

Synthesis of Platinum(II) Complexes from *N*-Alkyl-1,2-ethanediamine and *N*-Alkyl-1,3-propanediamine Derivatives

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Cisplatin, *cis*-diaminedichloroplatinum(II), is one of the most widely used drugs in cancer chemotherapy¹ even though its clinical usefulness has been limited by severe side effects, such as nephrotoxicity, ototoxicity and neurotoxicity, and by the emergence of resistant cancer cells lines.²

Several platinum complexes have been synthesized in an attempt to find new compounds that show antitumor properties, less severe side effects, and that can overcome cellular resistance.¹ Despite all efforts, only a few compounds have reached clinical use. Among those worth mentioning are the second generation drugs carboplatin which shows less severe nephrotoxicity³ and oxaliplatin which is active in some resistant cell lines.^{4,5} However, these complexes still present severe side effects and are active in a limited number of tumors.^{5,6}

We have recently described the synthesis and characterization of a series of platinum(II) complexes which have as ligands *N*-benzyl-1,2-ethanediamine and *N*-benzyl-1,3-propanediamine.⁷ Complexes containing diamine ligands have been shown to have relevant antitumor properties⁸ and the aromatic compounds could intercalate between the DNA base pairs,⁹ possibly increasing their cytotoxic properties.

In continuation of the work which has been developed by our research group, we describe in this article the synthesis and characterization of eight new platinum(II) complexes containing ligands derived from 1,2-ethanediamine and 1,3-propanediamine linked to phenylethyl and phenylpropyl groups. In the present work, we also describe the synthesis and characterization of new ligands prepared from 1,4-butanediamine and 1,6-hexanediamine containing phenylethyl and phenylpropyl groups. These ligands will be used in the future preparation of dinuclear platinum complexes.

Ligands **1** to **13** were synthesized by treating the corresponding diamine with an alkyl halide in ethanol. The only exception being compound **11** which was obtained through hydrogenation (H₂, Pd/C) of compound **9** in methanol (Scheme 1). In the ¹H NMR spectra for all the ligands, signals were observed in the δ 2.50 to 3.48 region corresponding to the methylene hydrogens CH₂N or CH₂Ar. Signals in the δ 6.70 to 8.12 region, attributable to the aromatic ring hydrogens, were also observed. For the others methylene hydrogens one observes signals in the δ 1.20 to 2.05 region. In the ¹³C NMR spectra, signals were observed

in the δ 18.5 to 52.0 region corresponding to the methylene carbons and signals in the δ 117.2 to 150.1 region attributed to the aromatic carbons.

The platinum(II) complexes (**14** to **21**) were synthesized by reaction of the corresponding ligands with K₂[PtCl₄]. For these complexes, one can see in the IR spectra absorptions corresponding to $\nu_{\text{Pt-N}}$ and $\nu_{\text{Pt-Cl}}$ at 530 and 320 cm⁻¹, respectively, in addition to the absorptions observed for the ligand. In the ¹H NMR spectra, one observes that the corresponding signals for the hydrogen atoms close to the platinum coordination site result in a more complex splitting pattern compared to the spectra of the free ligands. In the ¹⁹⁵Pt NMR spectra only one signal was observed around δ -2300, which can be anticipated based on data for similar compounds.¹⁰

