Self-assembling Properties of an N-Heterocyclic Carbene-based Metallosurfactant: Pd-Coordination Induced Formation of Reactive Interfaces in Water

Toshiaki Taira¹, Takaya Yanagimoto², Kenichi Sakai², Hideki Sakai², Akira Endo¹, and Tomohiro Imura¹*

¹ Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), Central 5-2, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, JAPAN
² Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, JAPAN

Abstract: In this study, an N-heterocyclic carbene (NHC)-based metallosurfactant (MS), NHC-PdMS, was synthesized, where Pd(II) was bound to the NHC framework via a robust Pd–carbene bond with NEt₃ as a co-ligand. Surface tension measurements revealed that the critical micelle concentration (CMC) of NHC-PdMS (1.8 × 10⁻⁴ M) was one order of magnitude lower than that of its MS precursor (imidazolium bromide). Coordination of the MS precursor and NEt₃ to Pd(II) also influenced micelle size; the hydrodynamic diameters of NHC-PdMS were observed to be 25.8 ± 5.6 nm and 2.5 ± 0.3 nm, respectively. Furthermore, small angle X-ray scattering measurements indicated that NHC-PdMS exhibited liquid crystalline behavior above 26 wt%, with a spacing ratio of 1:2:3 for the first, second, and third Bragg peaks. To understand the role of the reactive interface, NHC-PdMS was also applied to aqueous catalytic reactions. Owing to its low CMC value, a catalytic amount of NHC-PdMS (3 mol%) provided the reactive interface, which facilitated the aqueous Mizoroki–Heck reaction of various aryl iodides and styrene in good yields (72–95%). These results suggest that MS formation results in a drastic change in self-assembling properties, which are important for the development of highly reactive chemical interfaces in water.

Key words: metallosurfactant, liquid crystal, N-heterocyclic carbene, palladium, Mizoroki-Heck reaction

1 INTRODUCTION

Metallosurfactants (MSs) are emerging as a new class of surfactants, in which ligand moieties in the surfactant framework bind to various metal ions.²⁻⁴ Owing to the various functions derived from the metal centers together with their surface activity, MSs can be potentially used as catalysts,⁵ electronic materials,⁶ medicines,⁷ templates for mesoporous materials,⁸ and precursors for nanoparticles.⁹ Among these applications, the use of MSs as aqueous catalysts is one of the most promising because they can exhibit dual functions of a surfactant and a catalyst in water. By providing a reactive interface between water and the reactants, MSs can play a role in accelerating reaction rates without the addition of unnecessary extra surfactants, such as rate-enhancement of ester hydrolysis.⁹⁻¹¹

MSs typically consist of a cationic metal center bound to anionic surfactants via ionic or coordination bonds. Satake et al. reported the synthesis of ionic-type MSs with double-tailed structures, where two dodecyl sulfate (DS) anions were bound to divalent Ni²⁺, Co²⁺, Cu²⁺, and Mg²⁺ ions.¹²⁻¹³ The critical micelle concentration (CMC) of each MS was estimated to be ~1.2 mM. Thus, these MSs showed lower CMC values than DS with sodium as a counter cation, which indicated that changing the surfactant structure from single- to double-tailed decreased the CMC. Kobayashi et al. have shown the catalytic function of a MS with a triple-tailed structure, in which three DS anions were bound to one Sc³⁺ center.¹⁴⁻¹⁵ Although Sc³⁺ tends to be dissociated in water, several carbon–carbon bond-forming reactions are known to proceed under emulsion conditions. MSs in which a metal cation is coordinated to an amphiphilic ligand via a heteroatom have also been reported. Scrimin et al. reported the effect of surfactant self-assembly on the reactivity of a metal center.¹⁶ They revealed...
that the aggregate structure of an amphiphilic nitrogen ligand together with cetyltrimethylammonium bromide (CTAB) affected the rate of ligand exchange on the micelle surface.

Phosphine-based MSs with several transition metals have been reported to exhibit surface activity.\(^\text{17, 18}\) The MS with Pd(II) has been reported that the complexation of Pd(II) with amphiphilic phosphine ligands can induce the formation of vesicles in water. However, owing to the high reactivity of phosphine ligands, these MSs are typically obtained as a mixture of cis and trans isomers. Uozumi et al.\(^\text{19}\) have previously synthesized a pincer-type ligand-based MS, in which a chelating agent binds tightly to three adjacent coplanar sites of Pd. This complex showed good thermal and water stability, which allowed its successful application to the Miyaura–Michael reaction of α,β-unsaturated ketones and sodium tetraarylborates in aqueous solution.\(^\text{20, 21}\)

N-Heterocyclic carbenes (NHCs), which are derived from imidazolium salts, have attracted significant interest as the ligands for transition-metal-catalyzed reactions in water.\(^\text{22, 23}\) Compared with conventional phosphine ligands, NHCs exhibit superior bonding robustness, and several NHC-based Pd complexes have been reported to show excellent catalytic activities.\(^\text{23}\) Previously, we reported that surface-active imidazolium bromide forms an NHC in water and yields an NHC-based MS in the presence of Pd(OAc)\(_2\).\(^\text{24}\) Although this MS showed surface and catalytic activities in water, several of its isomers were observed. Thus, its detailed aqueous-phase behavior remains unclear.

