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# Oligoether substituted bis-NHC palladium and platinum complexes for aqueous Suzuki–Miyaura coupling and hydrosilylation

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ABSTRACT

The synthesis of four oligo ethylene glycol substituted, bis-NHC palladium(II) and platinum(II) complexes is reported. Two of them were characterized by solid state structures. All complexes show excellent solubility in a variety of organic solvents and water. The palladium complexes were tested in the Suzuki–Miyaura coupling reaction and the platinum complexes in the hydrosilylation reaction of alkynes in aqueous solvent mixtures. All show a high catalytic activity at ppm level catalyst-loading under very mild reaction conditions.



## Introduction

*N*-Heterocyclic carbene (NHC) ligands are ubiquitous in organometallic chemistry [1–3] and have found widespread application in cross coupling chemistry [4–8]. Chelated palladium and platinum bis-NHC complexes show exceptional high chemical stability, favorable electronic and steric properties, and have been shown to be very efficient catalysts for a variety of organic transformations [9–11]. They also showed very high catalytic activity in the Heck reaction [12–14] and the Suzuki–Miyaura coupling [15–17]. We found that bis-NHC platinum complexes are very efficient catalysts for the hydrosilylation of olefins [18,19], which is of extraordinary importance for the silicon industry [20–23]. Unfortunately, chelated palladium- and platinum-bis-NHC catalysts typically show very limited solubility in solvents like dichloromethane, tetrahydrofuran or water, which seriously complicates their use in homogeneous catalysis and also hinders mechanistic organometallic investigations [24–28]. To increase the solubility in organic solvents, we exchanged the halide anions for non-coordinating anions like $BF_4^-$ or $PF_6^-$ using the corresponding silver salts [24]. We found that the result was strongly dependent on the counterion. Especially the anion metathesis with AgOAc lead to an interesting result, since not the desired mononuclear complex, but instead a trinuclear Pd–Ag–Pd carbene acetato complex was isolated [29]. Furthermore, many organometallic reactions like also the Heck reaction with chelating bis-NHC ligands either produce or require nucleophilic ions [30]. In order to achieve high solubility even in the presence of these coordinating counterions, a different strategy is needed.

PEGylation is a widely used technique in pharmaceutical chemistry [31,32] and well known for not only improving the solubility, but also changing the physicochemical properties of transition metal complexes [33–36]. Therefore, we decided to synthesize oligoether substituted bis-NHC complexes, which we expected to show a significantly enhanced solubility in both organic solvents and water.

The Suzuki–Miyaura coupling is a very important reaction in the field of organic synthesis [37,38] and due to safety issues, environmental aspects, and increasing regulatory pressure, the development of modern reaction protocols under aqueous conditions has become more and more important in recent years [39–41]. Therefore, the synthesis and application of water soluble transition metal NHC complexes is currently of interest [42–46].

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[1] X-ray analysis.

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0022-328X/

Strategies to improve the activity of C–C coupling reactions in an aqueous environment typically rely either on additives like phase transfer agents [47,48], solid supported catalysts [48,49], or the attachment of polar groups [50,51] to the ligand.

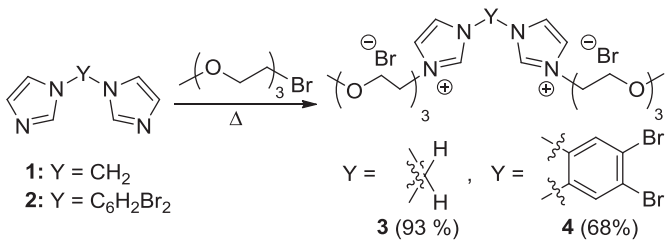
Reports on the hydrosilylation of olefins and alkynes in protic solvents [52–55] or ionic liquids [19,56] and especially under platinum catalysis [57–59] are, however, extremely rare.

Accordingly, we investigated the oligoether substituted palladium complexes as catalysts in the Suzuki–Miyaura coupling and the corresponding platinum complexes in the hydrosilylation reaction in aqueous solution.

## Results and discussion

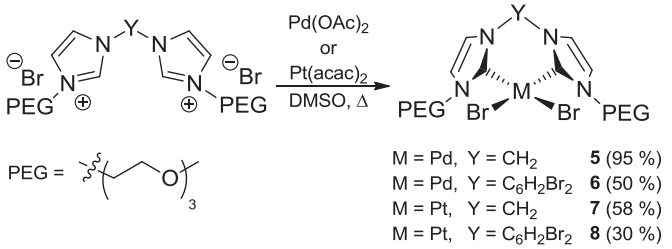
### *Synthesis*

The bisimidazolium salts were prepared in tetrahydrofuran (**3**) and acetonitrile (**4**) by alkylation of the corresponding bisimidazoles **1** and **2** with 2-[2-(2-methoxyethoxy)ethoxy]ethylbromide in 93% (**3**) and 68% (**4**) yield (Scheme 1).




