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Preparation of palladium(II) complexes with long alkyl chain ligand incorporated in micelle

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ABSTRACT

Three palladium(II) complexes with a bidentate nitrogen ligand having a long alkyl chain (**1**, [$PdCl_2$(C_8-tmen)], C_8-tmen = *N*,*N*,*N*′-trimethyl-*N*′-octylethylenediamine; **2**, [$PdCl_2$(C_{16}-tmen)], C_{16}-tmen = *N*,*N*,*N*′-trimethyl-*N*′-cetylethylenediamine; **3**, [$PdCl_2$(C_8-bpy)], C_8-bpy = 4-octyl-2,2′-bipyridine) were prepared. Addition of **1** to an aqueous solution of cetyltrimethylammonium bromide gave a metallomicelle containing the Pd(II) complex (**1A**). The other palladium complexes (**2** and **3**) were not incorporated into the CTABr micelle due to the unsuitable matching between the ligand and the micelle. **1A** showed good catalytic performance for Suzuki and Heck coupling reactions in water. The catalyst system for the Heck reaction in water was reusable.

1. Introduction

Transition metal complexes in micelle system have been utilized as catalysts for organic synthesis in water [1]. Palladium complex stabilized within polymer micelles in aqueous phase or in ionic liquid showed high catalytic activity for C–C coupling reactions [2]. For green sustainable chemistry, water is an important reaction media [3]. The composite system consisting of metal complex and cationic surfactant, such as cetylpyridinium chloride, or neutral polymer, such as polystyrene-co-poly(ethylene oxide), provides an active site for catalysis in water [4]. Since the Heck and Suzuki reactions are known to proceed through the redox cycle between Pd(II) and Pd(0) [5], both of palladium(II) complexes formed within micelle or polymer and palladium(0) nanoparticle stabilized by surfactants are efficient catalysts for these reactions [4,6,7]. In these C–C coupling reactions mediated in water, a number of stabilizing methods have been developed for the palladium nanoparticle using anionic, cationic, or neutral surfactants and polymer or solid supports [6,8,9]. In addition, some Pd(II) complexes anchored to organic and/or inorganic supports were also used as catalysts for the C–C coupling reactions in water [10].

In development of metallomicelle in aqueous media, metal ion as an active center for catalysis should stay not in the core of the micelle but at the periphery moiety, because easy transport of substrate and product through the oil–water surface is important for smoothly keeping the catalytic cycle. The incorporation of coordination ligand for transition metal into surfactant molecules provides a means of localizing many of the physicochemical properties of these ions at oil–water surface [11]. For this purpose, new Pd(II) complexes with a long alkyl chain are designed to be stabilized at the surface of the micelle system through hydrophobic interaction. Here, we describe a preparation of metallomicelle consisting of this palladium complex and cetyltrimethylammonium bromide (CTABr), and its catalytic performance for the Suzuki and Heck reactions in water. The Pd(II) complex within CTABr micelle smoothly proceeded both reactions, and moreover, it was reusable for the Heck reaction without the phosphine ligand.

2. Results and discussion

2.1. Preparations of palladium complexes with an N-alkyl-ethylenediamine ligand within micelle

For stabilizing palladium complex within micelle in aqueous phase, three bidentate ligands with a long alkyl chain were designed. Two ethylenediamine-type bidentate ligands, *N*,*N*,*N*′-trimethyl-*N*′-octylethylenediamine (C_8-tmen) and *N*,*N*,*N*′-trimethyl-*N*′-cetylethylenediamine (C_{16}-tmen), were prepared according to the methods previously reported [12]. A bipyridine-type ligand, 4-octyl-2,2′-bipyridine (C_8-bpy), was newly prepared through 4-octylpyridine as a synthetic intermediate [13]. The [$PdCl_2$(C_8-tmen)] complex (**1**) prepared from the reaction of [$PdCl_2(NCCH_3)_2$] and C_8-tmen in CH_2Cl_2 solution was dissolved easily in various