In this study, an NHC-based MS, NHC-PdMS, was synthesized in which Pd was located between the hydrophilic and hydrophobic parts of an MS precursor via a Pd-carbene bond with NEt\(_3\) as a co-ligand. Coordination of Pd(II) to the MS precursor changed its structural and electrical properties, and influenced its self-assembly behavior, as revealed by surface tension, dynamic light scattering (DLS), and small angle X-ray scattering (SAXS) measurements. Based on the promising self-assembling properties of NHC-PdMS, we examined the application of this MS to the Pd-catalyzed aqueous Mizoroki–Heck reaction, which is one of the most versatile C–C coupling reactions in organic synthesis. Because of its low CMC, a catalytic amount of NHC-PdMS could emulsify the reactants and provided a reactive interface between water and the reactants with a large interfacial area, which efficiently facilitated the aqueous Mizoroki–Heck reaction of various aryl iodides and olefins in good yields.

## 2 EXPERIMENTAL

### 2.1 Materials

Imidazolium bromide as a MS precursor was synthesized according to the literature method.\(^\text{24}\) Pd(OAc)\(_2\) (> 97.0%), NaBr (99.9%), dimethyl sulfoxide (99.0%), trimethylamine (99.0%), dichloromethane (99.0%), methanol (99.5%), chloroform (99.0%), iodobenzene (97.0%), chlorobenzene (99.0%), and 4-iodoacetophenone (90.0%) were purchased from Wako pure Chemical Industries, Ltd., Japan. Bromobenzene (99.0%), p-iodoanisole (96.0%), 4-iodobenzoic acid (> 98.0%), and methyl acrylate (> 99.0%) were procured from Tokyo Chemical Industry Co., Ltd., Japan. All chemicals were used as received.

### 2.2 Synthesis and characterization

\(^\text{1}\)H-NMR spectra were recorded using an NMR spectrometer (Avance 400, Bruker Biospin Co., Inc., USA) operated at 400 MHz. \(^\text{13}\)C-NMR spectra were recorded on the same instrument at 100 MHz. All NMR spectra were recorded in CDCl\(_3\) as a deuterated solvent and calibrated using tetramethylsilane as an internal reference. Elemental analyses were carried out using a Flash2000 instrument (Thermo Fisher Scientific Inc., USA).

#### 2.2.1 Pd-dimer

In a 15 mL test tube equipped with a magnetic stir bar, imidazolium bromide (1.00 g, 1.46 mmol), Pd(OAc)\(_2\) (0.38 g, 1.46 mmol), and NaBr (0.60 g, 5.85 mmol) were dissolved in 5 mL of DMSO. The mixture was stirred for 24 h at 90°C, the solvent was evaporated under reduced pressure and the crude product was purified by silica-gel chromatography (R\(_f\) = 0.35, CHCl\(_3\)/MeOH = 9/1). Pd-dimer was obtained as a pale red oil (1.14 g, 0.66 mmol, 90%).\(^\text{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.22 (s, 1H, NCH = CH), 6.89 (s, 1H, NCH = CH), 4.77 (br, 2H, NCH\(_2\)), 4.50 (br, 2H, CH\(_2\)), 4.05 (br, 2H, CH\(_2\)), 3.74-3.50 (m, 28H, OCH\(_3\)CH\(_2\)), 3.36 (s, 3H, OCH\(_3\)), 2.05 (t, \(J = 6.0\) Hz, 2H, CH\(_2\)), 1.49-1.19 (m, 18H, CH\(_2\)), 0.87 (t, \(J = 8.0\) Hz, 3H, CH\(_3\)).\(^\text{13}\)C NMR \(\delta\) 143.4, 124.3, 122.0, 71.9, 70.6, 70.5, 70.3, 70.0, 59.0, 51.4, 51.2, 39.3, 29.7, 29.7, 29.6, 29.4, 29.3, 26.8, 22.7, 14.1; Anal. Calcd. for C\(_{44}\)H\(_{83}\)Br\(_4\)N\(_4\)O\(_{16}\)Pd\(_2\): C, 43.93; H, 7.30; N, 3.32. Found: C, 44.23; H, 7.19; N, 3.22.