**Scheme 1.** Synthesis of the bisimidazolium salts.

Subsequently, the platinum and palladium complexes **5**–**8** could be synthesized from the bisimidazoliums salts with palladium acetate (**5, 6**) or platinum acetylacetonate (**7, 8**) in DMSO (Scheme 2).




**Scheme 2.** Synthesis of the palladium- and platinum-bis-NHC-complexes.

All four complexes are well soluble in a large variety of organic solvents like tetrahydrofuran, dichloromethane, acetone, acetonitrile or ethanol and show moderate solubility in toluene and water. Single crystals of **5** and **7** were obtained by slow diffusion of diethyl ether into a concentrated solution of the complexes in methanol. The solid state structures of both complexes are isostructural (Figs. 1 and 2) and both asymmetric units contain two independent metal complexes.

In both solid state structures, the oligo ethylene glycol chains are coiled up and situated below the plane of the bis-NHC moiety. The C–Pd–C (molecule A: 85.1(2)°; molecule B: 83.4(2)°) and C–Pt–C (molecule A: 85.6(2)°; molecule B: 84.4(2)°) bite angles of the ligands are considerably larger than these of the analogous bis-NHC complexes with methyl substituents (C–Pd–C: 83.2(2)°, C–Pt–C: 83.8(4)°) [60,61]. Likewise, the Pd–carbene (molecule A: 1.984(5) Å, 1.974(5) Å))°; molecule B: 1.983(5) Å, 1.986(5) Å) and the Pt–carbene (molecule A: 1.970(5) Å, 1.974(5) Å)°; molecule B: 1.961(5) Å, 1.967(5) Å) bond lengths seem to be slightly elongated in comparison to the complexes with methyl substituents (C–Pd: 1.983(5) Å, 1.971(5) Å, C–Pt: 1.963(10) Å, 1.950(10) Å) [60,61].

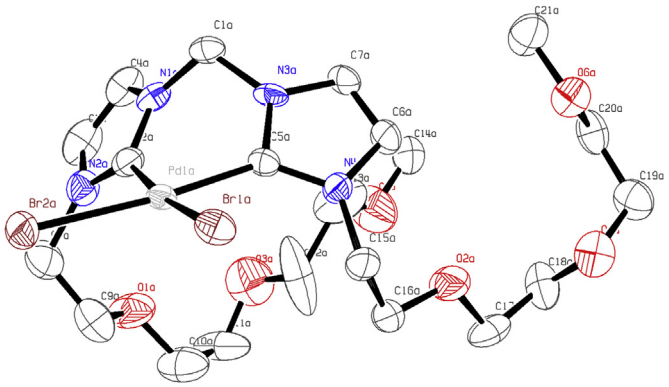



**Fig. 1.** Solid state structure of palladium bis-NHC complex **5**. Second molecule of **5** and hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) for molecule A: Pd1A–Br1A 2.4975(7), Pd1A–Br2A 2.4919(7), Pd1A–C2A 1.984(5), Pd1A–C5A 1.974(5), C2A–Pd1A–C5A 85.1(2), Br1A–Pd1A–Br2A 89.85(2). Selected bond lengths (Å) and angles (°) for molecule B: Pd1B–Br1B 2.4902(7), Pd1B–Br2B 2.4933(7), Pd1B–C2B 1.983(5), Pd1B–C5B 1.986(5), C2A–Pd1B–C5B 83.4(2), Br1B–Pd1B–Br2B 89.50(2).

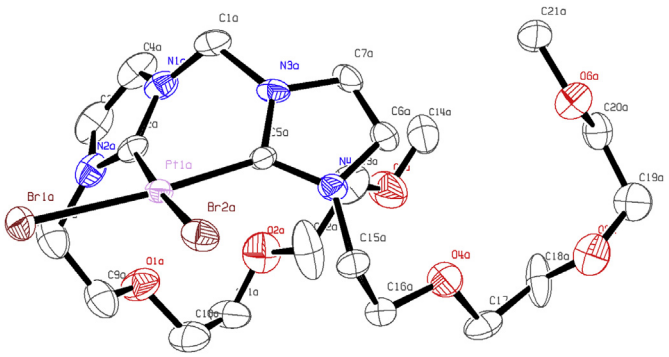



**Fig. 2.** Solid state structure of platinum bis-NHC complex **7**. Second molecule of **7** and hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) for molecule A: Pt1A–Br1A 2.4939(7), Pt1A–Br2A 2.4966(7), Pt1A–C2A 1.970(5), Pt1A–C5A 1.974(5), C2A–Pt1A–C5A 85.6(2), Br1A–Pt1A–Br2A 88.63(2). Selected bond lengths (Å) and angles (°) for molecule B: Pt1B–Br1B 2.4902(7), Pt1B–Br2B 2.4933(7), Pt1B–C2B 1.983(5), Pt1B–C5B 1.986(5), C2A–Pt1B–C5B 83.4(2), Br1B–Pt1B–Br2B 89.50(2).

