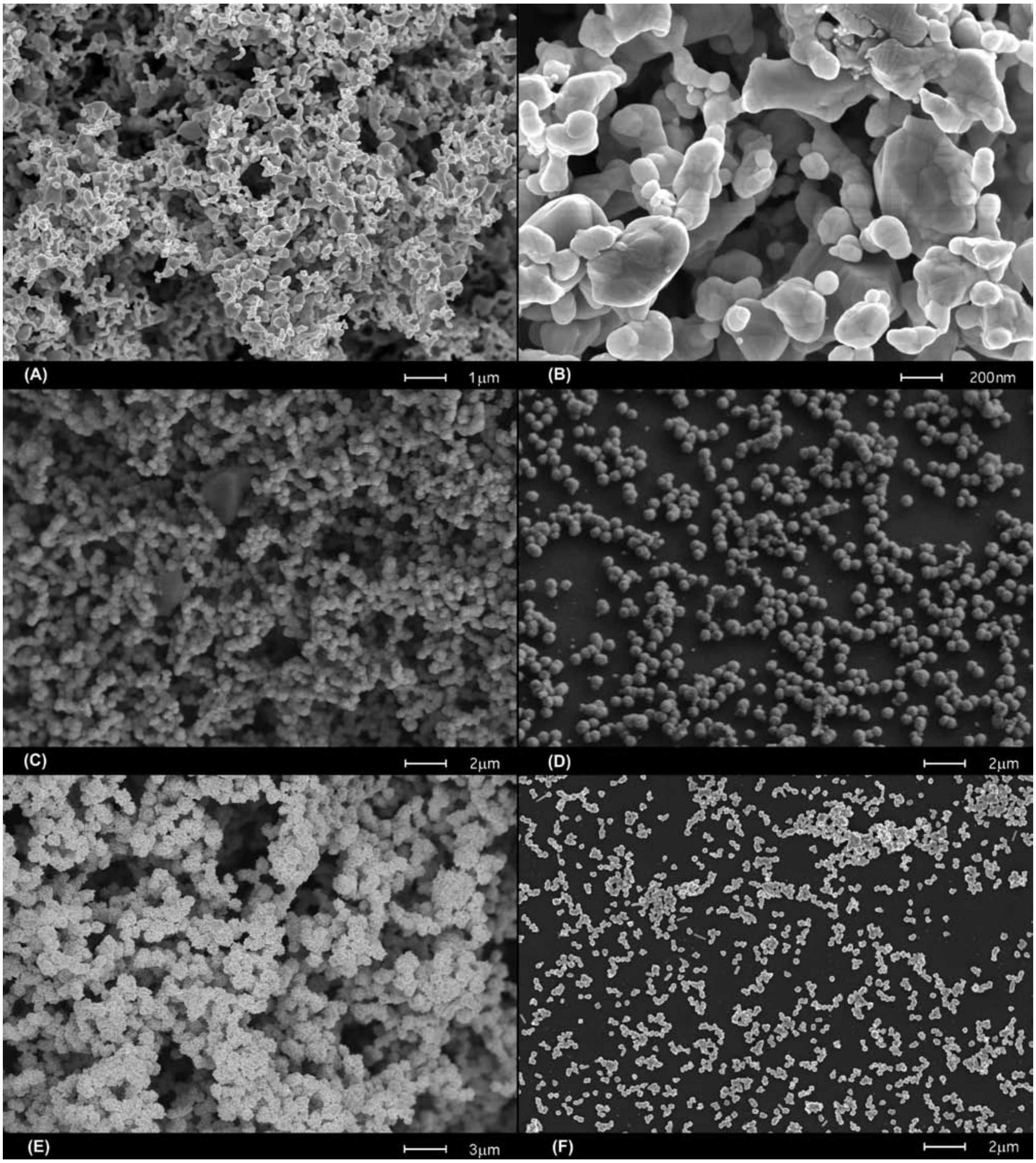


Figure 1. FE-SEM images of the metal particles formed in the reduction of $HAuCl_4$ by $NaBH_4$ (A and B), $N_2H_4 \cdot 2HCl$ (C and D), and hydroquinone (E and F); microscopy characterization of precipitates at ×10 000 (A), ×50 000 (B), ×5000 (C), and ×3000 (E) magnifications, and gold mirrors on the walls of the reaction vessel at ×5000 (D, F) magnification (corresponding micrometer and nanometer scale bars shown on each image).

types of structures may be attractive for heterogeneous catalysis because larger surface area and various types of corners and edges become available for the reaction with substrate.