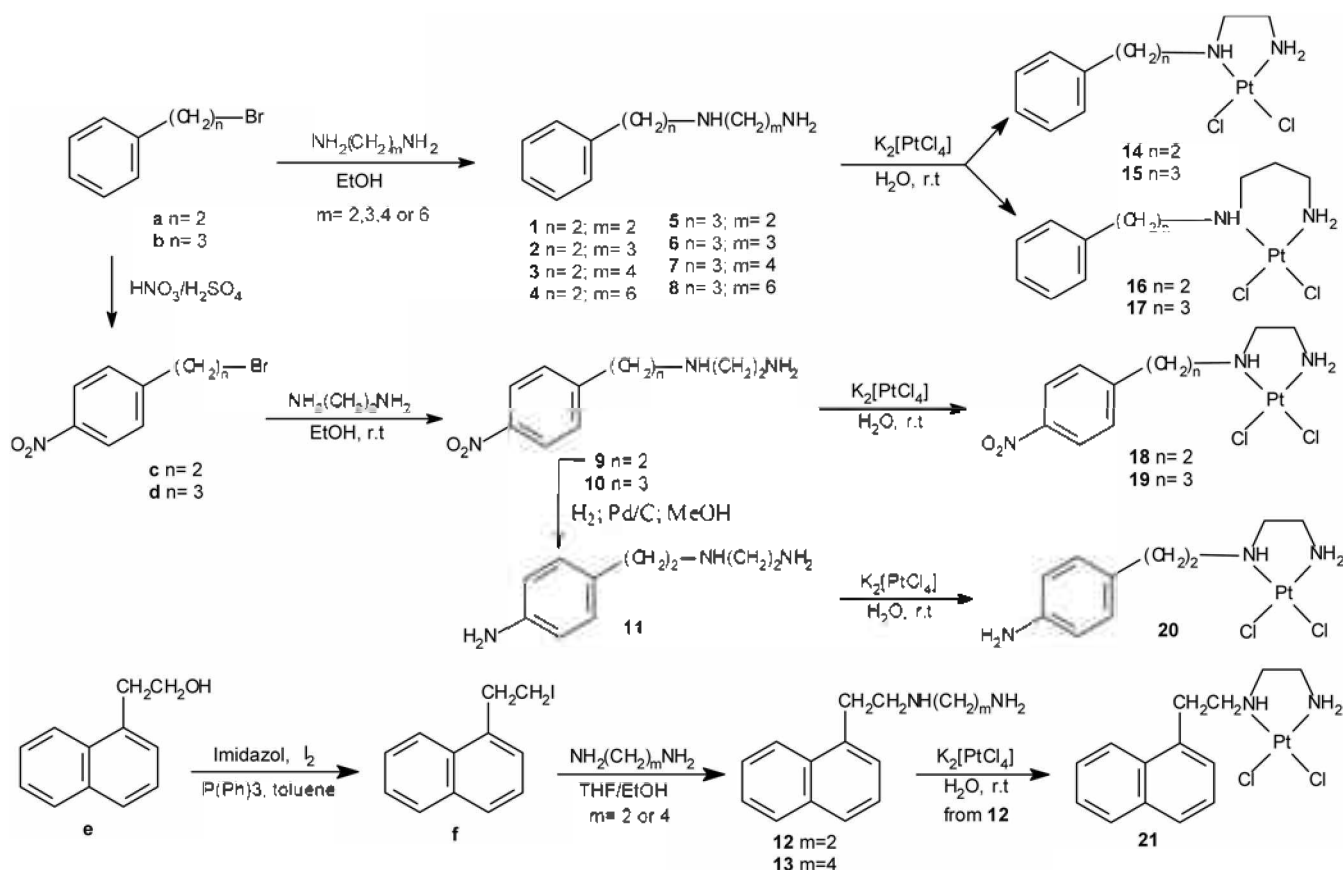
Experimental Section

Compounds **a** (2-bromoethyl)benzene, **b** (3-bromopropyl)benzene, and **e** 1-naphthaleneethanol are commercially available.

Synthesis of intermediates c and d. To nitric acid (7.0 mL) and sulfuric acid (3.5 mL) at 0 °C, the compounds (2-bromoethyl)benzene (6.8 mL; 50 mmol) or (3-bromopropyl)benzene (7.6 mL; 50 mmol) dissolved in dichloromethane were added. The reaction mixtures were stirred for 4 h at room temperature. Water was then added and a liquid/liquid extraction was performed (CH₂Cl₂/H₂O). The organic layer was separated and then evaporated. For compound **c**, the residue was recrystallized (hexane/ethyl acetate) and then filtered. For compound **d**, the residue was purified on silica gel, using CCl₄ as eluent.