#### 2.2.2 NHC-PdMS

Pd-dimer (365 mg, 0.42 mmol based on Pd) was charged in a screw cap vial equipped with a magnetic stirring bar and dissolved in dichloromethane (4 mL). An excess of NEt\(_3\) (2 mL) was added to the vial and the solution was stirred at room temperature for 1 h. Subsequently, the solvent was removed under reduced pressure and the crude product was filtered through a pad of Celite. NHC-PdMS was obtained as a pale brown oil (400 mg, 0.42 mmol, > 99%).\(^\text{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.10 (s, 1H, NCH = CH), 6.82 (s, 1H, NCH = CH), 4.60 (t, \(J = 4.0\) Hz, 2H, NCH\(_2\)), 4.36 (t, \(J = 8.0\) Hz, 2H, CH\(_2\)), 4.02 (t, \(J = 6.0\) Hz, 2H, CH\(_2\)), 3.71-3.48 (m, 28H, OCH\(_2\)CH\(_3\)), 3.35 (s, 3H, OCH\(_3\)), 2.96 (q, \(J = 8.0\) Hz, 6H, NCH\(_2\)), 2.03 (t, \(J = 6.0\) Hz, 9H, CH\(_3\)), 1.60 (t, \(J = 8.0\) Hz, 2H, CH\(_2\)), 1.56-1.20 (m, 18H, CH\(_2\)), 0.85 (t, \(J = 8.0\) Hz, 3H, CH\(_3\)).\(^\text{13}\)C NMR \(\delta\) 143.7, 123.7, 121.3, 71.9, 71.0, 70.6 70.5, 70.4, 69.9, 69.5, 59.0, 51.0, 50.8, 48.2, 47.6, 46.8.
Self-assembling Properties of an N-Heterocyclic Carbene Based Metallosurfactant

J. Oleo Sci. 67, (9) 1107-1115 (2018)

46.1, 31.9, 30.4, 29.9, 29.6, 29.6, 29.5, 29.3, 29.2, 26.9, 26.8, 22.7, 14.2, 10.3; Anal. Calcd. for C$_{38}$H$_{77}$Br$_2$N$_3$O$_8$Pd: C, 46.28; H, 7.97; N, 4.13. Found: C, 46.14; H, 8.15; N, 4.25.

2.3 Surface tension measurements
The surface tensions of the surfactant solutions were determined by the Wilhelmy plate method at 25°C using a DSY-500 surface tension meter (Kyowa Kaimen Kagaku Co., Japan), the accuracy of which was intermittently checked with ultrapure water. The Pt plate was cleaned by flaming, and glassware was rinsed sequentially with tap water and ultrapure water.

2.4 DLS measurements
The size distributions of the assemblies of synthesized NHC-PdMS and the MS precursor were measured with a DLS instrument (DLS-7000, Otsuka Electronics Co., Japan) using a 488 nm Ar laser (75 mW) as a light source (25°C). The autocorrelation function was analyzed using the histogram software provided with the instrument. In this study, the particle size distributions were determined using the software provided with the instrument. In this study, the autocorrelation function was analyzed using the histogram method.

2.5 2D NOESY NMR measurement
In an NMR tube, the MS precursor (10 mM) was dissolved in degassed D$_2$O. The 2D nuclear Overhauser effect spectroscopy (NOESY) spectrum of the solution was recorded at 300 K and 400 MHz with the phase-sensitive NOESY pulse sequence (Avance 400, Bruker Biospin Co., Inc., USA). The spectrum was collected with a mixing time of 400 ms.

2.6 SAXS measurements
To prepare NHC-PdMS/water samples for phase behavior studies, ultrapure water was added to sample tubes containing NHC-PdMS. The NHC-PdMS/water mixtures were then vigorously mixed using a vortex mixer. Before measuring, the samples were kept at room temperature for several hours. X-ray scattering data were then recorded on a SAXSeas camera (Anton Parr Co., Ltd., Austria) using a system equipped with a W3830 sealed glass bulb X-ray source (PANalytical Co., Ltd., Netherland, Cu-K$_\alpha$ (λ = 0.154 nm)). The diffraction pattern was recorded with an imaging plate and the exposure time was 20 min for each sample. The scattering vector $q$ was calculated using $q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle. The ratio of the interlayer spacing ($d$), where $d = 2\pi/q$, for the first and second Bragg peaks was used to confirm the type of liquid crystal.

