

Oxidative homo-coupling of potassium aryltrifluoroborates catalyzed by gold nanocluster under aerobic conditions

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Abstract

Gold(0) nanoclusters, stabilized by poly(*N*-vinyl-2-pyrrolidone) (**Au:PVP-*n***), catalyzed the oxidative homo-coupling reaction of potassium aryltrifluoroborate in water under air. Catalytic activity was dependent on the size of clusters. The smallest cluster **Au:PVP-1** ($d_{av} = 1.3 \pm 0.3$ nm) gave the highest activity, while **Au:PVP-7** ($d_{av} = 9.5 \pm 1.0$ nm) did not catalyze the homo-coupling. The catalyst was reusable for several times. Positively charged surface on the Au cluster, generated by the adsorption of molecular oxygen, would be the active site of the catalysis.

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Keywords: Gold nanocluster; Aerobic oxidation; Aryltrifluoroborate; Homo-coupling

1. Introduction

Since Haruta and co-workers reported that supported gold nanoclusters (NCs) exhibited high activity toward the oxidation of CO to CO₂ [1], heterogeneous catalyst system consisting of Au-NC has been extensively studied from both scientific and practical points of view [2]. In contrast, potentiality of colloidal Au-NCs stabilized by organic compounds/polymers as *quasi*-homogenous catalyst directly applicable to precise organic synthesis, still remains undeveloped subject [2,3]. Previously, we have reported preparative methods of Au nanoclusters with various sizes ranging from 1.3 ± 0.3 nm to 9.5 ± 1.0 nm, stabilized by water-soluble polymer, poly(*N*-vinyl-2-pyrrolidone) (**Au:PVP-*n***) using rapid reduction [4] and seed-mediated growth [5,6]. It was found that **Au:PVP-*n*** worked as an excellent *quasi*-homogenous catalyst which promoted the aerobic oxidations: oxidative homo-coupling reaction of arylbo-

ronic acids [4], oxidation of benzylic alcohols [5], and generation of H₂O₂ in the presence of ammonium formate [6] in water under ambient conditions. We have also demonstrated that the catalytic activity was strongly dependent on the size of the clusters, that is, the smaller cluster showed superior activity.

To the best of our knowledge, the oxidative homo-coupling of organoboron compounds [4] is the first and only example of the Au-NC catalyzed carbon–carbon bond forming reaction. The homo-coupling of organoboron compounds has been recognized as one of the convenient methods especially for the preparation of symmetrical biaryls [7,8]. In most cases Pd(II) catalyst system [7–9] has been utilized, therefore Suzuki–Miyaura type cross-coupling reaction should often compete against the homo-coupling in the presence of organohalide compounds. Some metallic oxidants such as Cu(II) [9a,10] or Mn(III) [11] have also been utilized. After our report, Au(III) supported on CeO₂ [12] and Au(III) Schiff base-complexes [13] were reported to promote the homo-coupling selectively without formation of Suzuki–Miyaura coupling product. These results indicate that Au catalyst would possess the charac-

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teristic feature for the specific promotion of homo-coupling. In this paper we report selective homo-coupling reaction of potassium aryltrifluoroborates [14] catalyzed by **Au:PVP** in water under ambient conditions.

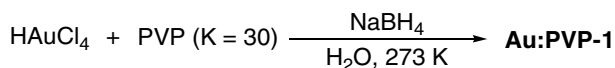
2. Results and discussion

2.1. Preparation of **Au:PVP-n**

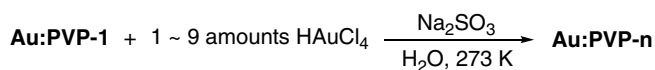
Preparation of **Au:PVP-n** of various sizes was performed according to the reported procedure. Rapid reduction of HAuCl_4 solution by NaBH_4 at 273 K in the presence of PVP (K-30) afforded the smallest cluster **Au:PVP-1** with good reproducibility (Scheme 1) [4]. The larger clusters **Au:PVP-n** ($n = 2-7$) were prepared by the seed-mediated growth method (Scheme 2) [5,6]. It is noteworthy that Au(III) is not reduced to Au(0) by Na_2SO_3 in the absence of Au-NC. The average diameters of **Au:PVP-n** used in this paper are listed in Table 1.