c. Yield: 6.90 g, 60%; white solid, m.p.: 70-73 °C; IR ν_{max} KBr (cm⁻¹): 3109, 3081, 2960, 2849, 1606, 1520, 1346, 703; ¹H NMR (300 MHz, CDCl₃): δ 3.29 (t, 2H, CH₂, *J* 7.1), 3.62 (t, 2H, CH₂), 7.39 (d, 2H, Ph, *J* 8.7), 8.17 (d, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃): δ 31.7, 38.5 (CH₂), 123.7, 129.5, 146.2, 146.9 (Ph).

d. Yield: 6.71 g, 55%; oil; IR ν_{max} KBr (cm⁻¹): 3109, 3076, 2942, 2854, 1598, 1517, 1345, 697; ¹H NMR (300 MHz, CDCl₃): δ 2.21 (m, 2H, CH₂), 2.91 (t, 2H, CH₂, *J* 7.4), 3.41 (t, 2H, CH₂, *J* 6.4), 7.37 (d, 2H, Ph, *J* 8.7), 8.13 (d, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃): δ 32.5, 33.4, 33.8 (CH₂), 123.7, 129.4, 146.5, 148.5 (Ph).



Scheme 1

Synthesis of intermediate f. To 1-naphthaleneethanol (1.72 g; 10 mmol) dissolved in toluene (20 mL), imidazole (1.36 g; 20 mmol), triphenylphosphine (5.24 g; 20 mmol), and iodine (5.08 g; 20 mmol) were added. The reaction mixture was stirred for 12 h under reflux and an extraction (toluene/water) was performed. The organic solvent was evaporated, and the residue was purified on silica gel, using hexane as eluent.

f. Yield: 1.74 g, 62%; oil; IR ν_{\max} KBr (cm⁻¹): 3058, 2960, 2872, 1596, 1509, 1171, 776, 529; ¹H NMR (300 MHz, CDCl₃): δ 3.48 (m, 2H, CH₂), 3.68 (m, 2H, CH₂), 7.35-7.62 (m, 4H, naph), 7.79, 7.89, 8.01 (3dd, 3H, naph); ¹³C NMR (75 MHz, CDCl₃): δ 4.4 (CH₂), 37.9 (CH₂), 123.0, 125.5, 125.7, 126.2, 126.5, 127.6, 128.9, 131.2, 133.9, 136.7 (naph).

Synthesis of the ligands (Scheme 1). To a solution of appropriate diamine (100 mmol) in ethanol (30 mL), the corresponding alkyl halide (20 mmol) was slowly added during 4 h. For the 1,2-ethanediamine and 1,3-propanediamine derivatives the reaction mixture was stirred for 48 h at room temperature. In the case of 1,4-butanediamine and 1,6-hexanediamine derivatives the reaction was maintained for 7 days at 60 °C. After which time, the solution was evaporated under reduced pressure, and the residue purified on silica gel 60 G (0.2-0.5 mm), using dichloromethane/methanol 9 : 1 as eluent.

Ligand 11 (Scheme 1) was obtained from the catalytic reduction (H₂, Pd/C 10%) of 0.580 g (2 mmol) of compound

9 dissolved in methanol (5 mL). The reaction was maintained under a hydrogen atmosphere with stirring for 48 hours at room temperature. The reaction mixture was then filtered and the solvent was evaporated. The residue was purified on silica gel 60 G (0.2-0.5 mm), using dichloromethane/methanol 9 : 1 as eluent.

1. Yield: 2.29 g, 47%; oil; Anal. (Found: C, 48.72; H, 7.39; N, 10.73. Calc. for C₁₀H₁₆N₂.HBr: C, 48.98; H, 6.93; N, 11.42%); IR ν_{\max} KBr (cm⁻¹): 3416, 3025, 2931, 2854, 1603, 1495, 1317, 750, 700; ¹H NMR (300 MHz, DMSO-*d*₆): δ 2.60-2.85 (m, 8H, CH₂), 7.21 (m, 5H, Ph); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 35.6, 39.0, 47.2, 50.5 (CH₂), 125.9, 128.3, 128.6, 140.1 (Ph).