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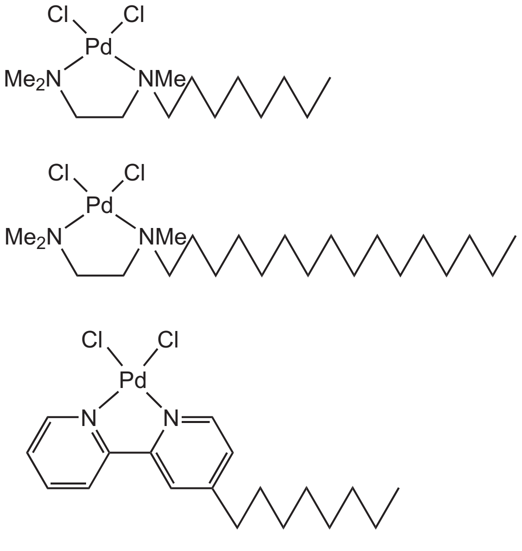
organic solvents such as chloroform, CH_2Cl_2, acetone, and DMSO. The $[PdCl_2(C_{16}\text{-tmen})]$ complex (**2**) with the longer alkyl chain was prepared from the reaction of $[PdCl_2(NCCH_3)_2]$ and C_{16}-tmen as well as the case of **1**. The $[PdCl_2(C_8\text{-bpy})]$ complex (**3**) was also prepared from the reaction of $[PdCl_2(NCCH_3)_2]$ and C_8-bpy. The structures of these complexes shown in Scheme 1 were identified by their elemental analyses and ^{1}H NMR spectroscopies. These complexes were unable to dissolve in water because of low polarity and the hydrophobic long alkyl chain. On the other hand, addition of surfactant, such as CTABr, to a suspension of **1** in water gave a clear yellow solution, **1A**, where the concentration of the surfactant was over critical micelle concentration (CMC) at 25 °C [14].

The ^{1}H NMR spectra of CTABr (10 mmol/L) in D_2O showed that several signals derived from the methylene and the terminal methyl hydrogens of the cetyl group were at 0.79, 1.21, 1.29, and 1.69 ppm and the methyl and the methylene hydrogens adjacent of the ternary nitrogen were at about 3.09 and 3.33 ppm, respectively. Addition of palladium complex to this solution showed the characteristic behavior of metallomicelle formation. In the case of **1**, the clear D_2O solution of **1A** showed characteristic methyl and methylene hydrogen signals derived from the coordinated C_8-tmen ligand at 2.76, 2.79, and 2.86 ppm, respectively, some of which were overlapped with the signals derived from CTABr. The dynamic light scattering (DLS) measurement revealed that the mean size of **1A**, consisting of 3.9 mg (1.0×10^{-3} mmol) of **1** and 182 mg (0.50 mmol) of CTABr in 3.0 mL of water, was 380–420 nm. Consequently, the palladium complex **1** with alkyl chain was incorporated into the micelle composed of CTABr to give the metallomicelle containing Pd(II) complex (**1A**) in water. In the case of **2** or **3**, however, clear solution was not formed when addition of these complexes to the CTABr micelle solution in D_2O. The characteristic NMR signals as observed in **1A** were not shown in **2** and **3**. These finding indicate the palladium complexes with the unfavorable ligands of the longer size of the alkyl chain (**2**) or of the rigid planar structure (**3**) were not incorporated into the CTABr micelle. Thus, tuning of the ligand is important to incorporate the metal complex into the micelle. The longer hydrophobic alkyl chain, such as cetyl, in comparison with octyl, was not incorporated into the micelle composed with CTABr. The more planar bipyridine unit, in comparison with alkyl ethylenediamine one, might be too more hydrophobic to incorporate into CTABr micelle or be less interaction with the alkyl chains of the micelle. Accordingly, the catalysis in water was investigated using **1A** consisting of the palladium(II) complex (**1**) with moderate-size *N*-alkyl ethylenediamine ligand and CTABr micelle.



