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Platinum(II) complexes with amide-functionalized NHC ligands

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ABSTRACT

We present the synthesis of neutral, amide-functionalized *N*-heterocyclic carbene (NHC) platinum(II) complexes with dianionic –N–C^{NHC}–C^{NHC}–N– (NC^*C^*N) tetradentate ligands. The imidazolium- and bisimidazolium bromide NHC ligand precursors with amide functionality in the side chain are reported together with the corresponding biscarbene bromido complexes and, after deprotonation, of the neutral NHC complexes without counterions. All compounds have been thoroughly characterized by standard techniques.

1. Introduction

The interest in *N*-heterocyclic carbenes (NHCs) in the last decade was mainly driven by new applications in homogeneous catalysis [1–6]. We explored the additional stability of chelating biscarbenes and synthesized different dihalogen complexes of palladium(II) and platinum(II), which turned out to be very stable, even in very acidic solutions [7–12].

Quite recently we and others found that they are also promising ligands for the synthesis of blue phosphorescent platinum compounds with interesting photophysical properties [13–16]. As rigid structures promise better photophysical properties (due to less geometrical changes between singlet and triplet state) we were looking for tetradentate dianionic ligands based on *N*-heterocyclic biscarbenes and explored different anionic side chains as it had previously been shown for monodentate NHC ligands [5,17].

For the general structure shown in Fig. 1 different Ag(I) and Au(I) [18–21] as well as Ni(II) and Pd(II) complexes [16,22–37] are known, but no homoleptic platinum(II) complexes have been reported yet. Examples of previously reported complexes are given in Fig. 1, e.g. the palladium complex **I** with one monodentate NHC ligand [24] or the *cis*- (Fig. 1, **II**) and *trans*-isomers (Fig. 1, **III**) of complexes with two bidentate ligands [23,25,27].

To exploit the well known additional stability of complexes with methylene bridged NHCs [7,10] we also decided to introduce a bridging methylene group between the two imidazolium fragments. While neutral –N–C^{NHC}–C^{NHC}–N– (NC^*C^*N) ligands can be found in the literature, e.g. the tetradentate di(imidazol-2-ylidene) ligand (Fig. 2, **IV**) [38–40] or the dianionic C^*NNC^* ligands (Fig. 2, **V**) [37,41] there have been (to the best of our knowledge) no reports of di(imidazol-2-ylidene) ligands with amide-functionalized side chains.

We herein describe the synthesis of platinum(II) complexes with the new dianionic N–C^*–C^*–N tetradentate amide-functionalized NHC ligands and their corresponding precursors.

2. Results and discussion

The synthesis of the acetamide- or propionamide di(imidazol-2-ylidene) platinum(II) dihalide complexes starts with the preparation of the corresponding chloroacetamides or -propionamides. 2-chloro-*N*-phenylacetamide **1** [25] and 2-chloro-*N*-(4-methoxyphenyl)acetamide **2** as well as 3-chloro-*N*-phenyl-propionamide **3** [42] and 3-chloro-*N*-(4-methoxyphenyl)-propionamide **4** were obtained in good yields by reaction of the corresponding aniline with chloroacetyl chloride or chloropropionyl chloride in the presence of triethylamine following a literature procedure [25] (Scheme 1).

The chloroacetamides or -propionamides **1**–**4** react with imidazole in refluxing toluene to form the corresponding imidazolylacetamides or -propionamides [25]. 2-Imidazol-1-yl-*N*-phenylacetamide **5** [25,44], 2-imidazol-1-yl-*N*-(4-methoxyphenyl) acetamide **6** [43], 3-imidazol-1-yl-*N*-phenylpropionamide **7** [42] and 3-imidazol-1-yl-*N*-(4-methoxyphenyl)-propionamide **8** were obtained in moderate yields (Scheme 1).

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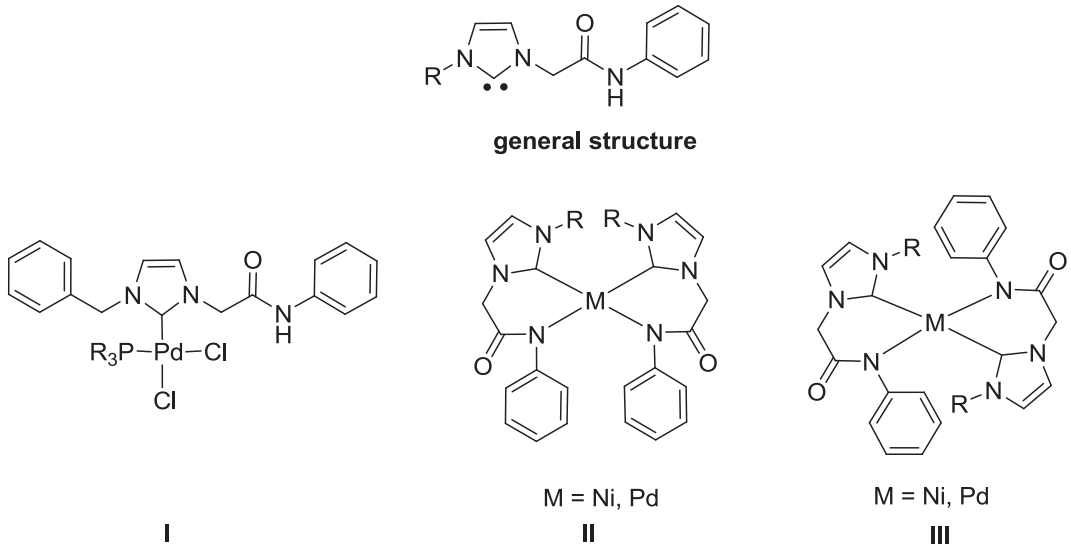


Fig. 1. Known structure-types of amide-functionalized NHC metal complexes with group 10 metals.

