



Effect of stabilizing ligands bearing ferrocene moieties on the gold nanoparticle-catalyzed reactions of arylboronic acids

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ABSTRACT

The homocoupling reaction of phenylboronic acid and demetalation reaction of ferrocenylboronic acid was inhibited and highly active, respectively, in the presence of gold nanoparticles stabilized by ligands containing ferrocene moieties.

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Nanoparticles (NPs) in catalysis have gained significant interest due to the mimicking of metal surface activation on nanoscale leading to the improvement of the efficiency and selectivity of reactions and also the recovery and recyclability of the catalysts.^{1,2} Gold nanoparticles (AuNPs) have been used as catalysts in many organic transformations^{3–5} due to their remarkable catalytic activities especially in the homocouplings of boronic acids.^{6–8} Most of the active catalysts are based on NPs stabilized by ligands with electron transfer properties⁹ or π -conjugated polymers⁷ that exhibit highly reversible redox behavior. Since the discovery of ferrocene in the 1950s, this fascinating molecule, which demonstrates reversible one-electron redox reactions, has been an attractive reagent for many chemical applications.¹⁰

Improvement of the efficiency and selectivity of reactions catalyzed by nanocatalysts can be achieved by particle size optimization and surface modification of the nanoparticles, the latter can be carried out simply by tuning the structures of the stabilizing ligands.^{11–15} In this study, the effect of ligands containing ferrocene moieties on the activities of AuNPs-catalyzed reactions of aryl boronic acids was investigated. Two substrates, phenylboronic acid (**A**) and ferrocenylboronic acid (**B**), were chosen for the reactions catalyzed by AuNPs, and two groups of stabilizing ligands, phenyl (1¹⁶) and ferrocenyl (2,¹⁷ 3,⁴,¹⁸ 5,¹⁹ and 6²⁰) groups, were utilized, Figure 1.

Here, AuNPs were prepared by a simple reduction method with stabilizing ligands consisting of a ferrocene moiety. HAuCl₄·3H₂O in THF (1 mM, 1.5 mL) and ligand **2** in THF (1 mM, 1.5 mL) were mixed without any other reducing reagent and stirred vigorously.

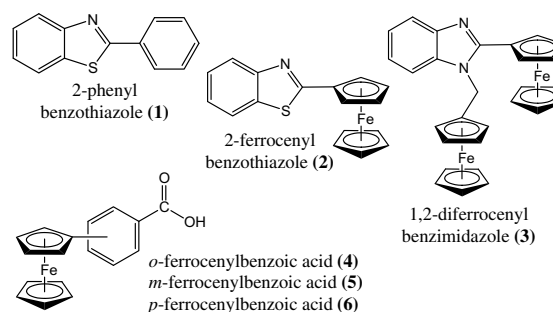


Figure 1. Stabilizing ligands in the formation of AuNPs.

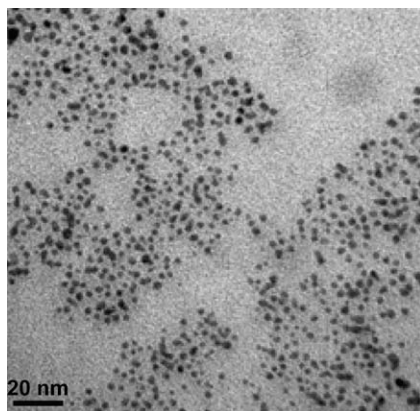
The solution became red-purple indicating the formation of AuNPs; a TEM image of the AuNPs is shown in Figure 2.

Au(III) ions can be reduced to Au(0) by ferrocene-attached ligand **2** giving a product with a ferricinium moiety which can be observed by EPR spectroscopy as a singlet paramagnetic signal at $g = 2.01$. The first-order characteristic curve for ligand **2** (Fig. 3) was observed in which the rate constant was determined by fitting to a single exponential with two adjustable parameters: the rate constant and the EPR intensity at infinite time. It should be noted that no EPR signal was observed for a mixed solution of Au(III) and ligand **1**.