1 :

2 :

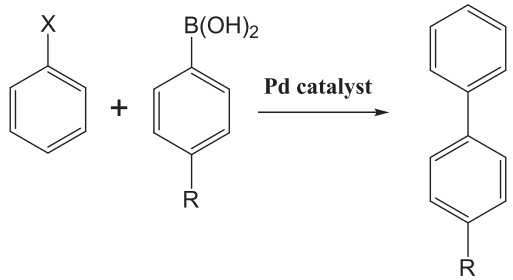
3 :

Scheme 1. Structures of three Pd(II) complexes with bidentate ligands.

Synthesis of metal nanoparticles requires the surfactants to inhibit aggregation of the ultra fine nanoparticles initially generated [15]. New preparation method through the stabilization of the Pd(II) complex within the micelle in aqueous phase was investigated to inhibit aggregation of Pd(0) species. Reduction of Pd(II) complex in metallomicelle **1A** in water was carried out under 1 atm of hydrogen gas bubbling at 25 °C. A gray suspension of metallomicelle containing Pd(0) species, **1B**, was obtained. The ^{1}H NMR spectrum of **1B** in D_2O showed new signals assignable to the protonated C_8-tmen moieties, which were different from the starting complex **1**. These findings indicate the formation of Pd(0) nanoparticles within the CTABr micelle. The distribution of the mean size of **1B** determined by the DLS had two peaks after reduction of **1A**. One was about 130 nm and another was about 20 nm. We estimated that the smaller size one was Pd(0) nanoparticle, which was also characterized by TEM image.

2.2. Suzuki reaction catalyzed by palladium micelle complex

The catalytic performance of Pd(II) species, **1A**, was investigated on the Suzuki reaction Eq. (1) in aqueous media under atmospheric condition. Phosphine-free palladium complexes were known to catalyze Heck and Suzuki reactions under aerobic condition [16]. Notably, phosphine-free and aqueous condition is environmentally friendly reaction. The catalytic activities of **1A** using some halogenobenzene derivatives are shown in Table 1. The reactions of iodobenzene and phenylboronic acid quantitatively gave biphenyl at 80 °C in aqueous condition under air (entries 1 and 2). Even at 60 °C, good reactivity for this reaction was shown, but very low at 25 °C (entries 3 and 4). The reaction using bromobenzene in the place of iodobenzene also gave biphenyl quantitatively at 80 °C (entries 5 and 6). The bromo- and/or chloro-benzenes are acceptable for the reactant of the Suzuki reaction [17], so that the less active chlorobenzene compared with iodo derivative also gave the corresponding coupling product at 100 °C under the extended reaction time (entry 8). Especially, 4-chloroacetophenone with electron-withdrawing group gave high yield of the corresponding coupling product at 100 °C (entry 10). Since the rate-limiting step in catalytic cycle of this cross-coupling reaction is considered the oxidative addition step, aryl halide with electron-withdrawing group smoothly proceeded the reaction [18]. The reaction of bromobenzene in the presence of small amount of the catalyst **1A** also gave the coupling product quantitatively under the extended reaction time (entry 7).



(1)

Notably, the catalytic activity in the Suzuki reaction using **1B** in the place of **1A** dramatically decreased. As shown in the entry 2 in Table 1, the reaction catalyzed by **1A** gave biphenyl quantitatively. In the same reaction condition using **1B**, however, the yield of the product decreased to 21% in 12 h reaction. Moreover, the reaction of iodotoluene with phenylboronic acid also gave 4-phenyltoluene at 80 °C in poor yield (18%, 8 h reaction). In this point, Hu et al. reported that the palladium nanoparticles, of

Table 1
Catalytic activity of **1A** for Suzuki reaction.