2.2. Morphology Change in the Presence of PPh_3. In the next step, we studied the influence of phosphine ligands to check if it would prevent precipitation of gold metal and favor $(Ph_3P)Au(I)$ complex formation. It is well-known that the (triphenylphosphine)gold chloride complex can be simply prepared by reaction of $HAuCl_4$ with excess PPh_3, so that an excess of PPh_3 partially serves as reducing agent.[35] This approach is rather simple and straightforward; however, it requires a large excess of phosphine (ca. 2−5 equiv) to be used.

With sodium borohydride, the reaction yielded insoluble dark precipitate without gold mirror formation. Low magnification analysis showed a structural array of gold material (Figure 3A). Higher magnification FE-SEM revealed ultrafine

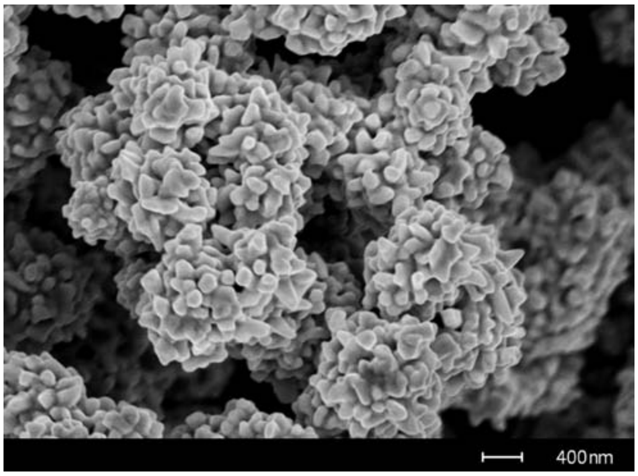


Figure 2. High magnification FE-SEM image (×20 000) showing the morphology of hierarchal gold particles formed upon reduction of $HAuCl_4$ with hydroquinone.

structure consisting of small sized particles of 5−10 nm in diameter (Figure 3B). It is evident that PPh_3 in this case plays an important role to control nanoparticles growth process (cf., Figures 1B and 3B). The nature of this process may be connected to the metal clusters generation and leaching involving nanoparticles;[16,29,30] molecules of triphenylphosphine coordinate to initially formed smaller clusters and nanoparticles, stabilizing them in solution and affecting the rate of their growth.

Reactions with hydrazine dihydrochloride and hydroquinone yielded both the precipitate and the gold mirror on the walls of the tube. In case of reduction with hydrazine dihydrochloride, characteristic spherical particles with a diameter of about 200−500 nm were formed (Figure 3C and D). High magnification FE-SEM showed some distortions from the spherical geometry and the presence of round-shaped corners. The same structural subunit was found in the precipitate and in the mirror, however, with a different degree of aggregation (cf., Figure 3C and D).

FE-SEM study of the precipitate formed during the reaction of $HAuCl_4$ and hydroquinone in the presence of triphenylphosphine revealed a complex 3D framework with particles sizes being significantly lower as compared to the experiment without phosphine ligand. The presence of PPh_3 resulted in ca. 2-fold decrease in the particles size (Figure 3E). In this case, the structure of the gold mirror was principally different as compared to the precipitate (cf., Figure 3E and F). The metal particles grown on the glass surface had almost the same size and morphology as those formed in the absence of phosphine (Figures 3F and 2F). Presumably, addition of triphenylphosphine changed the growth pattern of metal particles in solution to preserve a more fine structure in the isolated product; however, the phosphine has little effect (if any) on the morphology of the metal mirror.

2.3. Preparation of Soluble (R_3P)AuCl Complexes by Tuning the Reducing Agent. Despite our attempts, none of the reducing agents discussed above were suitable for the synthesis of gold(I) complexes because to a greater or lesser extent each of them led to the formation of Au nanoparticles. Contamination of soluble metal complexes with nanoparticles can seriously obscure application in catalysis and lead to ambiguous mechanistic picture.[17] Therefore, we have studied mild sulfur-based reductants and investigated whether it is possible to prepare a number of gold(I) phosphine complexes in one step starting from $HAuCl_4$ without the contamination with nanoparticles. Practically inconvenient sulfur compounds (see Introduction) have been excluded from the synthetic procedure.

