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A Recyclable Polystyrene-Supported Gold(I) Catalyst

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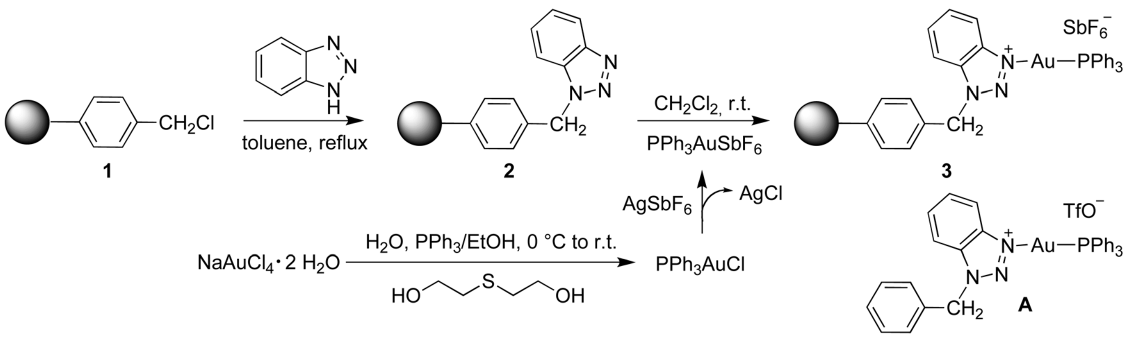
Abstract: A polystyrene-(benzotriazole)(triphenylphosphine)gold(I) [Btz·Au(I)PPh$_3$] resin, representing the first polystyrene-immobilized homogeneous gold(I) complex, was conveniently prepared, and showed remarkable catalytic activities and recyclability in three model transformations, including the tandem 3,3-rearrangement and Nazarov reaction of an enynyl acetate, the cyclization of a 1,6-enyne, and the rearrangement of an alkyne-furan.

Keywords: benzotriazole; gold; heterogeneous catalysis; polymer-supported gold(I) catalyst; polystyrene

Cationic gold(I) complexes have recently emerged as powerful homogeneous catalysts for the electrophilic activation of carbon-carbon multiple bonds towards nucleophiles to promote a number of unprecedented chemical transformations.[1,2] Immobilization of the gold(I) complexes onto solid supports would facilitate the recovery and reuse of these precious catalysts in practical synthesis. While polymer-supported transition metal catalysts have become a topic of intensive research,[3] such an interest has not been extended to gold(I) catalysts. The vast research efforts on the heterogeneous gold-catalyzed synthesis have thus far been dedicated to the gold particles supported on inorganic materials (mainly metal oxides) in which both the zerovalent gold clusters and the cationic gold(I) and gold(III) species are involved in the reactions.[4] Herein we report a polystyrene-supported gold(I) species which is highly effective and recyclable for the gold(I)-catalyzed reactions.

Shi and co-workers have recently developed triazole-Au(I) complexes, such as Ph$_3$PAu·BtzBn (**A**; BtzBn = N^1-benzylbenzotriazole), as a new class of gold(I) catalysts with improved thermal stability and reactivity.[5] Accordingly, we prepared conveniently a polystyrene-supported benzotriazole-Au(I) complex **3** as shown in Scheme 1.

The divinylbenzene (DVB) cross-linked polystyrenes (PS) are still the most popular polymeric materials used in organic synthesis due to their low cost, ready availability, mechanical robustness, chemical inertness, and facile functionalization;[3] we thus firstly chose Merrifield resin **1** (chloromethyl-polystyrene resin purchased from TCI, with 1% DVB, 200-400 mesh, and 1.2 mmol·g^{-1} as Cl) as the solid support. Treatment of resin **1** with a solution of benzotriazole (1.4 g, 12 mmol) in toluene (20 mL) under reflux for 48 h,[6] followed by precipitation from diethyl ether



Scheme 1. Preparation of a polystyrene-supported gold(I) catalyst **3**.

Table 1. XPS analysis of the PS-triazole resin **2** and the PS-supported gold(I) complex **3**.[a]

Resins	C [%]	Au [%]	P [%]	N [%]	Cl [%]	Sb [%]	F [%]
2	89.69			2.55	0.19		
3	82.67	0.79	0.80	2.11	0.14	0.42	3.07

[a] Surface concentrations are shown as atomic%.

