Platinum(II) Chloride Complexes of Linear Alkyl-bridged 2,2′-Bipyridine/Catechol Ligands

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Abstract. Platinum(II) chloride can selectively be coordinated to the 2,2′-bipyridine moiety of the alkyl bridged sequential catechol/2,2′-bipyridine ligand **1a-H$_2$** and of the related ligands **1a/b-Me$_2$** and **2**. Reaction of (**1b-Me$_2$**)$PtCl_2$ with BBr_3 produces the platinum(II) complex (**1b-H$_2$**)$PtCl_2$ while ether cleavage of the uncoordinated ligand **1b-Me$_2$** fails. Under basic conditions (**1a-H$_2$**)$PtCl_2$ forms polymeric/oligomeric species [(**1a**)Pt]$_n$ besides traces of the dinuclear complex [(**1a**)Pt]$_2$.

Keywords: 2,2′-Bipyridine; Catechol; Platinum; Sequential ligands

Platin(II)-chlorid-Komplexe von linearen alkylverbrückten Bipyridin/Brenzkatechin-Liganden

Inhaltsübersicht. Platin(II)-chlorid kann selektiv an die 2,2′-Bipyridineinheit des sequentiellen alkylverbrückten Brenzkatechin/2,2′-Bipyridin-Liganden **1a-H$_2$** und der analogen Derivate **1a/b-Me$_2$** und **2** binden. Die Reaktion von (**1b-Me$_2$**)$PtCl_2$ mit BBr_3 führt zu dem Platin(II)-Komplex (**1b-H$_2$**)$PtCl_2$, während die Etherspaltung bei dem freien Liganden **1b-Me$_2$** fehlschlägt. Bei der Reaktion von (**1a-H$_2$**)$PtCl_2$ mit Base werden neben Spuren des zweikernigen Komplexes [(**1a**)Pt]$_2$ polymere bzw. oligomere Spezies [(**1a**)Pt]$_n$ erhalten.

Introduction

Just recently linear sequential ligands with two or more different binding sites for metal cations became important building-blocks in metallo-supramolecular chemistry [1–5]. Using such ligands it is possible to design supramolecular functional devices which allow to investigate into energy transfer processes [2] or electrochemical switches [3]. In the self-assembly of helicates or helicate-type complexes the orientation of the sequential ligands can be controlled by the choice of appropriate metals or combinations of metals [4, 5].

We introduced alkyl-bridged 2,2′-bipyridine/catechol ligands **1-H$_2$** which can bind iron(II) ions using the bipyridine moieties to form tris(bipyridine)iron(II) complexes which possess uncoordinated catechol units as substituents. On the other hand, the same ligands in the presence of titanium(IV) ions and potassium carbonate form a tris(catecholato)titanium(IV) complex with "free" bipyridine units [6].

In this paper we discuss the coordination behavior of the ligands **1-H$_2$** and **1-Me$_2$** towards the platinum(II) chloride and the X-ray structure of [(**2**)$PtCl_2$] is presented.

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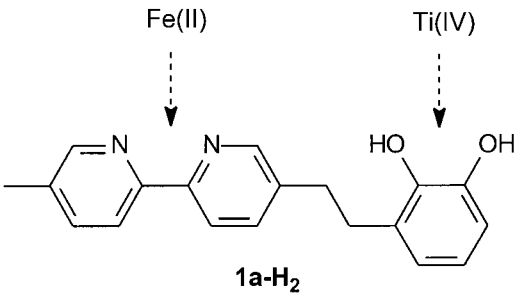


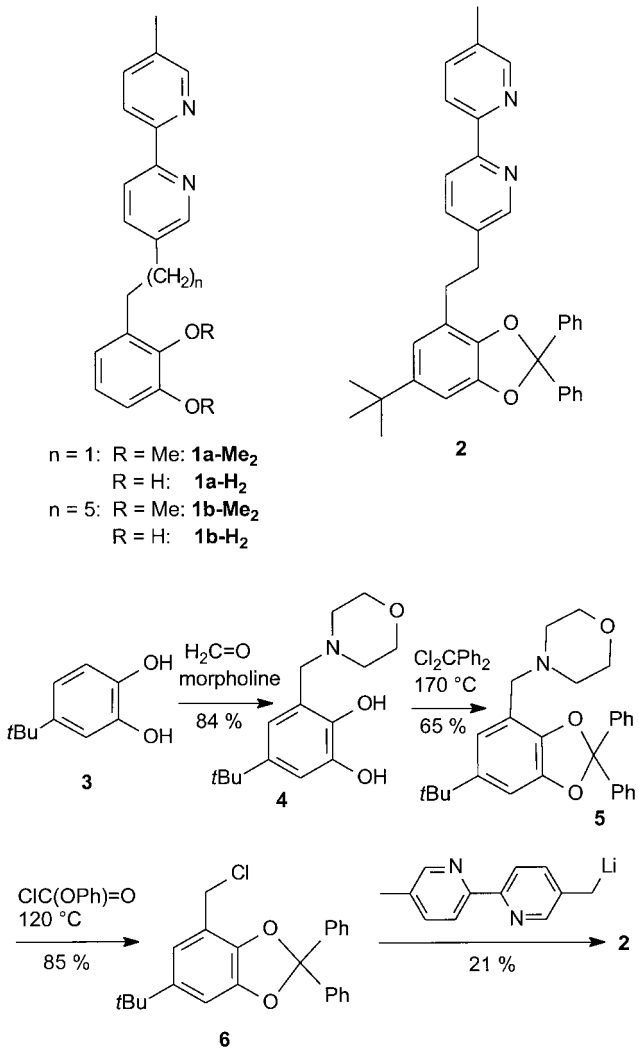
Fig. 1 Selective binding of Fe^{II}-ions to the 2,2′-bipyridine- and of Ti^{IV}-ions to the catecholate-binding site of **1a-H$_2$**.