Modification of the known procedure of reduction with sulfides has shown that a number of gold(I) complexes with various phosphine ligands can be accessed in excellent yields (90−99%) directly from $HAuCl_4$ (eq 1, Scheme 2).[36] Addition of Pr_2S to $HAuCl_4$ in ethanol led to a colorless clear solution, which indicated reduction of $HAuCl_4$ and formation of soluble Pr_2S−gold complex (10 min at 40 °C). Subsequent addition of R_3P ligand to the reaction mixtures led to the formation of the target (R_3P)AuCl complex (1 h at 40 °C). The procedure can be carried out in one pot without the need of separation and purification of intermediate gold(I) sulfide complex. Among the studied disulfides, the best yields were obtained using Pr_2S,[37] which was selected as a reagent of choice (a commercially available and easy to handle compound with weak odor).

Developed procedure is much more efficient as compared to the one pot reduction of $HAuCl_4$ with an excess of phosphine reported in the literature (eq 2, Scheme 2). The literature procedure gave good yield only for Ph_3P and poor yields for other ligands (34−69%), while only traces of product were detected for $CyPh_2P$.[36] Also, for cost-efficiency reasons, the synthesis of the complexes by reduction with an excess of biphenylphosphine and phosphite ligands is impractical. Another well-known method is based on the substitution of R_2S by a phosphine ligand, which proceeds with high yields (eq 3, Scheme 2). However, starting with $HAuCl_4$, it is a two-step procedure involving preparation of (R_2S)AuCl.[38] Both sulfur compounds (R_2S = Me_2S and tht) used in the first step are not as easy to handle as Pr_2S utilized in the present study. For the in situ reduction, the procedure using thiodiglycol as a reducing agent has been reported with the yield of 94% for $\{(2,4\text{-}(t\text{-Bu})_2C_6H_3O)_3P\}AuCl$,[39] 84% for ($Ph_3P$)AuCl, 49% for ($o$-Tol)$_3$PAuCl, 69% for $\{Cy_2(o\text{-biphenyl})P\}AuCl$, and 43% for $\{(t\text{-Bu})_2(o\text{-biphenyl})P\}AuCl$.[40]

One-pot $HAuCl_4$ reduction/complexation developed in the present study is a general procedure, and all tested ligands gave high yields (90−99%) and excellent product purity (eq 1, Scheme 2). The complexes were obtained in pure form without any dedicated purification steps. No signs of contamination of the product with corresponding phosphine oxides were observed (in contrast to reduction with an excess of PR_3). Even with rather complex and sterically demanding biphenylphosphine ligands (Buchwald-type), the proposed method results in the formation of the target complexes in one step with high yield using only 1.1 equiv of the phosphine. A challenging issue concerns the synthesis of gold(I) complexes with electron-poor phosphite ligand possessing weak coordination ability, where the developed procedure has also shown very good performance (eq 1, Scheme 2).[36] Structure and purity of the synthesized gold complexes were established with ^1H, ^{13}C, and ^{31}P NMR, and high-resolution ESI−MS in solution (see Experimental Section and the Supporting Information).

2.4. Synthesis of Ultrafine Nanoparticles by Reduction of Tightly Bound Gold−Phosphine Complex. It was of much interest to track the tendency of phosphine ligand to control nanoparticles formation; thus we have carried out the reaction of (Ph_3P)AuCl complex with the studied reducing agents. No reaction took place with hydrazine dihydrochloride