### *Suzuki–Miyaura coupling*

The palladium complexes **5** and **6** were tested as catalysts in the Suzuki coupling of phenylboronic acid with 4-bromo toluene, which is considered a challenging reactant in water due to its hydrophobicity. We decided to test the catalysts first in a 1:1 mixture of methanol and water with $K_2CO_3$ as base, which had been determined to be more or at least equally effective as $Cs_2CO_3$, KOH, or $K_3PO_4$.

Initially, we investigated the catalyst loading with complex **5** (Table 1) and found for catalyst loadings up to 0.001 mol-% similar yields of 80% at a reaction temperature of 100 °C (entries 1–4) demonstrating the high catalytic activity of our system with turnover numbers up to 81,000. Subsequently, we investigated the reaction temperature with a catalyst loading of 0.1 mol-% and obtained for temperatures of 40–100 °C similar yields of around 80%

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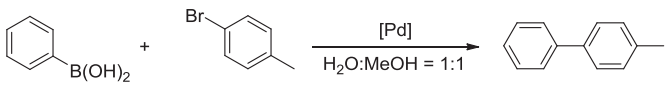
**Table 1**
Suzuki–Miyaura coupling in MeOH:$H_2O$ solvent mixture.[a]




| Entry | Catalyst | T [°C] | [mol-%] Cat. | Yield [%] | TON |
|---|---|---|---|---|---|
| 1 | **5** | 100 | 1 | 80 | 80 |
| 2 | **5** | 100 | 0.1 | 80 | 800 |
| 3 | **5** | 100 | 0.01 | 81 | 8100 |
| 4 | **5** | 100 | 0.001 | 81 | 81,000 |
| 5 | **5** | 80 | 0.1 | 79 | 790 |
| 6 | **5** | 60 | 0.1 | 80 | 800 |
| 7 | **5** | 40 | 0.1 | 79 | 790 |
| 8 | **5** | RT | 0.1 | 65 | 650 |
| 9 | **5** | 40 | 0.05 | 51 | 2550 |
| 10 | **5** | 40 | 0.01 | 28 | 280 |
| 11 | **6** | 40 | 0.1 | 25 | 250 |
| 12 | $Pd(OAc)_2$ | 40 | 0.1 | 12 | 120 |

[a] Reaction conditions: 0.5 mL $H_2O$, 0.5 mL MeOH, 1 mmol 4-bromo toluene, 1.1 mmol $PhB(OH)_2$, 2 mmol $K_2CO_3$, **[Pd]**, 12 h, under argon, GC yield.

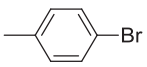
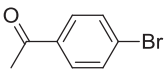
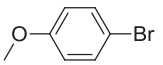
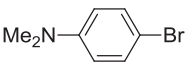
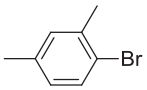
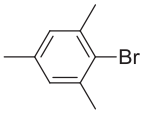
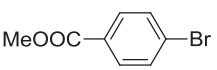
(entries 2, 5–7). However, at room temperature the yield decreased slightly (entry 8). We also reduced the catalyst loading at a temperature of 40 °C but obtained significantly lower yields with loadings of 0.05 mol-% and 0.01 mol-% (entries 9 and 10). Under the best reaction conditions (0.1 mol-%, 40 °C) we compared complexes **5, 6** and $Pd(OAc)_2$ (entries 7, 11 and 12). Complex **6** turned out to be significantly less catalytically active than complex **5** with a yield of only 25%, which clearly demonstrates that the methylene bridged ligand in **5** is superior to the phenyl bridged ligand in **6**. $Pd(OAc)_2$ gave only small amounts of the cross coupling product, which emphasizes the increase of activity by the bis-NHC ligand.

Additionally, we investigated the catalytic activity of **5** with other aryl bromides (Table 2). We obtained an excellent yield of 99% for the coupling of the acetophenone derivative (entry 2). Also for more challenging aryl bromides we obtained good yields, e.g. a yield of 81% for 4-bromo anisole (entry 3) and of 61% for *N,N*-dimethyl-4-bromo aniline (entry 4).

The presence of *ortho* substituents at the aryl bromide did not lead to a significant decrease of the yield as 1-bromo-2,4-dimethyl benzene (entry 5) and 1-bromo-2,4,6-trimethyl benzene (entry 6) could be converted in comparable yields. When the carboxylate ester (Table 2, entry 7) was used the corresponding biphenyl carboxylate ester was obtained in a yield of 72% with additional 8% of the biphenyl carboxylic acid demonstrating that the hydrolysis of the carboxylate ester occurred only to a small amount under the reaction conditions.