2. Yield: 2.59 g, 50%; oil; Anal. (Found: C, 49.90; H, 6.95; N, 10.70. Calc. for C₁₁H₁₈N₂.HBr: C, 50.96; H, 7.33; N, 10.81%); IR ν_{\max} KBr (cm⁻¹): 3380, 3015, 2986, 1598, 1444, 1029, 700; ¹H NMR (300 MHz, CDCl₃): δ 1.61 (m, 2H, CH₂), 2.65-2.87 (m, 8H, CH₂), 7.21 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃): δ 33.4, 36.3, 40.5, 47.7, 51.2 (CH₂), 126.2, 128.5, 128.7, 140.0 (Ph).

3. Yield: 0.57 g, 11%; oil; Anal. (Found: C, 51.90; H, 7.50; N, 10.42. Calc. for C₁₂H₂₀N₂.HBr: C, 52.74; H, 7.69; N, 10.25%); IR ν_{\max} KBr (cm⁻¹): 3400, 3368, 3058, 3025, 2934, 2870, 1570, 1500, 1495, 1454, 1311, 1103, 749, 740, 700; ¹H NMR (300 MHz, CDCl₃): δ 1.47 (m, 4H, CH₂), 1.73 (s, 2H, NH₂), 2.60-2.80 (2m, 8H, CH₂), 7.21 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃): δ 27.5, 31.5, 36.4, 42.1, 49.7, 51.2

(CH₂), 126.3, 128.6, 128.8, 140.1 (Ph).

4. Yield: 0.84 g, 14%; oil; Anal. (Found: C, 56.09; H, 8.45; N, 9.60. Calc. for C₁₄H₂₃N₂.HBr: C, 55.81; H, 8.30; N, 9.30%); IR ν_{\max} KBr (cm⁻¹): 3320, 3267, 3100, 3025, 2928, 2855, 1572, 1453, 1401, 1119, 1081, 1030, 850, 749, 699; ¹H NMR (300 MHz, CDCl₃): δ 1.20, 1.40 (2m, 8H, CH₂), 1.97 (s, 2H, NH₂), 2.57, 2.80 (2m, 8H, CH₂), 7.20 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃): δ 26.8, 27.3, 30.0, 33.6, 36.3, 42.1, 49.8, 51.2 (CH₂), 126.3, 128.6, 128.8, 142.1 (Ph).

5. Yield: 2.77 g, 54%; oil; Anal. (Found: C, 51.02; H, 7.70; N, 10.95. Calc. for C₁₁H₁₈N₂.HBr: C, 50.96; H, 7.33; N, 10.81%); IR ν_{\max} KBr (cm⁻¹): 3276, 3025, 2935, 2858, 1653, 1495, 1350, 750, 700; ¹H NMR (200 MHz, CDCl₃): δ 1.82 (m, 2H, CH₂), 2.60-2.71 (m, 4H, CH₂), 2.81 (t, 2H, CH₂), 3.13 (s, 2H, CH₂), 7.20 (m, 5H, Ph); ¹³C NMR (200 MHz, CDCl₃): δ 31.5, 33.6, 41.4, 49.2, 52.0 (CH₂), 125.7, 128.3, 128.3, 128.3, 142.0 (Ph).

6. Yield: 3.07 g, 57%; m.p.: 150-154 °C; Anal. (Found: C, 52.00; H, 7.39; N, 10.01. Calc. for C₁₂H₂₀N₂.HBr: C, 52.74; H, 7.69; N, 10.25%); IR ν_{\max} KBr (cm⁻¹): 3349, 3025, 2931, 2853, 1562, 1495, 1316, 750, 699; ¹H NMR (300 MHz, CD₃OD): δ 1.66-1.83 (m, 4H, CH₂), 2.50-2.90 (m, 8H, CH₂), 7.11 (m, 5H, Ph); ¹³C NMR (300 MHz, CD₃OD): δ 29.1, 31.2, 34.1, 39.8, 47.7, 49.4 (CH₂), 126.9, 129.2, 129.3, 142.6 (Ph).