2.2. **Au:PVP-1** catalyzed homo-coupling reaction of $\text{PhB}(\text{OH})_2$ and PhBF_3K

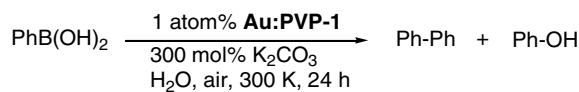
As reported in 2004, **Au:PVP-1** catalyzed the aerobic oxidation of $\text{PhB}(\text{OH})_2$ in aqueous K_2CO_3 solution under aerobic conditions, giving two products, biphenyl (Ph-Ph) and phenol (Ph-OH) (Scheme 3) [4]. The latter product may not have been produced by direct Au-catalyzed processes but by the oxidation of $\text{PhB}(\text{OH})_2$ with H_2O_2 co-produced in the coupling reaction. Time-dependent product ratio was monitored in the reaction of $\text{PhB}(\text{OH})_2$ and the results are shown in Fig. 1. Phenol was not detected at the early stage of the reaction, while the yield of phenol was drastically increased after the formation of Ph-Ph. Indeed, phenol can be selectively formed in the presence of appropriate reductant such as HCO_2NH_4 [6]. It is well known that the conversion of C–B bond to C–O bond by $\text{H}_2\text{O}_2/\text{OH}^-$ involves the



Scheme 1.



Scheme 2.



Scheme 3.

nucleophilic attack of HOO^- to form the hydroperoxyborate intermediate (R_3BOOH^-) and 1,2-migration of organic group (R) to give the C–O bond product [15]. In order to achieve the selective reaction for the biphenyl formation, generation of such a peroxyborate intermediate should be suppressed.

Potassium aryltrifluoroborates (ArBF_3K) are stable salts and has been utilized for the Suzuki–Miyaura coupling reactions [16]. In some cases the cross-coupling reaction using ArBF_3K did not require the addition of base but proceed under the neutral condition [17]. The fact indicated that the homo-coupling of ArBF_3K might also occur under neutral condition by virtue of slow ligand transfer between F^- and HOO^- . The results of the reaction of PhBF_3K with **Au:PVP-1** under the various conditions are listed as Table 2.

As shown in entries 1 and 2, the reaction was not influenced by the pH of the solution starting from $\text{PhB}(\text{OH})_2$, giving both biphenyl and phenol in approximately 3:1 ratio. The reaction using PhBF_3K was found to be dependent on the pH of the solution (entries 3–7). When PhBF_3K was treated with 1 atom% of **Au:PVP-1** in K_2CO_3 solution at 320 K under air, both biphenyl and phenol are obtained in approximately 3:1 ratio, indicating rapid ligand exchange between F^- and HOO^- under the conditions. As expected, in weakly basic to neutral solutions (pH 9.18–6.86), biphenyl was yielded as a sole product and phenol was not detected by ^1H NMR spectroscopy. In contrast, no oxidation occurred under the slightly acidic (pH 4.01) conditions (entry 7).

Next, reaction rate was monitored at various temperature under pH 6.86 solution condition (entries 8–11). At 300 K the reaction was slightly slower than that from $\text{PhB}(\text{OH})_2$. The reaction did not completed and phenol was also produced in 2% yield after 24 h. At 310 K, 320 K, and 370 K, the reaction proceeded quantitatively within 16 h, 10 h, and 1 h, respectively. Since the average size of **Au:PVP-1** (1.3 ± 0.3 nm) is estimated to be 55mer [4], TOF of the reaction at 370 K is calculated as $>50 \text{ h}^{-1} \text{ atom}^{-1}$ and $>2750 \text{ h}^{-1} \text{ cluster}^{-1}$. As described above, selective and quantitative formation of biphenyl was realized in the **Au:PVP-1** catalyzed aerobic oxidation reaction starting from PhBF_3K in place of $\text{PhB}(\text{OH})_2$ under the neutral condition (see Scheme 4).

Table 1
Average size of **Au:PVP-n**

<i>n</i>	1	2	3	4	5	6	7
Average diameter (nm)	1.3 ± 0.3	2.3 ± 0.4	3.3 ± 0.5	4.3 ± 0.6	4.7 ± 0.5	5.9 ± 0.5	9.5 ± 1.0

