Hybrid Surfactants with N-Heterocyclic Carbene Heads as a Multifunctional Platform for Interfacial Catalysis

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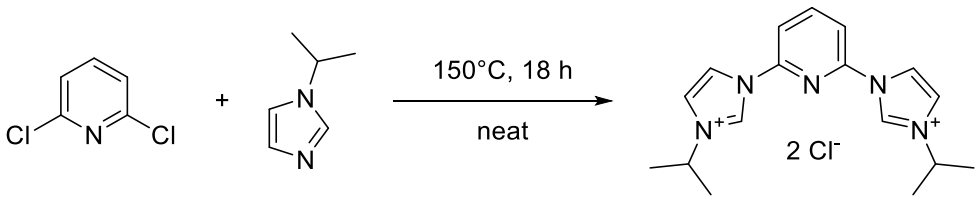
Supporting Information

Experimental Section

Synthetic procedures.

All reactions were carried out under nitrogen in a nitrogen filled glovebox (MBraun) or using common Schlenk-techniques. THF and diethyl ether were distilled from sodium/ benzophenone ketyl. Dichloromethane was distilled from CaH_2. The solvents were degassed by repetitive freeze/pump/thaw cycles and stored under dry nitrogen or argon. All other reagents were commercial grade and used as received. $Pd(MeCN)_2Cl_2$ [1] and $Fe(thf)_{1.5}Cl_2$ [2] were prepared according to literature procedures.

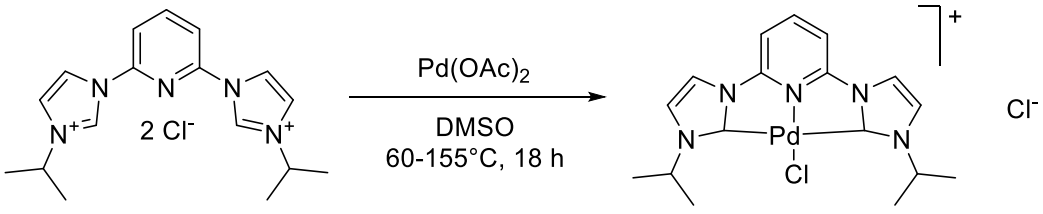
Synthesis of 2,6-Di-iso-propylimidazoliumpyridine



2,6-Dichloropyridine (2 g, 13.5 mmol) and N-*iso*-propylimidazole (4 ml, 35.2 mmol) were mixed together in a pressure tube. The mixture was heated to 150°C for 18 h. After cooling to room temperature, the brown mixture was dissolved in 40 ml MeOH. Addition of 100 ml ether lead to precipitation of a white solid, which was filtered off, washed with ether and dried in vacuo to yield the product (89%).

^{1}H-NMR (400 MHz, **DMSO-d_6**): δ (ppm) = 8.57 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, pyridine *para*-H), 8.54 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, –N–**C_H**–C_H–N–), 8.02 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, pyridine *meta*-H), 7.98 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, –N–C_H–**C_H**–N–), 5.61 (sep, $^3J_{HH}$ = 6.7 Hz, 2 H, Im-**(CH)**-$(CH_3)_2$), 1.46 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, Im-(CH)-**$(CH_3)_2$**).

Synthesis of $(iPrIm)_2Pd$ ***7***

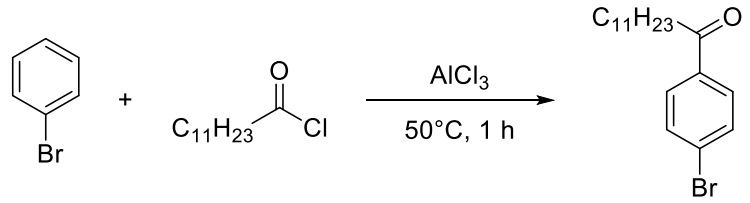


2,6-Di-iso-propylimidazoliumpyridine (760 mg, 2.06 mmol) and Palladium(II)-acetate were suspended in 12 ml of DMSO and heated to 60°C for 16, followed by 155°C for 1 h. The volatiles were removed in vacuo and the resulting brown residue was washed with a small portion of acetonitrile and pentane to yield the palladium NHC-complex as a light brown solid (59%).

^{1}H-NMR (400 MHz, **DMSO-d_6**): δ (ppm) = 8.57 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, pyridine *para*-H), 8.54 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, –N–**C_H**–C_H–N–), 8.02 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, pyridine *meta*-H), 7.98 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, Pyridinring), 5.61 (sep, $^3J_{HH}$ = 6.7 Hz, 2 H, Im-**(CH)**-$(CH_3)_2$), 1.46 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, Im-(CH)-**$(CH_3)_2$**).

ESI-MS (positive): m/z = 438.0452 (measured), 438.0481 (simulated) $[M\text{-}Cl]^+$.

Synthesis of 1-Bromo-4-dodecanoylbenzene

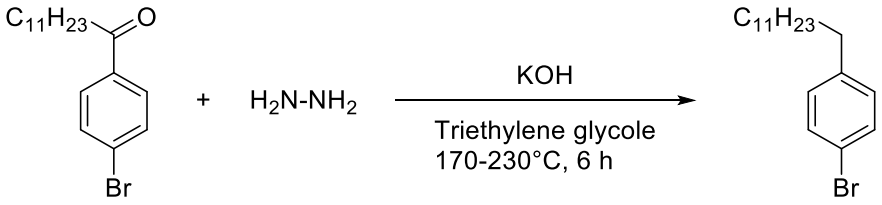


This compound was synthesized by a typical Friedel-Crafts procedure as previously published.[3]

Dodecanoylchloride (21.7 g, 114 mmol) was added dropwise to a stirred suspension of Aluminiumtrichloride (18.3 g, 137 mmol) in Bromobenzene (35.9 g, 228 mmol). After complete addition, the suspension was stirred for 1 h at 50 °C. The decreased evolution of HCl gas showed the complete conversion. The yellowish solution was carefully poured into 200 ml ice water and extracted three times with dichloromethane (100 ml). The combined organic phases were dried over $MgSO_4$ and the volatiles were removed under vaccum. The yellow residue was recrystallized from ethyl acetate to yield the final compound in form of a white powder (83%).

^{1}H-NMR (400MHz, **$CDCl_3$**): δ (ppm) = 7.81 (d, 3JHH = 8.5 Hz, 2 H, arom. H), 7.59 (d, 3JHH = 8.5 Hz, 2 H, arom. H), 2.91 (t, 3JHH = 7.3 Hz, 2 H, Ph–(CH2)), 1.72 (q, 3JHH = 7.3 Hz, 2 H, Ph–(CH2) –(CH2)), 1.12-1.47 (m, 12 H, alkyl chain), 0.88 (t, 3JHH = 6.7 Hz, 3 H, (CH2) –(CH3)).

Synthesis of 1-Bromo-4-dodecylbenzene

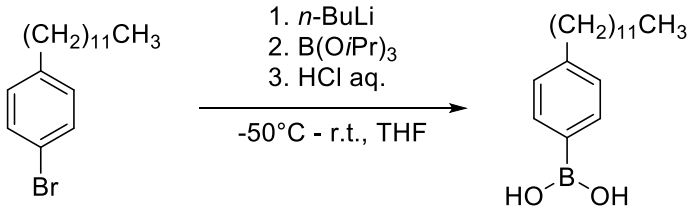


This compound was synthesized by a Wolff-Kishner reduction (Huang Minglon modification) as previously published. [3]

A mixture of 1-Bromo-4-dodecanoylbenzene (19.9 g, 58.9 mmol), KOH (13.2 g, 236 mmol) and hydrazine (9.45 g, 295 mmol, solution of 50 wt.%) in 100 ml of triethylene glycole was heated to reflux (170°C) for 5 h. The remaining hydrazine was distilled off by raising the temperature stepwise to 230°C for 1 h. The viscous orange residue was poured into 200 ml ice water and the pH of the suspension was adjusted to approximately 7 by adding conc. HCl. The mixture was extracted three times with dichloromethane (100 ml) and the combined organic phases were dried over $MgSO_4$. After removal of the solvent under vaccum, the orange residue was purified by flash chromatography (100% petrol ether) to yield the product as a clear, colorless oil (60%).

^{1}H-NMR (400MHz, **$CDCl_3$**): δ (ppm) = 7.28 (d, 3JHH = 8.5 Hz, 2 H, arom. H), 7.04 (d, 3JHH = 8.5 Hz, 2 H, arom. H), 2.55 (t, 3JHH = 7.5 Hz, 2 H, Ph–(CH2)), 0.77-1.67 (m, 23 H, alkyl chain).