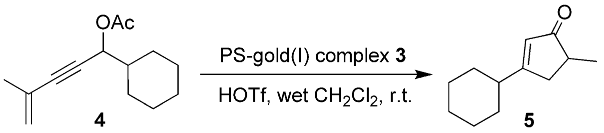
and drying under vacuum, provided the desired benzotriazole-functionalized resin **2** as a pale yellow powder. The elemental analysis of resin **2** revealed that the wt% contents of nitrogen and chloride were 4.65% and <0.5%, respectively, indicating 3.32 mmol·g^{-1} as N and less than 0.14 mmol·g^{-1} as Cl in the resin. These data were in good accordance with those implied from the X-ray photoelectron spectroscopy (XPS) analysis (Table 1), in that the wt% contents of nitrogen and chloride were calculated to be ~3.0% and ~0.5%, respectively. Prolongation of the reaction time did not increase considerably the loading of benzotriazole any more.

To a suspension of resin **2** in anhydrous CH_2Cl_2, PPh_3AuSbF_6 (freshly prepared as a solution in CH_2Cl_2 from PPh_3AuCl and $AgSbF_6$)[7] was then added at room temperature, and the resulting mixture was stirred overnight. The precipitate was filtered, washed with CH_2Cl_2 and diethyl ether, and dried under vacuum to afford the PS-supported gold(I) catalyst **3** as a gray powder. According to the weight gain of the resin before and after the reaction, the wt% content of Au was calculated to be 10.3%. This result was supported by the XPS analysis of resin **3**, which revealed the atomic% content of Au to be 0.79%, equal to a wt% of 11.1%. The Au atomic% (0.79%) was also in a satisfactory agreement with the stoichiometric proportions of atomic% of P, N, Sb, and F based on the structure of the complex **3**.

To evaluate the catalytic activity and recyclability of the PS-supported gold(I) complex **3**, three well documented homogeneous gold(I)-catalyzed transformations, i.e., **4**→**5**,[8] **6**→**7**,[9] and **8**→**9**,[5b,10] were examined as model reactions with **3** as a heterogeneous catalyst.

The transformation of enynyl acetates to cyclopentenones (e.g., **4**→**5**) *via* tandem 3,3-rearrangement and Nazarov reaction was disclosed by Zhang and Wang with $Ph_3PAuSbF_6$ as the most effective catalyst.[8] With the present PS-supported gold(I) complex **3** as catalyst (*ca.* 6 mol% Au) in the presence of 10 mol% HOTf in wet CH_2Cl_2 at room temperature, enynyl acetate **4** was converted to cyclopentenone **5** in excellent yields (Table 2). The filtered catalyst **3**, after being washed with CH_2Cl_2, was used directly for the next reaction cycle. It was remarkable that after 14 reaction cycles, the catalyst **3** was still effective to catalyze the reaction to completion, although the reaction rate slowed down gradually (from 30 min at the first cycle to 300 min at the 15th cycle).

Table 2. The transformation of enynyl acetate **4** to cyclopentenone **5** catalyzed by the PS-supported gold(I) complex **3** and the recycling experiments.[a]



Cycle	Time [min]	Yield [%][b]
1	30	94
2	35	93
3	70	93
4	80	93
5	90	94
6	120	95
7	120	92
8	150	94
9	150	93
10	180	94
11	180	93
12	210	95
13	240	94
14	270	92
15	300	93

[a] *Reaction conditions:* **4** (0.3 mmol), HOTf (0.03 mmol), and the PS-supported gold(I) complex **3** (36 mg, ca. 0.018 mmol Au) in wet CH_2Cl_2 (6 mL, 0.05 M) at room temperature.

[b] Isolated yield.

The reactivity/stability of the triazole-Au(I) complexes (e.g., **A**) has been attributed to the dynamic coordination of the triazole with Au(I) cation; the real catalytic species is still supposedly $Ph_3PAu(I)$.[5] After 15 cycles of reaction **4**→**5**, the Au atomic% in the recovered PS-supported gold(I) complex **3** had dropped to 0.30% (from the original 0.79%) as measured by XPS, indicating a lose of ~6% Au per cycle. To examine if the leached Au played the catalytic role in the transformation, the resin **3** was filtered off when half the amount of **4** was converted into **5**, the transformation of the remaining **4** in the filtrate was hardly observable on TLC, indicating that the PS-supported gold(I) complex **3** played the decisive role in the reaction.