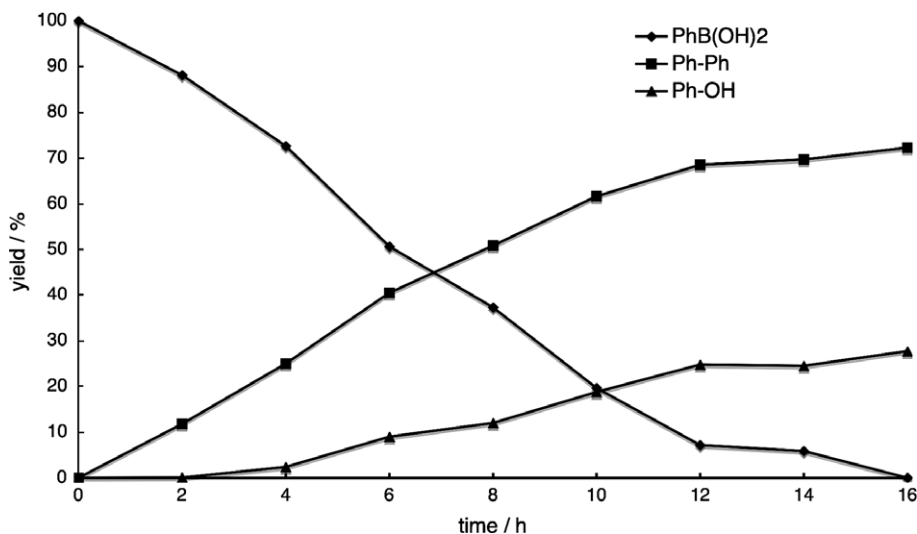
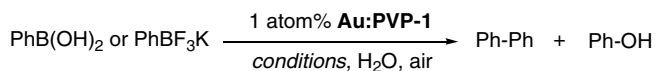


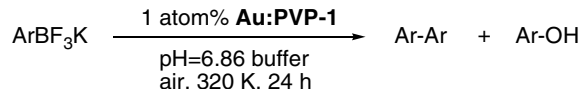
Fig. 1. Time-dependent product ratio of the Au:PVP-1 catalyzed homo-coupling of PhB(OH)₂.

Table 2
Optimization of the Au:PVP-1 catalyzed homo-coupling of phenylboron derivatives

Entry	Organoboron	Solution	Temperature (K)	Time (h)	Biphenyl (%)	Phenol (%)
1	PhB(OH) ₂	K ₂ CO ₃ aq.	320	24	72	27
2	PhB(OH) ₂	pH 6.86 buffer	320	24	75	24
3	PhBF ₃ K	K ₂ CO ₃ aq.	320	24	76	24
4	PhBF ₃ K	pH 9.18 buffer	320	24	>99	–
5	PhBF ₃ K	pH 7.41 buffer	320	24	>99	–
6	PhBF ₃ K	pH 6.86 buffer	320	24	>99	–
7	PhBF ₃ K	pH 4.01 buffer	320	24	–	–
8	PhBF ₃ K	pH 6.86 buffer	300	24	85	2
9	PhBF ₃ K	pH 6.86 buffer	310	16	>99	–
10	PhBF ₃ K	pH 6.86 buffer	320	10	>99	–
11	PhBF ₃ K	pH 6.86 buffer	370	1	>99	–



Scheme 4.



Scheme 5.

2.3. Substituent effect

Substituent effect on aryl group of borate was examined under the optimized reaction conditions at 320 K for 24 h (Table 3).

Steric effect was monitored using tolyl-substituted borates as shown in entries 2–4. As reported previously, remarkable effect was observed in the reaction of *ortho*-, *meta*-, and *para*-tolylboronic acid. That is, *o*-CH₃C₆H₄B(OH)₂ was not oxidized under Au:PVP-1 catalyzed conditions, yielding the corresponding bitolyl in only 4% after 24 h. The result was in sharp contrast with the fact that Pd(II) or Au(III) ions do catalyze the homo-coupling of *o*-CH₃C₆H₄B(OH)₂ [4]. Similar phenomena were also observed using tolyl-substituted trifluoroborates. Only 14% of bitolyl was produced with 80% recovery of boronic

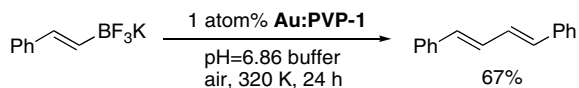
Table 3
Substituent effect

Entry	Ar	ArBF ₃ K (%)	Ar-Ar (%)	Ar-OH (%)
1	C ₆ H ₅	–	>99	–
2	<i>p</i> -CH ₃ C ₆ H ₄	–	>99	–
3	<i>m</i> -CH ₃ C ₆ H ₄	–	95	4
4	<i>o</i> -CH ₃ C ₆ H ₄	80 ^a	14	–
5	<i>p</i> -CH ₃ OC ₆ H ₄	–	89	11
6	<i>p</i> -FC ₆ H ₄	–	>99	–
7 ^b	<i>p</i> -BrC ₆ H ₄	–	98	1
8	<i>p</i> -CF ₃ C ₆ H ₄	–	>99	–

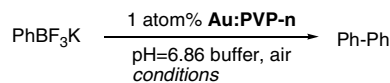
^a Recovered as ArB(OH)₂.