We did not observe signs of the formation of palladium black at a reaction temperature of 60 °C. Consequently the aqueous phase, which contains the palladium catalyst, could be recycled without a decrease in catalytic activity (Table 3, entries 1 and 2). Additional cycles led to reduced yields (entries 3 and 4), which we believe to be a consequence of the increasing salt load in the aqueous phase. The high concentration of potassium salt in the aqueous phase led to a highly viscous system in the case of entry 3 and especially entry 4.

**Table 2**
Variation of substrate.[a]

| Entry | Substrate | Yield [%] |
|---|---|---|
| 1 |  | 77 |
| 2 |  | 99 |
| 3 |  | 81 |
| 4 |  | 61 |
| 5 |  | 77 |
| 6 |  | 71 |
| 7 |  | 72[b] |

[a] Reaction conditions: 0.5 mL $H_2O$, 0.5 mL MeOH, 1 mmol aryl bromide, 1.1 mmol $PhB(OH)_2$, 0.01 mol-% **5**, 2 mmol $K_2CO_3$, 20 h, 60 °C, under air, isolated yield.
[b] Methyl (biphenyl carboxylate) was obtained in a yield of 72% next to biphenyl carboxylic acid in a yield of 8%.

**Table 3**
Recyclability of catalyst.[a]

| Entry | Run | Yield [%] |
|---|---|---|
| **1** | 1 | 81 |
| **2** | 2 | 81 |
| **3** | 3 | 61 |
| **4** | 4 | 54 |

[a] Reaction conditions: 1.5 mL $H_2O$, 1.5 mL MeOH, 1 mmol 4-bromo toluene, 1.1 mmol $PhB(OH)_2$, 0.01 mol-% **5**, 2 mmol $K_2CO_3$, 12 h, 60 °C, under air, GC yield.

Next, we briefly investigated the catalytic activity without the addition of methanol to the reaction mixture (Table 4). Although the yield for catalyst **5** was again considerable higher than for $Pd(OAc)_2$ and catalyst **6** (entries 1–5) we obtained only moderate yields of 55%. The addition of the phase transfer catalyst $NBu_4Br$ did not lead to higher yields (entry 7) indicating that the presence of methanol is very important in order to obtain a highly active catalytic system. Probably methanol increases the solubility of the organic compounds and increases the reactivity of the boronic acid.

**Table 4**
Suzuki–Miyaura coupling in water.[a]

| Entry | Catalyst | T [°C] | Yield [%] |
|---|---|---|---|
| 1 | **5** | 100 | 55 |
| 2 | **6** | 100 | 9 |
| 3 | $Pd(OAc)_2$ | 100 | 10 |
| 4 | **5** | 80 | 30 |
| 5 | **5** | 60 | 36 |
| 6 | **5** | 40 | 35 |
| 7 | **5** | 100 | 30[b] |

[a] Reaction conditions: 1 mL $H_2O$, 1 mmol 4-bromo toluene, 1.1 mmol $PhB(OH)_2$, 0.1 mol-% **[Pd]**, 2 mmol $K_2CO_3$, 12 h, GC Yield.
[b] Addition of 0.3 mmol $NBu_4Br$.

### *Hydrosilylation*

The platinum complexes **7** and **8** were tested as catalysts for the hydrosilylation of phenyl acetylene in a methanol:water = 1:1 mixture (Table 5).

Again, the methylene bridged complex (**7**) showed higher catalytic activity than the phenyl bridged (**8**) with yields of up to 83% (entry 1). The reactions proceeded with an excellent regioselectivity since only β-isomers (**A** and **B**) were obtained. However, we found only a moderate stereoselectivity demonstrated by *trans*:*cis* mixtures of 3:1 to 5.5:1 (entry 1). The lower reaction

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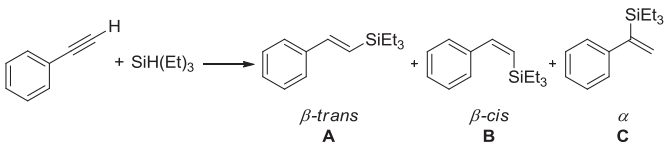
temperature slightly improved the stereoselectivity, but also decreased the yield.