Entry	R	X	T (°C)	Time (h)	Yield (%)
1	H	I	80	2	95
2	H	I	80	4	100
3	H	I	60	8	80
4	H	I	25	24	6
5	H	Br	80	2	91
6	H	Br	80	4	100
7[a]	H	Br	80	24	100
8	H	Cl	100	24	10
9	COMe	Cl	80	24	47
10	COMe	Cl	100	24	76

Reaction condition: phenylboronic acid 1.5 mmol, aryl halide 1.0 mmol, palladium content of **1A** 1.0×10^{-2} mmol, Na_2CO_3 2.0 mmol, CTABr 1.0 mmol, H_2O 3 mL, under air.

[a] 1.0×10^{-3} mmol of **1A**.

which size were about 3 nm, generated within poly(*N*,*N*-dialkylcarbodiimide) became a robust catalyst for Suzuki reaction under microwave heating.[19] Different from the case of the Heck reaction, the catalytic activity of the Suzuki reaction might depend on the size of the palladium nanoparticles.[7] The Pd(0) nanoparticles in the metallomicelles **1B** generated from the reduction of **1A** might be slightly larger size and not be suitable for the Suzuki reaction.

2.3. Heck reaction catalyzed by palladium micelle complex

The Pd(0) nanoparticle becomes suitable catalyst for the redox cycle reactions through the oxidative addition and reductive elimination [20]. Both **1A** and **1B** smoothly catalyzed the Heck reaction, because it was not influenced by the size of the palladium nanoparticle unlike the Suzuki reaction above mentioned.

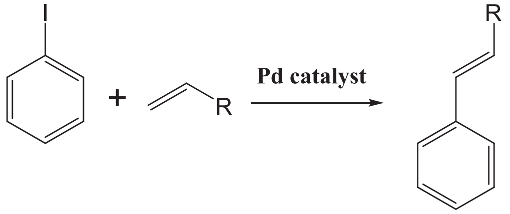
The Pd(0) species in **1B** within CTABr micelle was stable under aqueous, aerobic, and even phosphine-free conditions [6]. The coupling reaction of iodobenzene with styrene at 80 °C gave stilbene (43%) with small amount of biphenyl (4%) as shown in Table 2. The color change of **1B** from dark gray to orange during the reaction indicated that the oxidative addition of iodobenzene to Pd(0) species smoothly proceeded to give aryl-Pd(II) compound. The reactions of iodobenzene with *tert*-butylacrylate (entry 2) also gave the corresponding coupling products in moderate yields (66%). The reactivity of acrylate derivatives (entries 2–4) in this system showed the order, *tert*-butyl acrylate > ethyl acrylate > methyl acrylate, which is interpreted by the hydrophobicity of the acrylate derivatives. Using acrylic acid, the reaction with iodobenzene did not give any coupling product (entry 5). This finding is contrast to the previous reports, in which the reaction of acrylic acid with iodobenzene using solid support Pd(II) complex in aqueous ethanol [10] and latex-coated Pd nanocomposite in water [21] gave cinnamic acid in good yield. Consequently, the coupling reaction catalyzed by the palladium catalyst **1B** proceeded inner phase of the micelle through the incorporation of the substrate.

Table 2
Catalytic activity of **1B** for Heck reaction[a].

Entry	Substrate (R)	X	Time (h)	Yield (%)
1	Ph	I	8	43[b]
2	$CO_2{}^tBu$	I	8	66
3	CO_2Et	I	8	31
4	CO_2Me	I	8	10
5	COOH	I	8	0

[a] Reaction condition: substrate 1.2 mmol, aryl halide 1.0 mmol, palladium content of **1B** 1.0 μmol, K_2CO_3 2.0 mmol, CTABr 0.50 mmol, H_2O 3 mL, 80 °C, under air.

[b] 1,1-Diphenylethylene was formed as byproduct (4%).