From Table 1, the rates of the electron transfer were dependent on the number and position of the ferrocene moieties, binding atoms, and functional groups. AuNPs with ligand **3** were probably destabilized either by the number of ferrocene moieties or by weaker interactions between the AuNPs and nitrogen atoms of the benzimidazole moiety resulting in a lower rate of ferricinium

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$\bar{X} = 2.38 \text{ nm}$
Std. Dev = 0.99

Figure 2. The TEM micrograph of gold nanoparticles stabilized by ligand **2**. The scale bar is 20 nm.

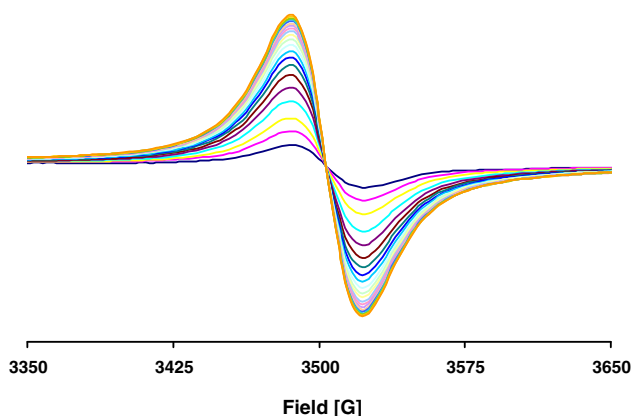


Figure 3. The kinetic EPR spectra of the ferricinium moiety generated from the reduction of Au(III) and ligand **2** were collected every 5 min for 100 min.

Table 1

The observed rate constants of ferricinium formation during the preparation of AuNPs as observed by EPR spectroscopy

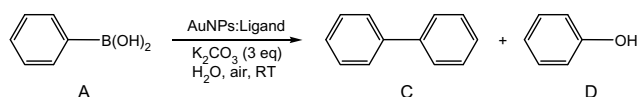
Entry	Ligand	$k \times 10^4 \text{ (s}^{-1}\text{)}$
1	2-Ferrocenylbenzothiazole (2)	4.51
2	1,2-Diferrocenylbenzimidazole (3)	0.17
3	<i>o</i> -Ferrocenylbenzoic acid (4)	2.89
4	<i>m</i> -Ferrocenylbenzoic acid (5)	9.53
5	<i>p</i> -Ferrocenylbenzoic acid (6)	6.04

formation and slower electron transfer rate. Ligands **4–6** were selected to compare with the thiazole group **2** to study the binding of the carboxylic group to AuNPs. Ligand **5** showed an excellent rate of ferricinium formation due to the *meta*-effect resulting from the electron withdrawing nature of the carboxylic acid while a slower rate was observed for ligand **4**, probably due to intramolecular interactions between the ferricinium and carboxylic groups. The higher rate of ferricinium formation using the *meta*- and *para*-isomers of ferrocenylbenzoic than that with the thiazole group indicated the presence of stronger interactions between the carboxylate groups and AuNPs probably resulting from electrostatic effects.^{1,2}

The C–C bond formation catalyzed by Au catalysts has been well exploited in synthetic chemistry.²¹ The excellent electron transfer

Table 2

Homocoupling reactions of **A** catalyzed by Au(III) and AuNPs stabilized by ligands **1–6**^a



Entry	AuNPs:Ligand	Au(III) (%)	% Yield ^b		
			A	C	D
1 ^c	AuNPs: 1	4	50	33	17
2 ^c	AuNPs: 2	4	80	14	6
3 ^c	AuNPs: 3	4	79	19	2
4 ^d	AuNPs: 4	1	86	8	6
5 ^d	AuNPs: 5	1	73	16	11
6 ^d	AuNPs: 6	1	72	19	9
7 ^c	Au(III)	4	54	37	9

^a Conditions: phenylboronic acid (0.82 mmol), K₂CO₃ (2.5 mmol), 5 mL of H₂O, and 5 mL of THF, stirred for 24 h.

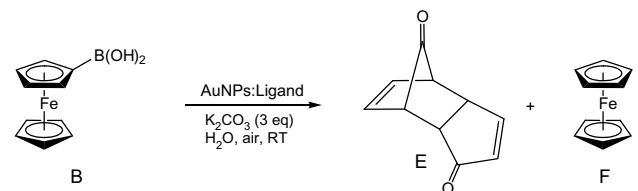
^b Estimated from ¹H NMR analysis.

^c [Au(III)] and [Ligand] = 3.13 mM.