**Table 5**
Hydrosilylation in methanol/water solvent mixture.[a]

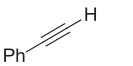
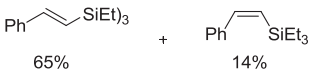
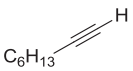
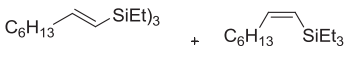
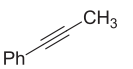
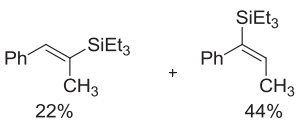
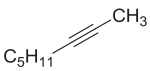
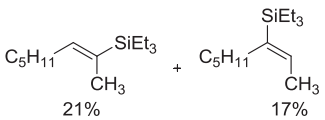
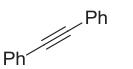
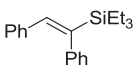



| Entry | Catalyst | T [°C] | [mol-%] Cat. | Yield [%] | Selectivity A/B/C[b] |
|---|---|---|---|---|---|
| 1 | **7** | 80 | 1 | 83 | 4/1/0 |
| 2 | **8** | 80 | 1 | 70 | 3/1/0 |
| 3 | **7** | 80 | 0.5 | 68 | 3/1/0 |
| 4 | **7** | 60 | 1 | 79 | 4.5/1/0 |
| 5 | **7** | 40 | 1 | 69 | 5.5/1/0 |

[a] Reaction conditions: 1 mL $H_2O$, 1 mL MeOH, 1 mmol phenyl acetylene, 1.1 mmol triethylsilane, **[Pt]**, 16 h, under air, isolated yields.
[b] Determined by $^1$H NMR.

As other silanes like triethoxysilane or dimethylphenylsilane are not stable in aqueous reaction mixtures the reaction conditions are limited to triethylsilane. But we ran the hydrosilylation at 60 °C with other alkynes to study the selectivities with these alkynes (Table 6). With 1-octyne (entry 2) an excellent yield of 92% was obtained. An excellent regioselectivity towards the corresponding β-isomers was found and the stereoselectivity increased to 9:1. With internal alkynes the yields decreased significantly, phenyl propylene (entry 3) led to a yield of 66% and 2-octyne (entry 4) to 38%. For both substrates we obtained an excellent stereoselectivity as only *cis* products were found, but only with moderate regioselectivities. Interestingly with phenyl propylene the α-isomer was obtained as the main product and the β-isomer as the minor product with an α:β ratio of 2:1 indicating that a phenyl ring activates its α-position in an internal alkyne. With 2-octyne there was no considerable bias for one position and we obtained a 1.2:1 mixture towards the less sterically hindered isomer. Using diphenyl acetylene (entry 5) only traces of the product were obtained, which points toward detrimental steric hindrance.

**Table 6**
Variation of substrate.[a]

| Entry | Alkyne | Products |
|---|---|---|
| 1 |  |  65% 14% |
| 2 |  |  |
| 3 |  |  22% 44% |
| 4 |  |  21% 17% |
| 5 |  |  traces |

[a] Reaction conditions: 1 mL $H_2O$, 1 mL MeOH, 1 mmol alkyne, 1.1 mmol triethylsilane, 1 mol % **7**, 60 °C, 16 h, under air, isolated yields.

## Conclusion

Four palladium- and platinum complexes with chelating, oligo ethylene glycol substituted bis-NHC ligands have been prepared. They show excellent solubility in a variety of organic solvents and water and could be characterized by their solid state structures. The palladium complexes show a very high catalytic activity at ppm catalyst loadings in the Suzuki–Miyaura reaction in an aqueous solvent under very mild reaction conditions with *TON*s higher than 80,000. The synthesized platinum complexes were tested in the hydrosilylation reaction in an aqueous solvent mixture as well and show reasonable catalytic activity.

## Experimental

### *General procedure*

Solvents of at least 99.5% purity were used throughout this study. All other chemicals were obtained from common suppliers and used without further purification. The bisimidazoles **1** and **2** and 1-[2-bromoethoxy-(2-methoxyethoxy)ethoxy]ethane were prepared as reported in the literature [62–64].

$^1$H and $^{13}$C NMR spectra were recorded with a Bruker AC 300 and Bruker DRX 500 P spectrometer. The spectra were referenced internally to the resonances of the solvent ($^1$H, $^{13}$C). Elemental analyses were performed by the microanalytical laboratory of our institute using a EuroVektor Euro EA-3000 Elemental Analyzer. Melting and decomposition points were determined with a Wagner&Munz PolyTherm A melting point apparatus and are uncorrected. Positive mode ESI-MS spectra for the synthesized compounds were recorded on a Bruker Esquire MS with Ion Trap Detector on samples dissolved in $NH_4OAc$ buffered methanol.