(2)

The Pd(II) metallomicelle, **1A**, showed the catalytic activity for both of the Heck and Suzuki reactions. The Heck reaction of styrene, iodobenzene, and $NaHCO_3$ in water was carried out in the presence of **1A** to give *trans*-stilbene (61%) accompanied with byproduct 1,1-diphenylethylene (5%) at 100 °C for 16 h. On the separation of the product from the reaction solution, heterogeneous catalyst systems have advantages in comparison with homogeneous ones.[8] Liquid/liquid phase separations are practical and viable to recover, separate, and reuse the metallomicelle catalyst. Using **1A** in the aqueous solution, the recycle catalytic reaction system was carried out under aerobic condition as shown in Scheme 2. At the first time, the Heck reaction catalyzed by **1A** in the reaction vessel [I] gave the coupling products under atmospheric condition. To extract the organic products, heptane (a) was added to the reaction mixture (b) [II], after the reaction. The organic phase [III] contained stilbene (a) and the aqueous one [IV] contained **1A** (b) were separated. The oxidation state of palladium species in [IV] was estimated as +2, since the precipitation of palladium black was not observed and the color of the solution was light yellow. The reaction products were easily isolated from [III] through evaporation. At the next run, styrene, iodobenzene, and $NaHCO_3$ were added again to the remaining aqueous solution, [IV]. The isolated yield of *trans*-stilbene at 100 °C for 16 h was 61% at the 1st run, and that at the 2nd run was 54%. At the 3rd run that decreased to 42%. The gradually decrease of yields of the products is probably due to destruction of the micelle phase by the generated inorganic salts. This problem is now improved for design of high performance catalyst.