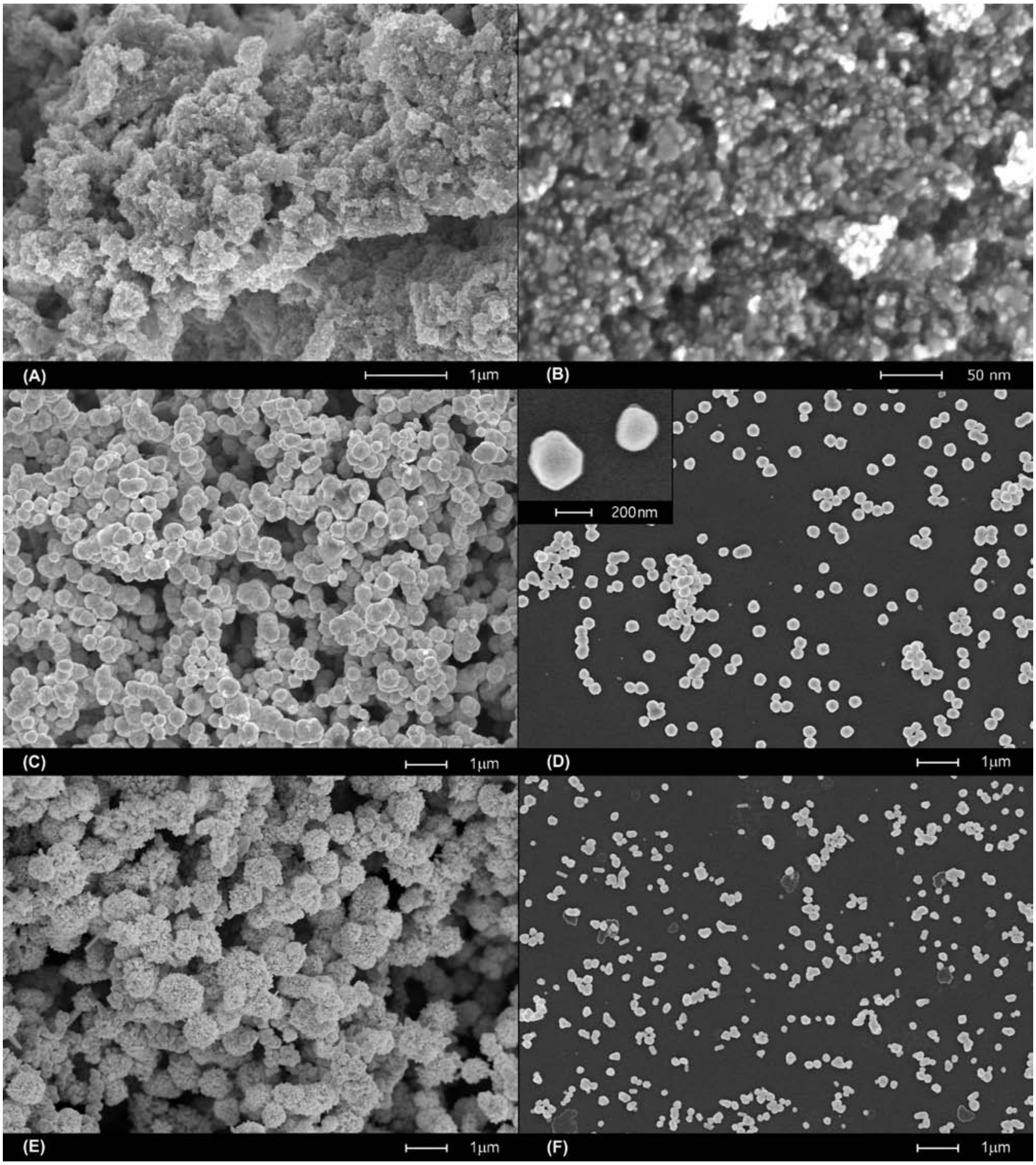
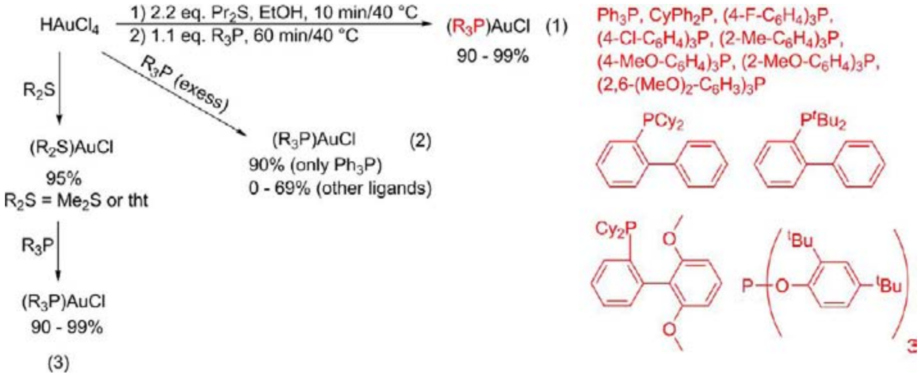