Results and Discussion

Ligand Syntheses

The ligands **1-H$_2$** and **1-Me$_2$** were prepared as described before [6]. The derivative **2** was synthesized as depicted in Scheme 1 starting from 4-t-butylcatechol **3** (s. Scheme 1).

In a mannich-type reaction **3** is transformed into the *N*-morpholino derivative **4** [7]. The catechol unit is protected as the benzophenone ketale by reaction of **4** with dichlorodiphenyl methane to obtain **5** [8]. Phenylchloroformate reacts with **5** and substitutes the morpholino substituent by chloride and the benzyl chloride **6** is isolated [9]. Ligand **2** is formed upon reaction with in situ lithiated 5,5′-dimethyl-2,2′-bi-



Scheme 1

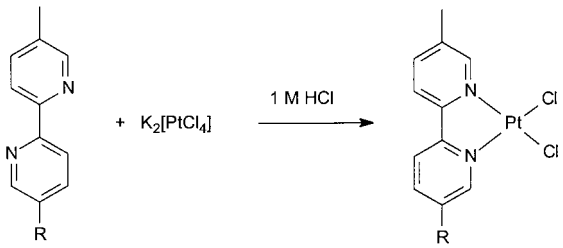
pyridine [6]. All our attempts (e. g.: H^+/H_2O [10]; H_2/Pd–C [11]; $(HOCH_2)_2/H^+$ [12]) to cleave the ketale moiety of **2** failed. However, the protected ligand **2** was used for comparison studies.

Preparation of Coordination Compounds

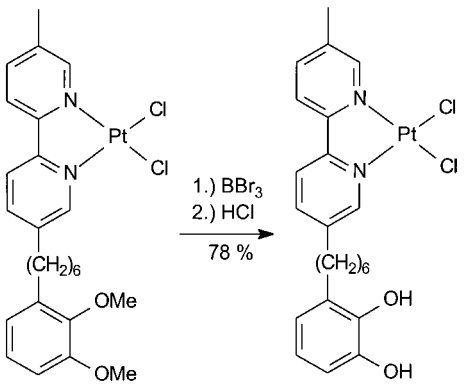
The $PtCl_2$ complexes are synthesized by reaction of the 2,2′-bipyridine derivatives **1** and **2** with potassium tetrachloroplatinate(II) in 1 M hydrochloric acid [13]. The complexes [(**1a-Me$_2$**)$PtCl_2$], [(**1a-H$_2$**)$PtCl_2$], [(**1b-Me$_2$**)$PtCl_2$], and [(**2**)$PtCl_2$] are obtained as yellow solids which precipitate and are isolated by filtration and recrystallized from acetone/diethyl ether. The coordination compounds are isolated in good to excellent yields (Table 1).

The $PtCl_2$ complex [(**1b-Me$_2$**)$PtCl_2$] by reaction with BBr_3 and workup with hydrochloric acid can be transformed into the corresponding derivative with a free catechol unit [(**1b-H$_2$**)$PtCl_2$]. This ether cleavage reaction only proceeds if the platinum complex is used. If similar reaction conditions are applied to the free ligand **1b-Me$_2$**, the BBr_3 attacks the bipyridine unit leading to an unspecific decomposition of the molecule. Thus the $PtCl_2$-moiety acts as a protecting group for the 2,2′-bipyridine unit of **1b**.