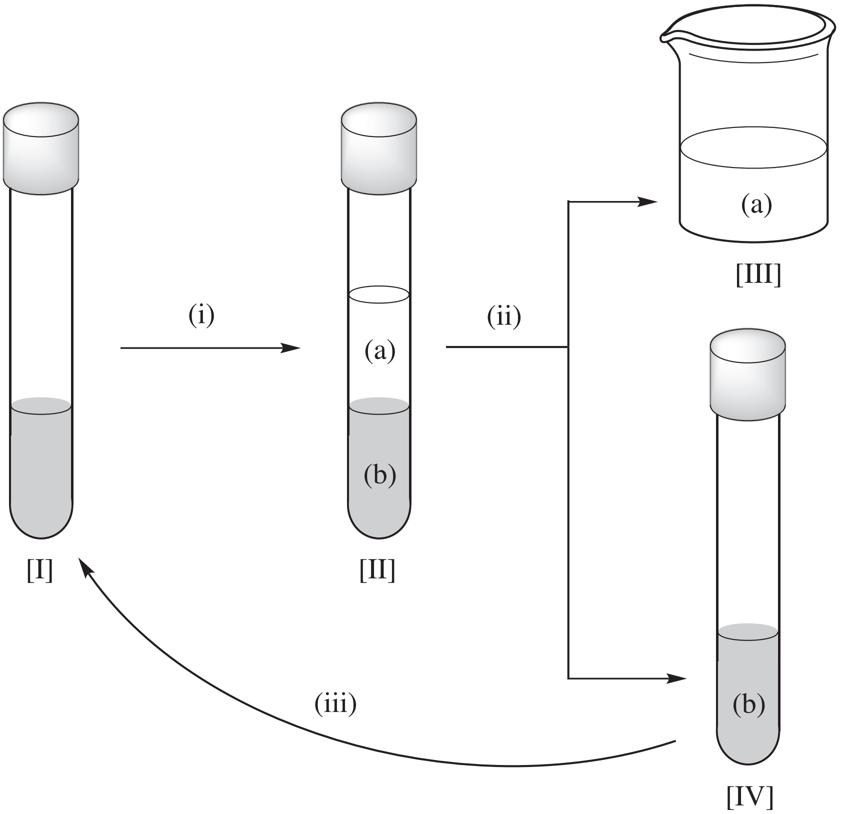
3. Conclusion

Pd(II) complex with a bidentate nitrogen ligand having a long alkyl chain (**1**, [$PdCl_2(C_8$-tmen)]) was incorporated into the micelle consisting of cetyltrimethylammonium bromide (CTABr) to give a metallomicelle (**1A**) in water. On the other hand, some palladium complexes (**2** and **3**) with unfavorable size of the alkyl chain or rigid structure were not incorporated into the CTABr micelle. Tuning of the alkyl chain length of the ligand is important to incorporate the complex into the micelle. The Pd(II) metallomicelle (**1A**) showed good catalytic activity for Suzuki and Heck reactions in water under atmospheric condition without phosphine ligand. The Pd(0) nanoparticle (**1B**) within CTABr generated from the reduction of **1A** was not good catalyst for Suzuki reaction, although **1B** promoted Heck reaction. The catalyst system **1A** was reusable for Heck reaction in aqueous media.

4. Experimental

4.1. General procedures

Manipulations of the palladium complexes were carried out under air. Chemicals were commercially available. The substituted ethylenediamine ligand, *N,N,N'-trimethyl-N'*-dodecylethylenediamine (C_{16}-tmen) [12], was prepared as reported previously, and *N,N,N'*-trimethyl-*N'*-octylethylenediamine (C_8-tmen) was prepared using a similar procedure. Micelle solutions containing CTAX



Scheme 2. Reuse System of Palladium Micelle Catalyst. [I] metallomicelle (1A) within aqueous phase. (i) Heck reaction catalyzed by palladium. [II] addition of heptane to the reaction mixture after the reaction. (ii) separation of organic (a) and aqueous phases (b). [III] organic phase (a) containing the coupling product. [IV] aqueous phase (b) containing catalyst. (iii) recycle use of the catalyst.

(X = Cl, Br) was prepared using the ultrapure water. The ^1H NMR spectra were recorded on Varian 300 and Bruker AV400N spectrometers. Elemental analyses were carried out using a Perkin Elmer 2400 series II CHNS/O Analyzer. Dynamic light scattering measurements were carried out using Otsuka DLS-8000. TEM measurements were carried out using JEOL JEM-3010.

4.2. Preparation of 2-bromo-4-octylpyridine

Preparation was performed according to a modified method of the lithiation of 4-picoline [13a]. To a solution of 2-(dimethylamino)ethanol (10.2 mL, 102 mmol) in dry hexane (100 mL) was added 2.71 M *n*-BuLi in hexane (75.0 mL, 203 mmol) at 0 °C under nitrogen. The mixture was stirred for 15 min at 0 °C, and a solution of 4-octylpyridine (9.71 g, 50.8 mmol) in dry hexane (63 mL) was added. After stirring for 1 h at 0 °C, the solution was cooled to −78 °C. A solution of CBr_4 (42.2 g, 127 mmol) in dry THF (40 mL) was added and stirred for 1 h at −78 °C, then the mixture was warmed to room temperature. To the mixture was added H_2O (150 mL) at 0 °C, and the organic layer was extracted with diethyl ether. The solution was dried with $MgSO_4$ and the solvents were removed. The crude product was purified by SiO_2 column chromatography with hexane/EtOAc (9:1) mixtures as eluent (4.03 g, 29.3%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3H, CH_3, J = 6.6 Hz), 1.26–1.30 (m, 10H, $(CH_2)_5CH_3$), 1.61 (m, 2H, $CH_2(CH_2)_5CH_3$), 2.57 (t, 2H, $CH_2(CH_2)_6CH_3$), J = 8.0 Hz), 7.07 (dd, 1H, py-H_5, J = 4.8, 1.2 Hz), 7.31 (d, 1H, py-H_3, J = 1.2 Hz), 8.24 (d, 1H, py-H_6, J = 4.8 Hz).

