Platinum(II) Compounds with Enantiomerically Pure Bis(pinene)-Fused Bipyridine Ligands − Diimine-Dichloro Complexes and Their Substitution Reactions

Brunhilde Kolp,[a] Dirk Abeln,[b] Helen Stoeckli-Evans,[c] and Alexander von Zelewsky*[a]

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The synthesis of chiral square-planar Pt^{II} complexes using symmetrical and unsymmetrical bis(pinene)-fused 2,2′-bipyridine is described. The neutral diimine dichloro complexes show a strong deviation of the coordination sphere from planarity if the pinene groups are attached at the 5- and 6-positions of the pyridine rings. However, this distortion does not occur in parallel with the chiral configuration at the diimine ligands. The substitution of the two *cis*-chloro ligands with diamines to form five-membered chelate rings shows little diastereoselectivity when racemic mixtures of chiral diamines are used. Also, ligands that are prochiral at the ligating centers show little selectivity upon coordination.

Introduction

Square-planar coordination geometry, the most frequent coordination mode of diamagnetic d^8-metals do not generally exhibit chirality, since genuinely planar structures cannot be chiral in three-dimensional space. Deviations from planarity can, however, lead to chiral configurations. An early example of this type was the platinum(II) complex containing one molecule of *meso*-stilbenediamine and one molecule of isobutylenediamine occuring as a pair of enantiomers.[1] Complexes in which a distortion from planarity occurs in a way that permits chirality have recently been found in the class of bis-cyclometallated compounds. These compounds have a very strong tendency to form *cis*-complexes, leading to helical configurations of ligands that interact strongly, thereby avoiding coplanarity.[2] The advent of nonracemic pyridine and bipyridine ligands derived from naturally occurring terpene compounds[3] has prompted us to investigate the possibility of a stereoselective synthesis of coordination species that show chiral elements within the ligand and around the metal center. It has been shown that metal chirality can be predetermined in "square-planar" complexes (SP-4-complexes) by using this type of ligand in *diastereoselective syntheses.*[4]

Here we present the preparation and characterization of a series of enantiomerically pure Pt^{II} complexes, in which the chirality is located in the "chiralized" bipyridine ligands. The investigations focus on the question whether the ligands **L1**−**L5** induce chiral distortions from planarity in the complex and whether chirality can be transferred in stereoselective reactions to ligands that occupy the coordination sites around the central metal (Scheme 1).

[a] Institute of Inorganic Chemistry, Pérolles, University of Fribourg, 1700 Fribourg, Switzerland
[b] Laboratory for Crystallography, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
[c] Institute of Chemistry, University of Neuchâtel, Avenue de Bellevaux 51, 2000 Neuchâtel, Switzerland

Results and Discussion

Chiral Bipyridine Ligands

For the synthesis of the substituted bipyridine ligands **L1**−**L5**, the method described by F. Kröhnke[5] was modified. The synthesis of the compounds **L1**, **L2**, and **L5** has already been described.[6,7] The preparation of ligand **L3** was similar to that of **L2** except that for one of the two 'Kröhnke cyclizations', (+)-α-pinene was used as starting material and for the second one (−)-α-pinene was used, which gave the *meso* ligand **L3**.

The preparation of compound **L4** is shown in Scheme 2. Chirality was introduced by using enantiomerically pure (−)-β-pinene (**1**) as starting material. Compound **1** was oxidized to the (+)-nopinone (**2**) following a 'one-pot' method described by Brown.[8] The nopinone was treated with $NaNH_2$ which resulted in the formation of enolate **3**. Treatment of **3** with formaldehyde in a Na_2CO_3 solution gave the α,β-methylene ketone **4**, which was used for the condensation with the 'Kröhnke salt' **5** in the same way as already described by von Zelewsky et al.[7] for **L2**.