The morphology of the recovered catalyst **3** (after 15th use in reaction **4**→**5**) together with the original **3** and the PS-triazole resin **2** were observed by scanning electron microscopy (SEM). As shown in Figure 1, the PS-triazole resin **2** remained largely spherical as the underivatized PS resin, the spherical beads fell apart after formation of the gold(I) complex in **3**, and the particles in **3** aggregated after several cycles of re-

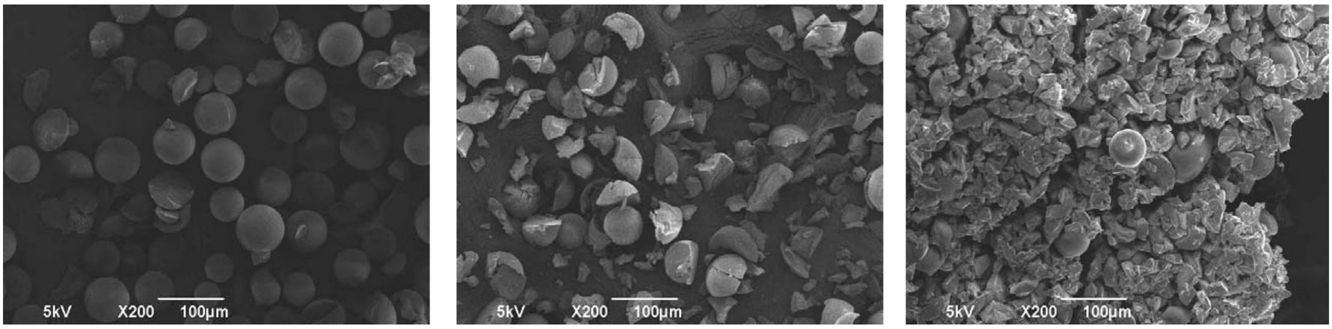


Figure 1. SEM of the PS-triazole resin **2** (*left*), the PS-supported gold(I) catalyst **3** (*middle*), and the recovered catalyst **3** after 15th use in reaction **4**→**5** (*right*).

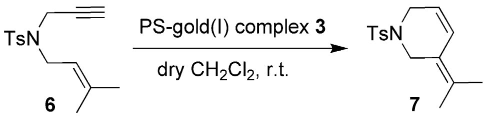
action. The aggregation of the PS-supported gold(I) complex might also account partly for the degradation of the catalytic activity.

We then examined the utility of the present PS-supported gold(I) complex **3** for the cyclization of 1,6-enyne **6** (to give **7**), a transformation well documented by Echavarren et al. with $Ph_3PAuSbF_6$ as an effective catalyst.[9] As shown in Table 3, complex **3** catalyzed this reaction effectively, and could be reused after simple filtration and washing with the solvent. At the first three cycles, the reaction proceeded smoothly, leading to product **7** in $>90\%$ yield within 90 min, however, the reaction with the recycled catalyst **3** became considerably more sluggish thereafter.

Lastly, the PS-supported gold(I) complex **3** was applied to the Hashmi phenol synthesis *via* alkyne-furan arrangement (i.e., **8**→**9**).[5b,10] As the results in Table 4 show, complex **3** was also demonstrated to be effective and reusable in this transformation. The reaction rate became considerably slower after each cyclization of the catalyst, nevertheless, within the tested 5 cycles, the yields of the phenol product **9** could be maintained at $>80\%$.

In summary, we have immobilized, for the first time, a homogeneous gold(I) catalyst onto a polystyrene support, the resulting PS-benzotriazole-gold(I) complex **3** showed comparable catalytic activities as those of the homogenous gold(I) catalysts and recyclability at least in the tested model transformations, including the tandem 3,3-rearrangement and Nazarov reaction of enynyl acetate **4**, the cyclization of 1,6-enyne **6**, and the rearrangement of alkyne-furan **8**. These preliminary results reveal the potential of the solid-supported gold(I) catalysts in future practical applications of the flourishing gold(I)-catalyzed chemical transformations.

Table 3. The cyclization of 1,6-enyne **6** catalyzed by the PS-supported gold(I) complex **3** and the recycling experiments.[a]

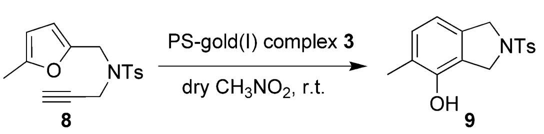


Cycle	Time [min]	Yield [%][b]
1	30	93
2	60	93
3	90	90
4	180	81
5	420	75
6	1440	70

[a] *Reaction conditions:* **6** (0.3 mmol) and the PS-supported gold(I) complex **3** (36 mg, *ca.* 0.018 mmol Au) in dry CH_2Cl_2 (3 mL, 0.1 M) at room temperature under an argon atmosphere.