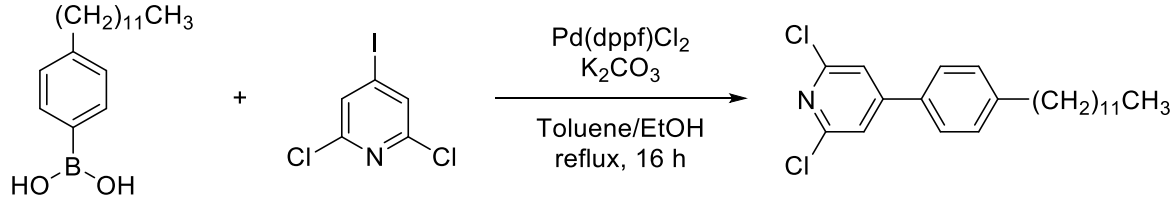
*Synthesis of 4-Dodecylphenylboronic acid **1***



To a solution of 1-Bromo-4-dodecylbenzene (1 g, 3 mmol) in 10 ml THF, *n*-Butyllithium (3.6 mmol, 1.6 M in hexane) was added dropwise at -50°C. After stirring one hour at -50°C, Tri-*iso*-propylborate (1 ml, 4.5 mmol) was added in one portion and the reaction mixture was stirred further over night at room temperature. The milky solution was treated with 100 ml of 2 M HCl for 1 h and extracted three times with dichloromethane (50 ml). The combined organic phases were washed with diluted $NaHCO_3$ solution and dried over $MgSO_4$. Removal of the solvent yielded the crude product as a white solid, which was used in the next step without further purification.

^{1}H-NMR (400MHz, **$CDCl_3$**): (ppm) = 8.15 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, arom. H), 7.32 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, arom. H), 2.69 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, Ph–**CH_2**), 1.67 (q, $^3J_{HH}$ = 7.5 Hz, 2 H, Ph–CH_2–**CH_2**–), 1.18-1.45 (m, 18 H, alkyl chain), 0.89 (t, $^3J_{HH}$ = 8.0 Hz, 3 H,
–CH_2–**CH_3**).

*Synthesis of 2,6-Dichloro-4-dodecylphenylpyridine **3***

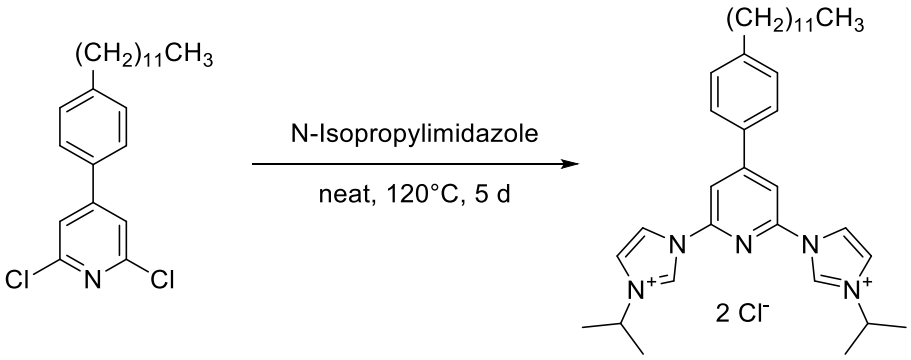


4-Dodecylphenylboronic acid (0.6 g, 2.07 mmol), 2,6-Dichloro-4-iodopyridine (0.57 g, 2.07 mmol), K_2CO_3 (0.86 g, 6.21 mmol) and $Pd(dppf)Cl_2$ (50 mg, 62 µmol) were suspended in a mixture of 8 ml toluene and 4 ml ethanol. The mixture was heated to reflux for 16 h and 50 ml of water was added after cooling to room temperature. After extraction with dichloromethane (3 x 50 ml), the combined organic phases were washed with brine and dried over $MgSO_4$. Removal of the solvent leaves a dark brown oily residue, which was purified by column chromatography (petrol ether:ethyl acetate, 1:0-20:1) to afford the product as colorless crystals (89%).

^{1}H-NMR (400MHz, **$CDCl_3$**): δ (ppm) = 7.51 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, arom. H, phenyl ring), 7.46 (s, 2 H, arom. H, pyridine ring), 7.31 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, arom. H, phenyl ring), 2.66 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, Ph–**(CH_2)**–), 1.64 (q, $^3J_{HH}$ = 7.6 Hz, 2 H, Ph–(CH_2)–**(CH_2)**–), 1.17-1.4 (m, 18 H, alkyl chain), 0.88 (t, $^3J_{HH}$ = 6.5 Hz, 3 H, –(CH_2)–**CH_3**).

GC-MS (EI+): m/z = 391.16 $[M]^+$, 356.16 $[M\text{-}Cl]^+$, 250.01 $[M\text{-}C_{10}H_{21}]^+$, 235.98 $[M\text{-}C_{11}H_{23}]^+$.

*Synthesis of the amphiphilic NHC-ligand **5b***

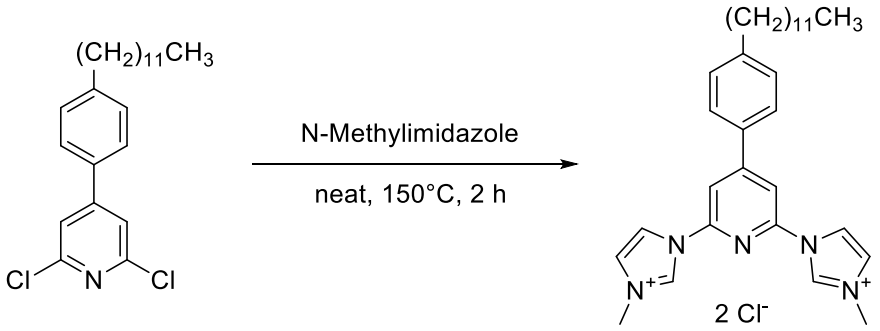


2,6-Dichloro-4-dodecylphenylpyridine (1 g, 2.5 mmol) and N-Isopropylimidazole (2 ml, 18 mmol) were combined in a sealed tube and heated to 150°C for 5 days. The brown residue was dissolved in dichloromethane and the volatiles were removed in vacuo. The resulting light brown solid was washed with a small portion of ether and dried in vacuo to yield the amphiphilic NHC-ligand.

^{1}H-NMR (400 MHz, **DMSO-d_6**): δ (ppm) = 11.00 (s, 2 H, –N–**C_H**–N–), 9.05 (s, 2 H, –N–**C_H**–C_H–N–), 8.69 (s, 2 H, pyridine ring), 8.17 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, phenyl ring), 8.31 (s, 2 H, –N–C_H–**C_H**–N–), 7.49 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, phenyl ring), 4.86 (sep, $^3J_{HH}$ = 6.7 Hz, 2 H, Im-**(CH)**-$(CH_3)_2$), 2.70 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, Ph–**CH_2**), 1.64 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, Im-(CH)-**$(CH_3)_2$**), 1.15-1.35 (m, 18 H, alkyl chain), 0.85 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, –CH2–**CH_3**).

ESI-MS (positive): m/z = 270.7105 (measured), 270.7080 (simulated) $[M\text{-}2Cl]^{2+}$.

*Synthesis of the amphiphilic NHC-ligand **5a***

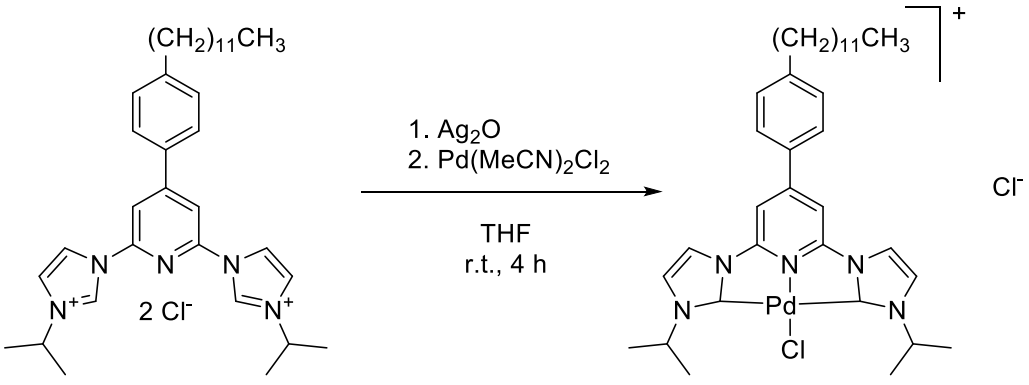


The ligand **5a** was synthesized according to the procedure described for the *iso*-propyl derivative **5b** using N-Methylimidazole at 150°C for two hours (49%).

^{1}H-NMR (400 MHz, **DMSO-d_6**): δ (ppm) = 10.88 (s, 2 H, –N–**C_H**–N–), 8.96 (s, 2 H, –N–**C_H**–C_H–N–), 8.62 (s, 2 H, pyridine ring), 8.13 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, phenyl ring), 8.08 (s, 2 H, –N–C_H–**C_H**–N–), 7.50 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, phenyl ring), 4.06 (s, 6 H, Im-**CH_3**), 2.71 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, Ph–**CH_2**), 1.64 (q, $^3J_{HH}$ = 7.05 Hz, 2 H, Ph–CH_2–**CH_2**), 1.15-1.38 (m, 18 H, alkyl chain), 0.86 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, –CH2–**CH_3**).