7. Yield: 0.86 g, 15%; oil; Anal. (Found: C, 54.60; H, 8.15; N, 10.01. Calc. for C₁₃H₂₂N₂.HBr: C, 54.35; H, 8.01; N, 9.75%); IR ν_{\max} KBr (cm⁻¹): 3350, 3100, 3025, 2930, 2856, 1582, 1500, 1453, 1382, 1314, 1119, 745, 688; ¹H NMR (300 MHz, CDCl₃): δ 1.49 (m, 4H, CH₂), 1.80 (m, 2H, CH₂), 2.10 (s, 2H, NH₂), 2.60 (m, 8H, CH₂), 7.18-7.29 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃): δ 27.4, 31.6, 33.8, 42.0, 49.5, 49.8, 50.4 (CH₂), 125.9, 128.5, 142.1 (Ph).

8. Yield: 0.60 g, 10%; oil; Anal. (Found: C, 56.01; H, 9.08; N, 8.73. Calc. for C₁₅H₂₆N₂.HBr: C, 57.14; H, 8.57; N, 8.88%); IR ν_{\max} KBr (cm⁻¹): 3320, 3290, 3019, 2928, 2855, 1576, 1510, 1454, 1320, 1312, 1119, 747, 699, 550; ¹H NMR (300 MHz, CDCl₃): δ 1.30, 1.50, 1.90 (3m, 12H, CH₂, NH₂), 2.57 (m, 8H, CH₂), 7.21 (m, 5H, Ph); ¹³C NMR (75 MHz, CDCl₃): δ 18.5, 26.9, 27.3, 30.1, 31.7, 33.7, 33.8, 42.2, 49.6, 50.0 (CH₂), 125.9, 128.4, 142.2 (Ph).

9. Yield: 2.51 g, 44%; oil; Anal. (Found: C, 41.87; H, 5.70; N, 14.73. Calc. for C₁₀H₁₅N₃O₂.HBr: C, 41.37; H, 5.51; N, 14.48%); IR ν_{\max} KBr (cm⁻¹): 3290, 2953, 2930, 2852, 1599, 1516, 1347, 1110, 855, 747, 699; ¹H NMR (300 MHz, CD₃OD): δ 2.72 (t, 2H, CH₂, *J* 6.4), 2.89 (s, 4H, CH₂), 3.27 (t, 2H, CH₂), 7.43, 8.11 (2d, 4H, Ph, *J* 8.6); ¹³C NMR (300 MHz, CD₃OD): δ 36.5, 39.8, 49.4, 51.0 (CH₂), 124.8, 131.0, 147.0, 149.1 (Ph).

10. Yield: 2.58 g, 43%; oil; Anal. (Found: C, 43.10; H, 5.81; N, 13.62. Calc. for C₁₁H₁₇N₃O₂.HBr: C, 43.42; H, 5.92; N, 13.81%); IR ν_{\max} KBr (cm⁻¹): 3435, 3109, 2995, 2961, 1598, 1514, 1345, 697; ¹H NMR (300 MHz, CD₃OD): δ 2.05 (m, 2H, CH₂), 2.85 (t, 2H, CH₂, *J* 7.5), 3.07 (t, 2H, CH₂, *J* 7.5), 3.27 (m, 4H, CH₂), 7.47, 8.12 (2d, 4H, Ph, *J* 8.8); ¹³C NMR (300 MHz, CD₃OD): δ 29.2, 33.6, 37.5, 46.2, 49.2 (CH₂), 124.9, 130.9, 148.0, 150.1 (Ph).

11. Yield: 0.26 g, 50%; oil; Anal. (Found: C, 46.35; H, 7.01; N, 16.33. Calc. for C₁₀H₁₇N₃.HBr: C, 46.15; H, 6.92; N, 16.15%); IR ν_{\max} KBr (cm⁻¹): 3410, 3310, 3010, 2926, 2852, 1615, 1517, 1376, 1122, 1073, 744; ¹H NMR (300 MHz, CD₃OD): δ 2.85 (t, 2H, CH₂, *J* 7.3), 3.12 (m, 4H, CH₂), 3.48 (t, 2H, CH₂), 6.70, 7.00 (2d, 4H, Ph, *J* 8.4); ¹³C NMR (300 MHz, CD₃OD): δ 32.8, 37.3, 49.1, 50.6 (CH₂), 117.2, 127.0, 130.6, 147.9 (Ph).