Complex Formation and Characterization in Solution

The complexation of **L1**, **L2**, **L3**, **L4**, and **L5** with Pt^{II} was carried out in aqueous hydrochloric acid solution using K_2PtCl_4 as starting material (Scheme 1). The yellow, uncharged dichloro complexes precipitated out of the aqueous solution and were isolated and purified. As expected, the formation of bis-diimine complexes was not observed, since the ligands are sterically bulky.

^1H NMR Spectroscopy

All compounds prepared were fully characterized by ^1H-, ^{13}C-, and ^{195}Pt NMR spectroscopy. Figure 1 shows the

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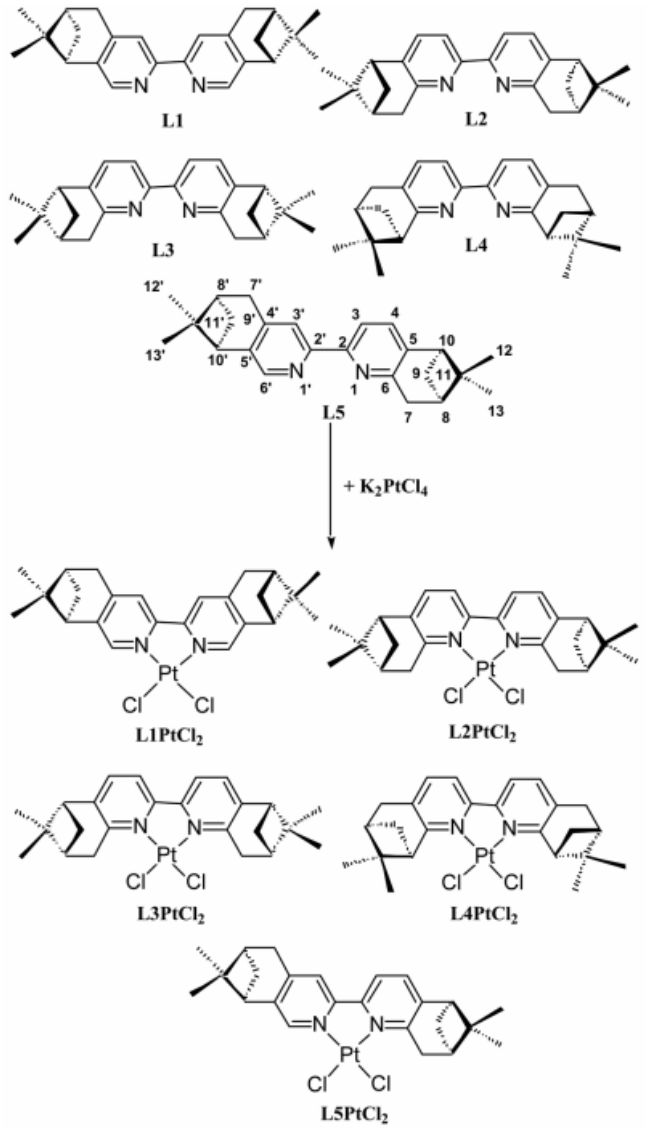


Scheme 1

^{1}H NMR spectra of **L1** and **L2**, and of their Pt-complexes. The pairs of diastereotopic protons H^7 (H^{7endo} and H^{7exo}) are isochronous in free **L1** and **L2**, as well as in **L3**, **L4**, and **L5**. However, a strong downfield shift with a concomitant splitting and a large geminal coupling occurs in the complexes **L2PtCl$_2$**, as well as in **L3PtCl$_2$** and **L5PtCl$_2$**, whereas **L1PtCl$_2$** and **L4PtCl$_2$** still show the same behavior as the free ligand. In **L1PtCl$_2$**, the complex formation strongly influences the aromatic proton H^6, whereas in the case of **L4PtCl$_2$**, the aliphatic proton H^{10} is shifted strongly downfield. The aliphatic protons, except for H^7 in **L2**, **L3**, and **L5**, H^{10} in **L4**, and the aromatic protons H^3 and H^4 are only very slightly influenced by complexation.