ESI-MS (positive): m/z = 520.3184 (measured), 520.3190 (simulated) $[M\text{-}Cl]^+$; 242.6772 (measured), 242.6758 (simulated) $[M\text{-}2Cl]^{2+}$.

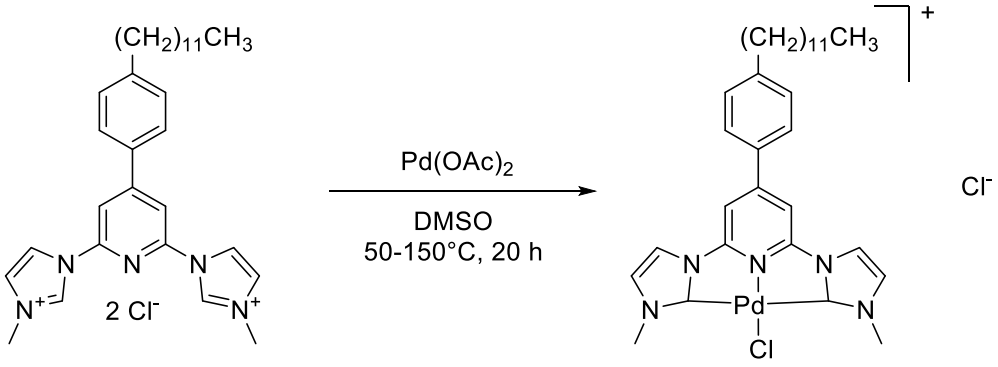
*Synthesis of the amphiphilic palladium(I)-complex **6bi***



The amphiphilic NHC-ligand (145 mg, 0.23 mmol) and silver(I)-oxide (27.5 mg, 0.12 mmol) were suspended in 10 ml of dichloromethane. The mixture was stirred for two hours at room temperature under the exclusion of light and filtrated over a 0.45 µm syringe filter. To the light brown solution, Bis(acetonitrile)dichloropalladium(I) (62 mg, 0.23 mmol) was added and the resulting solution was stirred for another two hours. The insolubles were removed by filtration over a 0.45 µm syringe filter and the filtrate was evaporated in vacuo. The resulting light brown solid was freeze dried out of benzene to yield the amphiphilic palladium NHC-complex **6bi** (79%).

ESI-MS (positive): m/z = 680.2824 (measured), 680.2780 (simulated) $[M\text{-}Cl]^+$.

*Synthesis of the amphiphilic palladium(I)-complex **6ai***

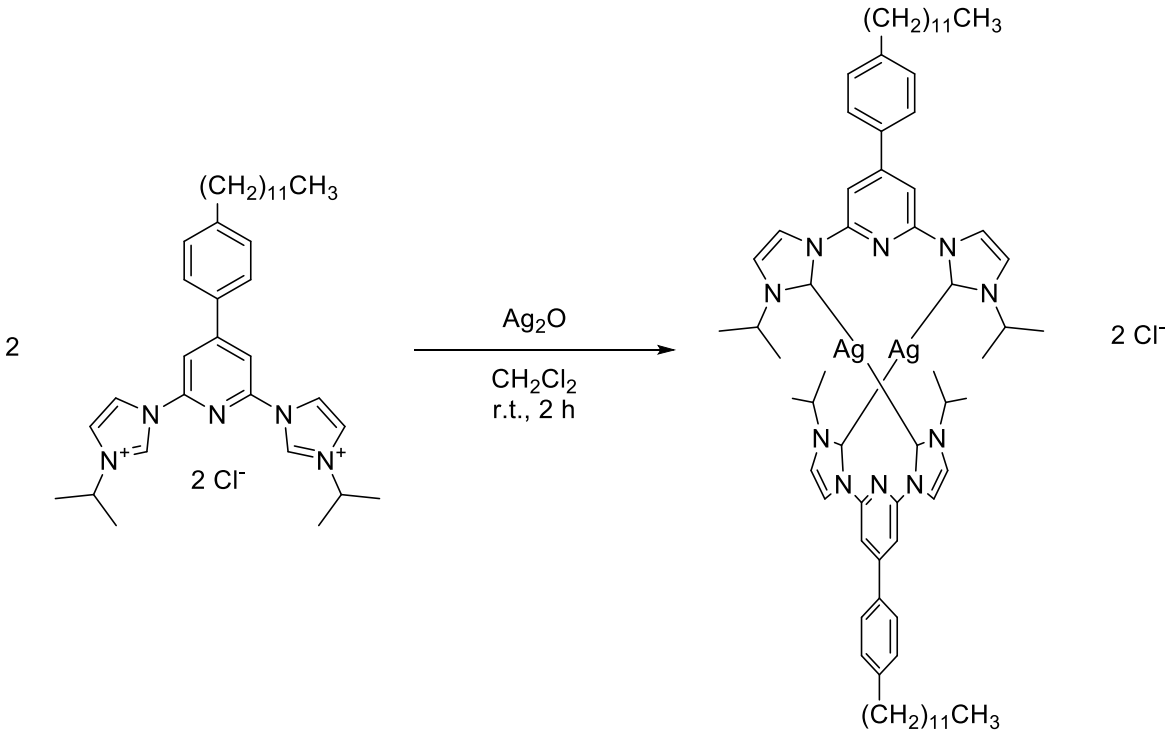


The complex **6ai** was synthesized according to the procedure described for the *iso*-propyl derivative **7** using palladium(II)-acetate with an elongated reaction time of 19 h at 50°C. The product was isolated by slow addition of diethyl ether to the crude DMSO solution, followed by filtration (39%).

^{1}H-NMR (400 MHz, DMSO-d6): δ (ppm) = 8.53 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, –N–**C_H**–C_H–N–), 8.39 (s, 2 H, pyridine ring), 8.00 (d, $^3J^{HH}$ = 8.1 Hz, 2 H, phenyl ring), 7.63 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, –N–C_H–**C_H**–N–), 7.47 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, phenyl ring), 4.00 (s, 6 H, Im-**CH_3**), 2.70 (t, $^3J_{HH}$ = 7.05 Hz, 2 H, Ph–**CH_2**), 1.64 (q, $^3J_{HH}$ = 7.05 Hz, 2 H, Ph–CH_2–**CH_2**), 1.15-1.38 (m, 18 H, alkyl chain), 0.85 (t, 3 J HH = 7.1 Hz, 3 H, –CH2–**CH_3**).

ESI-MS (positive): m/z = 624.2094 (measured), 624.2082 (simulated) $[M\text{-}Cl]^+$.

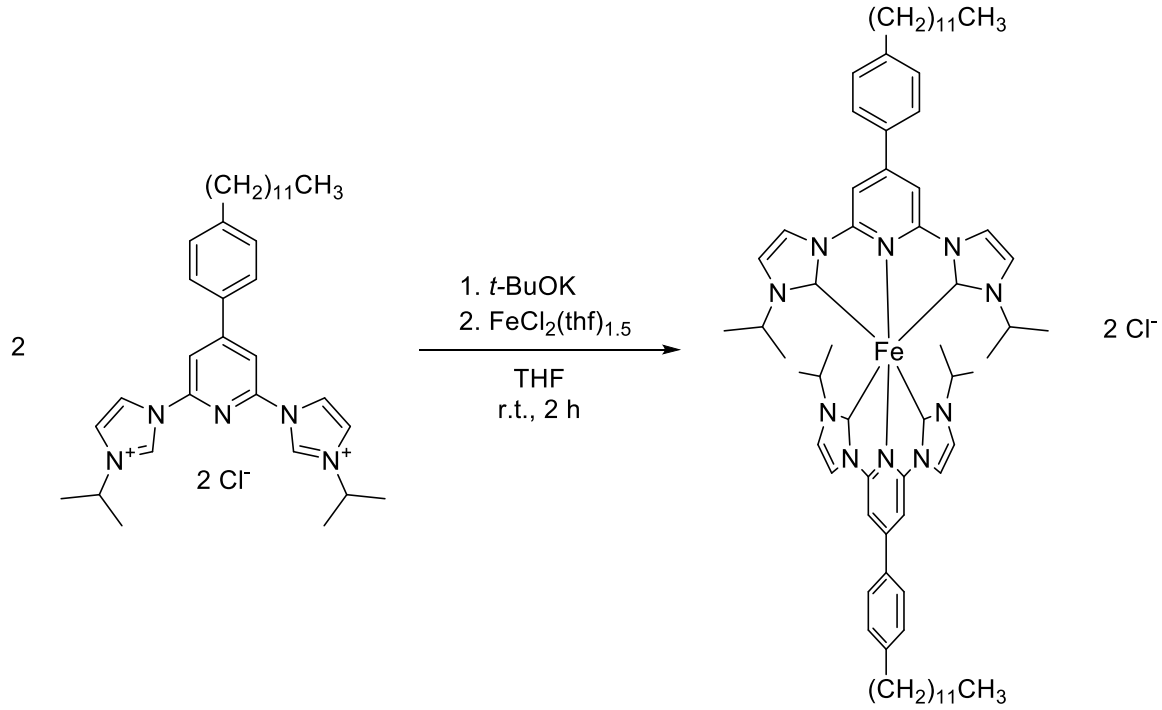
*Synthesis of the amphiphilic silver(I)-complex **6biv***



The amphiphilic NHC-ligand (145 mg, 0.23 mmol) and silver(I)-oxide (27.5 mg, 0.12 mmol) were suspended in 10 ml of dichloromethane. The mixture was stirred for two hours at room temperature under the exclusion of light and filtrated over a 0.45 µm syringe filter. The solvent was removed in vacuo and the resulting white solid was washed with pentane to yield the dimeric NHC-silver complex **6biv** (95%). Decomposition to silver(0) occurs within several days.