12. Yield: 3.93 g, 58%; m.p.: 140-145 °C; Anal. (Found: C, 48.95; H, 5.39; N, 8.01. Calc. for C₁₄H₁₈N₂.HI: C, 49.12; H, 5.55; N, 8.18%); IR ν_{\max} KBr (cm⁻¹): 3224, 3064, 2944, 2851, 1597, 1496, 1110, 1023, 768; ¹H NMR (300 MHz, D₂O): δ 2.90 (m, 2H, CH₂), 2.98 (m, 2H, CH₂), 3.03 (m, 2H, CH₂), 3.29 (m, 2H, CH₂), 7.41-7.54 (m, 4H, naph), 7.79, 7.90, 8.03 (3dd, 3H, naph); ¹³C NMR (75 MHz, D₂O): δ 31.5, 38.3, 47.0, 49.0 (CH₂), 123.9, 126.3, 126.6, 127.0, 127.6, 127.9, 129.3, 131.7, 134.2, 134.9 (naph).

13. Yield: 0.82 g, 11%; oil; Anal. (Found: C, 52.01; H, 6.32; N, 7.73. Calc. for C₁₆H₂₂N₂.HI: C, 51.89; H, 6.21; N, 7.56%); IR ν_{\max} KBr (cm⁻¹): 3353, 3051, 3025, 2935, 2856, 1558, 1473, 1410, 1395, 1312, 1113, 799, 788; ¹H NMR (300 MHz, CDCl₃): δ 1.50 (m, 4H, CH₂), 2.65 (m, 4H, CH₂), 3.01 (t, 2H, CH₂, *J* 7.23), 3.29 (t, 2H, CH₂, *J* 7.26), 7.33-7.57 (m, 4H naph), 7.74, 7.87, 8.08 (3dd, 3H, naph); ¹³C NMR (75 MHz, CDCl₃): δ 27.5, 31.5, 33.6, 42.1, 49.8, 50.5 (CH₂), 123.9, 125.7, 126.1, 126.8, 127.2, 129.0 (naph).

Synthesis of the complexes (Scheme 1). To a solution of K₂[PtCl₄] (0.415 g; 1 mmol) in water (10 mL), the appropriate ligand (1 mmol), dissolved in water (5 mL), was added slowly with stirring. After 24 h at room temperature, the solid that formed was filtered off, washed with water, and dried.

14. Yield: 0.34 g, 80%; yellow solid, m.p.: 296-300 °C (dec); Anal. (Found: C, 27.45; H, 3.65; N, 6.22; Cl, 16.10. Calc. for C₁₀H₁₆N₂Cl₂Pt: C, 27.90; H, 3.72; N, 6.51; Cl, 16.51%); IR ν_{\max} KBr (cm⁻¹): 3243, 3129, 2916, 1605, 1456, 1031, 742, 696, 540, 316; ¹H NMR (300 MHz, DMSO-*d*₆): δ 2.35 (m, 2H, CH₂), 2.81 (m, 2H, CH₂), 2.98 (m, 2H, CH₂), 3.24 (m, 2H, CH₂), 5.37, 5.42 (2s, 2H, NH₂), 6.48 (s, 1H, NH), 7.25 (m, 5H, Ph); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 33.1, 46.6, 53.2, 55.3 (CH₂), 126.2, 128.4, 128.6, 138.7 (Ph); ¹⁹⁵Pt NMR (86 MHz, DMSO-*d*₆): δ -2365.