Reaction of **5**–**8** with dibromomethane yielded the corresponding bisimidazolium bromide salts **9**–**12** (Scheme 1). These have been reacted with the basic metal precursor platinum(II) acetylacetonate [7,8] in dimethylsulfoxide (DMSO) following a temperature program for several hours (see Experimental details) according to the method first described by Öfele [45–47]. The platinum(II) complexes **13**–**16** could be synthesized in good yields (Scheme 1).

Complexes **17** and **18** could be synthesized by reaction of 1,1′-methylene-bis(3-*N*-phenylacetamide-imidazol-2-ylidene)platinum-(II) dibromide **13** and 1,1′-methylene-bis(3-*N*-(4-methoxyphenyl)-acetamide-imidazol-2-ylidene)platinum(II) dibromide **14** with potassium carbonate in DMSO (Scheme 2).

Although the deprotonation of the amide by potassium carbonate in dimethylsulfoxide and the synthesis of the corresponding metal complex were successful for the shorter chain lengths, we unfortunately were not able to make the corresponding compounds with the longer alkyl chain from precursors **15** and **16**. Multiple unsuccessful attempts included changing the reaction time and the use of different bases like cesium carbonate Cs_2CO_3, potassium carbonate K_2CO_3 and lithium di*iso*propylamide (LDA). It is well known that the protons of the N–CH_2–N group between the two imidazole heterocycles are acidic and susceptible to attack by strong bases, therefore it is no surprise that in the case of the strong base LDA, we did observe decomposition products. We also tried deprotonation by a proton sponge e.g. 1,8-(dimethylamino)naphthalene [48,49], which only lead to the reisolation of the starting material.

Exchange of the bromide ligands against non-coordinating counterions followed by deprotonation with potassium carbonate also did not result in the formation of the desired halide-free complexes. We believe that the formation of the seven-membered ring is sterically too unfavorable, why we only succeeded in synthesizing complexes **17** and **18**.

In the context of this study the signal of the hydrogen atom at the amide nitrogen was of special interest to us. Already in the ^{1}H NMR spectra of the bisimidazolium salts **9**–**12** and also in the platinum(II) complexes **13**–**16** the proton is shifted to higher field by more than 2 ppm compared to the imidazolylamides **5**–**8**, in agreement with an earlier publication which proposed the formation of a hydrogen bond between the halide atom and the hydrogen atom at the amide nitrogen to be responsible for this shift [21]. This implies that the amide fragment in complexes **13**–**16** should be orientated toward the bromide ligands. The downfield shift of the amide-NH is less pronounced (ca. 0.3 ppm) in **15** and **16** compared to **13** and **14**. For the *para*-methoxy substituted complexes **14** and **16** this signal is shifted downfield compared to the unsubstituted complexes **13** and **15**, which can be attributed to the electron donating group (signal of amide proton: **13**: 10.3 ppm, **14**: 10.1 ppm, **15**: 10.0 ppm, **16**: 9.8 ppm).