ESI-MS: m/z = 647.2962 (measured), 647.3000 (simulated) $[M\text{-}2Cl]^{2+}$.

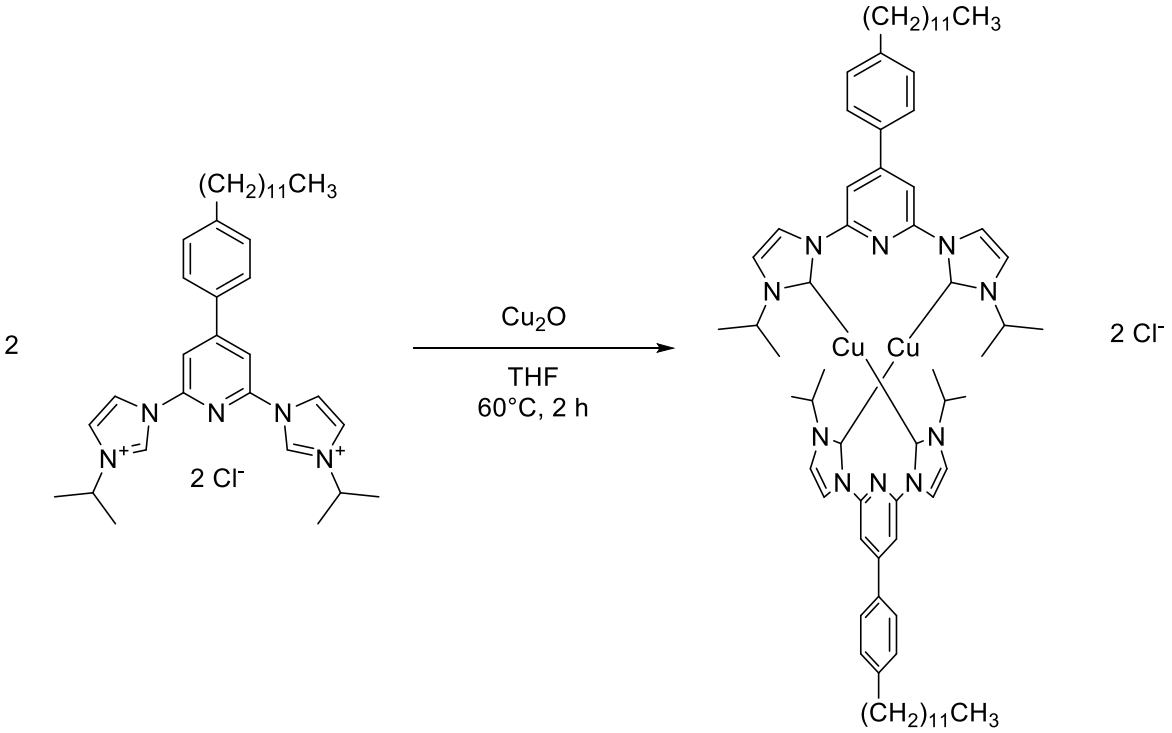
Synthesis of the amphiphilic iron(II)-complex **6bii**



The amphiphilic NHC-ligand (4 mg, 0.0065 mmol) and potassium tert-butanolate (1.5 mg, 1.5 ml of a 1 mM stock solution in THF) were combined in 2 ml of THF and heated to 40°C for 30 min. To the yellow solution, $Fe(thf)_{1.5}Cl_2$ (1.5 mg, 0.0065 mmol) was added and the resulting solution was stirred for one hour. A sample of 50 µl was taken for ESIMS analysis.

ESI-MS (positive): m/z = 566.3669 (measured), 566.3668 (simulated) $[M\text{-}2Cl]^{2+}$.

Synthesis of the amphiphilic copper(I)-complex ***6biii***



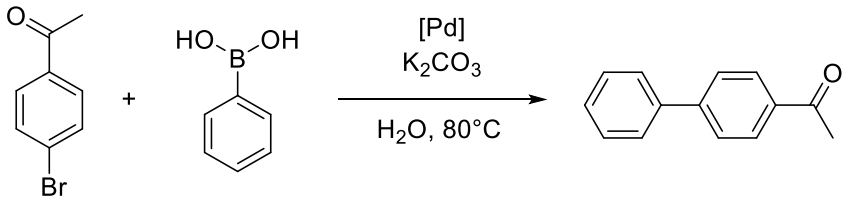
The amphiphilic NHC-ligand (5 mg, 0.0081 mmol) and copper(I) oxide (2 mg, 0.014 mmol) were combined in 2 ml of THF and heated to 60°C for two hours. A sample of 50 µl was taken for ESIMS analysis.

ESI-MS (positive): m/z = 603.3358 (measured), 603.3300 (simulated) $[M\text{-}2Cl]^{2+}$.

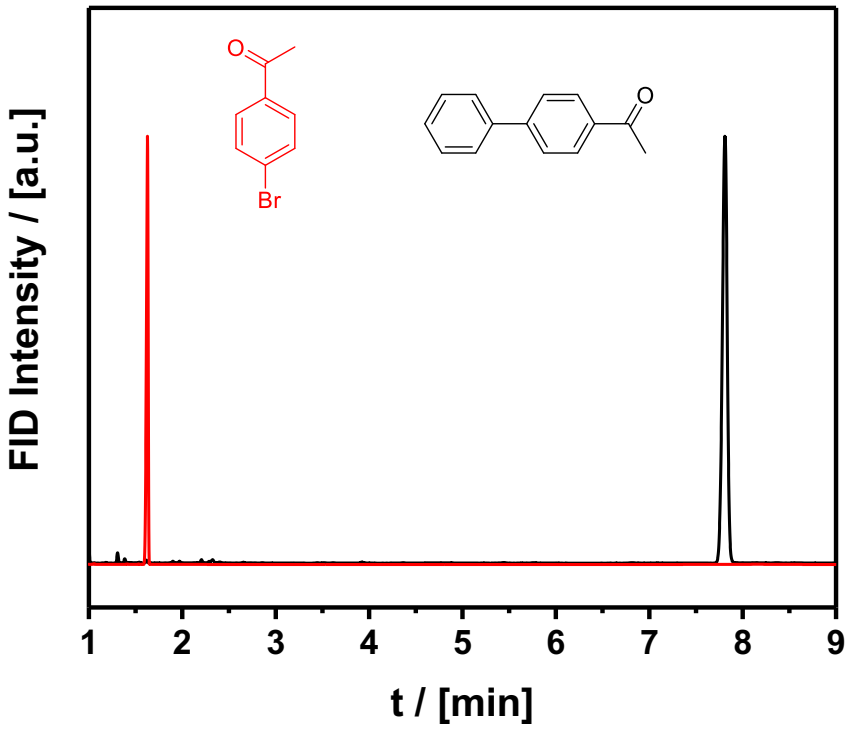
Analytic procedures.
GC-MS measurements were carried out on a Thermo-Fisher Trace 1310 (FID detection, injection temperature 200°C, temperature gradient 50°C-230°C within 10 min) coupled to a ISQ QD single quadrupole mass spectrometer. ESI mass spectra were recorded on a Bruker micrOTOF focus II mass spectrometer coupled to a Dionex 3000 UHPLC (RP-C18, water/acetonitrile, 0,1% formic acid). DLS size distributions were measured on a Malvern Zetasizer Nano ZSP at 20°C in water or methanol. For the surface tension measurements and determination of the CMC, a Krüss K100 force tensiometer with Metrohm Dosino units was used. For cryo-TEM studies, a 2 µL droplet of dispersion was put on a lacey carbon-coated copper grid, where most of the liquid was removed with blotting paper in a temperature- and humidity-controlled freezing unit (Leica EM GP, Germany), leaving a thin film stretched over the lace. The specimens were instantly vitrified by rapid immersion into liquid ethane and cooled to approximately 90 K. The temperature and the humidity as monitored and kept constant in the environmental chamber during all of the sample preparation steps. After freezing, the specimen was inserted into a cryo-transfer holder (CT3500, Gatan, Germany) and transferred to a Zeiss EM922 OMEGA EFTEM (Zeiss Mikroskopie, Germany). Examinations were carried out at temperatures around 95 K. Zero-loss filtered micrographs (E ~ 0 eV) were recorded under reduced dose conditions (100-1000 e/nm^2). Geometry optimization was performed using Density-Functional Theory (DFT) with the TURBOMOLE Program Package for ab initio Electronic Structure Calculations using B3LYP/def2-TZVP level of theory. TURBOMOLE V7.1, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com. The authors acknowledge support by the state of Baden-Württemberg through bwHPC.