Ligands **L1**−**L4** and their Pt complexes all show equivalent halves in the ^{1}H NMR spectra (Figure 1). This equivalence is due to a C_2 axis in **L1**, **L2**, and **L4**, whereas **L3** has a mirror plane. These symmetry elements are no longer present in the solid state, as will be discussed later. In the unsymmetrical ligand **L5**, all the protons of the two halves are nonequivalent, as expected.

^{13}C NMR

In all cases, the ^{13}C NMR spectra show the expected features. Contrary to the ^{1}H NMR spectra, the ^{13}C NMR spectra of the diastereomeric ligands **L2** and **L3** exhibit differences in the chemical shift values of C^5. However the complexes **L2PtCl$_2$** and **L3PtCl$_2$** don't show any differences in the ^{1}H NMR or in the ^{13}C NMR spectra.

^{195}Pt NMR

More information about the isomeric purity of the complexes can be obtained by ^{195}Pt NMR spectroscopy, since chemical shifts are usually very large for this nucleus. All compounds show a single Pt-signal. The values in Table 1 show a small influence ($\Delta\delta$ = 14 ppm) of the pinene groups at the 4- and 5-positions when compared to the complex with unsubstituted 2,2′-bipyiridine. The shift values for the complexes with the 5,6-pinene-bipyridine ligands are much larger, in the order of $\Delta\delta \approx 400$ ppm. The diastereomeric complexes **L2PtCl$_2$** and **L3PtCl$_2$** are not distinguishable.

Electronic and CD Spectra

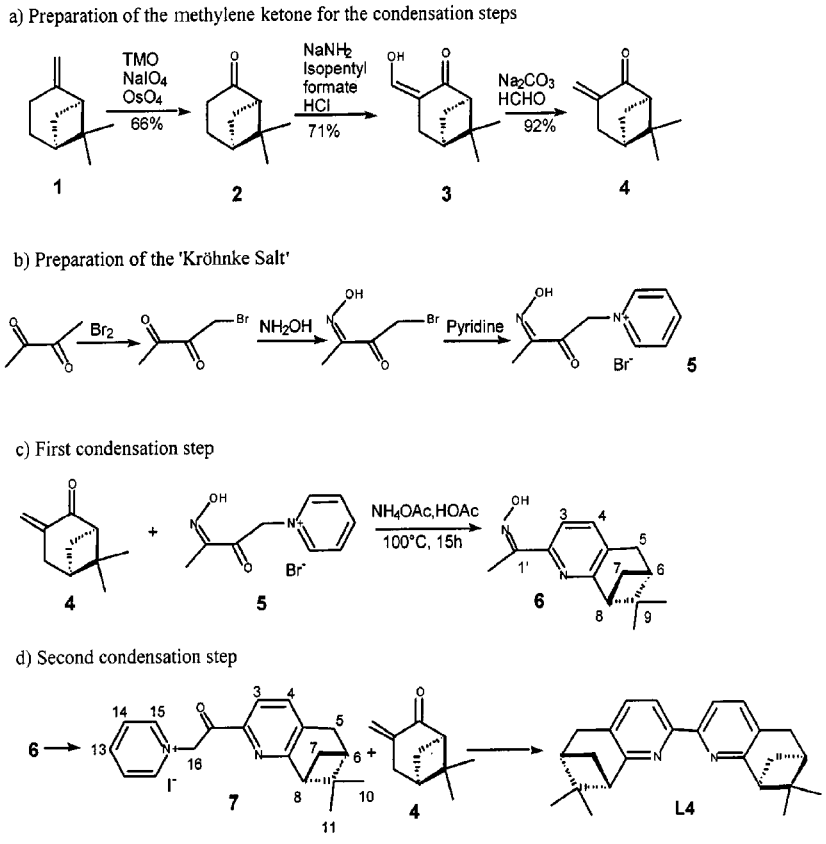
Neither the UV or the CD spectra are very strongly influenced by complex formation. All free ligands show two absorption maxima in the UV region. Complexation with $PtCl_4^-$ leads to a red shift of these ligand transitions as well as to two additional bands above 300 nm (Table 2). The CD activity, which is very small in the accessible spectral range (250 nm−700 nm) is hardly enhanced through complex formation. This is in marked contrast to complexes where two or three chiral bipyridine ligands coordinate to one metal center.[9]