Figure 3. FE-SEM images of the metal particles formed in the reduction of $HAuCl_4$ in the presence of PPh_3 using $NaBH_4$ (A and B), $N_2H_4{\cdot}2HCl$ (C and D), and hydroquinone (E and F); microscopy characterization of precipitates at ×20 000 (A), ×300 000 (B), and ×10 000 (C, E) magnifications, and gold mirrors at ×10 000 (D, F) and ×50 000 (inset on D) magnifications with corresponding micrometer and nanometer scale bars shown on each image.

and hydroquinone; however, reduction with $NaBH_4$ led to the formation of metal mirror and a small amount of precipitate. As evidenced by FE-SEM, the particles of this precipitate (Figure 4A) had significantly different morphology as compared to those discussed earlier (Figure 1A). The aggregates had a diameter of 20−150 of nm, while the diameter of the small particles was in the range of 5−10 nm in diameter (Figure 4A).

The most interesting finding was the microscopic structure of gold mirror; in fact, it consisted of very small nanoparticles with a mean diameter of about 5 nm. The borders between individual particles were clearly visible with a negligible degree of aggregation (Figure 4B). In addition to application in catalysis, such thin metal films consisting of perfectly shaped particles are in demand for material science studies[41] and the development of new nanoelectronic devices.[42] Synthetic

Scheme 2. (1) Synthesis of $(R_3P)AuCl$ Complexes from $HAuCl_4$ Using One-Pot Procedure Developed in the Present Study (90−99% Yield for the Shown Ligands); and (2 and 3) Comparison with the Literature Methods



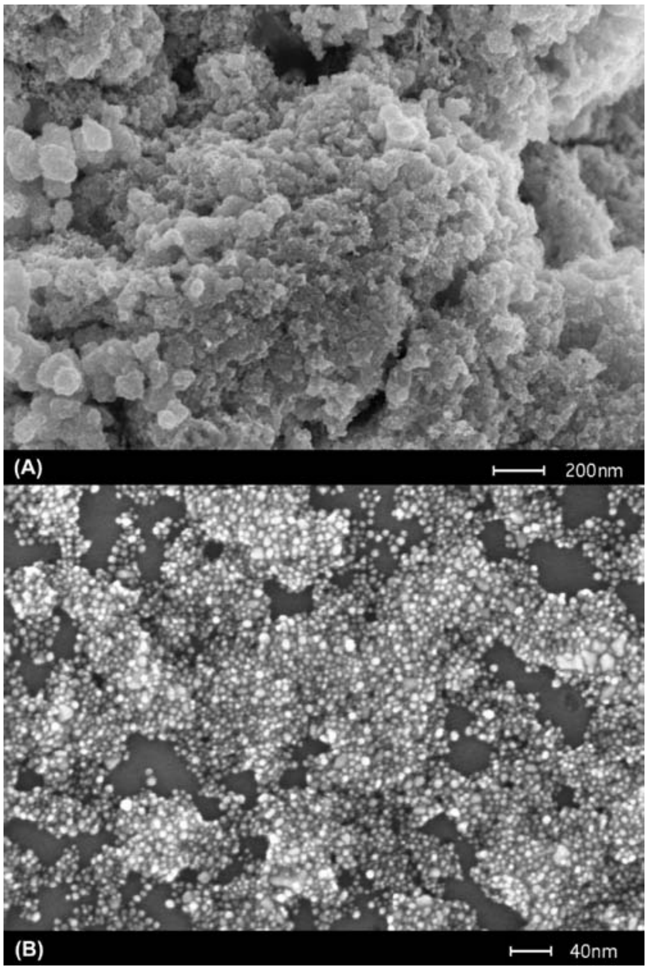


Figure 4. High magnification FE-SEM images of the metal particles formed in the reduction of $(Ph_3P)AuCl$ in solution with $NaBH_4$: (A) precipitate (×50 000) and (B) metal mirror (×200 000) with corresponding nanometer scale bars shown on each image.

procedures reported so far to obtain such structures were based on complicated techniques including galvanic displacement reactions,[43] electrodeposition,[44] and electrohydrodynamic atomization.[45] The procedure described in the present study provides a simple and straightforward approach to this class of gold materials.