Catalytic performance test (Suzuki coupling, Heck reaction)

Suzuki coupling of 1-bromoacetophenone and phenylboronic acid



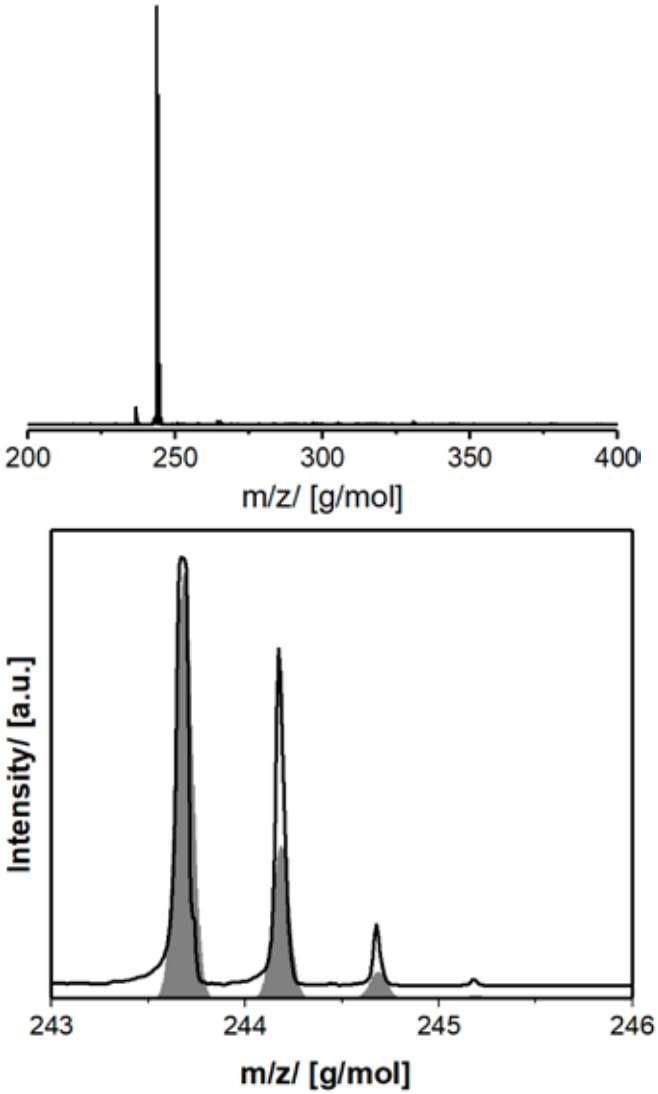
4-Bromoacetophenone (0.31 mmol, 62 mg), phenylboronic acid (50 mg, 0.41 mmol), potassium carbonate (87 mg, 0.63 mmol) and the corresponding palladium catalyst **7** or **6bi** (5 mol%, 0.016 mmol) were dispersed in 15 ml of water and the mixture was heated to 80°C. In regular time periods, a sample of 0.4 ml was taken and extracted with 2 ml of diethyl ether. The ether phase was directly analyzed via GC-MS using 1-buatanol as an internal standard.



Exemplary GC-FID chromatogram showing a conversion of >99% (red: chromatogram of the starting material 1-bromoacetophenone, black: chromatogram of the reaction mixture after a reaction time of 30 min).

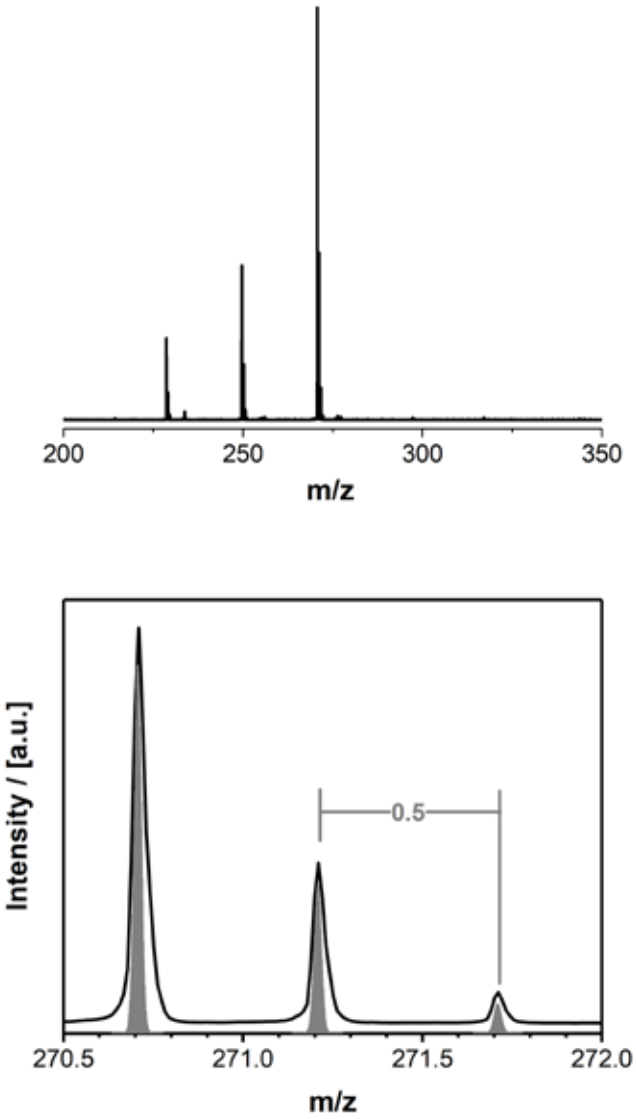
Fig. S1. ESIMS spectra of organic ligands.

(a) Compound 5a



black: experimental pattern
grey: signals expected for $[M]^{2+}$

(b) Compound 5b



black: experimental pattern
grey: signals expected for $[M]^{2+}$

Fig. S2.
Determination of surface excess and minimum area per molecule in the interface.

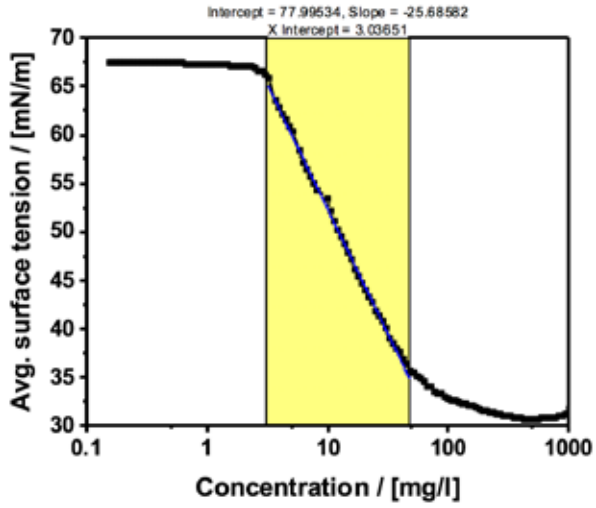
The surface excess is given by:

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d\ln c}$$

The minimum area per molecule at the air/water interface can be calculated as follows:

$$A_m = \frac{10^{20}}{N\,\Gamma}$$

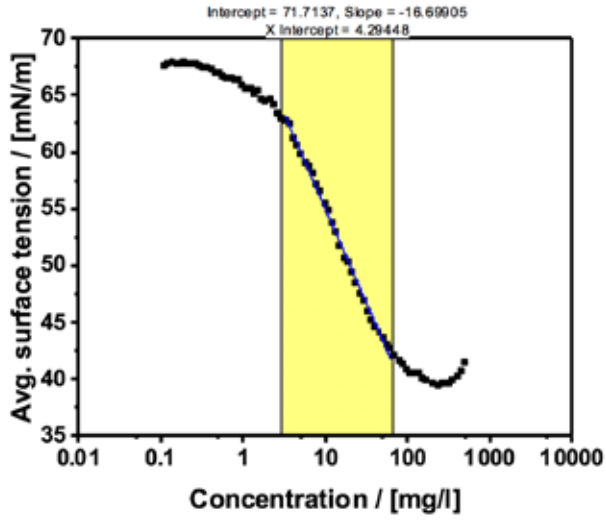
Compound 5a



$$\Gamma = -\frac{-25.686 * 10^{-3}}{298 * 8.314} = 1.04 * 10^{-5}\ mol/m2$$

$$a = \frac{10^{20}}{1.04 * 10^{-5} * 6.023 * 10^{23}} = 16.0\ \text{Å}^2$$

Compound 5b



$$\Gamma = -\frac{-16.70 * 10^{-3}}{298 * 8.314} = 6.74 * 10^{-6}\ mol/m2$$

$$a = \frac{10^{20}}{6.74 * 10^{-6} * 6.023 * 10^{23}} = 24.6\ \text{Å}^2$$

Fig. S3.
Molecular extension of a single surfactant molecule determined by DFT calculations.