X-ray Structure Determination

One of the ligands, **L2** gave suitable crystals for structure determination. Tables 3, 6, and 8 contain the relevant crystallographic data. Figure 2 reveals an approximately C_2-symmetric structure with a *transoid* conformation of the two pyridine rings. The values of all the internal coordinates (bond lengths and bond angles) are as expected. A feature that is worth noting is the banana-like deformation of the bpy moiety, which can be expressed in terms of the angle γ, as defined in Scheme 3 and given in Table 6. Although, the ligand changes its conformation from *transoid* to *cisoid*, this type of distortion is preserved and even significantly enhanced (vide infra) upon coordination.

The X-ray structures of the complexes **L2PtCl$_2$**, **L3PtCl$_2$**, and **L4PtCl$_2$** (no suitable crystals of **L1PtCl$_2$** and **L5PTCL$_2$** could be obtained), allow for an investigation of the question as to whether the metal itself assumes a chiral configuration induced by the chiral ligands. Figures 3, 4, and 5 show representations of these molecules in a projection that stresses the out-of-plane position of the ligand atoms. Selected bond lengths and angles are listed in Tables 3, 4, and 5.

L2PtCl$_2$ and **L4PtCl$_2$** crystallize in the triclinic space group *P*1. In the former case, there are two independent complex molecules per asymmetric unit, whereas the latter contains four independent molecules. Compound **L3PtCl$_2$**



Scheme 2. Synthesis overview for **L4**

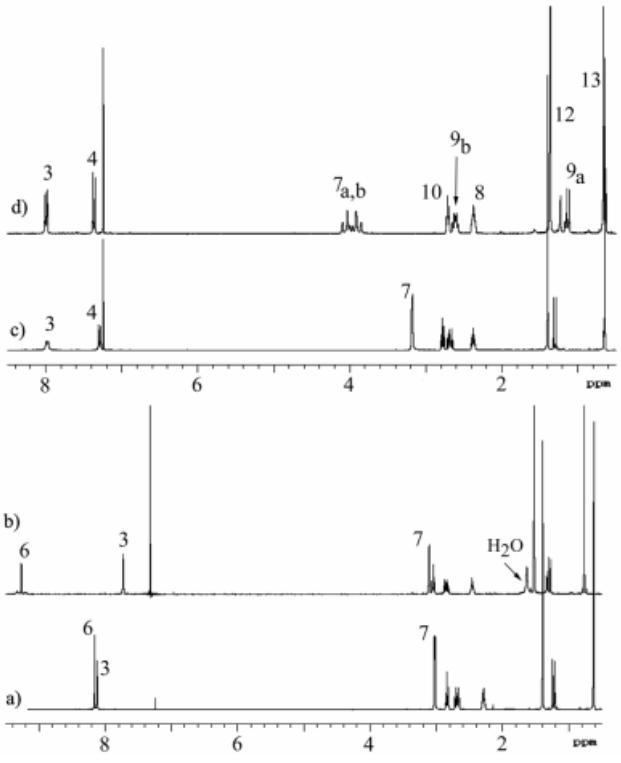


Figure 1. ^{1}H NMR spectra of the ligands **L1** and **L2**, and their platinum complexes: a) free ligand **L1**, b) **$L1PtCl_2$**, c) free ligand **L2**, d) **$L2PtCl_2$**

Table 1. ^{195}Pt NMR spectroscopic data [referenced to $NaPtCl_6$ ($\delta = 0.0$)]

Compound	δ
$[Pt(2,2'\text{-bpy})Cl_2]$	−2315
$L1PtCl_2$	−2329
$L2PtCl_2$	−1884
$L3PtCl_2$	−1887
$L4PtCl_2$	−1939
$L5PtCl_2$	−2066