15. Yield: 0.38 g, 85%; light brown solid, m.p.: 280-288 °C (dec); Anal. (Found: C, 30.00; H, 4.15; N, 6.45; Cl, 16.02. Calc. for C₁₁H₁₈N₂Cl₂Pt: C, 29.73; H, 4.05; N, 6.31; Cl, 16.00%); IR ν_{\max} KBr (cm⁻¹): 3244, 3195, 3133, 3026, 2926, 1603, 1453, 1285, 752, 699, 540, 321; ¹H NMR (300 MHz, DMSO-*d*₆): δ 2.07 (m, 2H, CH₂), 2.31 (m, 2H, CH₂), 2.49 (m, 2H, CH₂), 2.59 (t, 2H, CH₂, *J* 7.7), 2.84 (m, 2H, CH₂), 5.28, 5.36 (2s, 2H, NH₂), 6.28 (s, 1H, NH), 7.22 (m, 5H, Ph); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 28.7, 32.5, 46.4, 51.5, 54.9 (CH₂), 124.4, 126.7, 126.8, 139.8 (Ph); ¹⁹⁵Pt NMR (86 MHz, DMSO-*d*₆): δ -2353.

16. Yield: 0.37 g, 83%; brown solid, m.p.: 220-228 °C (dec); Anal. (Found: C, 29.30; H, 4.08; N, 6.58; Cl, 16.52. Calc. for C₁₁H₁₈N₂Cl₂Pt: C, 29.73; H, 4.05; N, 6.31; Cl, 16.00%); IR ν_{\max} KBr (cm⁻¹): 3207, 3142, 3026, 2945, 1600,

1454, 1179, 1057, 752, 529, 320; ^1H NMR (300 MHz, DMSO- d_6): δ 1.71 (m, 2H, CH₂), 2.59 (m, 2H, CH₂), 2.79 (m, 2H, CH₂), 2.90 (m, 2H, CH₂), 3.40 (m, 2H, CH₂), 4.92, 5.15 (2s, 2H, NH₂), 5.99 (s, 1H, NH), 7.29 (m, 5H, Ph); ^{13}C NMR (75 MHz, DMSO- d_6): δ 22.5, 33.8, 42.3, 50.1, 54.0 (CH₂), 125.7, 127.9, 128.1, 138.2 (Ph); ^{195}Pt NMR (86 MHz, DMSO- d_6): δ -2260.

17. Yield: 0.38 g, 83%; gray solid, m.p.: 224-228 °C (dec); Anal. (Found: C, 30.66; H, 4.27; N, 5.82; Cl, 15.89. Calc. for C₁₂H₂₀N₂Cl₂Pt: C, 31.44; H, 4.37; N, 6.11; Cl, 15.50%); IR ν_{max} KBr (cm⁻¹): 3241, 3198, 3127, 3024, 2942, 1598, 1452, 1181, 751, 520, 321; ^1H NMR (300 MHz, DMSO- d_6): δ 1.69 (m, 2H, CH₂), 1.99 (m, 2H, CH₂), 2.30 (m, 2H, CH₂), 2.64 (m, 4H, CH₂), 2.88, 3.10 (2m, 2H, CH₂), 4.85, 5.10 (2s, 2H, NH₂), 5.85 (s, 1H, NH), 7.24 (m, 5H, Ph); ^{13}C NMR (75 MHz, DMSO- d_6): δ 22.9, 29.7, 32.7, 42.8, 50.7, 53.0 (CH₂), 125.8, 128.2, 128.3, 141.7 (Ph); ^{195}Pt NMR (86 MHz, DMSO- d_6): δ -2256.

18. Yield: 0.34 g, 71%; orange solid, m.p.: 253-260 °C (dec); Anal. (Found: C, 25.02; H, 3.01; N, 8.55; Cl, 14.72. Calc. for C₁₀H₁₅N₃Cl₂O₂Pt: C, 25.26; H, 3.15; N, 8.84; Cl, 14.94%); IR ν_{max} KBr (cm⁻¹): 3197, 3118, 2959, 2919, 1600, 1517, 1458, 1348, 1110, 746, 699, 527, 323; ^1H NMR (300 MHz, DMSO- d_6): δ 2.36 (m, 2H, CH₂), 2.95-3.15 (m, 4H, CH₂), 3.35 (m, 2H, CH₂), 5.36, 5.43 (2s, 2H, NH₂), 6.55 (s, 1H, NH), 7.52, 8.15 (2d, 4H, Ph, *J* 7.1); ^{13}C NMR (75 MHz, DMSO- d_6): δ 33.0, 46.4, 52.1, 55.0 (CH₂), 122.2, 128.5, 144.5, 145.3 (Ph); ^{195}Pt NMR (86 MHz, DMSO- d_6): δ -2366.