2.5. "All-from-One" Gold Complexes/Particles Kit. In the present study, we have developed a series of practically useful procedures to access various gold species starting from $HAuCl_4$ (Scheme 3). An important issue was to localize the interface between soluble molecular complexes of gold and insoluble gold particles. Large and medium-sized particles were prepared by reaction in solution carried out in the presence or in the absence of ligand. Nanoparticles of gold were synthesized by stabilization of molecular complexes with PPh_3 prior to the self-assembly procedure. From the other hand, individual molecular complexes were prepared in high yields without nanoparticles contamination. The best results were achieved using Pr_2S as reducing and complexation agent. Therefore, the approach was developed to access gold complexes and particles to cover homogeneous and heterogeneous chemical systems (Scheme 3).

The scope and structural summary of the developed approach are shown in Table 1, with the highlight on the preparation of a variety of soluble gold complexes and particles. Current study constitutes an attempt to develop a so-called "all-from-one" gold kit for application in the fields of homogeneous/heterogeneous catalysis as well as in solid-state chemistry of gold. The approach should be especially useful for screening procedures, where a diversity of metal complexes and materials should be rapidly generated from a single source.

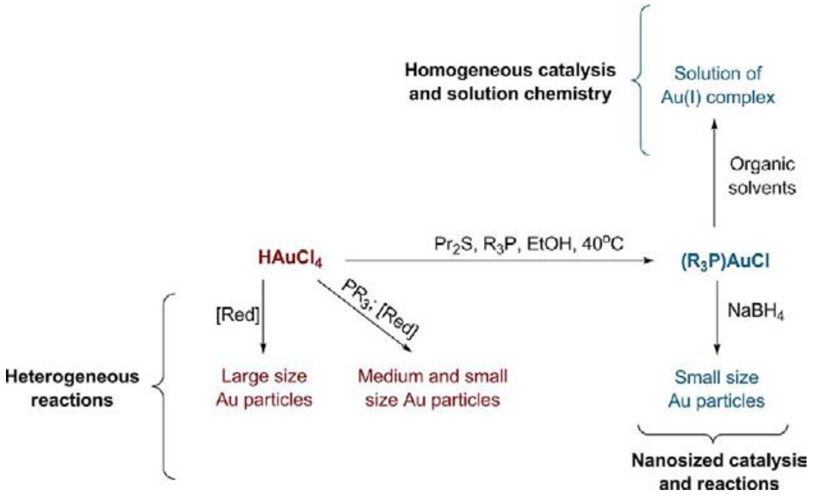
The study of $HAuCl_4$ reduction with sulfides allowed us to develop an easy to use and efficient method for the synthesis of various $(R_3P)AuCl$ complexes, which are valuable precatalysts for gold-mediated reactions. The application of developed method was successfully tested on various phosphine ligands. The complexes were prepared in excellent yields under verified conditions that avoid contamination by metal nanoparticles.

A diversity of microsized and nanosized gold particles was prepared using well-known reducing agents (Table 1). Gold particles were characterized in detail by FE-SEM study. Gold particles formed as a precipitate and as metal mirror on the glass surface can be easily separated from each other and potentially used in various catalytic reactions. Because of a noticeable difference in size and morphology of the particles assembled on the glass surface and in solution, one should expect varying chemical and catalytic properties.

3. CONCLUSIONS

We have shown that a number of challenging gold structures can be formed by reduction of $HAuCl_4$ under controlled conditions. An interesting effect of triphenylphosphine stabilization of nanoparticles upon formation was observed. This allowed us to tune the size and shape of the particles

Scheme 3. Summary of Possible Pathways for the Preparation of Gold Materials from the Known "Platform Chemicals" $HAuCl_4$ and R_3PAuCl^a



[a] [Red] = $N_2H_4{\cdot}2HCl$, $NaBH_4$, or hydroquinone.

Table 1. Preparation of Molecular Complexes, Particles, and Metal Mirrors Starting from $HAuCl_4$[a]