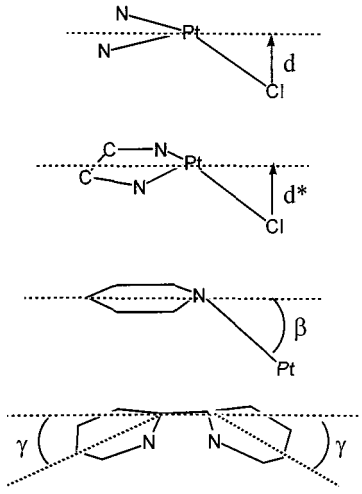
crystallizes in the triclinic, centrosymmetric space group $P\bar{1}$ with one independent molecule per asymmetric unit.

The independent molecules in the lattice of **$L2PtCl_2$** and **$L4PtCl_2$** do not show strong variations in their structural parameters (Tables 3, 4, and 8). In both cases, the molecules designated as I (Tables 3 and 4), serve as a basis for further discussion.

All three complexes **$L2PtCl_2$**, **$L3PtCl_2$**, and **$L4PtCl_2$** show strong deviation from planarity. Table 6 lists bond angles and distances that characterize these deviations, as given in Scheme 3. In the complex with the *meso*-form ligand **L3**, a strong out-of-plane distortion is observed, whereby both chlorine ligands are displaced to the same side of the coordination plane defined by the five-membered chelate ring. Figure 3 shows how the two chloride ligands are located on the same side as the methyl groups of the pinene moieties of the bent pinene-bpy-ligand. Most surprisingly, exactly the same type of deformation is ad-

Table 2. Absorption data and extinction coefficients from UV/Vis spectra

Ligands	nm	ε	Complexes	nm	ε
L1	256	15200	**L1PtCl$_2$**	289	29400
	295	21200		324	11700
				339	16700
				387	3400
L2	261	12500	**L2PtCl$_2$**	277	21200
	302	22100		291	20100
				341	10800
				356	11300
L3	261	12500	**L3PtCl$_2$**	277	20600
	303	18900		295	21000
				341	11900
				356	13300
L4	258	11500	**L4PtCl$_2$**	291	18700
	304	28200		338	15400
				354	17200
L5	259	14600	**L5PtCl$_2$**	274	24600
	298	20900		287	24100
				334	14900
				348	18800



Scheme 3. Definition of parameters from planar coordination geometry for the distortion in the crystal structures for the **L2PtCL$_2$**, **L3PtCl$_2$**, and **L4PtCl$_2$** complexes. **α**, **β**, and **γ** are defined as in ref.[10], **d*** is the distance of a Cl ligand to the best plane defined by the chelate ring

Table 3. Selected bond lengths [Å], angles and dihedral angles [°] of the free ligand **L2** and the complex **L2PtCl$_2$**

L2		**L2PtCl$_2$**: Molecule I		Molecule II	
N1−C6	1.335	Pt1−N1	2.046	Pt2−N3	2.002
N1−C2	1.349	Pt1−N2	2.027	Pt2−N4	2.054
N1′−C6′	1.341	Pt1−Cl1	2.303	Pt2−Cl3	2.306
N1′−C2′	1.354	Pt1−Cl2	2.319	Pt2−Cl4	2.307
C6−N1−C2	118.3	N1−Pt−N2	80.0	N3−Pt2−N4	79.3
C6′−N1′−C2′	117.0	Cl1−Pt1−Cl2	85.2	Cl4−Pt2−Cl4	86.0
N1−C2−C3	121.5	N1−Pt1−Cl1	96.0	N3−Pt2−Cl3	96.2
N1−C2−C2′	115.4	N2−Pt1−Cl2	97.1	N4−Pt2−Cl4	96.6
N1−C2−C2′−N1′	−166.9	C5−N1−Pt1−Cl1	37.8	C29−N3−Pt2−Cl3	−25.5
C3−C2−C2′−C3′	−172.9	C17−N2−Pt1−Cl2	−30.5	C41−N4−Pt2−Cl4	34.2