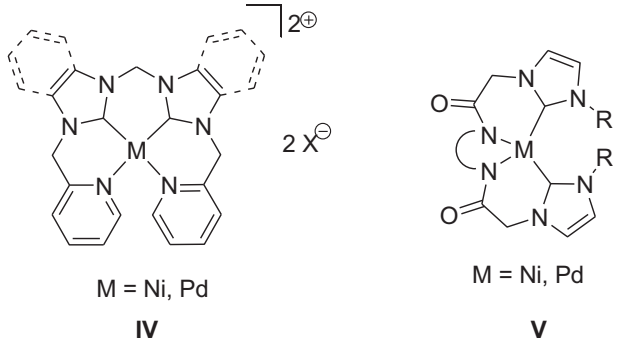


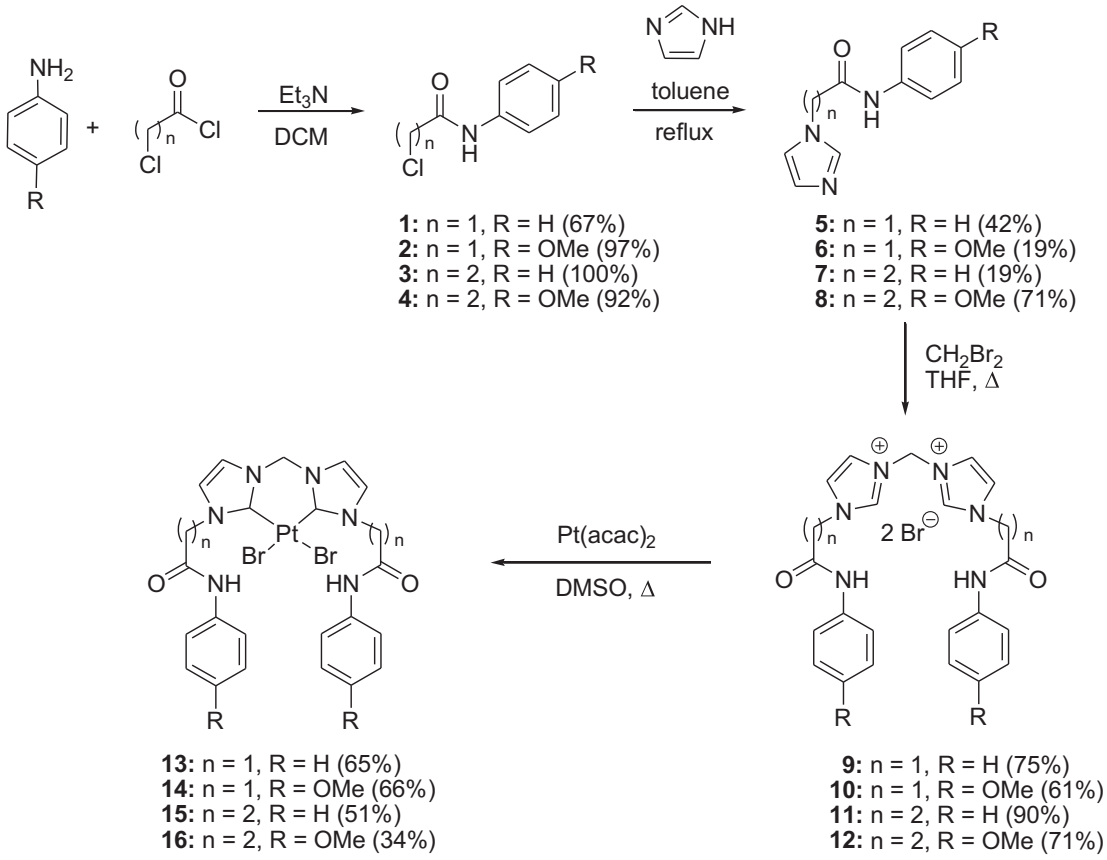
Fig. 2. NHC metal(II) complexes with tethered tetradentate ligand.

3. Conclusion

We could synthesize and characterize new platinum(II) complexes with NHC ligands carrying amide-functionalized side chains. Next to platinum(II) biscarbene (C^*–C^*) complexes with halide ligands we were also able to synthesize halide-free tethered platinum(II) complexes with tetradentate N–C^*–C^*–N ligands by deprotonation of the amide group.

4. Experimental

Solvents of 99.5% purity were used throughout this study. All other chemicals, platinum(II) acetylacetonate and platinum(II) chloride were obtained from common suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with



Scheme 1. Synthesis of acetamide- or propionamide di(imidazol-ylidene)platinum(II) dihalide complexes.

a Bruker AC 300 P or Bruker DRX 500 spectrometer. The spectra were referenced internally to the references of the solvent ($CDCl_3$, DMSO). Elementary analyses were performed by the microanalytical laboratory at our institute using an Eurovektor Hekatech EA-3000 Elemental Analyzer. The melting points were measured with a Wagner&Munz PolyTherm A melting-point apparatus and are uncorrected.

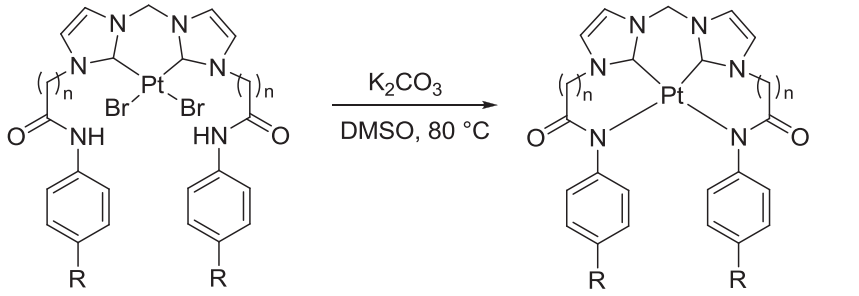
4.1. Synthesis of chloroacetamides and -propionamides

4.1.1. General procedure

1 equiv aniline was slowly added to a dichloromethane solution of 0.91 equiv triethylamine at 0 °C. 1.18 equiv chloroacetyl chloride or chloropropionyl chloride were dissolved in dry dichloromethane. This solution was slowly added to the aniline solution at 0 °C and the mixture was stirred at 0 °C for 2 h. The solution was allowed to slowly warm up to room temperature, extracted with dichloromethane and washed with 2 M HCl. The organic phase was separated from the aqueous phase and dried with anhydrous $MgSO_4$. Filtration and removal of the solvent under reduced pressure gave the desired product.

4.1.2. 2-Chloro-N-phenylacetamide ***1***

Aniline (42.5 mmol, 3.958 g, 3.87 mL) reacts with triethylamine (38.7 mmol, 3.916 g, 5.40 mL) in 15 mL dichloromethane and



Scheme 2. Synthesis of tethered di(imidazol-2-ylidene)platinum(II) complexes.

chloroacetyl chloride (50.26 mmol, 5.676 g, 4.0 mL) in 10 mL dry dichloromethane.