^b Other products derived by the reaction in which bromo group participates are not detected.

acid in the reaction of *o*-CH₃C₆H₄BF₃K even after 24 h at 320 K. As for *meta* or *para* derivatives, quantitative oxidation proceeded under the same conditions.



Scheme 6.



Scheme 7.

Electronic effect was monitored using various *para*-substituted substrates, but no apparent tendency was found (entries 5–8). Yield of ArOH was increased in the electron donative *p*-CH₃OC₆H₄BF₃K reaction. As shown in entries 7 and 8, however, quantitative yield was obtained in the reaction of more electron accepting CF₃-substituted borate, while 1% of ArOH was detected in the less accepting Br-substituted borate.

It should be pointed out that bromo group on arene was tolerant under the reaction conditions as shown in entry 7. Haloarenes were not capable for oxidative addition to Au(0) cluster, generating Ar-Au intermediate [18]. Such a resistant character of Au nanocluster toward the oxidative addition of haloarenes is in sharp contrast with the reactivity of Pd:PVP nanocluster, which readily catalyzes Suzuki–Miyaura type cross-coupling reaction [19,20] (see Scheme 5).

The **Au:PVP-1** catalyzed reaction condition was also applicable to the alkenylborate as a substrate. The reaction of potassium 2-(*E*)-phenylethenyltrifluoroborate under the above conditions afforded the homo-coupling product, 1,4-(*E,E*)-diphenylbutadiene, in 67% yield (Scheme 6).

2.4. Size effect of Au cluster

We have already demonstrated remarkable differences dependent on the cluster size in catalytic activity toward homo-coupling of PhB(OH)₂ [4], oxidation of benzylic alcohols [5], and generation of H₂O₂ [6]. Unfortunately it was unable to investigate quantitative kinetic studies in the present reaction due to the size growth of the clusters during the reaction as shown in the following section. Therefore, the size effect was evaluated by comparing the yields of biphenyl in the 1 atom% **Au:PVP-*n*** catalyzed reaction of PhBF₃K at three different reaction conditions, 15 h at 300 K, 15 h at 320 K, and 24 h at 320 K (Table 4). No side reaction such as a formation of PhOH was observed in most of the reactions except for **Au:PVP-6** catalyst for 24 h at 320 K.

Biphenyl was obtained when **Au:PVP-1–3** were used as a catalyst at 300 K for 15 h in 32%, 16%, and 9% yield, respectively. Normalization by the surface areas of the corresponding nanoclusters by assuming spherical shapes with the diameters gave the relative reaction rate as **PVP-1:PVP-2:PVP-3** = 1:0.88:0.71. Only trace amounts of biphenyl (lower than 1%) were detected by ¹H NMR under the **Au:PVP-4** or **-5** catalyzed reaction conditions. No biphenyl formation was observed using **Au:PVP-6** or **-7**. These results indicated that the smaller clusters showed superior reactivity to the larger clusters.

Table 4
Size effect of Au cluster

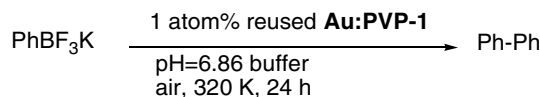
Entry	Catalyst	Yield (300 K, 15 h) (%)	Yield (320 K, 15 h) (%)	Yield (320 K, 24 h) (%)
1	Au:PVP-1 (1.3 ± 0.3 nm)	32	>99	>99
2	Au:PVP-2 (2.3 ± 0.4 nm)	16	50	>99
3	Au:PVP-3 (3.3 ± 0.5 nm)	9	39	>99
4	Au:PVP-4 (4.3 ± 0.6 nm)	Trace	23	89
5	Au:PVP-5 (4.7 ± 0.5 nm)	Trace	17	66
6	Au:PVP-6 (5.9 ± 0.6 nm)	–	10	34 ^a
7	Au:PVP-7 (9.5 ± 1.0 nm)	–	–	–

^a Phenol was also detected in 3% yield.

At 320 K, the reaction was completed within 10 h using **Au:PVP-1** (see Table 2 entry 10), while the yields were diminished to 50%, 39%, 23%, 17%, and 10%, respectively, using **Au:PVP-2–6** catalysts even after 15 h stirring. In particular, **Au:PVP-7** ($d_{av} = 9.5 \pm 1.0$ nm) no longer possessed the catalytic activity. However, from the practical viewpoint, **Au:PVP-2** ($d_{av} = 2.3 \pm 0.4$ nm) and **Au:PVP-3** ($d_{av} = 3.3 \pm 0.5$ nm) were also applicable to accomplish the reaction quantitatively by prolonging the reaction time to 24 h at 320 K, although **Au:PVP-1** ($d_{av} = 1.3 \pm 0.3$ nm) obviously showed the highest performance (see Scheme 7).