^d [Au(III)] and [Ligand] = 0.83 mM.

Table 3

Demetalation reactions of **B** catalyzed by Au(III) and AuNPs stabilized by ligands **1–6**^a



Entry	AuNPs:Ligand	Au(III) (%)	% Yield ^b		
			B	E	F
1 ^c	AuNPs: 1	7	–	47	53
2 ^c	AuNPs: 2	7	–	>99	–
3 ^c	AuNPs: 3	7	–	>99	–
4 ^d	AuNPs: 4	2	–	>99	–
5 ^d	AuNPs: 5	2	–	>99	–
6 ^d	AuNPs: 6	2	–	>99	–
7 ^c	Au(III)	7	–	34	66

^a Conditions: ferrocenylboronic acid (0.44 mmol), K₂CO₃ (1.3 mmol), 5 mL of H₂O, and 5 mL of THF, stirred for 24 h.

^b Estimated from ¹H NMR analysis.

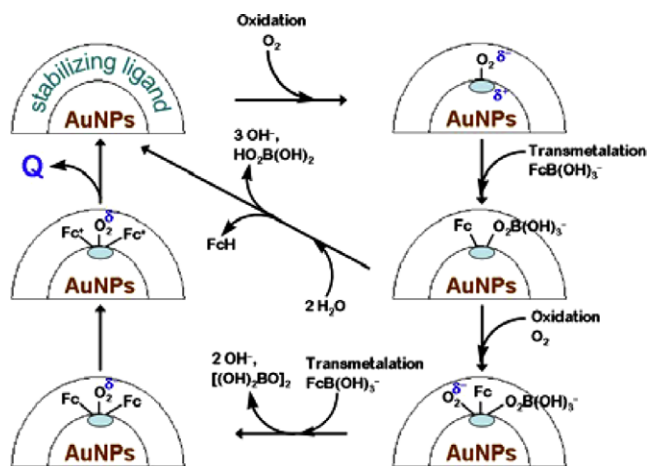
^c [Au(III)] and [Ligand] = 3.13 mM.

^d [Au(III)] and [Ligand] = 0.83 mM.

properties of ferrocene moieties were proposed here to study their activities in AuNPs-catalyzed reactions of arylboronic acids, **A** (Table 2) and **B** (Table 3), in a mixed solvent of THF/water under aerobic conditions for 24 h.

The results of the homocoupling of **A** showed similar conversions (~50%) for entries 1 and 7 (Table 2) indicating the low catalytic activity of ligand **1** while low conversions (14–28%) were observed for entries 2–6 (Table 2). It was surprising to find that the addition of stabilizing ligands containing ferrocene moieties inhibited the homocoupling of **A** even at a low %loading of Au(III).

In contrast to **A**, the AuNPs-catalyzed demetalation reactions of **B** showed excellent catalytic activities with complete conversions. Biferrocene and ferrocenyl alcohol were not observed but an unexpected dicyclopentadienone^{22–24} (**E**) and ferrocene (**F**) were obtained as decomposition products. Moreover, the catalysts containing ferrocene moieties (Table 3, entries 2–6) showed excellent selectivity giving product **E**, exclusively.



Scheme 1. Proposed mechanisms for the demetallation reaction of **B** catalyzed by AuNPs. **Q** = $Fc^+ - O - O - Fc^+$.

The mechanisms for the reactions of **B** catalyzed by AuNPs are modified from the literature⁷ and proposed as shown in Scheme 1. Initially, the oxidation by O_2 occurred on the surface of the AuNPs leading to a superoxo species. Subsequently, transmetalation of **B** produced ferrocenyl and boron peroxy adsorbed on AuNPs in which ferrocene and boron peroxide may be partly released and then circulated back to the initial step. Next, the oxidation and 2nd-transmetalation occurred sequentially providing two ferrocenyl and a superoxo group on the AuNPs. Two ferricinium species were next formed and then bridged by the superoxo species to produce the species **Q** which was further oxidized to form dicyclopentadienone (**E**) as reported.^{22–24} It should be noted that this is a rare example of the demetallation of ferrocene derivatives catalyzed by gold nanocatalysts in which a bicyclic ketone can be synthesized quantitatively on large scale with a good yield for potential applications in host-guest chemistry.