### *Suzuki–Miyaura cross coupling*

A 10 mL crimp vial with a magnetic stir bar was charged with the catalyst, boronic acid (1.1 mmol), aryl bromide (1 mmol), and powdered base (2 mmol). The vial was capped with a PTFE-faced butyl rubber septum and evacuated and filled with argon twice. Distilled water was added through the septum with a syringe and degased for 2 min. The resulting mixture was stirred at the given temperature for the given time. For the determination of GC–MS yields, the reaction mixture was extracted with dichloromethane (3x 10 mL), dried over $Na_2SO_4$, and filtered through a thin pad of silica gel. Dodecane (170 mg) was added as internal standard.

### *Hydrosilylation*

A 10 mL screw top vial with a magnetic stir bar was charged with the catalyst, alkyne (1.0 mmol), triethylsilane (128 mg, 1.1 mmol), and a 1:1 water:methanol mixture (2 mL) and the reaction mixture was stirred at the indicated temperature. Subsequently, the aqueous phase was extracted with diethyl ether (3x 5 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (isohexane:ethyl acetate 4:1) and the selectivity was determined by $^1$H NMR spectroscopy.

### *Synthesis of the bisimidazolium salts*

#### *3,3′-Bis{1,1′-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-(1,1′-diimidazolium)}-methylene-dibromide **(3)***

0.60 g (4.1 mmol) of the methylene bridged bisimidazol **1** was stirred with 2.20 g (9.7 mmol) of 1-[2-bromoethoxy-(2-methoxyethoxy)ethoxy]ethane in 10 mL of THF at 120 °C for

72 h in an ACE pressure tube, during which a second phase formed. Volatiles were removed *in vacuo* and the residue was dissolved in acetonitrile. The product was precipitated by addition of diethyl ether, washed with 2 mL of THF and dried *in vacuo* to afford the very hygroscopic, colorless product (2.27 g, 93%). M.p. 103 °C. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ = 9.43 (s, 2*H*, NC*H*N), 8.00 (s, 2*H*, NC*H*), 7.86 (s, 2*H*, NC*H*), 6.68 (s, 2*H*, C$H_2$), 4.42 (t, $J$ = 4.7 Hz, 4*H*, C$H_2$), 3.79 (t, 4.8 Hz, 4*H*, C$H_2$), 3.60−3.35 (m, 16*H*, C$H_2$), 3.24 (s, 6*H*, C$H_3$) ppm. $^{13}$C NMR NMR (151 MHz, DMSO-$d_6$): $\delta$ = 137.8 (*C*H), 123.6 (*C*H), 121.8 (*C*H), 71.2 (*C*$H_2$), 69.5 (*C*$H_2$), 69.5 (*C*$H_2$), 69.4 (*C*$H_2$), 67.81 (*C*$H_2$), 58.1 (*C*$H_3$), 57.8 (*C*$H_2$), 49.2 (*C*$H_2$) ppm. Anal. Calcd. for $C_{21}H_{38}Br_2N_4O_6$ (602.36): C 41.87, H 6.36, N 9.30% found C 41.86, H 6.59, N 9.41%.

*3,3′-Bis{1,1′-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-[4,5-dibromo-(1,1′-diimidazolium)}-1,2-phenylene]-dibromide* ***(4)***

0.23 g (0.63 mmol) of the dibromo phenylene bridged bisimidazol **2** was stirred with 0.31 g (1.37 mmol) of 1-[2-bromoethoxy-(2-methoxyethoxy)ethoxy]ethane in 5 mL of acetonitrile at 120 °C for 72 h in an ACE pressure tube. The product was precipitated by addition of 50 mL of diethyl ether at 3 °C, washed with 5 mL ethyl acetate and dried *in vacuo* to afford the very hygroscopic, colorless product (0.35 g, 68%). M.p. 60 °C. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ = 9.54 (s, 2*H*, NC*H*N), 8.52 (s, 2*H*, C*H*), 7,90 (s, 2H, C*H*), 7.75 (s, 2*H*, C*H*), 4.43 (t, 4*H*, $J$ = 4.5 Hz, C$H_2$), 3.81 (t, 4*H*, $J$ = 4.5 Hz, C$H_2$), 3.57 (m, 4*H*, C$H_2$), 3.51 (m, 8*H*, C$H_2$), 3.40 (m, 4*H*, C$H_2$), 3.20 (s, 6*H*, C$H_3$) ppm. $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ = 138.4 (NCHN), 132.6 (*C*H), 129.8 ($C_{ipso}$), 127.2 ($C_{ipso}$), 123.7 (*C*H), 122.7 (*C*H), 71.2 (*C*$H_2$), 69.6 (*C*$H_2$), 69.5(*C*$H_2$), 67.9 (*C*$H_2$), 67.0 (*C*$H_2$), 58.1 (*C*$H_3$), 49.4 (*C*$H_2$) ppm. Anal. Calcd. for $C_{26}H_{38}N_4O_6Br_4$ (822.22): C 37.98, H 4.66, N 6.81% found C 37.54, H 4.40, N 6.68%.