2.5. Reusability

Au:PVP catalyst was able to be recovered by centrifugal ultrafiltration. Reusability of **Au:PVP-1** was tested by the reaction of PhBF₃K (Scheme 8). Reaction conditions were set up at 320 K for 24 h on the basis of the result in Section 2.4, and the results with TEM images of the recovered nanoclusters are shown in Table 5 and Fig. 2. Apparent size growth was observed after the first cycle from 1.3 ± 0.3 nm to 2.3 ± 0.7 nm. In contrast, average size of



Scheme 8.

Table 5
Reusability of **Au:PVP-1**

	Yield (%)	<i>d</i> (nm)
First cycle	>99	1.3 ± 0.3 → 2.3 ± 0.7
Second cycle	>99	2.3 ± 0.7 → 2.3 ± 0.7
Third cycle	98	2.3 ± 0.7 → 2.4 ± 0.7

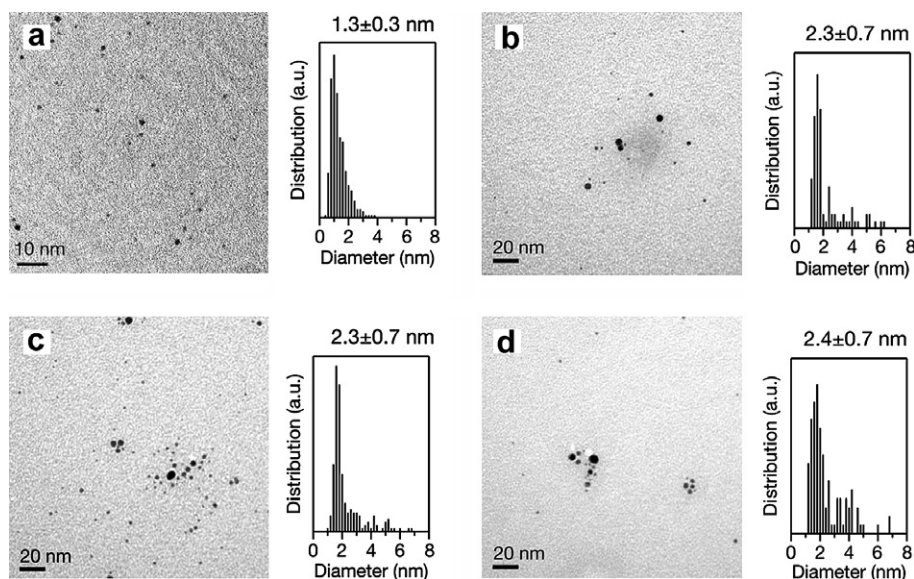


Fig. 2. Typical TEM images and cluster size distributions of **Au:PVP-1** (a) and recycled catalyst after (b) first, (c) second, and (d) third cycles.

the cluster did not change appreciably after second cycle; 2.3 ± 0.7 nm and 2.4 ± 0.7 nm in the second and third cycles, respectively. Similar phenomenon was also obtained in the PhB(OH)_2 homo-coupling reaction [4]. As described in Section 2.4, gold clusters of 2–3 nm in size still possess enough catalytic activity toward homo-coupling of PhBF_3K so that the reaction proceeded quantitatively at 320 K for 24 h. In fact, biphenyl was obtained quantitatively both in the first and second cycle, and in 98% yield in the third cycle. The reason why the activity of the third cycle catalyst was slightly diminished was probably due to the formation of gigantic clusters over 6 nm, which are inert in the reaction. In conclusion, **Au:PVP-1** was found to be applicable as a reusable catalyst at least for several times.

2.6. Possible mechanisms

As described above, **Au:PVP** showed excellent catalytic activities toward the aerobic oxidations. After our report, some heterogeneous and homogeneous Au(III) catalysts were found to promote aerobic oxidations such as homo-coupling of ArB(OH)_2 [12,13] or benzylic alcohols [21] in a similar fashion. Very recently, Corma et al. reported that Au(I) Schiff base complexes do catalyze Suzuki–Miyaura coupling predominantly whereas Au(III) complexes with same ligand catalyze only homo-coupling [22]. These facts imply that the reactivity of **Au:PVP** clusters rather resembles to that of Au(III) species. However, as confirmed in the previous study, gold in **Au:PVP** is in essentially zero valence state and contamination of ionic species such as AuX_n is not detected by XPS and other measurements [4]. Remarkable interference by *ortho* substitution (Section 2.3) also indicates that active catalytic site would not be atomic/ionic gold, which would possibly be leached out through the reaction, but the two dimensional surface of Au(0) cluster. On