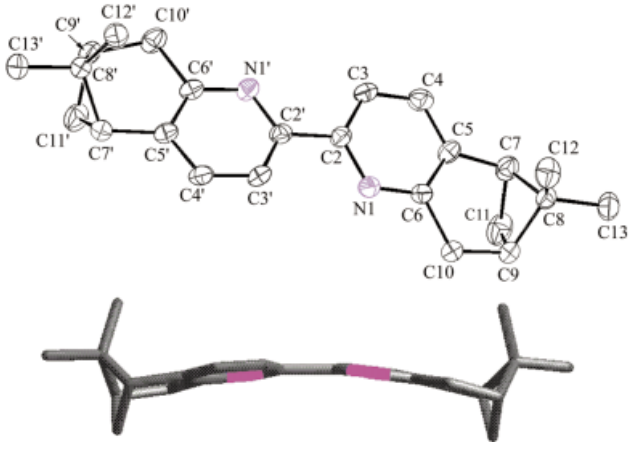


Figure 2. ORTEP[16] plot and Cerius2[17] representation of the crystal structure of the free ligand **L2**

opted by the C_2-symmetric (in the uncoordinated form) ligands in their complexes **L2PtCl$_2$** and **L4PtCl$_2$**. Again, both chlorine ligands are displaced towards the same side of the coordination plane. Even the crystal packing is very similar in all three cases. These three complexes are all strongly distorted from square-planar geometry, yet it seems that the stereogenic centers are not decisive for the type of distortion. In addition, the distortions occur in a counter-intuitive way. We would have expected that both chloride ligands lie on the opposite side of the plane to the methyl groups of the pinene moieties in the *meso*-form complex, and that the complex with the enantiomerically pure ligand would adopt approximately C_2 symmetry.

A similar phenomenon (mismatched symmetry) was observed by Newkome et al.[10] for palladium complexes with bipyridine ligands substituted at the 6- and 6,6′-positions. The parameters **d1** and **d2** in Table 6 are defined in the same way as in literature[10] (Scheme 3). In addition, we introduce the distances **d1*** and **d2***, respectively (Scheme 3), which we consider to be a more reliable measure of the distortion from a square-planar arrangement. It is difficult to know whether these distortions are due to packing effects (e.g.

Table 4. Selected bond lengths [Å], angles and dihedral angles [°] of **L3PtCl$_2$**

Molecule I	
Pt1−N1	2.063
Pt1−N2	2.015
Pt1−Cl1	2.307
Pt1−Cl2	2.305
N1−Pt−N2	80.3
Cl1−Pt1−Cl2	85.9
N1−Pt1−Cl1	96.1
N2−Pt1−Cl2	96.1
C5−N1−Pt1−Cl1	34.3
C17−N2−Pt1−Cl2	−30.3

Table 5. Selected bond lengths [Å], bond angles and dihedral angles [°] of **L4PtCl$_2$**

Molecule I		Molecule II		Molecule III		Molecule IV	
Pt1−N1	2.041	Pt2−N3	2.025	Pt3−N5	2.045	Pt4−N7	2.030
Pt1−N2	2.048	Pt2−N4	2.022	Pt3−N6	2.022	Pt4−N8	2.023
Pt1−Cl1	2.294	Pt2−Cl3	2.305	Pt3−Cl5	2.306	Pt4−Cl7	2.289
Pt1−Cl2	2.306	Pt2−Cl4	2.292	Pt3−Cl6	2.293	Pt4−Cl8	2.311
N1−Pt−N2	97.7	N3−Pt2−N4	80.4	N5−Pt3−N6	80.2	N7−Pt4−N8	80.1
Cl1−Pt1−Cl2	86.0	Cl4−Pt2−Cl4	85.6	Cl5−Pt3−Cl6	85.6	Cl7−Pt4−Cl8	86.6
N1−Pt1−Cl1	95.2	N3−Pt2−Cl3	96.9	N5−Pt3−Cl5	96.4	N7−Pt4−Cl7	94.8
N2−Pt1−Cl2	97.6	N4−Pt2−Cl4	95.7	N6−Pt3−Cl6	96.4	N8−Pt4−Cl8	97.0
C5−N1−Pt1−Cl1	23.5	C29−N3−Pt2−Cl3	31.3	C53−N5−Pt3−Cl5	26.4	C77−N7−Pt4−Cl7	24.4
C17−N2−Pt1−Cl2	−24.7	C41−N4−Pt2−Cl4	−25.3	C65−N6−Pt3−Cl6	−25.1	C89−N8−Pt4−Cl8	−26.8