Table 1 Preparation of platinum(II) chloride complexes



Platinum(II) complex	R =	Yield
[(**1a-Me$_2$**)$PtCl_2$]	2-(2,3-dimethoxyphenyl)ethyl	80%
[(**1a-H$_2$**)$PtCl_2$]	2-(2,3-dihydroxyphenyl)ethyl	100%
[(**1b-Me$_2$**)$PtCl_2$]	6-(2,3-dimethoxyphenyl)hexyl	72%
[(**2**)$PtCl_2$]	2-(5-*t*butyl-2,3-((diphenyl-methylene)dioxy)phenyl)ethyl	68%



Scheme 2

All $PtCl_2$ complexes give characteristic ^1H and ^{13}C NMR spectra and can be characterized by mass spectrometry. Molar peaks are detected at m/z = 599 ([(**1a-Me$_2$**)$PtCl_2$]; EI), 573 ([(**1a-H$_2$**)$PtCl_2H]^+$, FAB(+)), 656 ([(**1b-Me$_2$**)$PtCl_2H]^+$, FAB(+)), 593 ([(**1b-H$_2$**) · $PtCl_2H]^+$, FAB(+)), and 792 ([(**2**)$PtCl_2H]^+$, FAB(+)). (**1b-H$_2$**)$PtCl_2$ is not obtained in analytically pure form because of a partial exchange of chloro by bromo substituents at platinum during BBr_3 deprotection.

X-ray Structural Analysis of [(2)PtCl$_2$]

The complexes [(**1**)$PtCl_2$] crystallize from acetone/diethyl ether in the form of yellow plates. Due to the two dimensional character of the crystals we were not

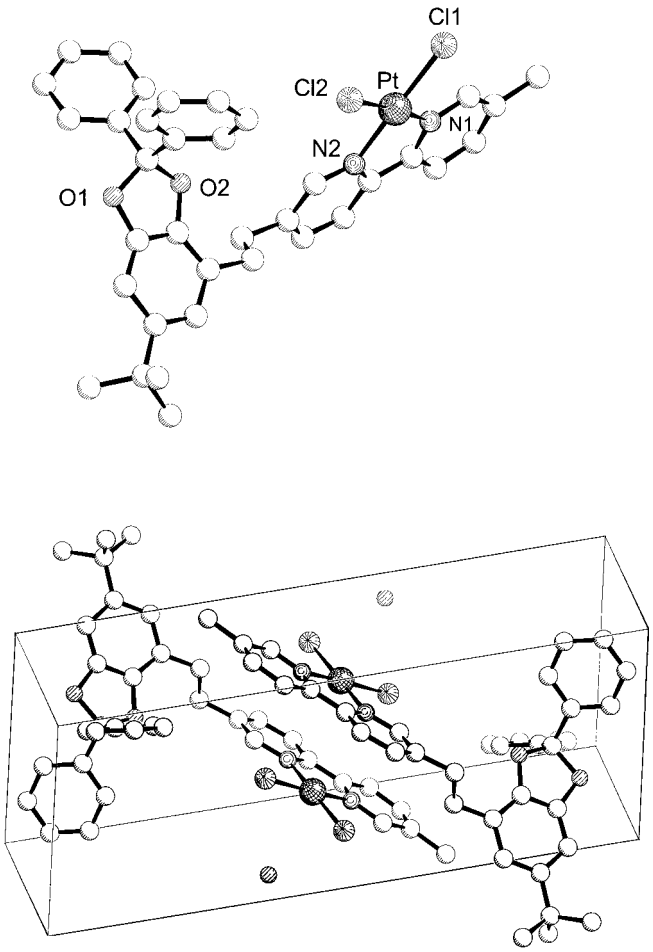


Fig. 2 Molecular structure of $[(\mathbf{2})PtCl_2]$ in the solid state and representation of the corresponding unit cell.

Table 2 Selected bond lengths and angles of $[(\mathbf{2})PtCl_2]$

	Distance Å		Angle °
Pt–Cl1	2.298(3)	Cl1–Pt–Cl2	89.25(10)
Pt–Cl2	2.291(3)	N1–Pt–N2	79.9(4)
Pt–N1	2.002(8)	Cl1–Pt–N1	95.6(3)
Pt–N2	2.019(8)	Cl2–Pt–N2	95.2(3)
Pt···Pt	3.92		

able to obtain an X-ray structural analysis of one of the derivatives $[(\mathbf{1})PtCl_2]$. The derivative $[(\mathbf{2})PtCl_2]$ on the other hand led to crystals which were suitable to determine an X-ray structure.

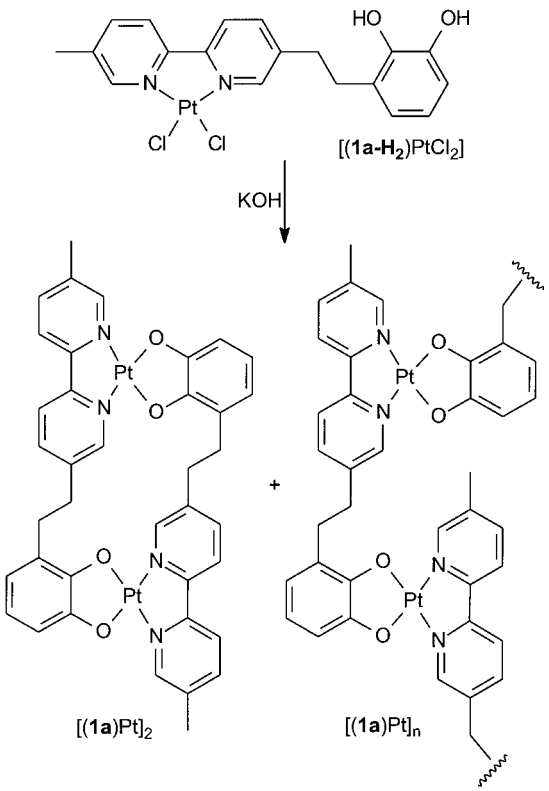
$[(\mathbf{2})PtCl_2] \cdot 0.5\,H_2O$ crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$) with the cell constants $a = 8.273(1)$, $b = 9.485(3)$, $c = 21.467(4)$ Å, $\alpha = 101.51(2)$, $\beta = 90.86(2)$, $\gamma = 100.05(2)°$. The structure was refined to $R = 0.045$. The crystal contains half a molecule of water per asymmetric unit.