2.7 Polarized optical microscopy
A polarized optical microscope (BX41, OLYMPUS, Japan) equipped with cross-polarizing filters and a charge-coupled-device camera (DP12, OLYMPUS, Japan) was used to observe the lyotropic liquid crystalline phase of NHC-PdMS. Phase behavior was investigated by using the water-penetration scan technique. Birefringent textures observed by optical microscopy allowed the assignment of particular lyotropic-phase types to the samples.

2.8 Aqueous Mizoroki–Heck reaction
NHC-PdMS (0.018 mmol), aryl halide (0.54 mmol), and olefin (0.78 mmol) were added to a test tube equipped with a stir bar and a screw cap. Then, 600 µL of water was added and the mixture was vortexed for several seconds. Subsequently, NEt$_3$ (0.69 mmol) was added and the mixture was vigorously stirred for 24 h at 70°C. The stirring speed was set at a constant of 1200 rpm. The reaction was monitored by $^1$H-NMR spectroscopy based on the signal intensity. After completion of the reaction, the mixture was cooled to room temperature and filtered, and the remaining solid was washed with ethyl acetate. After washing with brine, the organic phase was extracted and dried over MgSO$_4$. The organic solvent was evaporated to obtain the crude product. Further purification was conducted by column chromatography (hexane/ethyl acetate).

3 RESULTS AND DISCUSSION
3.1 Synthesis and structural properties
Figure 1 shows the molecular structure of NHC-PdMS, where the Pd(II) center is located at the linkage between the hydrophilic and hydrophobic parts of the molecule. This led to the catalytic center being placed at the air–water interface. Generally, reactions between imidazolium and Pd salts generate several isomers and dimers of NHC-Pd because of the high reactivity and electron-rich nature of the obtained Pd complex. In this work, we focused on a pyridine-enhanced precatalyst preparation, stabilization, and initiation (PEPSI) approach to synthesize a single isomer of the NHC-based MS$^{25–27}$. This design
principle is based on the introduction of a hemilabile nitrogen ligand that not only stabilizes the Pd(II) species but is also readily displaced to give the catalytically active Pd(0) species. We synthesized a PEPSI-type MS with NEt₃ as a hemilabile co-ligand because of its less bulk and σ-donating capability, which allowed it to stabilize the Pd complex, even in aqueous conditions²⁸⁻²⁹. The synthesis of NHC-PdMS was achieved by stepwise ligand substitution reactions. First, a reaction of imidazolium bromide with Pd(OAc)₂ in the presence of NaBr afforded [(NHC)-PdBr₂]₂ dimer (Pd-dimer) in 90% yield. Pd-dimer was then treated with an excess of NEt₃ in CH₂Cl₂ at room temperature. After 1 h, the desired MS was isolated in >99% yield by evaporating the solvent. NHC-PdMS was fully characterized by means of elemental analysis and ¹H and ¹³C NMR spectroscopy.

3.2 Surface tension measurements

To explore the effects of Pd on the surface activity, the surface tension lowering activities of the synthesized NHC-PdMS were determined using the Wilhelmy plate method. Figure 2 shows the relationship between the surface tension of water and the sample concentration. Both NHC-PdMS and the MS precursor gradually reduced the surface tension by adsorption at the air–water interface, with the surface tension becoming constant above the CMC. The CMC and γcmc values were estimated from the crossover point of the two fitted lines for each surfactant (Fig. 2). The CMC of NHC-PdMS (1.8 × 10⁻⁵ M) was found to be one order of magnitude lower than that of the MS precursor (3.9 × 10⁻³ M)²⁴, whereas the γcmc of NHC-PdMS (36.7 mN·m⁻¹) was higher than that of the MS precursor (27.6 mN·m⁻¹). In situ formation of an NHC-based MS by mixing imidazolium bromide with Pd(OAc)₂ also had the ability to lower the surface tension, but its CMC (1.2 × 10⁻³ M) was higher than that of NHC-PdMS³⁰. This difference arose from the use of NEt₃ as a co-ligand in NHC-PdMS. Coordination of NEt₃ to Pd(II) in the trans position led to increased hydrophobicity as well as steric bulkiness at the air–water interface, resulting in the lower CMC and higher γcmc of NHC-PdMS. Suades et al. have previously reported a phosphine-based MS, in which two amphiphilic phosphine ligands were coordinated to one Pd(II) to give the Gemini form, leading to a reduced CMC value³⁷. Osakada et al. have reported bipyridine-based MSs with two amphiphilic bipyridine ligands bound to one Pd(II) or Pt(II) center (Gemini forms) also reduced CMC relative to that of the amphiphilic bipyridine ligand³⁸. Interestingly, the CMCs were independent of the kind of the metal. Thus, structural changes to form Gemini-type MSs after complexation could be the main factor responsible for this effect. In contrast, such structural changes did not occur in our NHC-PdMS system. Thus, the reduction of the CMC value after complexation could be attributed to an increase in hydrophobicity as well as a decrease in electronic repulsion via complexation of Pd(II) together with NEt₃ to the MS precursor.