*Synthesis of the bis-NHC complexes*

*3,3′-Bis{1,1′-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-(1,1′-diimidazoline-2,2′-diylidene)}-methylene-palladium(II)dibromide* ***(5)***

0.45 g (2.0 mmol) of palladium acetate was stirred with 1.20 g (2.0 mmol) of the bisimidazolium salt **3** in 15 mL of DMSO for 2 h at 40 °C, 2 h at 60 °C, 2 h 80 °C, 2 h at 100 °C and 2 h at 120 °C. The solvent was removed *in vacuo* at 60 °C, the residue was dissolved in 4 mL of dichloromethane and it was washed with 5 mL of water. The organic layer was dried with $Na_2SO_4$, reduced to 3 mL, and the crude product was precipitated by addition of 40 mL of diethyl ether at 3 °C. After filtration, the solid was dissolved in 3 mL of dichloromethane, layered with 40 mL of diethyl ether and stored at 3 °C. After three days 1.34 g (95%) of colorless, hygroscopic crystals had formed, which were collected and dried *in vacuo*. M.p. 81 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.48 (d, $J$ = 1.9 Hz, 2*H*, NC*H*), 7.24 (d, $J$ = 1.9 Hz, 2*H*, NC*H*), 6.39 (dd, $J$ = 13.24 Hz, $J$ = 17.02 Hz, 2*H*, C$H_2$), 4.7−4.6 (m, 4*H*, C$H_2$), 4.7−3.7 (m, 4*H*, C$H_2$), 3.50−3.65 (m, 16*H*, C$H_2$), 3.37 (s, 6*H*, $CH_3$) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 159.3 (NCN), 123.0 (*C*H), 121.2 (*C*H), 71.9 (*C*$H_2$), 70.9 (*C*$H_2$), 70.4 (*C*$H_2$) 70.3 (*C*$H_2$), 70.2 (*C*$H_2$), 64.0 (*C*$H_2$), 59.1 (*C*$H_3$), 51.4 (*C*$H_2$) ppm. Anal Calcd. for $C_{21}H_{36}Br_2N_4O_6Pd$ (706.76): C 35.69, H 5.13, N 7.93% found 35.77, H 5.08, N 8.04%. ESI-MS: $m/z$ = 627.1 $[PdL{\cdot}Br]^+$.

*3,3′-Bis{1,1′-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-[4,5-dibromo-(1,1′-diimidazoline-2,2′-diylidene)}-1,2-phenylene]palladium(II) dibromide* ***(6)***

94 mg (0.35 mmol) of palladium acetate was stirred with 250 mg (0.30 mmol) of the bisimidazolium salt **4** in 8 mL of DMSO for 12 h at 40 °C and 1 h at 60 °C. The solvent was removed *in vacuo* at 60 °C, the residue was dissolved in 5 mL of THF and solids were filtered off. The THF was removed under reduced pressure, the residue was dissolved in 10 mL of dichloromethane and washed with 1 mL of water. The crude product was further purified by fractionate precipitation: The organic phase was reduced to 4 mL and 10 mL of diethyl ether were added, upon which a brown precipitate formed. Solids were rapidly filtered off, and the solvent was removed *in vacuo*. Subsequently it was again dissolved in 4 mL of dichloromethane, 10 mL of diethyl ether were added and the yellow precipitate, which formed, was again filtered off. The solution was layered with further 30 mL of diethyl ether and stored at 3 °C. After one week 160 mg (50%) of colorless, hygroscopic crystals had formed, which were collected and dried *in vacuo*. M.p. 78 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.87 (s, 2*H*, C*H*), 7.57 (d, 2*H*, $J$ = 1.9 Hz, NC*H*), 7.15 (d, 2*H*, $J$ = 1.9 Hz, NC*H*), 4.93 (m, 2*H*, C$H_2$), 4.65 (m, 2*H*, C$H_2$), 4.07 (m, 2*H*, C$H_2$), 3.87 (m, 2*H*, C$H_2$), 3.64 (s, 8*H*, C$H_2$), 3.62 (m, 4*H*, C$H_2$), 3.56 (m, 4*H*, C$H_2$), 3.38 (s, 6*H*, C$H_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 164.0 (NCN), 132.6 ($C_{ipso}$), 131.3 (*C*H), 126.3 ($C_{ipso}$), 125.1 (*C*H), 121.9 (CH), 71.9 (*C*$H_2$), 70.3 (*C*$H_2$), 70.3(*C*$H_2$), 70.1 (*C*$H_2$), 70.1 (*C*$H_2$), 59.0 (*C*$H_3$), 51.6 (*C*$H_2$) ppm. Anal. Calcd. for $C_{26}H_{36}N_4Br_4O_6Pd$ (926.62): C 33.70, H 3.92, N 6.05% found C 34.02, H 3.97, N 6.19%. ESI-MS: $m/z$ = 847.0 $[PdL{\cdot}Br]^+$.