The central part of $[(\mathbf{2})PtCl_2]$ is the square planar (2,2′-bipyridine)platinum(II) chloride moiety. The angles and bond length which are found for $[(\mathbf{2})PtCl_2]$ (Table 2) are in accordance with those observed for related (bipyridine)platinum(II) chloride complexes [14]. The plane of the aromatic moiety of the protected t-butylcatechol substituent which is attached to the Pt-complex unit via an ethylene spacer is twisted by 53.1° compared to the plane of the square planar complex unit.

In the unit cell two of the molecules $[(\mathbf{2})PtCl_2]$ are oriented anti-parallel to each other with an Pt–Pt separation of 3.92 Å. Due to the sterically hindered side chain this distance is large compared to the one observed for $[(bpy)PtCl_2]$ ($d_{Pt-Pt} = 3.40$ Å) [14]. The chloro substituents of one of the molecules $[(\mathbf{2})PtCl_2]$ in the solid state are located on top of the plane of the bipyridine unit of the second complex which is reasonable because of electrostatic interactions.

Attempts to Synthesize [(1 a)Pt]$_2$

(2,2′-Bipyridine)(catecholato)platinum(II) derivatives are prepared by reaction of (2,2′ bipyridine)platinum(II) chloride with catechol in the presence of base [15]. Reaction of $[(\mathbf{1\,a\text{-}H_2})PtCl_2]$ with methanolic KOH in acetone leads to the precipitation of a purple solid material which is insoluble in common solvents. In propylene carbonate it can be partly dissolved at elevated temperatures. However, UV-spectroscopy of the solution indicates that decomposition of the (catecholato)(bipyridine)platinum complex takes place upon dissolution.



Scheme 3

For the insoluble material an elemental analysis is obtained which is consistent with the composition "$[(\mathbf{1a})Pt]_2 \cdot 8\,H_2O$" and FAB(+) mass spectrometry shows the presence of the dinuclear species $[(\mathbf{1a})Pt]_2$ (HRMS: calcd. 998.1720, found 998.1514). However, the insolubility of the material indicates that only traces of the dinuclear complex are formed while mainly oligomers or polymers are produced during the reaction. Attempts to optimize the reaction conditions (high temperatures, high dilution conditions) did not lead to isolable quantities of the pure dinuclear complex $[(\mathbf{1a})Pt]_2$.

The isolation of mixtures of oligomeric as well as dimeric species shows, that here not a selective self-assembly process but unspecific complex formation takes place. Unfortunately the ligand **1a** does not allow to control the assembly of the complexes by addition of e. g. appropriate templates as was recently done to obtain defined metalla-cryptates instead of complex mixtures of coordination compounds [16].

Conclusions

Platinum(II) chloride complexes $[(\mathbf{1\text{-}H_2})PtCl_2]$, $[(\mathbf{1\text{-}Me_2})PtCl_2]$, and $[(\mathbf{2})PtCl_2]$ can be prepared by standard methods. In $[(\mathbf{1\text{-}H_2})PtCl_2]$ the platinum(II) chloride selectively binds to the 2,2′-bipyridine units while an uncoordinated catecholate moiety still is present. Complexes of this type are ideal precursors for the formation of large polymetallic arrays using the catechol sites for further binding to other metal centers. Reaction of $[(\mathbf{1a\text{-}H_2})PtCl_2]$ with base does not produce significant amounts of the desired dinuclear platinum complex $[(\mathbf{1a})Pt]_2$. However, this dinuclear species can be characterized by mass spectrometry as one component of the formed mixture of oligomers or polymers.

The X-ray structure of $[(\mathbf{2})PtCl_2]$ shows that the square-planar (2,2′-bipyridine)dichloroplatinum units staple in the solid state and lead to columns with Pt–Pt separations of 3.92 and 5.21 Å.

Experimental Part

General

IR: Bruker IFS 88. – EI (70 eV) or FAB(+) MS/HRMS: Finnigan MAT 90; matrix for FAB(+): 3-nitrobenzoic acid (3-NBA). – UV/Vis: Perkin Elmer UV-Vis Lambda 2. – ^{1}H NMR and ^{13}C NMR (BB/DEPT): Bruker DRX 500 or AM 400; internal standard: $CHCl_3$, $HD_2CC(=O)CD_3$, or $HD_2CS(=O)CD_3$.