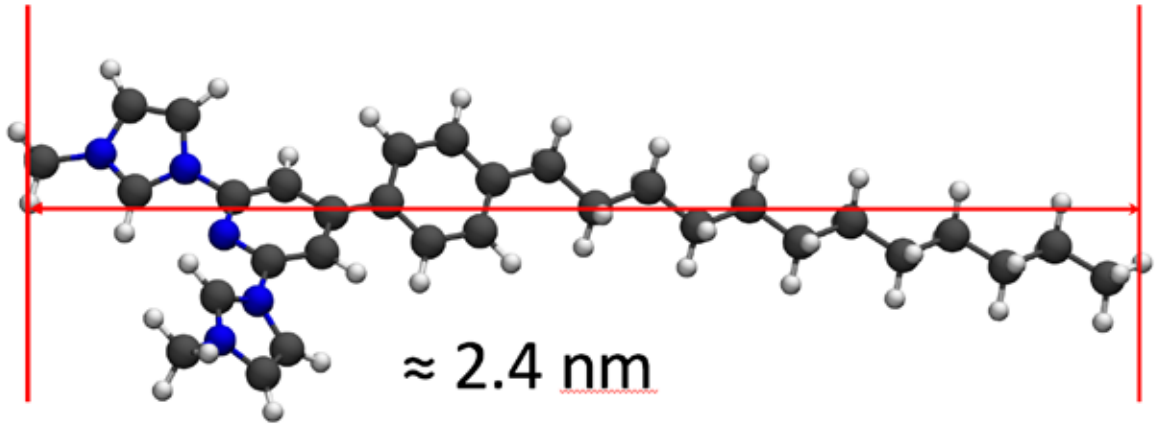
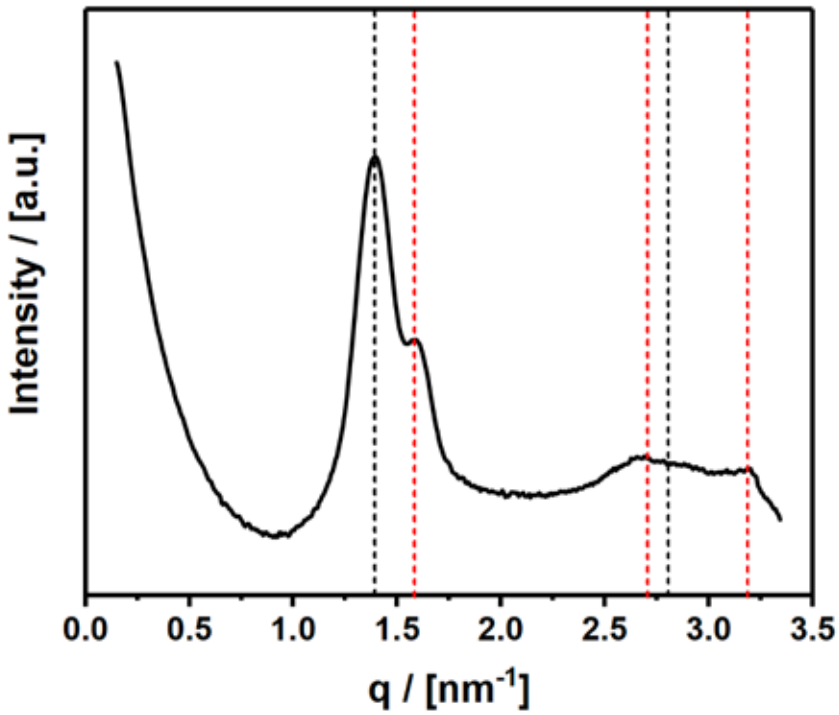


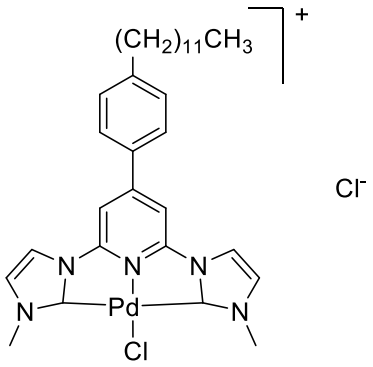
Fig. S4.
SAXS pattern of the LC phase formed by surfactant 5b.



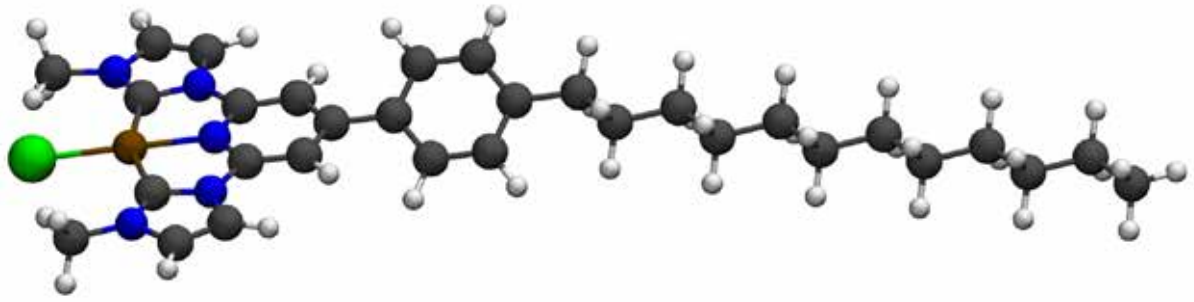
black bars ≅ lamellar phase (periodicity 4.5 nm)
red bars ≅ hexagonal phase (periodicity 4.5 nm)

Fig. S5.
Additional information for complexes 6a,b(i-iv).

Compound 6ai:

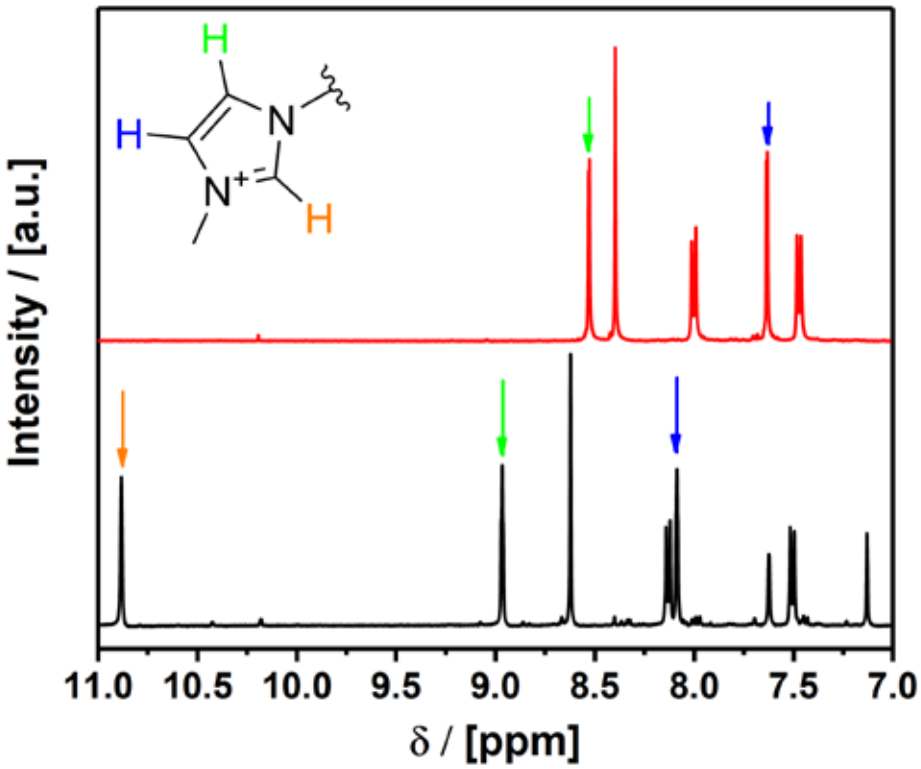


Molecular structure (DFT)