3.3 DLS measurements

DLS measurements were performed to examine the effect of Pd complexation on micelle formation in water, as shown in Fig. 3. Based on the histograms, the hydrodynamic diameter (Dh) of NHC-PdMS micelles (25.8 ± 5.6 nm) was larger than that of the MS precursor micelles (2.5 ± 0.3 nm)²⁴. Based on molecular modeling (Chem3D, molecular mechanics (MM) calculation), the fully extended molecular length of the surfactant was expected to be ca. 4 nm. As the micellar diameter is generally almost twice the molecular length, the obtained Dh value for the MS precursor was shorter than expected. To confirm this, 2D NOESY NMR measurements were conducted for the MS precursor (10 mM) in D₂O. The spectrum showed cross peaks between octaethylene glycol and imidazolium moieties, suggesting that the former surrounded the imidazolium group. This result indicated that the MS precursor does not adopt a fully extended conformation but instead forms a contracted conformation with a relatively larger head group. Thus, we expected that the MS precursor formed spherical micelles, whereas NHC-PdMS could form different types of aggregates. This different aggregation behavior may arise from the increased hydrophobicity induced by the coordination of Pd(II) as a heavy metal to the MS precursor. NEt₃, which was coordinated to Pd(II) in a trans position, also contributed by increasing the steric bulkiness as shown in Fig. 1. It has also been reported that complexation of Pd(II) to amphiphilic phosphine ligands increases the aggregation number, and leads to the formation of vesicles in water³⁷.
3.4 Aqueous phase behavior of NHC-PdMS

As described above, MS formation promoted self-assembly in dilute aqueous solution. It is known that MSs show lyotropic phase behavior at high concentrations\(^{31,32}\). Thus, the lyotropic phase behavior of NHC-PdMS at high concentrations was examined based on a combination of visual inspection, polarized optical microscopy, and SAXS measurements. First, the phase behavior of the MS precursor was preliminarily investigated using the water-penetration scan technique. The MS precursor did not provide an anisotropic phase at any concentration. In contrast, NHC-PdMS provided an optically anisotropic phase. To directly determine the structure of the lyotropic liquid crystals, SAXS measurements were conducted at 25°C. Typical scattering curves for 20 and 60 wt% samples are shown in Fig. 4. At 20 wt%, the SAXS pattern exhibited a broad peak around 2 nm\(^{-1}\), whereas at 60 wt%, the SAXS pattern exhibited three clear peaks, with a spacing ratio of 1:2:3 for the first, second, and third Bragg peaks. These results indicate that Pd(II) induced the formation of a lamellar structure. To obtain further insight into the lamellar structure of NHC-PdMS, the lamellar d-spacing of the [100] plane was estimated from the primary peak position at various concentrations. The obtained lamellar d-spacings were plotted as a function of NHC-PdMS concentrations. The d-spacing was constant between 5 and 20 wt%, but an increased d-spacing (8.7 nm) was observed for the lamellar structure at 40 wt%, followed by a decrease of the d-spacing at higher NHC-PdMS concentrations (6.9 nm for 50 wt%, 6.0 nm for 60 wt%, and 2.1 nm for 80 wt%), suggesting shrinkage of the water pool in the bilayer. The d-spacing at 80 wt% was almost equal to the molecular length of contracted octaethylene glycol (ca. 2 nm based on a calculation), suggesting the formation of an interdigitated bilayer.

Fig. 3 Size distributions of (a) MS precursor (10 mM) and (b) NHC-PdMS (10 mM) in water at 25°C.

Fig. 4 SAXS patterns for the lyotropic liquid crystals of NHC-PdMS at (a) 20 wt% and (b) 60 wt% at 25°C.
the MS precursor, as coordination of NEt₃ to Pd(II) at the trans position led to increased hydrophobicity and steric bulkiness. Consequently, the decreased electric charge of the MS precursor after complexation influenced its self-assembling properties.