*5-tButyl-3-(morpholinomethyl)benzene-1,2-diol (**4**).* Compound **4** was prepared in 84% yield according to a literature procedure [7].

*5-tButyl-1,2-[(diphenylmethylene)dioxy]-3-(N-morpholinomethyl)benzene (**5**).* The catechol derivative **4** (2.65 g, 10.0 mmol) and dichlorodiphenyl methane (1.92 ml, 10.0 mmol) are heated to 170 °C for 20 minutes. The obtained derivative **5** is recrystallized from methanol. Yield: 2.79 g (65%).

M. p. 166–167 °C – ^{1}H NMR ($CDCl_3$): $\delta = 7.62$ (m, 4 H), 7.40–7.34 (m, 6 H), 6.88 (d, $J = 1.9$ Hz, 1 H), 6.83 (d, $J = 1.9$ Hz, 1 H), 3.72 (t, $J = 4.5$ Hz, 4 H), 3.61 (s, 2 H), 2.50 (t, $J = 4.5$ Hz, 4 H), 1.29 (s, 9 H). – ^{13}C NMR ($CDCl_3$): $\delta = 146.7$ (C), 145.0 (C), 143.8 (C), 140.7 (C), 129.0 (CH), 128.2 (CH), 126.4 (CH), 119.8 (CH), 117.6 (C), 116.3 (C), 105.3 (CH), 67.1 (CH_2), 57.0 (CH_2), 53.3 (CH_2), 34.6 (C), 31.7 (CH_3). – IR (KBr): $\nu = 2967$, 2851, 1485, 1450, 1295, 1119, 1070, 760 cm^{-1}. – MS (EI, 70 eV): m/z = 429 (34%) $[M]^+$, 344 (100%), 287 (15%), 262 (51%). – High resolution MS calcd. for $C_{28}H_{31}NO_3$: 429.2304; found: 429.2293. – Calcd. for $C_{28}H_{31}NO_3 \cdot {}^1/_2\,CH_3OH$: C 76.82; H 7.47, N 3.14; found: C 76.84, H 7.23, N 3.51.

*5-tButyl-1,2-[(diphenylmethylene)dioxy]-3-(chloromethyl)-benzene (**6**).* Compound **5** (215 mg, 0.50 mmol) is dissolved in phenyl chloroformate (118 mg, 0.75 mmol) and heated for 20 h to 120 °C. The mixture is dissolved in hexane and filtered over silica gel to obtain after removal of the solvent **6** as a white solid. Yield: 160 mg (85%).

M. p. 97 °C – ^{1}H NMR ($CDCl_3$): $\delta = 7.62$ (m, 4 H), 7.39 (m, 6 H), 6.92 (d, $J = 1.8$ Hz, 1 H), 6.84 (d, $J = 1.8$ Hz, 1 H), 4.66 (s, 2 H), 1.28 (s, 9 H). – ^{13}C NMR ($CDCl_3$): $\delta = 147.1$ (C), 145.6 (C), 143.2 (C), 140.3 (C), 129.1 (CH), 128.2 (CH), 126.4 (CH), 118.7 (CH), 117.5 (C), 117.2 (C), 106.8 (CH), 40.9 (CH_2), 34.7 (C), 31.5 (CH_3). – IR (KBr): $\nu = 2965$, 2868, 1486, 1451, 1430, 1267, 1063 cm^{-1}. – MS (EI, 70 eV): m/z = 380/378 (21/100%) $[M]^+$, 365/363 (26/81%), 343 (17%), 303/301 (49/15%), 165 (37%). – High resolution MS calcd. for $C_{24}H_{23}ClO_2$: 378.1387; found: 378.1401. – Calcd. for $C_{24}H_{23}ClO_2$: C 76.08; H 6.12; found: C 75.87, H 6.27.

*5-(2-{5-tButyl-2,3-[(diphenylmethylene)dioxy]phenyl}ethyl)-5′-methyl-2,2′-bipyridine (**2**).* 1.6 M *n*BuLi in hexane (1.3 ml, 2.08 mmol) at 0 °C is added to a solution of diisopropyl amine (0.3 ml, 2.30 mmol) in 5 ml of dry THF. The mixture is cooled to –78 °C and 5,5′-dimethyl-2,2′-bipyridine (382 mg, 2.07 mmol) in 10 ml of THF is added. At 0 °C this mixture is transferred to a solution of **6** (786 mg, 2.07 mmol) in 40 ml of THF. After 65 h at room temperature the solvent is removed and the residue is dissolved in dichloromethane, washed with water and dried ($MgSO_4$). **2** is obtained by column chromatography (hexane/ethyl acetate/Et_3N 20 : 1 : 2) as a yellow solid. Yield: 221 mg (21%).