Yield: 4.818 g (66.8%). Mp: 125 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 8.19 (s, 1H, N*H*); 7.48 (m, 2H, J = 7.5 Hz, o-C*H*); 7.29 (m, 2H, J = 7.5 Hz, m-C*H*); 7.12 (m, 1H, J = 7.4 Hz, p-C*H*); 4.12 (s, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ = 163.8; 136.6; 129.1; 125.3; 120.1; 42.9 ppm. Anal. Calcd for C_8H_8NOCl: C, 56.65; H, 4.75; N, 8.26%. Found: C, 56.42; H, 4.88; N, 8.10%.

4.1.3. 2-Chloro-N-(4-methoxyphenyl)acetamide **2**

p-Anisidine (42.5 mmol, 5.234 g) reacts with triethylamine (38.7 mmol, 3.916 g, 5.40 mL) in 15 mL dichloromethane and chloroacetyl chloride (50.26 mmol, 5.676 g, 4.0 mL) in 10 mL dry dichloromethane.

Yield: 7.507 g (97.2%). Mp: 103 °C–104 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 8.12 (bs, 1H, N*H*); 7.38–7.36 (dd, 2H, J = 2.2 Hz, C*H*); 6.83–6.80 (dd, 2H, J = 2.2 Hz, C*H*); 4.11 (s, 2H, CH_2); 3.73 (s, 3H, OCH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ = 163.7; 157.1; 129.7; 122.1; 114.2; 55.5; 42.8 ppm. Anal. Calcd for $C_9H_{10}NO_2Cl$: C, 54.14; H, 5.05; N, 7.02%. Found: C, 54.01; H, 5.16; N, 7.17%.

4.1.4. 3-Chloro-N-phenylpropionamide **3**

Aniline (42.5 mmol, 3.958 g, 3.87 mL) reacts with triethylamine (38.7 mmol, 3.916 g, 5.40 mL) in 15 mL dichloromethane and 3-chloropropionyl chloride (50.26 mmol, 6.382 g, 5.95 mL) in 10 mL dry dichloromethane.

Yield: 7.532 g (100%). Mp: 90.8–91.5 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.45 (d, 3H, J = 7.8 Hz, o-C*H*, N*H*); 7.25 (t, 2H, J = 7.6 Hz, m-C*H*); 7.05 (t, 1H, J = 7.4 Hz, p-C*H*); 3.80 (t, 2H, J = 6.4 Hz, ClCH_2CH$_2$CO); 2.74 (t, 2H, J = 6.4 Hz, ClCH$_2$CH_2CO) ppm. ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ = 167.8; 137.4; 129.0; 124.7; 120.1; 40.4; 39.9 ppm.

4.1.5. 3-Chloro-N-(4-methoxyphenyl)propionamide **4**

p-Anisidine (85 mmol, 10.469 g) reacts with triethylamine (77.4 mmol, 7.832 g, 10.8 mL) in 30 mL dichloromethane and 3-chloropropionyl chloride (100.52 mmol, 12.760 g, 11.9 mL) in 20 mL dry dichloromethane.

Yield: 15.226 g (92.1%). Mp: 78.6 °C–78.8 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.83 (bs, 1H, N*H*); 7.36 (d, 2H, J = 9.0 Hz, C*H*); 6.77 (d, 2H, J = 9.0 Hz, C*H*); 3.80 (t, 2H, J = 6.5 Hz, ClCH_2CH$_2$CO); 3.71 (s, 3H, OCH_3); 2.72 (t, 2H, J = 6.5 Hz, ClCH$_2$CH_2CO) ppm. ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ = 167.8; 156.5; 130.7; 122.0; 114.0; 55.4; 39.1 ppm. Anal. Calcd for $C_{10}H_{12}NO_2Cl$: C, 56.21; H, 5.66; N, 6.56%. Found: C, 56.38; H, 5.82; N, 6.63%.

4.2. Synthesis of imidazolylacetamides and -propionamides

4.2.1. General procedure

A mixture of 5 equiv imidazole and 1 equiv 2-chloroacetamide or 3-chloropropionamide was dissolved in toluene and heated at 110 °C over night. After cooling to room temperature the solvent was removed under vacuum. The residue was then extracted with dichloromethane. The organic phase was washed with water, separated and dried with anhydrous $MgSO_4$. After filtration and removal of the solvent under reduced pressure the product was obtained.

4.2.2. 2-Imidazol-1-yl-N-phenylacetamide **5**

Imidazole (70.0 mmol, 4.766 g) reacts with 2-chloro-*N*-phenylacetamide (14.0 mmol, 2.374 g) in 40 mL toluene.

Yield: 1.174 g (41.7%). Mp: 130 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.91 (s, 1H, N*H*); 7.55 (s, 1H, NC*H*N); 7.39 (d, 2H, J = 7.7 Hz, o-C*H*); 7.25 (t, 2H, J = 7.6 Hz, m-C*H*); 7.13 (s, 1H, NC*H*CHN); 7.06 (t, 1H, J = 7.4 Hz, p-C*H*); 7.01 (s, 1H, NCHC*H*N); 4.74 (s, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 125.75 MHz): δ = 164.7; 138.0; 136.8; 130.2; 129.1; 125.2; 120.2; 120.0; 50.6 ppm.