*3,3′-Bis{1,1′-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-(1,1′-diimidazoline-2,2′-diylidene)}-methylene-platinum(II)dibromide* ***(7)***

0.29 g (0.75 mmol) of platinum(II) acetylacetonate was stirred with 0.45 g (0.75 mmol) of the bisimidazolium salt **3** in 10 mL of DMSO for 3 h at 60 °C, 3 h at 80 °C and 3 h at 110 °C. The solvent was removed *in vacuo* at 60 °C, the residue was dissolved in 5 mL of dichloromethane and washed with 3 mL of water. The crude product was further purified by fractionate precipitation: Diethyl ether was added to the organic phase, until a brown precipitate formed. Solids were rapidly filtered off, and the solution was layered with further 50 mL of diethyl ether and stored at 3 °C. After one week 0.34 g (58%) of colorless, hygroscopic crystals had formed, which were collected and dried *in vacuo*.

M.p. 78 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.31 (d, $J$ = 1.9 Hz, 2*H*, NC*H*), 7.24 (d, J = 1.9 Hz, 2*H*, NC*H*), 6.10 (dd, $J$ = 12.9 Hz, J = 105.6 Hz 2*H*, C$H_2$), 4.75−4.50 (m, 4*H*, C$H_2$), 4.0−3.7 (m, 4*H*, C$H_2$), 3.7−3.65 (m, 16*H*, C$H_2$), 3.46 (s, 6*H*, C$H_3$) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 145.1 (NCN), 122.5 (*C*H), 119.9 (*C*H), 71.9 (*C*$H_2$), 70.8 (*C*$H_2$), 70.4 (*C*$H_3$), 70.3 (*C*$H_3$), 70.1 (*C*$H_3$), 60.4 (*C*$H_2$), 59.1 (*C*$H_3$), 50.6 (*C*$H_2$) ppm. ESI-MS: $m/z$ = 715.1 $[PtL{\cdot}Br]^+$. Anal. Calcd. for $C_{21}H_{36}Br_2N_4O_6Pt$ (795.43): C 31.71, H 4.56, N 7.04% found C 31.60, H 4.29, N 7.01%.

*3,3′-Bis{1,1′-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-[4,5-dibromo-(1,1′-diimidazoline-2,2′-diylidene)}-1,2-phenylene]platinum(II) dibromide* ***(8)***

0.12 g (0.31 mmol) of platinum(II) acetylacetonate was stirred with 250 mg (0.30 mmol) of the bisimidazolium salt **4** in 8 mL of DMSO for 2 h at 40 °C, 2 h at 60 °C, 2 h at 80 °C, 2 h at 80 °C and 3.5 h at 120 °C. The solvent was removed *in vacuo* at 60 °C, the residue was dissolved in 5 mL of THF and solids were filtered off. The THF was removed under reduced pressure and the crude product was further purified by fractionate precipitation: The residue was dissolved in 3 mL of dichloromethane and diethyl ether was added until the precipitation of a brown solid. The solution was filtered off and the solvent was removed *in vacuo*. The residue was dissolved in 3 mL of dichloromethane and precipitated with diethyl ether. 0.09 g (29%) of a light brown solid was collected and dried *in vacuo*.

M.p. 121 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.81 (s, 2*H*, C*H*), 7.54 (d, 2*H*, $J$ = 2.1 Hz, NC*H*), 7.07 (d, 2*H*, $J$ = 2.3 Hz, NC*H*), 4.89 (m, 2*H*, C$H_2$), 4.62 (m, 2*H*, C$H_2$), 4.04 (m, 2*H*, C$H_2$), 3.86 (m, 2*H*, C$H_2$), 3.68−3.60 (m, 12*H*, C$H_2$), 3.59−3.50 (m, 4*H*, C$H_2$), 3.38 (s, 6*H*, C$H_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 152.1 (NCN), 133.3 ($C_{ipso}$), 131.0 (CH), 126.0 ($C_{ipso}$), 124.3 (CH), 120.8 (CH), 71.9 (CH$_2$), 70.34 (CH$_2$), 70.30 (CH$_2$), 70.13 (CH$_2$), 70.10 (CH$_2$), 59.0 (CH$_3$), 50.9 (CH$_2$) ppm.

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Anal. Calcd. for $C_{26}H_{36}Br_4N_4O_6Pt$ (1015.29): C 30.76, H 3.57, N 5.52% found C 30.96, H 3.77, N 5.60%. ESI-MS: $m/z$ = 935.1 $[PdL \cdot Br]^+$.

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## Appendix A. Supplementary material

CCDC 1054106 and 1054107 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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