3.5 Catalytic activity of NHC-PdMS for aqueous Mizoroki–Heck reactions

As described above, NHC-PdMS showed distinctive self-assembly behavior in water. To apply the reactive interface formed by the MS in aqueous catalytic reaction systems, we conducted Mizoroki–Heck reactions under dilute conditions (Table 1). First, as a typical protocol, iodobenzene was reacted with styrene together with NHC-PdMS (3 mol%) as a catalyst in DMF. Further, NEt₃ was also added, as an extra amount of NEt₃ was required to regenerate Pd(0) during the catalytic cycle. The typical protocol in an organic solvent afforded stilbene as the quantitative coupling product (entry 1). The aqueous cross-coupling reaction of iodobenzene and styrene was also examined. The concentration of NHC-PdMS was fixed to be above the CMC (30 mM, 3 mol% relative to substrates). The solution formed an oil-in-water (O/W) emulsion and with the vigorous stirring of the emulsion at 70°C for 24 h, stilbene was obtained in quantitative conversion (entry 2). After SiO₂ column chromatography, stilbene was isolated in 95% yield. The reaction did not provide any regioisomers such as 1,1-diphenylethylene. These results clearly demonstrate that NHC-PdMS retained its activity under aqueous conditions and facilitated the Mizoroki–Heck reaction. It should be noted that NHC-Pd MS, whose reactivity was equal to that of a previously reported in situ generate MS, did not provide Pd black after the reaction. This result indicates that the NEt₃ was not only readily displaced to give a catalytically active Pd(0) species, but that it also stabilizes the Pd species. Navarro et al. have reported that NEt₃ co-coordinated to the Pd center after the transition from stable Pd(II) to active Pd(0) without isomerization or dimerization of the complex. Indeed, surface tension measurements of the resulting aqueous solution revealed that the γ_CM value remained constant (36.7 mN·m⁻¹), indicating that NHC-PdMS retained its molecular structure after the catalytic reaction. After the reaction, the residual oily substrate within the O/W emulsion was completely converted to stilbene as an insoluble solid, which was separated by simple filtration (52% isolated yield). As NHC-PdMS in the aqueous phase retained both its surface and catalytic activities, it could be recycled for a second reaction (48% isolat-
Self-assembling Properties of an N-Heterocyclic Carbene Based Metallosurfactant

ed yield). Several control reactions served to highlight the role of NEt₃. N, N-Dimethyloctylamine as a hydrophobic amine provided stilbene in 68% conversion (entry 3). Inorganic salts such as Na₂CO₃, K₂CO₃, and Cs₂CO₃ were less effective than NEt₃ and gave stilbene in 13, 21, and 17% conversion, respectively (entries 4, 5, and 6). These results suggested that NEt₃ plays an important role in the aqueous Mizoroki-Heck reaction. Inorganic salts would destabilize the emulsion and led to poor conversion. Lipshutz et al. have reported that the use of NEt₃ as a base for the reaction could most successfully be carried out using a nonionic amphiphile such as Triton X-100 or a vitamin E-based synthetic surfactant.

| entry | aryl halide | olefin | product | conv. (%) | isolated yield (%) |
|-------|-------------|--------|---------|-----------|--------------------|
| 1     | I           |       |         | >99       | 95                 |
| 2     | Br          |       |         | 9         | -                  |
| 3     | Cl          |       |         | 0         | -                  |
| 4     | MeO         |       | MeO     | 75        | 72                 |
| 5     | H           |       | H       | >99       | 94                 |
| 6     | O           |       | O       | >99       | 95                 |
| 7     | HO           | MeO   | HO      | >99       | 91                 |
| 8     | MeO         | MeO   | MeO     | >99       | 90                 |

4 CONCLUSIONS

In this study, an NHC-based MS (NHC-PdMS) where the Pd center was located between the hydrophilic and hydrophobic parts of the surfactant via a Pd–carbene bond, was synthesized by stepwise ligand substitution reactions. The use of NEt₃ as a hemilabile ligand regulated Pd isomerization to give NHC-PdMS as a single isomer. Interestingly, the CMC value of the surfactant decreased after complexation.

J. Oleo Sci. 67, (9) 1107-1115 (2018)
with Pd. In contrast to the MS precursor, NHC-PdMS formed larger aggregates in dilute aqueous solution. Furthermore, it was found that Pd(II) affects the lyotropic liquid crystal structure, with coordination of the MS precursor and NEt₃ to Pd(II) resulting in distinctive self-assembly to form a lamellar structure over a wide concentration range (>26 wt.%).

Based on the advantageous aqueous phase behavior of NHC-PdMS, the applicability of the MS as an aqueous catalyst was examined for the Mizoroki–Heck reaction under dilute conditions. The reaction of iodobenzene and styrene by complexation of transition metals allows reactions to take place under environmentally attractive conditions. Thus, NHC-PdMS has the potential for catalyzing various organometallic reactions in water, while realizing the philosophy of green sustainable chemistry.