4.2.3. 2-Imidazol-1-yl-N-(4-methoxyphenyl)acetamide **6**

Imidazole (64.0 mmol, 4.357 g) reacts with 2-chloro-*N*-(4-methoxyphenyl)acetamide (12.8 mmol, 2.555 g) in 40 mL toluene.

Yield: 0.562 g (18.9%). Mp: 161.7 °C–163.2 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.60 (s, 1H, NC*H*N); 7.25 (d, 2H, J = 9.0 Hz, C*H*); 7.15 (s, 1H, NC*H*CHN); 7.05 (s, 1H, N*H*); 7.00 (s, 1H, NCHC*H*N); 6.74 (d, 2H, J = 9.1 Hz, C*H*); 4.74 (s, 2H, CH_2); 3.71 (s, 3H, OCH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ = 164.6; 157.1; 138.2; 131.0; 129.3; 122.1; 119.7; 114.3; 55.5; 50.5 ppm.

4.2.4. 3-Imidazol-1-yl-N-phenylpropionamide **7**

Imidazole (64.0 mmol, 4.357 g) reacts with 3-chloro-*N*-phenylpropionamide (12.8 mmol, 2.351 g) in 40 mL toluene.

Yield: 0.522 g (18.9%). Mp: 139.8 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 8.87 (s, 1H, NC*H*N); 7.45 (d, 2H, J = 7.7 Hz, o-C*H*); 7.26 (t, 2H, J = 7.7 Hz, m-C*H*); 7.03 (t, 1H, J = 7.4 Hz, p-C*H*); 6.95 (s, 1H, NC*H*CHN); 6.91 (s, 1H, NCHC*H*N); 4.27 (t, 2H, J = 6.4 Hz, NCH_2CH$_2$CO); 2.71 (t, 2H, J = 6.4 Hz, NCH$_2$CH_2CO); (NH not visible) ppm. ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ = 168.0; 152.6; 138.0; 136.9; 134.1; 129.0; 124.4; 119.9; 43.0; 39.0 ppm. Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.95; H, 6.09; N, 19.53%. Found: C, 66.68; H, 6.22; N, 19.37%.

4.2.5. 3-Imidazol-1-yl-N-(4-methoxyphenyl)propionamide **8**

Imidazole (128 mmol, 8.714 g) reacts with 3-chloro-*N*-(4-methoxyphenyl)propionamide (25.6 mmol, 5.470 g) in 80 mL toluene.

Yield: 4.424 g (70.5%). Mp: 100.6 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 9.48 (s, 1H, N*H*); 7.35 (d, 2H, J = 9.0 Hz, C*H*); 7.20 (s, 1H, NC*H*N); 6.88 (d, 2H, J = 9.0 Hz, NC*H*C*H*N); 6.73 (d, 2H, J = 9.0 Hz, C*H*); 4.23 (t, 2H, J = 6.2 Hz, NCH_2CH$_2$CO); 3.69 (s, 3H, OCH_3); 2.67 (t, 2H, J = 6.4 Hz, NCH$_2$CH_2CO) ppm. ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ = 168.0; 156.3; 136.8; 131.3; 128.6; 121.7; 119.7; 114.0; 55.4; 43.1; 38.5 ppm. Anal. Calcd for $C_{13}H_{15}N_3O_2$: C, 63.66; H, 6.17; N, 17.13%. Found: C, 63.19; H, 6.18; N, 16.82%.

4.3. Synthesis of the methylene-bisacetamide or propionamide-imidazolium salts

4.3.1. General procedure

2 equiv imidazoleamide or -propionamide and 1 equiv dibromomethane were dissolved in THF. The reaction mixture was heated at 110 °C in a pressure tube. After cooling to room temperature the solid formed was filtrated, washed with THF and dried under vacuum.

4.3.2. 1,1′-Methylene-bis(3-N-phenylacetamide-1H-imidazolium) dibromide **9**

2-Imidazol-1-yl-*N*-phenylacetamide (2.5 mmol, 0.500 g) and dibromomethane (1.25 mmol, 0.216 g, 0.09 mL) were stirred in 5 mL THF at 110 °C for 3 days.

Yield: 0.540 g (74.7%). Mp: 149.7 °C. ^{1}H NMR (d_6-DMSO, 300.13 MHz): δ = 10.69 (s, 2H, N*H*); 9.62 (s, 2H, NC*H*N); 8.13 (s, 2H, NC*H*CHN); 7.93 (s, 2H, NCHC*H*N); 7.62 (d, 4H, J = 7.6 Hz, o-C*H*); 7.36 (t, 4H, J = 7.6 Hz, m-C*H*); 7.11 (t, 2H, J = 7.4 Hz, p-C*H*); 6.89 (s, 2H, NCH_2N); 5.36 (s, 4H, NCH_2CO) ppm. ^{13}C NMR (d_6-DMSO, 75.475 MHz): δ = 163.3; 138.9; 138.2; 129.0; 125.0; 123.9; 121.5; 119.1; 58.3; 51.7 ppm. Anal. Calcd for $C_{23}H_{24}N_6O_2Br_2$: C, 47.93; H, 4.20; N, 14.59%. Found: C, 47.79; H, 4.30; N, 14.32%.