M. p. 64–65 °C – ^{1}H NMR ($CDCl_3$): $\delta = 8.50$ (m, 1 H), 8.46 (m, 1 H), 8.23 (m, 2 H), 7.62–7.55 (m, 6 H), 7.33 (m, 6 H), 6.82 (d, $J = 1.7$ Hz, 1 H), 6.56 (d, $J = 1.7$ Hz, 1 H), 3.01 (m, 4 H), 2.39 (s, 3 H), 1.22 (s, 9 H). – ^{13}C NMR ($CDCl_3$): $\delta = 154.2$ (C), 153.8 (C), 149.6 (CH), 149.4 (CH), 146.7 (C), 142.9 (C), 140.7 (C), 137.4 (CH), 136.9 (CH), 136.8 (C), 133.1 (C), 129.0 (CH), 128.2 (CH), 126.3 (CH), 120.9 (C), 120.4 (CH), 120.3 (CH), 119.1 (CH), 116.2 (C), 104.5 (CH), 34.6 (C), 33.0 (CH_2), 31.8 (CH_2), 31.6 (CH_3), 18.4 (CH_3). – IR (KBr): $\nu = 2962$, 1488, 1467, 1450, 1206, 1065, 1021, 834, 700 cm^{-1}. – MS (EI, 70 eV): m/z = 526 (100%) $[M]^+$, 511 (32%), 449 (13%), 343 (34%), 184 (14). – High resolution MS calcd. for $C_{36}H_{34}N_2O_2$: 526.2620; found: 526.2634. – Calcd. for $C_{36}H_{34}N_2O_2$: C 82.10; H 6.51, N 5.32; found: C 81.95, H 6.49, N 4.69.

General Procedure for the Preparation of (2,2′-Bipyridine)platinum(II) Chloride Complexes

Equimolar amounts of the 2,2′-bipyridine ligand and of potassium tetrachloroplatinate in a mixture of 10 M HCl and ethanol (10 : 1) are heated to reflux. The yellow precipitate is collected, washed with a small amount of water and recrystallized from acetone/diethyl ether.

$[(\mathbf{1a\text{-}Me_2})PtCl_2]$

Yield: 23 mg (80%). – ^{1}H NMR (dmso-d_6): $\delta = 9.24$ (br, 1 H), 9.21 (br, 1 H), 8.38 (m, 2 H), 8.19 (m, 2 H), 6.96 (m, 1 H), 6.89 (m, 1 H), 6.78 (m,

1 H), 3.77 (s, 3 H), 3.71 (s, 3 H), 3.32 (s, 3 H), 3.02 (t, J = 7.7 Hz, 2 H), 2.91 (t, J = 7.7 Hz, 2 H). – ^{13}C NMR (dmso-d_6): δ = 154.6 (C), 154.1 (C), 152.4 (C), 147.9 (CH), 147.6 (CH), 146.6 (C), 141.3 (C), 140.7 (CH), 140.2 (CH), 137.9 (C), 133.3 (C), 123.8 (CH), 123.4 (CH), 123.3 (CH), 121.6 (CH), 111.3 (CH), 60.1 (CH_3), 55.6 (CH_3), 33.0 (CH_2), 30.2 (CH_2), 18.3 (CH_3). – IR (KBr): ν = 3051, 2939, 2838, 1584, 1479, 1271, 1080, 1013, 829, 754 cm^{-1}. – UV/Vis (methanol): λ = 198, 261, 276, 318, 331 nm. – MS (EI, 70 eV): m/z = 600 (0.2%) $[M]^+$, 334 (100%). – High resolution MS calcd. for $C_{21}H_{22}Cl_2N_2O_2Pt$: 599.0707; found: 599.0674. – Calcd. for $C_{21}H_{22}Cl_2N_2O_2Pt$: C 42.01, H 3.69, N 4.67; found: C 41.86, H 3.69, N 4.70.

*[(**1a-H$_2$**)PtCl$_2$]*

Yield: 574 mg (quant.). M.p. 209–212 °C (dec.). – ^{1}H NMR (acetone-d_6): δ = 9.49 (m, 1 H), 9.43 (m, 1 H), 8.37 (br, OH), 8.23 (m, 2 H), 8.17 (m, 1 H), 8.12 (m, 1 H), 7.34 (br, OH), 6.73 (m, 1 H), 6.65–6.57 (m, 2 H), 3.15 (m, 2 H), 3.03 (m, 2 H), 2.55 (s, 3 H). – ^{13}C NMR (acetone-d_6): δ = 156.5 (C), 156.2 (C), 150.2 (CH), 150.0 (CH), 146.2 (C), 144.9 (C), 143.5 (C), 141.8 (CH), 141.3 (CH), 139.6 (C), 128.4 (C), 124.3 (CH), 124.2 (CH), 122.7 (CH), 120.8 (CH), 115.1 (CH), 34.3 (CH_2), 32.5 (CH_2), 19.4 (CH_3). – IR (KBr): ν = 3372, 2924, 1609, 1595, 1477, 1282, 1250, 827, 781, 725, 717 cm^{-1}. – UV/Vis (methanol): $\lambda(\varepsilon)$ = 198 (96800), 261 (36900), 275 (40000), 319 (19000), 332 nm (25900). – MS (FAB(+), 3-NBA): m/z = 573 $[M + H]^+$, 536 $[M–Cl]^+$. – Calcd. for $C_{19}H_{18}Cl_2N_2O_2Pt$: C 39.87, H 3.17, N 4.89; found: C 39.53, H 3.26, N 4.89.