References
1) Griffiths, P.C.; Fallis, I.A.; Chuenpratoom, T.; Watanask, R. Metallosurfactants: Interfaces and micelles. Adv. Colloid Interface Sci. 122, 107-117 (2006).
2) Griffiths, P.C.; Fallis, I.A.; Tatchell, T.; Bushby, L.; Beeby, A. Aqueous solutions of transition metal containing micelles. Adv. Colloid Interface Sci. 144, 13-23 (2008).
3) Griffiths, P.C.; Fallis, I.A.; James, C.; Morgan, I.R.; Brett, G.; Heenan, R.K.; Schweins, R.; Giillo, I.; Paul, A. Structure–property relationships in metallosurfactants. Soft Matter 6, 1981-1989 (2010).
4) Polarch, S.; Landsmann, S.; Kleiber, A. Hybrid surfactant systems with inorganic constituents. Angew. Chem. Int. Ed. 53, 946-954 (2014).
5) Zhang, J.; Meng, X.-G.; Zeng, X.-C.; Yu, X.-Q. Metallo-micellar supramolecular systems and their applications in catalytic reactions. Coord. Chem. Rev. 253, 2166-2179 (2009).
6) Mauro, M.; Paolo, G.D.; Otter, M.; Donghi, D.; D’Alfonso, G.; De Cola, L. Aggregation induced color change for phosphorescent iridium(III) complex-based anionic surfactants. Dalton Trans. 40, 12162-12167 (2011).
7) Gong, P.; Chen, Z.; Chen, Y.; Wang, W.; Wang, X.; Hu, A. High-relaxivity MRI contrast agents prepared from miniemulsion polymerization using gadolinium(III)-based metallosurfactants. Chem. Commun. 47, 4240-4242 (2011).
8) Jervis, H.B.; Bruce, D.W.; Raimondi, M.E.; Seddon, J.M.; Maschmeyer, T.; Raja, T. R. Templating mesoporous silicates on surfactant ruthenium complexes: A direct approach to heterogeneous catalysts. Chem. Commun. 2031-2032 (1999).
9) Kaur, R.; Mehta, S.K. Self aggregating metal surfactant complexes: Precursors for nanostructures. Coord. Chem. Rev. 262, 37-54 (2014).
10) Sorella, G.L.; Strukul, G.; Scarso, A. Recent advances in catalysis in micellar media. Green Chem. 17, 644-683 (2015).
11) Bhattacharyya, S.; Kumari, N. Metallo-micelles as potent catalysts for the ester hydrolysis reactions in water. Coord. Chem. Rev. 253, 2133-2149 (2009).
12) Satake, I.; Iwamatsu, I.; Hosokawa, S.; Matuura, R. The surface activities of bivalent metal alkyl sulfates. I. On the micelles of some metal alkyl sulfates. Bull. Chem. Soc. Jpn. 36, 204-209 (1963).
13) Satake, I.; Matuura, R. The surface activities of bivalent metal alkyl sulfates. II. The solubilization of some hydrocarbons in aqueous solutions of bivalent metal alkyl sulfates. Bull. Chem. Soc. Jpn. 36, 813-817 (1963).
14) Kobayashi, S.; Wakabayashi, T. Scandium trisdodecyl-sulfate (STDS). A new type of Lewis acid that forms stable dispersion systems with organic substrates in water and accelerates aldol reactions much faster in water than in organic solvents. Tetrahedron Lett. 39, 5389-5392 (1998).
15) Manabe, K.; Mori, Y.; Wakabayashi, T.; Nagayama, S.; Kobayashi, S. Organic synthesis inside particles in water: Lewis acid–surfactant-combined catalysts for organic reactions in water using colloidal dispersions as reaction media. J. Am. Chem. Soc. 122, 7202-7207 (2000).
16) Scrimin, P.; Tecilla, P.; Tonellato, U.; Vendrame, T. Aggregates of Cu(II) and Cu(I) and their binding ability of cationic metallosurfactants. J. Org. Chem. 54, 5988-5991 (1989).
17) Valls, E.; Solsona, A.; Suades, J. Synthesis and characterization of new amphiphilic phosphines and palladium metallosurfactants. Organometallics 21, 2473-2480 (2002).
18) Parera, E.; Comelles, P.; Barnadas, R.; Suades, J. New surfactant phosphine ligands and platinum(II)metallosurfactants. Influence of metal coordination on the critical micelle concentration and aggregation properties. Langmuir 26, 743-751 (2010).
19) Hamasaka, G.; Muto, T.; Uozumi, Y. Molecular-architecture-based administration of catalysis in water: Self-assembly of an amphiphilic palladium pincer complex. Angew. Chem. Int. Ed. 50, 4876-4878 (2011).
20) Hamasaka, G.; Muto, T.; Uozumi, Y. A novel amphiphilic palladium pincer complex: Design, preparation and
self-assembling behavior. \textit{Dalton Trans.} \textbf{40}, 8859-8868 (2011).