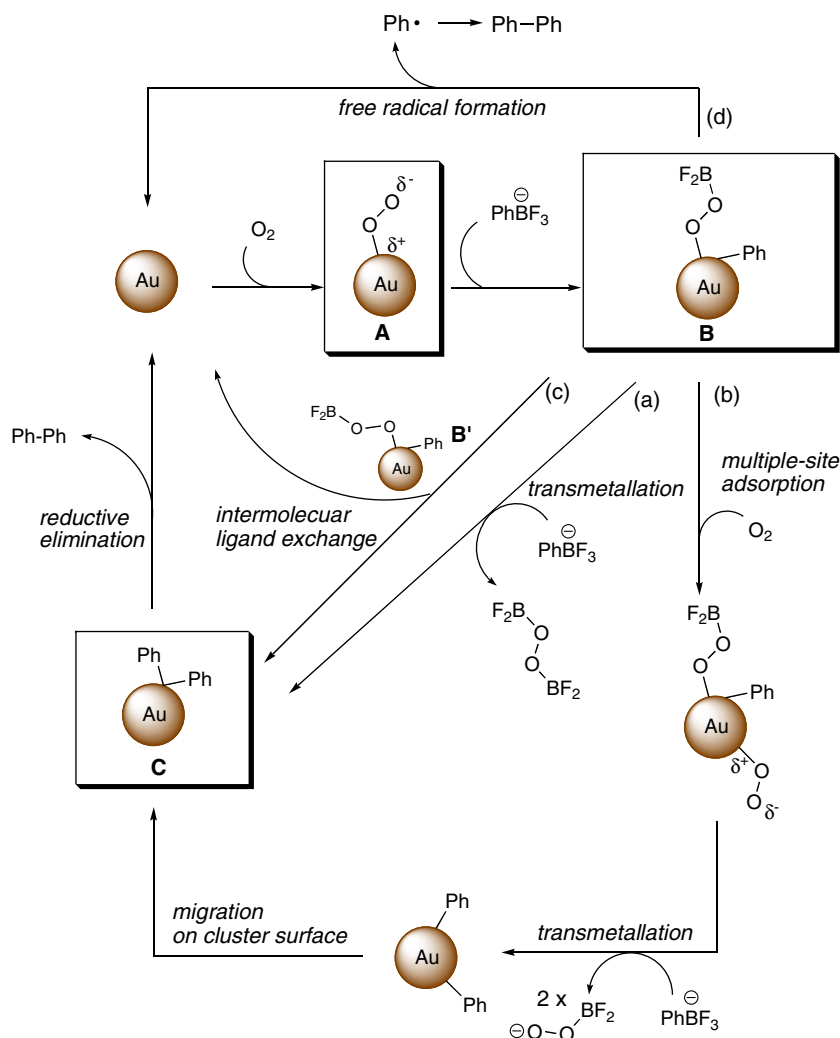
the contrary, it has been proposed that atomic Pd species leached out from the clusters are involved as the real catalyst in Pd(0) nanocluster-catalyzed reaction [23].

It is known that nanosized gold cluster readily adsorbs O_2 , generating superoxo complex-like intermediate [24]. Therefore, unique character of **Au:PVP** as an aerobic oxidation catalyst is reasonably explained in such a way that positively charged site on surface of Au cluster (**A**) would be generated by O_2 adsorption (Scheme 9). Positively charged Au site is likely to show a similar reactivity as ionic Au such as Au(III) and to undergo the attack of nucleophile such as PhBF_3K , generating Au–C bond (**B**) as equal as *transmetallation*. On the other hand, larger clusters such as **Au:PVP-7**, which scarcely adsorb O_2 , may not undergo nucleophilic attack.

Several reaction pathways are plausible once the Au–C intermediate **B** is generated and the schematic mechanisms are drawn in Scheme 9. Pathway (a) involves second nucleophilic attack (*transmetallation*) on the same site according to the hypothesis that the site where aryl group attaches is still positively charged due to the coordination of peroxy group. Pathway (b) is based on the assumption that multi-active sites exist on the same cluster. After multiple organic groups adsorb onto the same cluster, the organic groups migrate on the surface of Au cluster. Collision of each group at the same site (**C**) affords spontaneously reductive elimination. At present other mechanisms such as intermolecular ligand transfer (c) [25] or radical coupling (d) [11,26] cannot be excluded. Further study should be required to clarify the mechanism.