Table 6. Distortion measurements for the complexes **L2PtCl$_2$**, **L3PtCl$_3$**, and **L4PtCl$_2$**

	L2	L2PtCl$_2$	L3PtCl$_2$	L4PtCl$_2$	Newkome[10]
d1 [Å]	–	0.427	0.380	0.371	0.277
d2 [Å]	–	0.363	0.368	0.345	0.496
d1* [Å]	–	0.814	0.829	0.720	0.699
d2* [Å]	–	0.778	0.831	0.721	0.908
β1 [°]	–	12.3	15.5	16.4	18.8
β2 [°]	–	11.4	13.5	15.9	16.8
γ1 [°]	3.4	17.1	14.4	6.8	7.5
γ2 [°]	7.0	11.1	11.6	7.1	8.5

π-stacking) or whether they are properties of the isolated molecules. In solution, all complexes show the expected symmetrical behavior of the two ligand halves on the NMR time scale.

Substitution Reactions

In order to determine the influence of a chiral ligand on the substitution reactions of the two *cis*-chloride ligands, a series of diamine ligands were treated with the [Pt(pinene-bpy)]Cl$_2$ complexes, as shown in Scheme 4. Table 7 shows the diamines that were treated with the complexes of Scheme 1. The products are numbered according to their position in this 'matrix'. The main point of interest is the stereoselectivity in these cases, where the incoming ligands can adopt a chiral configuration. Coordinated ethylenediamine adopts a chiral conformation.[11] In the complex [Pt(bpy)(en)]$^{2+}$, which was also synthesized for reference purposes[12], the CH$_2$-protons of 'en' appear as a singlet at δ = 2.82. Two satellites due to ^{1}H-^{195}Pt coupling are clearly resolved (Figure 6, a). Here, the λ- and δ- conformers of the five-membered chelate ring of ethylenediamine are enantiomers. The achiral time average between the two conformers has a C_{2v} symmetry, which results in one signal for the four CH$_2$ protons of 'en' (Scheme 5). In the case of the complex **13**, with the *meso*-form of the ligand, two signals for the methylene protons are expected, since the time-averaged symmetry is reduced to C_S, rendering the two protons 'above' and 'below' the coordination plane nonequivalent. With complex **12**, the two conformers are the (*RR*δ)- and (*RR*λ)-diastereomers. Again, two signals for the CH$_2$ protons are expected. Figure 6, b and c, show the relevant parts of the ^{1}H NMR spectra of these compounds. In both cases, the four protons (assigned as '15' in Figure 6) appear as one broad signal. Complexes **11**, **14**, and **15** behave in a very similar way as **12** and **13**, except that the lack of C_2 symmetry in **15** is clearly discernible in its NMR spectrum.