21) Diez-González, S.; Marion, N.; Nolan, S.P. \textit{N}-Heterocyclic carbene in late transition metal catalysis. \textit{Chem. Rev.} \textbf{109}, 3612-3676 (2009).

22) Hopkinson, M.H.; Richter, C.; Schedler, M.; Glorius, F. An overview of \textit{N}-heterocyclic carbenes. \textit{Nature} \textbf{510}, 485-496 (2014).

23) Levin, E.; Ivry, E.; Diesendruck, C.E.; Lemcoff, N.G. \textit{N}-Heterocyclic carbenes in late transition metal catalysis. \textit{Chem. Rev.} \textbf{109}, 3612-3676 (2009).

24) Taira, T.; Yanagimoto, T.; Sakai, K.; Sakai, H. Endo, A.; Imura, T. Synthesis of surface-active \textit{N}-heterocyclic carbene ligand and its Pd-catalyzed aqueous Mizoroki-Heck reaction. \textit{Tetrahedron} \textbf{72}, 4117-4122 (2016).

25) Organ, M.G.; Çalimsiz, S.; Sayah, M.; Hoi, K.H.; Lough, A.J. Pd-PEPPSI-I-Pent: An active, sterically demanding cross-coupling catalyst and its application in the synthesis of tetra-ortho-substituted biaryl. \textit{Angew. Chem. Int. Ed.} \textbf{48}, 2383-2387 (2009).

26) Valente, C.; Çalimsiz, S.; Hoi, K.H.; Mallik, D.; Sayah, M.; Organ, M.G. The development of bulky palladium NHC complexes for the most-challenging cross-coupling reactions. \textit{Angew. Chem. Int. Ed.} \textbf{51}, 3314-332 (2012).

27) Zhong, R.; Pothig, A.; Feng, Y.; Riener, K.; Herrmann, W.A.; Kuhn, F.E. Facile-prepared sulfonated water-soluble PEPPSI-Pd-NHC catalysts for aerobic aqueous Suzuki-Miyaura cross-coupling reactions. \textit{Green Chem.} \textbf{16}, 4955-4962 (2014).

28) Chen, M.T.; Vicic, D.A.; Turner, M.L.; Navarro, O. (\textit{N}-Heterocyclic carbene)PdCl\textsubscript{2}(TEA) complexes: Studies on the effect of the “throw-away” ligand in catalytic activity. \textit{Organometallics} \textbf{30}, 5052-5056 (2011).

29) Chen, M.T.; Vicic, D.A.; Chain, W.J.; Turner, M.L.; Navarro, O. Inhibited catalyst activation in (\textit{N}-heterocyclic carbene)PdCl\textsubscript{2}(diethylamine) complexes: by intramolecular hydrogen bonding. \textit{Organometallics} \textbf{30}, 6770-6773 (2011).

30) Taira, T.; Suzuki, Y.; Osakada, K. Pd\textsuperscript{II} and Pt\textsuperscript{II} complexes with amphiphilic ligands: Formation of micelles and [5]rotaxanes with \textit{α}-cyclodextrin in aqueous solution. \textit{Chem. Asian J.} \textbf{3}, 895-902 (2008).

31) Donnio, B.; Bruce, D.W. Metallomesogens. \textit{Struct. Bonding} \textbf{95}, 193-247 (1999).

32) Donnio, B. Lyotropic metallomesogens. \textit{Curr. Opin. Colloid Interface Sci.} \textbf{7}, 371-394 (2002).

33) Anderson, D.; Wennerstöm, H. Olsson, U. Isotropic biphasic solutions in surfactant–solvent systems: The L3 phase. \textit{J. Phys. Chem.} \textbf{93}, 4243-4253 (1989).

34) Imura, T.; Ohta, N.; Inoue, K.; Yagi, N.; Negishi, H.; Yanagishita, H.; Kitamoto, D. Naturally engineered glycolipid biosurfactants leading to distinctive self-assembled structures. \textit{Chem. Eur. J.} \textbf{12}, 2434-2440 (2006).

35) Imura, T.; Hikosaka, Y.; Worakitkanchanakul, W.; Sakai, H.; Abe, M.; Konishi, M.; Minamikawa, H.; Kitamoto, D. Aqueous-phase behavior of natural glycolipid biosurfactant mannosylerythritol lipid A: Sponge, cubic, and lamellar phases. \textit{Langmuir} \textbf{23}, 1659-1663 (2007).

36) Lipshitz, B.H.; Taft, B.R. Heck coupling at room temperature in nanometer aqueous micelles. \textit{Org. Lett.} \textbf{10}, 1329-1332 (2008).