3. Summary

In summary, we have demonstrated that **Au:PVP-1** works as a selective, quantitative, and reusable catalyst for the homo-coupling reaction of potassium aryltrifluo-



Scheme 9. Possible mechanisms.

robates in neutral aqueous media under ambient condition. The reaction can be carried out at reflux conditions and the estimated TOF at 370 K is more than $2750 \text{ h}^{-1} \text{ cluster}^{-1}$. Characteristic feature of **Au:PVP** catalyst is that it behaves as if it is positively charged, not as zero-valent metals. For example, haloarenes do not oxidatively add to **Au:PVP**, which realizes the selective homocoupling with prevention of competitive Suzuki–Miyaura type cross-coupling. Further improvement by changing the stabilizing polymer from PVP to proper polymers/molecules would lead us to develop more precise and robust catalyst for synthetic organic chemistry.

4. Experimental

4.1. General

Potassium aryltrifluoroborates were prepared according to the literature procedure [14]. Other reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. The water is of a Milli-Q grade. The ¹H NMR spectra were recorded on

a JEOL Lambda 400 (400 MHz) spectrometer. UV–Vis spectra were obtained by using a Hitachi U-2010 spectrophotometer. Transmission electron microscopy (TEM) images were recorded with electron microscopes operated at 100 kV (Hitachi H-7500). Preparative thin layer chromatography (PTLC) was conducted on silica gel (Wako gel B-5F).

Preparation of **Au:PVP-*n*** was followed by the reported procedure [4–6].

4.2. General procedure of **Au:PVP-*n*** catalyzed homocoupling reaction of aryltrifluoroborate

All the reaction was carried out using an EYELA PPS-2510. A test tube ($\varnothing = 30 \text{ mm}$) was placed with ArBF₃K (0.25 mmol) and 3 mL of pH 6.86 phosphate buffer (Wako Pure Chemical Industries). The aqueous solution of **Au:PVP-*n*** (0.5 mM, 5 mL, 1 atom%) was added and the reaction mixture was stirred ($1300 \pm 5 \text{ rpm}$) at a given temperature. The reaction was quenched by adding 5 mL of AcOEt and the aqueous phase was extracted twice with 10 mL of AcOEt. The combined organic phase was dried

over Na₂SO₄, and evaporated in vacuo. Products were characterized by ¹H NMR. If necessary, further purification was performed by PTLC.

All products are known compounds and their ¹H NMR spectra are in good accordance with those of authentic samples.

4.3. Recycle experiment

All the reaction was carried out according to the standard procedure described in Section 4.2. After quenching and extraction with AcOEt, the aqueous phase was filtered and deionized three times (10 mL H₂O) by using centrifugal ultrafiltration (Vivascience, Vivaspin 20) featuring a membrane with a cutoff molecular-weight of 10 kDa. The deionized hydrosol of Au:PVP was diluted to 5 mL and was used for the next cycle. Yields of the products were determined according to the standard procedure above.