*[(**1b-Me$_2$**)PtCl$_2$]*

Yield: 47 mg (72%). M. p. 185–188 °C. – ^{1}H NMR (acetone-d_6): δ = 9.53 (d, J = 1.8 Hz, 1 H), 9.48 (br s, 1 H), 8.33 (d, J = 8.3 Hz, 1 H) 8.32 (d, J = 8.2 Hz, 1 H), 8.24 (dd, J = 8.3, 1.8 Hz, 1 H), 8.21 (dd, J = 8.2, 1.1 Hz, 1 H), 6.94 (t, J = 7.9 Hz, 1 H), 6.84 (dd, J = 7.9, 1.5 Hz, 1 H), 6.76 (dd, J = 7.9, 1.5 Hz, 1 H), 3.82 (s, 3 H), 3.76 (s, 3 H), 2.86 (m, 2 H), 2.61 (m, 2 H), 2.56 (s, 3 H), 1.73 (m, 2 H), 1.57 (m, 2 H), 1.49–1.43 (m, 4 H). – ^{13}C NMR (acetone-d_6): δ = 153.8 (C), 152.9 (C), 149.6 (CH), 149.2 (CH), 148.2 (C), 144.2 (C), 143.4 (C), 141.1 (CH), 140.5 (CH), 139.0 (C), 136.9 (C), 124.4 (CH), 123.8 (CH), 123.7 (CH), 122.7 (CH), 111.3 (CH), 60.6 (CH_3), 56.0 (CH_3), 33.4 (CH_2), 31.5 (CH_2), 31.3 (CH_2), 30.7 (CH_2), 18.7 (CH_3), two CH_2-signals are hidden under the solvent peak. – IR (KBr): ν = 3055, 2923, 2855, 1609, 1582, 1481, 1429, 1262, 1226, 1082, 1058, 1020, 836, 797, 765 cm^{-1}. – UV/Vis (methanol): λ = 198, 260, 275, 318, 331 nm. – MS (FAB(+), 3-NBA): m/z = 656 $[M + H]^+$, 621 $[M – Cl]^+$. – High resolution MS calcd. for $C_{25}H_{30}Cl_2N_2O_2Pt$: 655.1333; found: 655.1392. – Calcd. for $C_{25}H_{30}Cl_2N_2O_2Pt$: C 45.75, H 4.61, N 4.27; found: C 46.05, H 4.79, N 4.54.

*[(**2**)PtCl$_2$]*

Yield: 27 mg (68%). M. p. 238 °C. – ^{1}H NMR (dmso-d_6): δ = 9.26 (br s, 1 H), 9.25 (d, J = 1.6 Hz, 1 H), 8.33 (d, J = 8.3 Hz, 1 H), 8.29 (d, J = 8.3 Hz, 1 H), 8.21 (d, J = 8.3 Hz, 1 H), 8.06 (dd, J = 8.3, 1.8 Hz, 1 H), 7.44 (d, J = 7.5 Hz, 4 H), 7.35 (t, J = 7.5 Hz, 4 H), 7.26 (t, J = 7.5 Hz, 2 H), 6.87 (d, J = 1.7 Hz, 1 H), 6.74 (d, J = 1.7 Hz, 1 H), 3.11 (t, J = 7.2 Hz, 2 H), 2.99 (t, J = 7.2 Hz, 2 H), 1.20 (s, 9 H), CH_3-signal is hidden under solvent peak. – ^{13}C NMR (dmso-d_6): δ = 154.6 (C), 154.2 (C), 147.9 (CH), 147.8 (CH), 145.9 (C), 145.2 (C), 142.4 (C), 140.8 (C), 140.7 (CH), 140.2 (CH), 140.1 (C), 138.0 (C), 129.0 (CH), 128.4 (CH), 125.6 (CH), 123.3 (CH), 123.0 (CH), 120.0 (C), 119.1 (CH), 115.5 (C), 104.5 (CH), 34.5 (C), 32.5 (CH_2), 31.4 (CH_3), 29.9 (CH_2), 18.3 (CH_3). – IR (KBr): ν = 3047, 2962, 2867, 1644, 1609, 1488, 1477, 1450, 1430, 1206, 1020, 754, 704, 642 cm^{-1}. – UV/Vis (methanol): λ = 193, 262, 278, 318, 332 nm. – MS (FAB(+), 3-NBA): m/z = 792 $[M + H]^+$, 756 $[M – Cl]^+$. – Calcd. for $C_{36}H_{34}Cl_2N_2O_2Pt \cdot 0.5\,H_2O$: C 53.94, H 4.40, N 3.49; found: C 53.71, H 4.20, N 3.10.