4.3.3. 1,1′-Methylene-bis(3-N-(4-methoxyphenyl)-acetamide-1H-imidazolium) dibromide **10**

2-Imidazol-1-yl-*N*-(4-methoxyphenyl)acetamide (1.05 mmol, 0.243 g) and dibromomethane (0.53 mmol, 0.091 g, 0.04 mL) were stirred in 3 mL THF at 110 °C for 3 days.

Yield: 0.205 g (60.8%). Mp: decomposition >292 °C. ^{1}H NMR (d_6-DMSO, 300.13 MHz): δ = 10.57 (s, 2H, NH); 9.63 (s, 2H, NCHN); 8.14 (s, 2H, NCHCHN); 7.92 (s, 2H, NCHCHN); 7.53 (d, 4H, J = 7.1 Hz, CH); 6.92 (d, 6H, J = 8.6 Hz, CH, NCH_2N); 5.33 (s, 4H, NCH_2CO); 3.73 (s, 6H, OCH_3) ppm. ^{13}C NMR (d_6-DMSO, 75.475 MHz): δ = 162.7; 155.6; 138.9; 131.3; 124.9; 121.5; 120.7; 114.1; 58.3; 55.2; 51.6 ppm. Anal. Calcd for $C_{23}H_{24}N_6O_2Br_2$: C, 47.18; H, 4.44; N, 13.21%. Found: C, 46.98; H, 4.31; N, 13.05%.

4.3.4. 1,1′-Methylene-bis(3-N-phenylpropionamide-1H-imidazolium) dibromide **11**

3-Imidazol-1-yl-*N*-phenylpropionamide (2 mmol, 0.421 g) and dibromomethane (1 mmol, 0.170 g, 0.07 mL) were stirred in 2 mL THF at 110 °C for 3 days.

Yield: 0.542 g (89.7%). Mp: 161 °C. ^{1}H NMR (d_6-DMSO, 500.15 MHz): δ = 10.25 (s, 2H, NH); 9.61 (s, 2H, NCHN); 8.05 (s, 2H, NCHCHN); 7.92 (d, 2H, J = 1.4 Hz, NCHCHN); 7.58 (d, 4H, J = 7.7 Hz, o-CH); 7.30 (t, 4H, J = 7.9 Hz, m-CH); 7.04 (t, 2H, J = 7.4 Hz, p-CH); 6.72 (s, 2H, NCH_2N); 4.52 (t, 4H, J = 6.1 Hz, NCH_2CH$_2$CO); 3.03 (t, 4H, J = 6.1 Hz, NCH$_2$CH$_2$CO) ppm. ^{13}C NMR (d_6-DMSO, 125.75 MHz): δ = 167.9; 138.8; 138.2; 128.7; 123.4; 122.0; 119.2; 58.0; 45.5; 35.6 ppm. Anal. Calcd for $C_{25}H_{28}N_6O_2Br_2$: C, 49.68; H, 4.67; N, 13.91%. Found: C, 49.72; H, 4.89; N, 13.86%.

4.3.5. 1,1′-Methylene-bis(3-N-(4-methoxyphenyl)-propionamide-1H-imidazolium) dibromide **12**

3-Imidazol-1-yl-*N*-(4-methoxyphenyl)propionamide (1.75 mmol, 0.430 g) and dibromomethane (0.88 mmol, 0.153 g, 0.06 mL) were stirred in 3 mL THF at 110 °C for 2 days.

Yield: 0.413 g (71.0%). Mp: 180.7 °C–181.8 °C. ^{1}H NMR (d_6-DMSO, 500.15 MHz): δ = 10.10 (s, 2H, NH); 9.60 (s, 2H, NCHN); 8.04 (s, 2H, NCHCHN); 7.91 (s, 2H, NCHCHN); 7.49 (d, 4H, J = 8.3 Hz, CH); 6.88 (d, 4H, J = 8.5 Hz, CH); 6.72 (s, 2H, NCH_2N); 4.51 (t, 4H, J = 5.7 Hz, NCH_2CH$_2$CO); 3.72 (s, 6H, OCH_3); 3.0 (t, 4H, J = 5.7 Hz, NCH$_2$CH$_2$CO) ppm. ^{13}C NMR (d_6-DMSO, 125.75 MHz): δ = 167.3; 155.3; 138.2; 131.9; 123.4; 122.0; 120.7; 113.8; 58.0; 55.2; 45.6; 35.4 ppm. Anal. Calcd for $C_{27}H_{32}N_6O_4Br_2$: C, 48.81; H, 4.85; N, 12.65%. Found: C, 48.52; H, 4.73; N, 12.56%.

4.4. Synthesis of acetamide- or propionamide-imidazol-ylidene platinum(II) dihalide complexes

4.4.1. General procedure

1 equiv bisimidazolium dibromide and 1 equiv platinum(II) acetylacetonate were dissolved in DMSO. The reaction mixture was stirred for 3 h at 60 °C, at 80 °C, and at 110 °C. The solvent was removed under reduced pressure to give a crude product, which for purification was washed with water, MeOH and THF. The obtained product was dried under vacuum.