4.3. Preparation of 4-octyl-2,2′-bipyridine

Preparation of 4-octyl-2,2′-bipyridine was performed according to a modified method of the syntheses of polypyridine [13b]. To a solution of 2-bromo-4-octylpyridine (3.57 g, 13.2 mmol) and $Pd(PPh_3)_4$ (718 mg, 0.621 mmol) in dry THF (20 mL) was added 0.5 M 2-pyridylzinc bromide in THF (45.0 mL, 22.5 mmol) under nitrogen. The mixture was stirred for 1.5 day at rt, and an alkaline solution containing an excess of EDTA was added. The organic layer was extracted with CH_2Cl_2 and the solvents were removed. The crude product was purified by SiO_2 column chromatography with hexane/acetone (2:1) mixtures as eluent (2.44 g, 68.9%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, CH_3, J = 6.9 Hz), 1.25–1.38 (m, 10H, $(CH_2)_5CH_3$), 1.69 (m, 2H, $CH_2(CH_2)_5CH_3$), 2.69 (t, 2H, $CH_2(CH_2)_6CH_3$, J = 7.8 Hz), 7.14 (dd, 1H, bpy-H_5, J = 5.0, 1.7 Hz), 7.30 (ddd, 1H, bpy-$H_{5'}$, J = 7.5, 4.8, 1.2 Hz), 7.81 (ddd, 1H, bpy-$H_{4'}$, J = 8.0, 7.5, 1.8 Hz), 8.23 (d, 1H, bpy-H_3, J = 1.7 Hz), 8.39 (dd, 1H, bpy-$H_{3'}$, J = 8.0, 1.2 Hz), 8.56 (d, 1H, bpy-H_6, J = 5.0 Hz), 8.69 (dd, 1H, bpy-$H_{6'}$, J = 4.8, 1.8 Hz).

*4.4. Preparation of [$PdCl_2(C_8$-tmen)] (**1**)*

A mixture of $PdCl_2(CH_3CN)_2$ (0.528 g, 2.04 mmol) in CH_2Cl_2 (350 mL) and 0.434 g (2.02 mmol) of C_8-tmen in CH_2Cl_2 (15 mL) was stirred for 5 min at room temperature. After evaporation of the solvent, the residue was crystallized from CH_2Cl_2-hexane (0.410 g, 52.0%). Calc. for $C_{13}H_{30}Cl_2N_2Pd$ (391.72): C, 39.86; H, 7.72; N, 7.15. Found: C, 39.63; H, 7.73; N, 6.77%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 3H, CH_2CH_3, J = 5.9 Hz), 1.28 (m, 10H, $(CH_2)_5CH_3$), 1.78 (m, 1H, CH_2), 2.2–2.3 (m, 2H, CH_2), 2.45 (m, 1H, CH_2), 2.58 (m, 1H, CH_2), 2.82 (s, 3H, NCH_3), 2.83 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 3.1 (m, 2H, CH_2), 3.30 (m, 1H, CH_2).

*4.5. Preparation of [$PdCl_2(C_{16}$-tmen)] (**2**)*

The complex was prepared by a procedure similar to that for [$PdCl_2(C_8$-tmen)], using C_{16}-tmen as the starting material. The product (45.9%) was obtained as orange powder. Calc. for

$C_{21}H_{46}Cl_2N_2Pd$ (503.93): C, 50.05; H, 9.20; N, 5.56. Found: C, 49.53; H, 9.18; N, 5.27%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3H, CH_2CH_3, J = 6.9 Hz), 1.26 (m, 26H, $(CH_2)_{13}CH_3$), 1.79 (m, 1H, CH_2), 2.2–2.3 (m, 2H, CH_2), 2.45 (m, 1H, CH_2), 2.56 (m, 1H, CH_2), 2.81 (s, 3H, NCH_3), 2.82 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 3.13 (m, 1H, CH_2), 3.18 (m, 1H, CH_2), 3.30 (m, 1H, CH_2).