*X-ray Structural Analysis of [(**2**)PtCl$_2$] · 0.5 H$_2$O*

X-ray quality crystals of [**(2)**PtCl$_2$] · 0.5 H$_2$O were obtained by slow diffusion of diethyl ether into a solution of [**(2)**PtCl$_2$] in wet acetone. Formula $C_{36}H_{34}N_2O_2Cl_2Pt \cdot 1/2\,H_2O$, M = 801.65, yellow crystal, 0.1 × 0.1 × 0.03 mm, a = 8.273(1), b = 9.485(3), c = 21.467(4) Å, α = 101.51(2), β = 90.86(2), γ = 100.05(2)°, V = 1632.1(6) Å^3, ρ_{calc} = 1.640 g · cm^{-3}, $F(000)$ = 794 e, μ = 45.24 cm^{-1}, empirical absorption correction via φ scan data ($0.912 \le C \le 0.999$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 293 K, $\omega/2\theta$ scans, 6134 reflections collected ($-h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.59 Å^{-1}, 5702 independent and 3146 observed reflections [$I \ge 2\sigma(I)$], 401 refined parameters, R = 0.045, wR^2 = 0.085, max. residual electron density 0.99 (–0.70) e Å^{-3}, hydrogens calculated and refined as riding atoms, hydrogens of the water molecule could not be located.

Data set was collected with an Enraf Nonius CAD4 diffractometer on a rotating anode generator. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102662. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44(12 23)3 36-0 33, e-mail: deposit@ccdc.cam.ac.uk].

*[(**1b-H$_2$**)PtCl$_2$]*

At 0 °C a 1 M solution of BBr_3 in CH_2Cl_2 (0.2 ml) is added to [(**1b-Me$_2$**)PtCl$_2$] (17.1 mg, 0.026 mmol) in 5 ml of CH_2Cl_2. The mixture is allowed to warm to room temperature and is stirred for 15 hours. Methanol (2 ml) is added and solvent is removed in vacuo. The residue is refluxed in 2 N HCl. The product is isolated by filtration and recrystallized from acetone/diethyl ether. [(**1b-H$_2$**)PtCl$_2$] can not be obtained in analytically pure form due to the presence of traces of [(**1b-H$_2$**)PtClBr].

Yield: 12.8 mg (~78%). – ^{1}H NMR (acetone-d_6): δ = 9.74 (d, J = 1.8 Hz, 1 H), 9.69 (dd, J = 1.3, 0.6 Hz, 1 H), 8.32 (d, J = 8.3 Hz, 1 H), 8.31 (d, J = 8.2 Hz, 1 H), 8.27 (s, OH), 8.23–8.18 (m, 2 H), 7.11 (s, OH), 6.68 (dd, J = 7.3, 2.0 Hz, 1 H), 6.59 (dd, J = 7.6, 2.0 Hz, 1 H), 6.57 (dd, J = 7.6, 7.3 Hz, 1 H), 2.85 (m, 2 H), 2.61 (m, 2 H), 2.54 (s, 3 H), 1.73 (m, 2 H), 1.62 (m, 2 H), 1.44 (m, 4 H). – ^{13}C NMR (acetone-d_6): δ = 155.8 (C), 155.6 (C), 150.7 (CH), 150.4 (CH), 145.4 (C), 144.1 (C), 143.5 (C), 141.1 (CH), 140.5 (CH), 139.0 (CH), 130.1 (C), 124.4 (CH), 124.0 (CH), 121.9 (CH), 119.9 (CH), 113.8 (CH), 33.4 (CH_2), 31.2 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 18.7 (CH_3), two CH_2-signals are hidden under the solvent peak. – MS (FAB(+), 3-NBA): m/z = 593 $[M – Cl]^+$.

*Attempt to Synthesize [(**1a**)$_2$Pt$_2$]*

A 1 M solution of KOH in methanol (1.1 ml) is added to 10 ml of acetone and the mixture is heated to reflux. A solution of [(**1a-H$_2$**)PtCl$_2$] (31.7 mg, 0.055 mmol) in 120 ml of acetone is added slowly. After the addition is complete, the mixture is heated for another 15 h. A purple precipitate is formed, which is collected and successively washed with water, methanol and acetone and dried in vacuo. Yield: "25.6 mg (81%)."

IR (KBr): ν = 3051, 2924, 2512, 1794, 1476, 1267, 877, 830, 713 cm^{-1}. – MS (FAB(+), 3-NBA): m/z = 998 $[M]^+$. – High resolution MS calcd. for $C_{38}H_{32}N_4O_4Pt_2$: 998.1720; found: 998.1514. – Calcd. for $C_{38}H_{32}N_4O_4Pt_2 \cdot 8\,H_2O$: C 39.93, H 4.23, N 4.90; found: C 39.75, H 3.90, N 5.08.

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