4.4.2. 1,1′-Methylene-bis(3-N-phenylacetamide-imidazol-2-ylidene) platinum(II) dibromide **13**

1,1′-Methylene-bis(3-*N*-phenylacetamide-1*H*-imidazolium) dibromide (0.35 mmol, 0.200 g) and platinum(II) acetylacetonate (0.35 mmol, 0.137 g) react in 4 mL DMSO.

Yield: 0.174 g (64.6%). Mp: decomposition >350 °C. ^{1}H NMR (d_6-DMSO, 300.13 MHz): δ = 10.25 (s, 2H, NH); 7.59 (d, 2H, J = 1.6 Hz, NCHCHN); 7.53 (d, 4H, J = 7.9 Hz, o-CH); 7.37 (d, 2H, J = 1.7 Hz, NCHCHN); 7.26 (t, 4H, J = 7.6 Hz, m-CH); 7.03 (t, 2H, J = 7.3 Hz, p-CH); 6.21 (AB, 1H, J = 13.1 Hz, NCH_2N); 6.04 (AB, 1H, J = 13.1 Hz, NCH_2N); 5.55 (AB, 2H, J = 16.7 Hz, NCH_2CO); 5.15 (AB, 2H, J = 16.8 Hz, NCH_2CO) ppm. ^{13}C NMR (d_6-DMSO, 75.475 MHz): δ = 164.7; 146.6; 138.8; 128.7; 123.3; 123.2; 120.1; 118.9; 62.1; 52.6 ppm. Anal. Calcd for $C_{23}H_{22}N_6O_2PtBr_2\cdot 1H_2O$: C, 35.09; H, 3.07; N, 10.67%. Found: C, 35.25; H, 2.84; N, 10.31%.

4.4.3. 1,1′-Methylene-bis(3-N-(4-methoxyphenyl)-acetamide-imidazol-2-ylidene)platinum(II) dibromide **14**

1,1′-Methylene-bis(3-*N*-(4-methoxyphenyl)-acetamide-1*H*-imidazolium) dibromide (0.31 mmol, 0.200 g) and platinum(II) acetylacetonate (0.31 mmol, 0.124 g) react in 4 mL DMSO.

Yield: 0.170 g (66.1%). Mp: 347.6 °C. ^{1}H NMR (d_6-DMSO, 300.13 MHz): δ = 10.11 (s, 2H, NH); 7.58 (d, 2H, J = 1.7 Hz, NCHCHN); 7.44 (d, 4H, J = 8.9 Hz, CH); 7.36 (d, 2H, J = 1.7 Hz, NCHCHN); 6.82 (d, 4H, J = 9.0 Hz, CH); 6.20 (AB, 1H, J = 13.2 Hz, NCH_2N); 6.03 (AB, 1H, J = 13.0 Hz, NCH_2N); 5.57 (AB, 2H, J = 16.6 Hz, NCH_2CO); 5.08 (AB, 2H, J = 16.7 Hz, NCH_2CO); 3.69 (s, 6H, OCH_3) ppm. ^{13}C NMR (d_6-DMSO, 75.475 MHz): δ = 164.1; 155.1; 146.6; 132.0; 123.3; 120.5; 120.0; 113.8; 55.1; 52.6 ppm. Anal. Calcd for $C_{25}H_{26}N_6O_4PtBr_2\cdot 1H_2O$: C, 35.43; H, 3.33; N, 9.92%. Found: C, 35.59; H, 3.16; N. 9.67%.

4.4.4. 1,1′-Methylene-bis(3-N-phenylpropionamide-imidazol-2-ylidene)platinum(II) dibromide **15**

1,1′-Methylene-bis(3-*N*-phenylpropionamide-1*H*-imidazolium) dibromide (0.41 mmol, 0.250 g) and platinum(II) acetylacetonate (0.41 mmol, 0.163 g) react in 4 mL DMSO.

Yield: 0.168 g (51.4%). Mp: 293–305 °C. ^{1}H NMR (d_6-DMSO, 300.13 MHz): δ = 9.99 (s, 2H, NH); 7.53 (s, 2H, NCHCHN); 7.51 (d, 4H, J = 7.2 Hz, o-CH); 7.35 (s, 2H, NCHCHN); 7.26 (t, 4H, J = 7.4 Hz, m-CH); 7.02 (t, 2H, J = 7.2 Hz, p-CH); 6.08 (AB, 1H, J = 13.1 Hz, NCH_2N); 6.00 (AB, 1H, J = 13.1 Hz, NCH_2N); 4.74–4.53 (m, 4H, J = 13.3 Hz, NCH_2CH$_2$CO); 3.02 (m, 4H, J = 13.3 Hz, NCH$_2$CH$_2$CO) ppm.

^{13}C NMR (d_6-DMSO, 75.475 MHz): δ = 168.5; 145.2; 138.9; 128.7; 123.2; 121.5; 120.7; 119.2; 67.0; 45.8; 37.2 ppm. Anal. Calcd for $C_{25}H_{26}N_6O_2PtBr_2$: C, 37.65; H, 3.29; N, 10.54%. Found: C, 37.56; H, 3.17; N, 10.45%.