black = carbon
grey = hydrogen
blue = nitrogen
red = palladium
yellow = chlorine

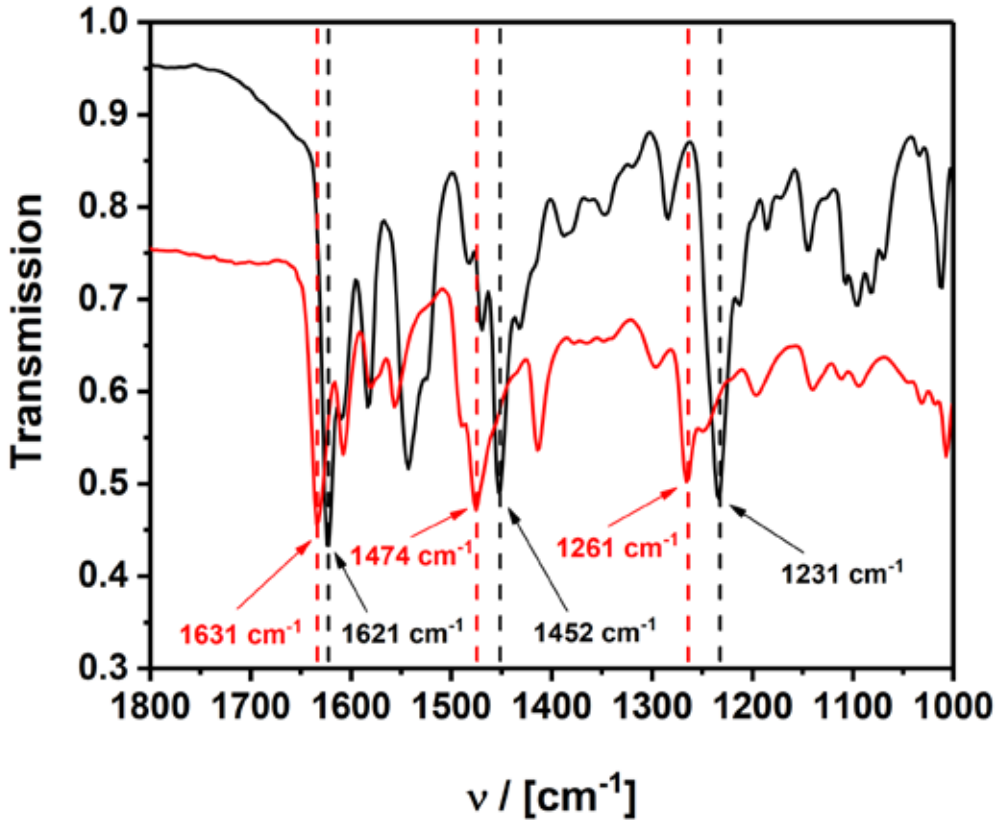
NMR-spectroscopy; imidazolium region.



black spectrum ≅ before coordination (free ligand **5a**)
red spectrum ≅ after Pd-coordination (**6ai**)

The proton at the immidazolium ring (orange arrow) disappears due to the formation of the carbene species. The remaining protons are shifted to lower field because of the transfer of electon density to the metal center.

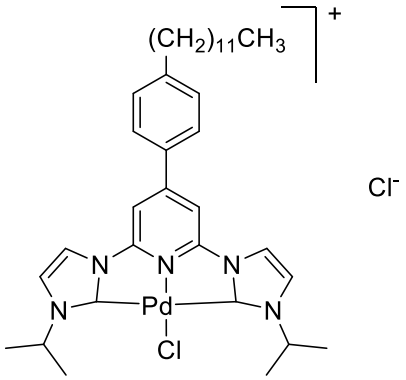
IR-spectroscopy.



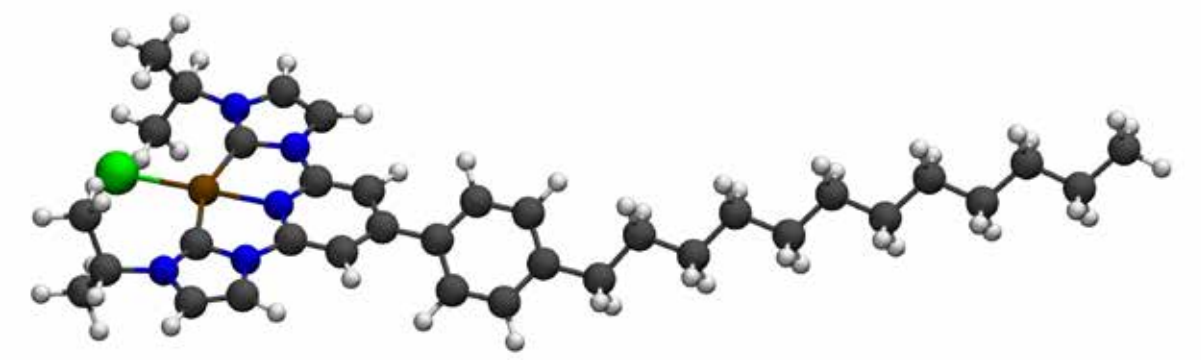
black spectrum ≅ before coordination (free ligand **5a**)
red spectrum ≅ after Pd-coordination (**6ai**)

Because of the coordination one sees a strong shift of the bands associated with the pyridine ring (1452 cm^{-1}) and the immidazole (1231 cm^{-1}).

Compound 6bi:

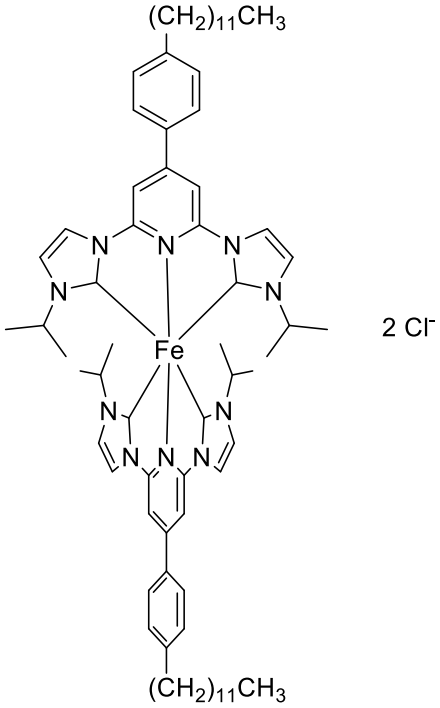


Molecular structure (DFT)

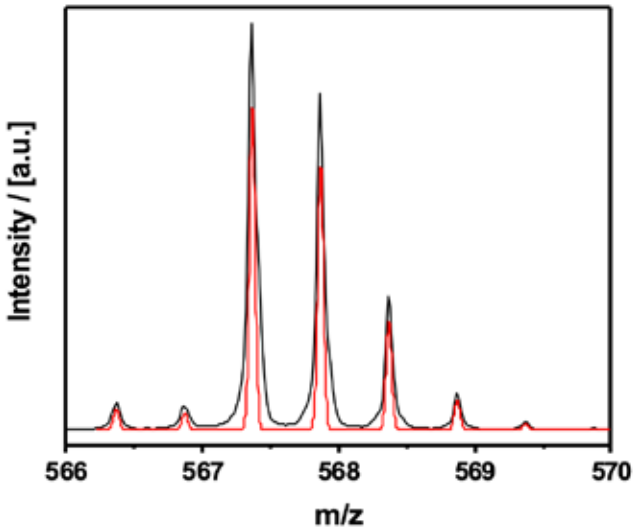


black = carbon
grey = hydrogen
blue = nitrogen
red = palladium
yellow = chlorine

Compound 6bii:

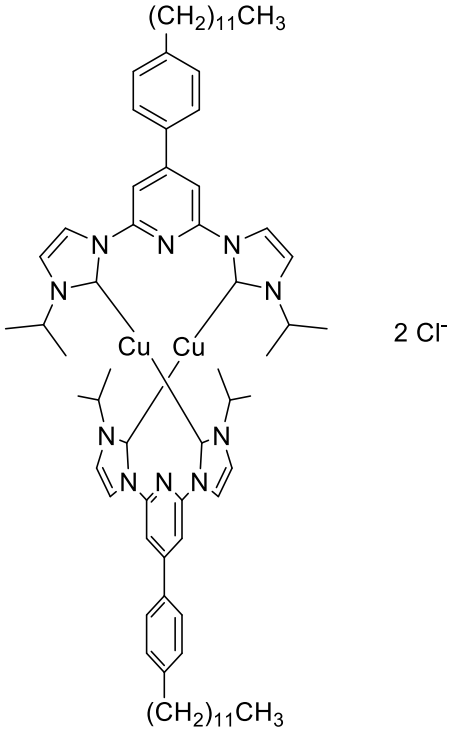


ESIMS.

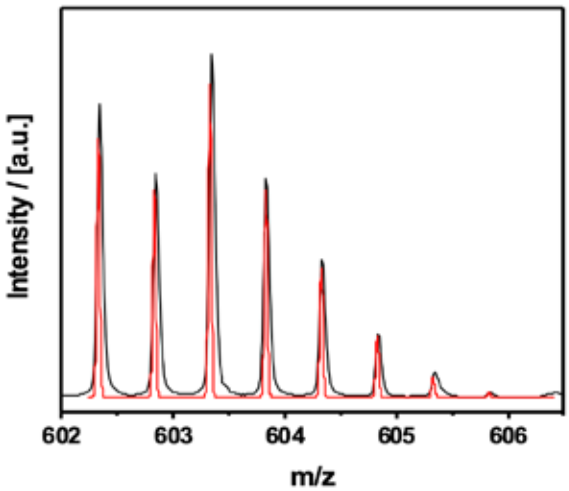


black line = experimental pattern
red line = pattern expected for $[M]^{2+}$

Compound 6biii.