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References

- [1] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, *J. Catal.* 115 (1989) 301.
- [2] (a) M. Haruta, *Nature* 437 (2005) 1098;
(b) G. Schmid, B. Corain, *Eur. J. Inorg. Chem.* (2003) 3081;
(c) D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, D.W. Knight, G.J. Hutchings, *Science* 311 (2006) 362.
- [3] D. Astruc, F. Lu, J.R. Aranzaes, *Angew. Chem., Int. Ed.* 44 (2005) 7852.
- [4] H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, T. Tsukuda, *Langmuir* 20 (2004) 11293.
- [5] (a) H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, *J. Am. Chem. Soc.* 127 (2005) 9374;
(b) H. Tsunoyama, H. Sakurai, T. Tsukuda, *Chem. Phys. Lett.* 429 (2006) 528.
- [6] H. Sakurai, H. Tsunoyama, T. Tsukuda, *Trans. Mater. Res. Soc. Jpn.* 31 (2006) 521.
- [7] M. Moreno-Mañas, M. Pérez, R. Pleixats, *J. Org. Chem.* 61 (1996) 2346.
- [8] H. Hata, H. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* 127 (2005) 8264.
- [9] (a) K.A. Smith, E.M. Campi, W.R. Jackson, S. Marcuccio, C.G.M. Naeslund, G.B. Deacon, *Synlett* (1997) 131;
(b) M.S. Wang, X.L. Zhang, *Tetrahedron Lett.* 42 (2001) 4087;
(c) J.P. Perrish, Y.C. Jung, R.J. Floyd, K.W. Jung, *Tetrahedron Lett.* 43 (2002) 7899;
(d) H. Yoshida, Y. Yamaryo, J. Ohshita, A. Kunai, *Tetrahedron Lett.* 44 (2003) 1541;
(e) S. Punna, D.D. Díaz, M.G. Finn, *Synlett* (2004) 2351.
- [10] A.S. Demir, Ö. Reis, M. Emrullahoglu, *J. Org. Chem.* 68 (2003) 10130.
- [11] A.S. Demir, Ö. Reis, M. Emrullahoglu, *J. Org. Chem.* 68 (2003) 578.
- [12] S. Carrettin, J. Guzman, A. Corma, *Angew. Chem., Int. Ed.* 44 (2005) 2242.
- [13] C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, *Chem. Commun.* (2005) 1990.
- [14] E. Vedejs, R.W. Chapman, S.C. Fields, S. Lin, M.R. Schrimpf, *J. Org. Chem.* 60 (1995) 3020.
- [15] A. Pelter, K. Smith, H.C. Brown, *Borane Reagents*, Academic Press, London, 1988.
- [16] (a) G.A. Molander, B. Biolatto, *Org. Lett.* 4 (2002) 1867;
(b) G.A. Molander, B. Biolatto, *J. Org. Chem.* 68 (2003) 4302;
(c) R.A. Batey, T.D. Quach, *Tetrahedron Lett.* 42 (2001) 9099.
- [17] (a) S. Darses, J.-P. Genêt, J.-L. Brayer, J.-P. Demoute, *Tetrahedron Lett.* 38 (1997) 4393;
(b) Z.-C. Chen, M. Xia, *Synth. Commun.* 29 (1999) 2457.
- [18] When 1:1 mixture of PhBF₃K and *m*-iodophenol in pH 6.86 buffer was treated with **Au:PVP-1**, cross-coupling product, *m*-hydroxybiphenyl, was not detected but homo-coupling product, biphenyl, was obtained as a sole product. Details of such competitive reactions will be described elsewhere.
- [19] (a) Y. Li, X.M. Hong, D.M. Collard, M.A. El-Sayed, *Org. Lett.* 2 (2000) 2385;
(b) Y. Li, E. Boone, M.A. El-Sayed, *Langmuir* 18 (2002) 4921;
(c) R. Narayanan, M.A. El-Sayed, *J. Am. Chem. Soc.* 125 (2002) 8340;
(d) R. Narayanan, M.A. El-Sayed, *J. Phys. Chem. B* 108 (2004) 8572.
- [20] H. Sakurai, T. Hirao, Y. Negishi, H. Tsunakawa, T. Tsukuda, *Trans. Mater. Res. Soc. Jpn.* 27 (2002) 185.
- [21] B. Guan, D. Xing, G. Cai, X. Wan, N. Yu, Z. Fang, L. Yang, Z. Shi, *J. Am. Chem. Soc.* 127 (2005) 18004.
- [22] C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, *J. Catal.* 238 (2006) 497.
- [23] (a) M.T. Reetz, J.G. de Vries, *Chem. Commun.* (2004) 1559;
(b) M.B. Thathagar, P.J. Kooyman, R. Boerleider, E. Jansen, C.J. Elsevier, G. Rothenberg, *Adv. Synth. Catal.* 347 (2005) 1965.
- [24] (a) A. Henglein, *Langmuir* 15 (1999) 6738;
(b) B.E. Salisbury, W.T. Wallace, R.L. Whetten, *Chem. Phys.* 262 (2000) 131;
(c) M. Okumura, Y. Kitagawa, M. Haruta, K. Yamaguchi, *Chem. Phys. Lett.* 346 (2001) 163;
(d) D.H. Wells Jr., W.N. Delgass, K.T. Thomson, *J. Chem. Phys.* 117 (2002) 10597;
(e) B. Yoon, H. Häkkinen, U. Landman, *J. Phys. Chem. A* 107 (2003) 4066;
(f) D. Stolcic, M. Fischer, G. Ganteför, Y.D. Kim, Q. Sun, P. Jena, *J. Am. Chem. Soc.* 125 (2003) 2848;
(g) J.D. Stiehl, T.S. Kim, S.M. McClure, C.B. Mullins, *J. Am. Chem. Soc.* 126 (2004) 1606;
(h) A. Bongiorno, U. Landman, *Phys. Rev. Lett.* 95 (2005) 106102.
- [25] (a) Y. Suzaki, K. Osakada, *Bull. Chem. Soc. Jpn.* 77 (2004) 139;
(b) Y. Suzaki, K. Osakada, *Organometallics* 23 (2004) 5081.
- [26] P. Ionita, B.C. Gilbert, V. Chechik, *Angew. Chem., Int. Ed.* 44 (2005) 3720.