19. Yield: 0.24 g, 50%; brown solid, m.p.: 200-215 °C (dec); Anal. (Found: C, 26.80; H, 3.55; N, 8.45; Cl, 14.62. Calc. for C₁₁H₁₇N₃Cl₂O₂Pt: C, 26.99; H, 3.47; N, 8.58; Cl, 14.51%); IR ν_{max} KBr (cm⁻¹): 3276, 3137, 2958, 2919, 1599, 1517, 1347, 1109, 853, 540, 326; ^1H NMR (300 MHz, DMSO- d_6): δ 1.96 (m, 2H, CH₂), 2.31 (m, 2H, CH₂), 2.65-2.97 (m, 6H, CH₂), 5.32, 5.39 (2s, 2H, NH₂), 6.34 (s, 1H, NH), 7.50, 8.14 (2d, 4H, Ph, *J* 7.4); ^{13}C NMR (75 MHz, DMSO- d_6): δ 27.8, 32.1, 45.2, 50.4, 53.8 (CH₂), 123.5, 129.6, 145.9, 149.6 (Ph); ^{195}Pt NMR (86 MHz, DMSO- d_6): δ -2358.

20. Yield: 0.25 g, 57%; brown solid, m.p.: 250-267 °C (dec); Anal. (Found: C, 27.10; H, 4.00; N, 9.25; Cl, 16.05. Calc. for C₁₀H₁₇N₃Cl₂Pt: C, 26.96; H, 3.82; N, 9.43; Cl, 15.95%); IR ν_{max} KBr (cm⁻¹): 3342, 3204, 3091, 2915, 1653, 1511, 1438, 1369, 1176, 761, 527, 323; ^1H NMR (300 MHz,

DMSO- d_6): δ 2.80-3.20 (m, 6H, CH₂), 3.33 (m, 2H, CH₂), 7.12 (m, 4H, Ph), 8.12 (s, 1H, NH), 8.62 (s, 2H, NH₂); ^{13}C NMR (75 MHz, DMSO- d_6): δ 31.0, 35.2, 46.5, 47.8 (CH₂), 122.6, 128.6, 133.5, 140.1 (Ph); ^{195}Pt NMR (86 MHz, DMSO- d_6): δ -2360.

21. Yield: 0.37 g, 77%; brown solid, m.p.: 240-247 °C (dec); Anal. (Found: C, 34.87; H, 3.81; N, 5.95; Cl, 14.68. Calc. for C₁₄H₁₈N₂Cl₂Pt: C, 35.00; H, 3.75; N, 5.83; Cl, 14.79%); IR ν_{max} KBr (cm⁻¹): 3241, 3196, 3050, 2946, 1595, 1461, 1027, 798, 493, 317; ^1H NMR (300 MHz, DMSO- d_6): δ 2.36 (m, 2H, CH₂), 2.64 (m, 2H, CH₂), 3.10 (m, 2H, CH₂), 3.67 (m, 2H, CH₂), 5.39, 5.46 (2s, 2H, NH₂), 6.65 (s, 1H, NH), 7.40-7.59 (m, 4H, naph), 7.78, 7.91, 8.18 (3 dd, 3H, naph); ^{13}C NMR (75 MHz, DMSO- d_6): δ 30.3, 46.8, 52.8, 55.4 (CH₂), 123.8, 125.6, 125.7, 126.1, 126.7, 126.9, 128.5, 131.3, 133.4, 134.8 (naph); ^{195}Pt NMR (86 MHz, DMSO- d_6): δ -2362.

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