The low conversions for the homocouplings of **A** inhibited by AuNPs:2–6 were further investigated in the reactions catalyzed by AuNPs stabilized by polyanilines²⁵ and its derivatives (**7M–10M**), the structures of the polymers are shown in Figure 4. In addition, ferricinium-doped polyaniline and its derivatives (**7N–10N**)

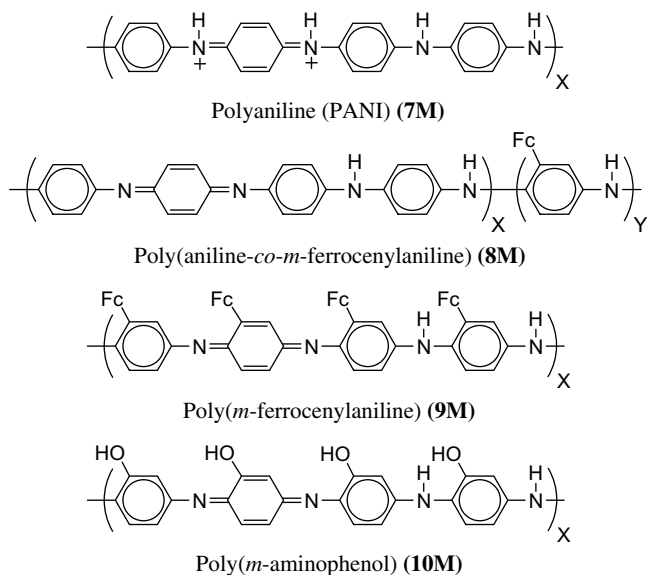


Figure 4. Polyaniline (PANI) and its derivatives.

Table 4

Homocoupling reactions of **A** catalyzed by AuNPs stabilized by polyaniline and its derivatives (**7–10**)^a

Entry	AuNPs:Polymer	Au(III) %	% Yield ^b		
			A	C	D
1	AuNPs: 7M	4	90	7	3
2	AuNPs: 8M	4	2	61	37
3	AuNPs: 9M	4	—	60	40
4	AuNPs: 10M	4	2	53	45
5	AuNPs: 7N^c	4	93	7	—
6	AuNPs: 8N^c	4	95	5	—
7	AuNPs: 9N^c	4	84	12	4
8	AuNPs: 10N^c	4	95	5	—

^a Conditions: phenylboronic acid (0.82 mmol), Au(III) (0.03 mmol), polymer (12.34 mg), K_2CO_3 (2.5 mmol), 5 mL of H_2O , and 5 mL of THF, stirred for 24 h.

^b Estimated from 1H NMR analysis.

^c N = ferricinium-doped polymer (50 mol % of monomer).

were also used for the stabilization of AuNPs. The result of the reactions of **A** catalyzed by AuNPs:polymers (**7–10**) are shown in Table 4.

The ferricinium-doped polymers (Table 4, entries 5–8) gave very low conversions (5–16%). However, it was unexpected that the polyaniline (entry 1) would show a similar result. The form of polyaniline (**7M**) used in this experiment was as the emeraldine salt²⁶ with a positive charge on the backbone of the polymer. The lower positive charge density on the backbone of polymers (**8M–9M**) was evident from the smaller EPR intensities compared to polyaniline (**7M**). Hence, it is proposed here that cationic species destabilized the transition state during homocoupling of **A**. The electrostatic interactions^{1,2} between ferricinium or cations and the peroxy species might inhibit the transmetalation of **A**.

In summary, we have demonstrated the catalytic activities of AuNPs stabilized by ligands containing ferrocene moieties in the homocoupling of **A** and demetallation of **B**.

General procedure for reactions of boronic acid: Arylboronic acid (1 equiv) and K_2CO_3 (3 equiv) were mixed in 5 mL of H_2O . Gold nanoparticles in 5 mL of THF were added, and the reaction mixture was stirred vigorously at room temperature under aerobic conditions for 24 h. The reaction was quenched with 1 M HCl solution and the products were extracted with EtOAc (20 mL \times 3). The combined organic layer was dried over Na_2SO_4 and evaporated in vacuo. The resulting mixture was analyzed by 1H NMR spectroscopy.

Acknowledgments

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Supplementary data

Experimental methods, kinetic curves, and NMR spectra of **3** and dicyclopentadienone (**E**) are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.10.040.

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