[b] Isolated yield.

Table 4. Synthesis of phenol **9** *via* rearrangement of alkyne-furan **8** catalyzed by the PS-supported gold(I) complex **3** and the recycling experiments.[a]



Cycle	Time [min]	Yield [%][b]
1	5	88
2	30	86
3	180	82
4	2160	85
5	2160	80

[a] *Reaction conditions:* **8** (0.2 mmol) and the PS-supported gold(I) complex **3** (24 mg, *ca.* 0.012 mmol Au) in dry nitromethane (10 mL, 0.02 M) at room temperature under an argon atmosphere.

[b] Isolated yield.

Experimental Section

Preparation of the PS-benzotriazole-Gold(I) Complex 3

To a solution of benzotriazole (1.4 g, 12 mmol) in toluene (20 mL) were added Merrifield resin **1** (chloromethyl-polystyrene resin, 1% DVB, 200–400 mesh, 1.2 mmol$\cdot$g^{-1} as Cl, 2.0 g). After being refluxed for 48 h, the mixture was poured into ethyl ether (200 mL). The precipitate was filtered, washed with ethyl ether several times, and then dried under oil pump vacuum for 12 h to provide the PS-benzotriazole resin **2** as a pale yellow powder; yield: 2.2 g.

To a suspension of the resin **2** (0.6 g) in anhydrous CH_2Cl_2 (10 mL), PPh_3AuSbF_6 [freshly prepared as a CH_2Cl_2 solution (10 mL) by mixing PPh_3AuCl[13] (0.5 g, 1.0 mmol with $AgSbF_6$ (0.35 g, 1.0 mmol) followed by filtration through a celite plug to remove precipitated AgCl][7] was added at room temperature. After being stirred overnight, the precipitate was filtered, washed with CH_2Cl_2 and ethyl ether three times in turn, and dried under oil pump vacuum for 12 h to give the desired PS-supported gold (10.3 wt%) catalyst **3** as a gray powder; yield: 0.94 g.

Transformation of Enynyl Acetate 4 to Cyclopentenone 5 Catalyzed by the PS-Supported Gold(I) Complex 3 and the Recycling Experiments

To a solution of enynyl acetate **4**[8] (66 mg, 0.3 mmol) in wet CH_2Cl_2[14] (6 mL, 0.05 M) were added the PS-supported gold(I) complex **3** (36 mg, *ca.* 0.018 mmol Au) and HOTf (2.7 μL, 0.03 mmol) at room temperature with stirring. The reaction was monitored by TLC. When the reaction was over, the resin **3** was filtered, then washed with CH_2Cl_2 several times, and was used directly for the next reaction cycle. The organic phases were combined and treated with several drops of Et_3N and then concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 12/1) to give cyclopentenone **5**.

Cyclization of 1,6-Enyne 6 Catalyzed by the PS-Supported Gold(I) Complex 3 and the Recycling Experiments

Enyne **6**[11] (83 mg, 0.3 mmol) in dry CH_2Cl_2 (3 mL, 0.1 M) was added *via* a syringe to a round-bottomed flask containing the PS-supported gold(I) complex **3** (36 mg, *ca.* 0.018 mmol Au) under argon atmosphere at room temperature. The stirring continued until TLC showed the completion of the reaction. The solid was filtered, washed with dry CH_2Cl_2 for several times, and then dried under oil pump vacuum for 12 h, which was used for the next reaction cycle under similar conditions. The organic layers were combined and concentrated, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/dichloromethane = 20/1/1) to give compound **7**.

Synthesis of Phenol 9 *via* Rearrangement of Alkyne-furan 8 Catalyzed by the PS-Supported Gold(I) Complex 3 and the Recycling Experiments

To a solution of **8**[12] (60 mg, 0.2 mmol) in dry nitromethane (10 mL, 0.02 M) was added the PS-supported gold(I) complex **3** (24 mg, 0.012 mmol Au) at room temperatur under an argon atmosphere. The stirring was continued until TLC showed the completion of the reaction. The solid was filtered, washed with dry CH_2Cl_2 several times, then dried under oil pump vacuum for 12 h, and used for the next reaction cycle under similar conditions. The organic layers were combined and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/dichloromethane = 5/1/1) to provide phenol **9**.

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