no.	initial compound	reagents	products molecular compounds	 particles	 metal mirror
1	$HAuCl_4$	$NaBH_4$		particles with diameter of 100−400 nm arranged in a well-developed porous network (Figure 1A,B)	
2	$HAuCl_4$	$N_2H_4{\cdot}2HCl$		slightly distorted spheres with diameter of 300−600 nm (Figure 1C)	slightly distorted spheres with diameter of 500−700 nm (Figure 1D)
3	$HAuCl_4$	hydroquinone		polygonal particles with smoothed edges (diameter of 100−300 nm) incorporated in the sphere-like structures with diameter of 1.5 ± 0.2 μm (Figures 1E, 2)	polygonal particles with smoothed edges (diameter of 100−400 nm) (Figure 1F)
4	$HAuCl_4$	$NaBH_4$ + PPh_3		structural array of gold material consisting of ultrafine subunits with diameter of 5−10 nm; (Figure 3A,B)	
5	$HAuCl_4$	$N_2H_4{\cdot}2HCl$ + PPh_3		slightly distorted spheres with diameter of 200−500 nm (Figure 3C)	slightly distorted spheres with diameter of 200−300 nm (Figure 3D)
6	$HAuCl_4$	hydroquinone + PPh_3		polygonal particles with smoothed edges (diameter of 50−100 nm) incorporated in the sphere-like structures with diameter of 0.7 ± 0.1 μm (Figure 3E)	polygonal particles with smoothed edges and diameter of 200−300 nm (Figure 3F)
7	$(Ph_3P)AuCl$	$NaBH_4$		highly aggregated particles with a small subunit of 5−10 nm (Figure 4A)	individual spherical particles with diameter of 5−10 nm (Figure 4B)
8	$HAuCl_4$	Pr_2S + PR_3	$(R_3P)AuCl$		

[a] In case of nonspherical shape, the reported size of the particles corresponds to Feret diameter.

simply by addition of a ligand. Very interesting results came out from the reaction of gold tetrachloroaurate with hydroquinone and reduction of $(Ph_3P)AuCl$ in solution with $NaBH_4$. These reactions proceeded smoothly at room temperature, yielding the formation of an agglomerated porous three-dimensional framework consisting of nanosized gold subunits (Figures 2, 3F) and gold mirror composed of ultrafine smoothly shaped particles (Figure 4B). Surprisingly, the unique nanostructured organization of gold particles in demand for material science applications and catalysis[41,42] became accessible via such a simple and practical procedure.

For homogeneous catalytic systems, gold(I) phosphine complexes represent one of the most used types of catalysts and precatalysts in various transformations, including their cationic derivatives, which are easily made by treatment with an equivalent of silver salt. Practical application of $(R_3P)AuCl$ complexes prepared in high yield in the present study (Scheme 2) has demonstrated unquestionable utility.[46] Complexes of gold(I) with bulky biphenylphosphines were explored in several catalytic transformations and revealed amazing ability of ligand effect tuning.[40a,47,48] Synthesis and isolation of stable complexes with electron-poor ligands is another challenging goal achieved using the developed procedure. Gold(I) complex with phosphite ligand gives rise to most electrophilic metal species and new types of catalytic applications.[40a,48−50] Thus, a general synthetic procedure was developed for the preparation of a series of the key gold(I) complexes in demand for homogeneous catalysis.

It should be pointed out that we focused our attention on simple reducing agents and efficient procedures with proven utility in transition metal chemistry. Individual reactions of these types under different conditions and varying target applications were employed in gold chemistry for many years. However, detailed study and comprehensive FE-SEM characterization in the solid state coupled with NMR in solution reported in this article have clearly shown that the potential of these practically simple procedures remains largely unexplored. We anticipate further research in the area of tuning the properties of gold complexes and particles at the molecular level and finding new chemical applications.

4. EXPERIMENTAL SECTION

4.1. General Considerations. NMR spectra were recorded on Bruker DRX-500 and Avance-600 spectrometers with working frequencies 500.1 and 600.1 MHz for ^1H, respectively. Chemical shifts are reported in ppm relative to residual solvent signal for ^1H and ^{13}C, and external 85% H_3PO_4/H_2O for ^{31}P.

High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II and Maxis instruments using electrospray ionization (ESI).[51] The measurements were performed in a positive ion mode (interface capillary voltage −4500 V); mass range from m/z 50 to m/z 3000 Da; external or internal calibration was performed with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set to 180 °C.

For the FE-SEM measurements, samples were mounted on a 25 mm aluminum specimen stub and fixed by conductive silver paint. The observations were carried out using a Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 10 kV accelerating voltage and at the working distance of 8−10 mm. For the samples of gold mirror obtained from the $HAuCl_4$, metal coating with a thin film of chromium was performed using magnetron sputtering method as described earlier.[52] Morphology of the coated samples was studied adjusted for the metal coating surface effects. SEM magnification values given on the figures refer to the standard 1280 × 960 (256 dpi) picture frame.