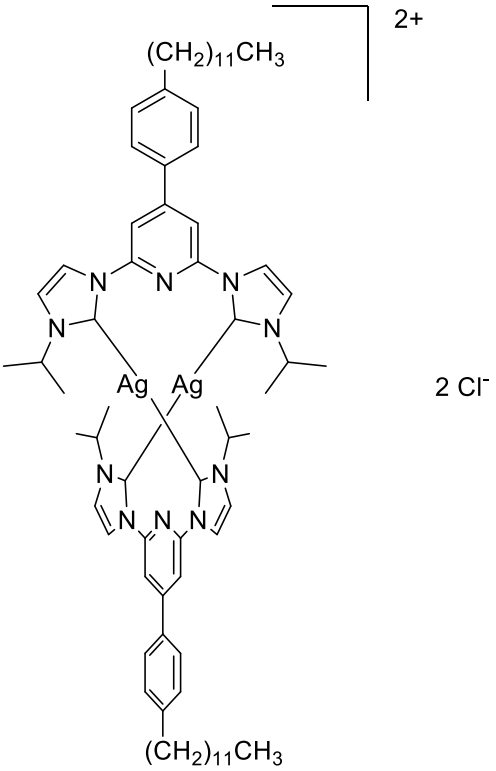


ESIMS.



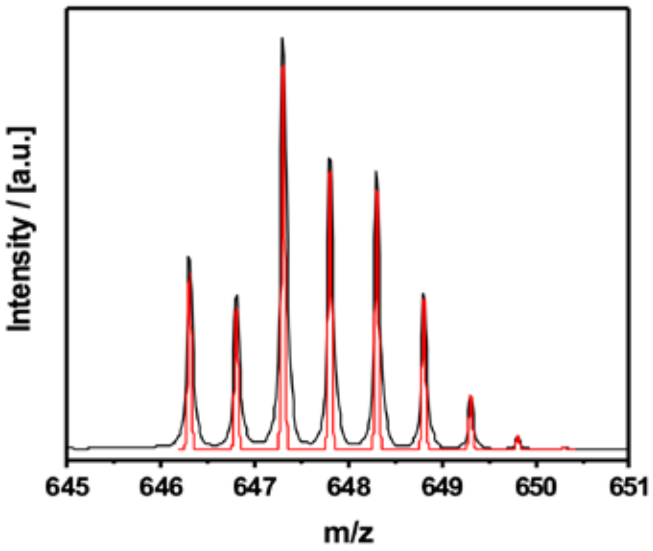
black line = experimental pattern
red line = pattern expected for $[M]^{2+}$

Compound 6biv.



2 Cl^-

ESIMS.



black line = experimental pattern
red line = pattern expected for $[M]^{2+}$

Fig. S6.
TEM micrograph of the LC phase of 6ai.

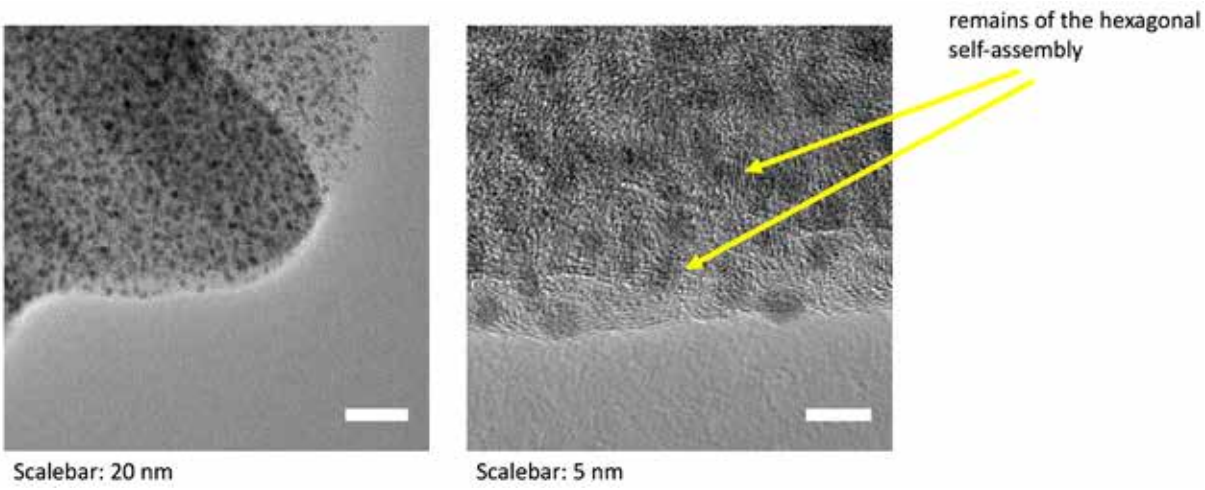
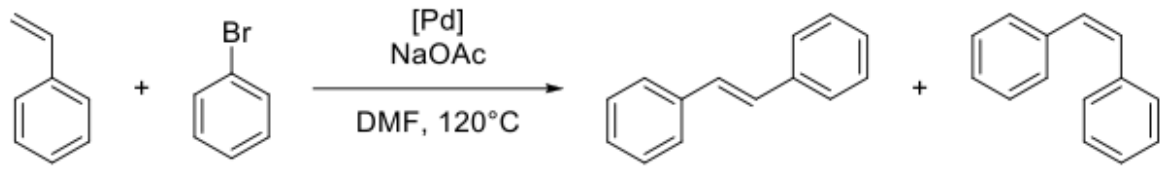
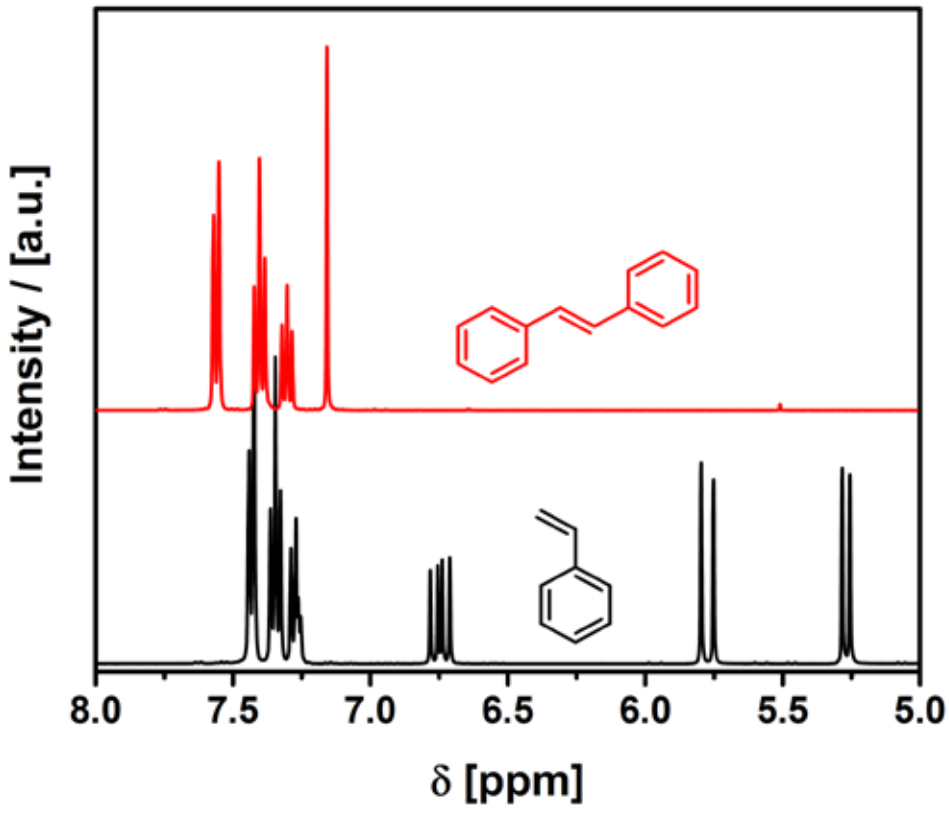


Fig. S7.
Heck reaction catalysed by Pd-NHC surfactants.



Bromobenzene (628 mg, 4 mmol), freshly distilled styrene (583 mg, 5.6 mmol), sodium acetate (984 mg, 12 mmol) and the corresponding palladium-catalyst (5 mol%) were dispersed in 10 ml of dimethyl formamide. The mixture was heated to 120°C for two hours, followed by the removal of the solvent in vacuo. The resulting product was analyzed by ^{1}H-NMR spectroscopy.



black spectrum: Styrene, t = 0
red spectrum: t = 2h; all signals can be assigned to stilbene

References

[1] C. J. Mathews, P. J. Smith, T. Welton, *J. Mol. Catal. A Chem.* **2004**, *214*, 27–32.
[2] R. J. Kern, *J. Inorg. Nucl. Chem.* **1962**, *24*, 1105–1109.
[3] C. J. Mathews, P. J. Smith, T. Welton, *J. Mol. Catal. A Chem.* **2004**, *214*, 27–32.