4.6. Preparation of [PdCl$_2$(C$_8$-bpy)] (**3**)

The complex was prepared by a procedure similar to that for [PdCl$_2$(C$_8$-tmen)], using C$_8$-bpy as the starting material. The product (60.5%) was obtained as beige powder. Calc. for $C_{18}H_{24}Cl_2N_2Pd$ (445.72): C, 48.51; H, 5.43; N, 6.28. Found: C, 48.44; H, 5.61; N, 6.10%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 3H, CH_3, J = 7.4 Hz), 1.28–1.35 (m, 10H, $(CH_2)_5CH_3$), 1.73 (m, 2H, $CH_2(CH_2)_5CH_3$), 2.83 (t, 2H, $CH_2(CH_2)_6CH_3$, J = 7.8 Hz), 7.31 (d, 1H, bpy-H$_5$, J = 5.8 Hz), 7.50 (m, 1H, bpy-H$_{5'}$), 7.90 (s, 1H, bpy-H$_3$), 8.14 (m, 2H, bpy-H$_{3'}$and H$_{4'}$), 9.09 (d, 1H, bpy-H$_6$, J = 5.8 Hz), 9.27 (d, 1H, bpy-H$_{6'}$, J = 6.0 Hz).

4.7. Dynamic light scattering measurement

Micelle sample solution was prepared as 182 mg (0.50 mmol) of CTABr in 3.0 mL of water. Sample of metallomicelle including Pd(II) complex (**1A**) was prepared by addition of 3.9 mg (1.0×10^{-2} mmol) of **1** into that micelle solution, then ultrasonication. Sample of metallomicelle including Pd(0) particles (**1B**) was prepared by stirring the solution of **1A** under H_2 (1 atm) at 25 °C overnight. The averages of particle size of micelles of these solutions were measured after filtration (pore size 0.1 or 0.22 μm).

4.8. General procedure for Suzuki coupling reaction catalyzed by **1A** in water

Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), and Na_2CO_3 (2.0 mmol) were added to the metallomicelle solution (**1A**) composed of 363 mg (1.0 mmol) of CTABr and 3.9 mg (0.010 mmol) of **1** in 3.0 mL of water. The mixture was stirred under air. Et_2O and 1-butanol were added to the reaction solution, and then the solvents were removed. The products and unreacted substrate were extracted with Et_2O from the residue and their amounts were determined by GC.

4.9. General procedure for Heck reaction catalyzed by **1B** in water

Preparation of **1B** was performed by the same procedure as mentioned above. Aryl halide (1.0 mmol), olefin (1.2 mmol), and base (K_2CO_3 or $NaHCO_3$, 2.0 mmol) were added to the metallomicelle solution including Pd(0) particles (**1B**) composed of 182 mg (0.50 mmol) of CTABr and 3.9 mg (0.010 mmol) of **1** in 3.0 mL of water under air. The mixture was stirred at 80 °C. Et_2O and 1-butanol were added to the reaction solution, then solvents were removed. Products and unreacted substrate were extracted with Et_2O from the residue and their amounts were determined GC method using diethylene glycol di-*n*-butyl ether as standard.

4.10. Reuse performance for Heck reaction of **1A**

To a metallomicelle solution containing 363 mg (1.0 mmol) of CTABr and 3.9 mg (0.010 mmol) of **1** in 3.0 mL of water were added the iodobenzene (1.0 mmol), styrene (2.0 mmol), and $NaHCO_3$ (2.0 mmol) in sealed tube under air. The mixture was stirred at 100 °C for 20 h. The products and unreacted substrates were extracted with heptane, and the heptane solution was analyzed by GC. To the opposite water solution remaining Pd complex and surfactant was added the new substrate and base.

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