4.2. Reaction of $HAuCl_4$ with Reductants. The solution of the reductant (0.08 mmol) in ethanol (1 mL) was added to a solution of $HAuCl_4 \cdot 4H_2O$ (0.005 g, 0.0126 mmol) in ethanol (1 mL) at room temperature (25 °C).[53]

$NaBH_4$. After addition of the reductant, the solution instantly became black and gas evolution was observed. Black solid precipitate was washed with 4 mL of dichloromethane, 2 mL of ethanol, 2 mL of hexanes, 2 mL of water, and 2 mL of acetone.

$N_2H_4 \cdot 2HCl$. Reaction was completed in 5 min after addition of the reductant, and the solution became colorless. Brown solid precipitate and the gold mirror from the walls of the reaction vessel were washed with 2 mL of dichloromethane, 2 mL of ethanol, 2 mL of water, and 2 mL of acetone.

Hydroquinone. Brown suspension was formed in 5 min after addition of the reductant. The solid and the gold mirror from the walls of the reaction vessel were washed with 2 mL of dichloromethane, 2 mL of ethanol, and 2 mL of acetone.

4.3. Reaction of $HAuCl_4$ with Reductants in the Presence of PPh_3. The solution of the reductant (0.08 mmol) and PPh_3 (0.0033 g, 0.0126 mmol) in ethanol (1 mL) was added to a solution of $HAuCl_4 \cdot 4H_2O$ (0.005 g, 0.0126 mmol) in ethanol (1 mL).

$NaBH_4$. After addition of the reductant, the solution instantly became black and gas evolution was observed. Black solid precipitate was washed with 4 mL of dichloromethane, 2 mL of ethanol, 2 mL of hexanes, 2 mL of water, and 2 mL of acetone.

$N_2H_4 \cdot 2HCl$. The reaction was completed in 5 min after addition of the reductant, and the solution became colorless. Brown solid precipitate and gold mirror on the walls of the reaction vessel were washed with 2 mL of dichloromethane, 2 mL of ethanol, 2 mL of water, and 2 mL of acetone.

Hydroquinone. Brown suspension was formed in 5 min after addition of the reductant and the solution became dark. Solid precipitate and gold mirror on the walls of the reaction vessel were washed with 2 mL of dichloromethane, 2 mL of ethanol, and 2 mL of acetone.

4.4. Reaction of $(Ph_3P)AuCl$ with Sodium Borohydride. The solution of $NaBH_4$ (0.0038 g, 0.10 mmol) in ethanol (1.5 mL) was added to the solution of $(Ph_3P)AuCl$ (0.005 g, 0.01 mmol) in dichloromethane (0.5 mL). After addition of the reductant, the solution instantly became black and gas evolution was observed. Black solid and the internal walls of the reaction vessel were washed with 4 mL of ethanol, 4 mL of dichloromethane, 4 mL of acetone, and 4 mL of water.

4.5. General Procedure for the Developed One-Pot Synthesis of Au(I) Complexes from $HAuCl_4$ by Reduction with Pr_2S. Pr_2S (0.088 mL, 0.535 mmol) was added to the solution of $HAuCl_4 \cdot 4H_2O$ (0.100 g, 0.243 mmol) in ethanol (2 mL). After 10 min of stirring at 40 °C, the solution became colorless. The solution of corresponding phosphine or phosphite ligand (0.2673 mmol) in ethanol (2 mL) was added to the reaction mixture, and the formation of precipitate was initiated upon addition. Stirring was continued for 60 min at 40 °C followed by cooling the reaction mixture to room temperature and evaporation to a 5−10% of initial volume under reduced pressure. The white precipitate was separated by centrifugation (3500 rpm; 2 min) and washed with 1.5 mL of ethanol and 7.5 mL of hexanes (in the centrifuge tube). After that it was washed with 0.5 mL of ethanol and 4.5 mL of hexanes (in the centrifuge tube). The product was isolated by centrifugation (3500 rpm; 2 min) and redissolved in DCM. The evaporation of the solvent gave pure products with the isolated yield 90−90% for the studied ligands (eq 1, Scheme 2).[36] The complexes were characterized by NMR and ESI−MS.

■ ASSOCIATED CONTENT

Supporting Information

Optimization of the reaction conditions, and NMR spectra and ESI−MS spectra of the synthesized gold complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

val@ioc.ac.ru

Notes

The authors declare no competing financial interest.

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