4.4.5. 1,1′-Methylene-bis(3-N-(4-methoxyphenyl)-propionamide-imidazol-2-ylidene)platinum(II) dibromide **16**

1,1′-Methylene-bis(3-*N*-(4-methoxyphenyl)-propionamide-1*H*-imidazolium) dibromide (0.38 mmol, 0.250 g) and platinum(II) acetylacetonate (0.38 mmol, 0.148 g) react in 4 mL DMSO. The solid formed was washed twice with water, MeOH and THF–water mixture.

Yield: 0.109 g (33.5%). Mp: 305.1 °C. ^{1}H NMR (d_6-DMSO, 300.13 MHz): δ = 9.84 (s, 2H, NH); 7.52 (d, 2H, J = 2.0 Hz, NCHCHN); 7.42 (d, 4H, J = 9.0 Hz, CH); 7.35 (d, 2H, J = 1.9 Hz, NCHCHN); 6.83 (d, 4H, J = 9.0 Hz, CH); 6.10 (AB, 1H, J = 13.1 Hz, NCH_2N); 5.99 (AB, 1H, J = 13.1 Hz, NCH_2N); 4.77–4.70 (m, 2H, J = 13.4 Hz, NCH_2CH$_2$CO); 4.59–4.51 (m, 2H, J = 13.4 Hz, NCH_2CH$_2$CO); 2.99–2.93 (m, 4H, NCH$_2$CH$_2$CO) ppm. ^{13}C NMR (d_6-DMSO, 75.475 MHz): δ = 168.0; 155.2; 145.2; 132.0; 121.5; 120.8; 120.7; 113.8; 62.0; 55.1; 45.9; 37.1 ppm. Anal. Calcd for $C_{27}H_{30}N_6O_4PtBr_2\cdot 1H_2O$: C, 37.04; H, 3.68; N, 9.60%. Found: C, 36.90; H, 3.42; N, 9.50%.

4.5. Synthesis of acetamide-imidazol-ylidene platinum(II) complexes

4.5.1. 1,1′-Methylene-bis(3-N-phenylacetamide-imidazol-2-ylidene) platinum(II) **17**

1,1′-Methylene-bis(3-*N*-phenylacetamide-imidazoline-2-ylidene)-platinum(II) dibromide (0.20 mmol, 0.155 g) and potassium carbonate (0.40 mmol, 0.056 g) react in 4 mL DMSO. The reaction mixture was stirred at 80 °C for 8 h. The mixture was filtrated, the solvent removed in vacuo and the crude product was washed with water. The obtained product was dried in vacuo.

Yield: 0.093 g (76.5%). Mp: decomposition >365 °C. ^{1}H NMR (d_6-DMSO, 300.13 MHz): δ = 7.60 (d, 2H, J = 2.0 Hz, NCHCHN); 7.50 (d, 2H, J = 2.0 Hz, NCHCHN); 6.70 (t, 4H, J = 8.9 Hz, o-CH); 6.66 (t, 4H, J = 8.9 Hz, m-CH); 6.63 (t, 2H, J = 4.4 Hz, p-CH); 6.32 (s, 2H, NCH_2N); 4.66 (s, 4H, NCH_2CO) ppm. ^{13}C NMR (d_6-DMSO, 75.475 MHz):

δ = 166.1; 149.0; 145.8; 126.8; 126.0; 121.5; 121.0; 120.3; 61.9; 54.7 ppm. Anal. Calcd for $C_{23}H_{20}N_6O_2Pt \cdot 0.3$ DMSO $\cdot 1H_2O$: C, 43.36; H, 3.67; N, 12.85; S, 1.47%. Found: C, 43.34; H, 3.61; N, 13.08; S, 1.20%.

4.5.2. 1,1′-Methylene-bis(3-N-(4-methoxyphenyl)-acetamide-imidazol-2-ylidene)platinum(II) ***18***

1,1′-Methylene-bis(3-*N*-(4-methoxyphenyl)-acetamide-imidazoline-2-ylidene)-platinum(II) dibromide (0.18 mmol, 0.150 g) and potassium carbonate (0.36 mmol, 0.050 g) react in 4 mL DMSO. The reaction mixture was stirred at 80 °C for 8 h. The mixture was filtrated, the solvent removed in vacuo and the crude product was washed with water. The obtained product was dried in vacuo.

Yield: 0.075 g (57.3%). Mp: 255–266.9 °C. ^{1}H NMR (d_6-DMSO, 300.13 MHz): δ = 7.59 (d, 2H, J = 1.9 Hz, NC*H*CHN); 7.48 (d, 2H, J = 1.9 Hz, NCHC*H*N); 6.52 (d, 4H, J = 8.8 Hz, C*H*); 6.30 (s, 2H, NCH_2N); 6.28 (d, 4H, J = 8.7 Hz, C*H*); 4.63 (s, 4H, NCH_2CO); 3.66 (s, 6H, OCH_3) ppm. ^{13}C NMR (d_6-DMSO, 75.475 MHz): δ = 166.3; 154.4; 146.2; 142.1; 127.2; 120.9; 120.3; 111.5; 61.4; 54.9; 54.7 ppm. Anal. Calcd for $C_{25}H_{24}N_6O_4Pt \cdot 0.5$KBr: C, 41.30; H, 3.33; N, 11.56%. Found: C, 41.75; H, 3.94; N, 11.00%.

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