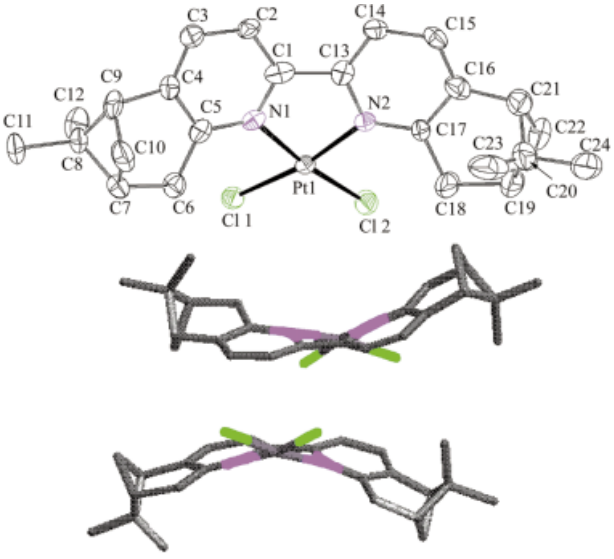


Figure 3. ORTEP[16] plot and Cerius2[17] packing representation of the crystal structure of **L2PtCl$_2$**

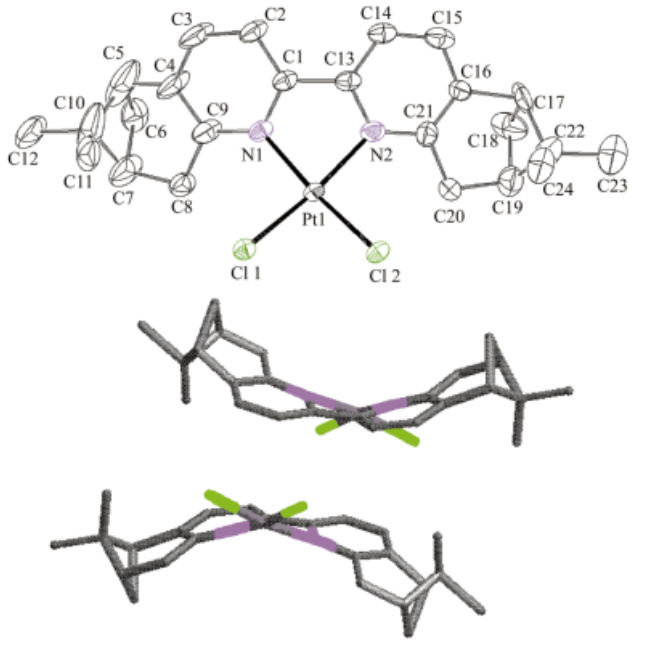


Figure 4. ORTEP[16] plot and Cerius2[17] packing representation of the crystal structure of **L3PtCl$_2$**

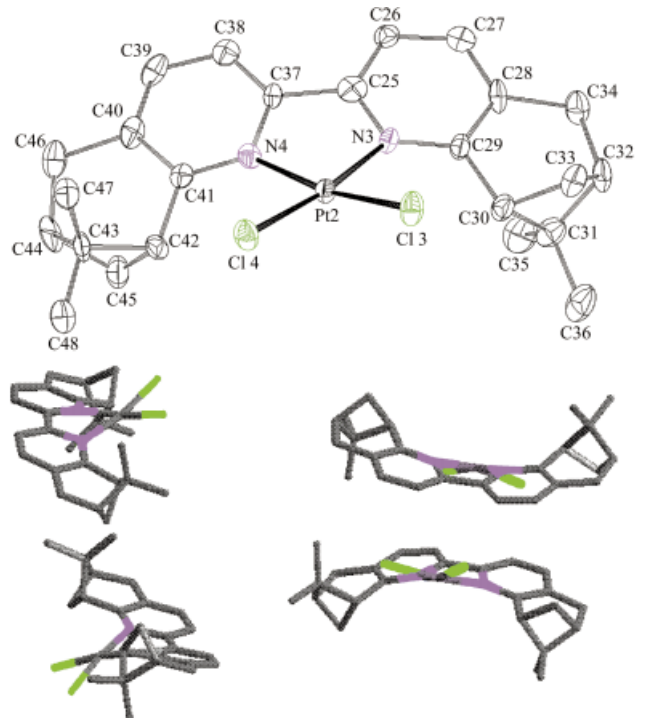
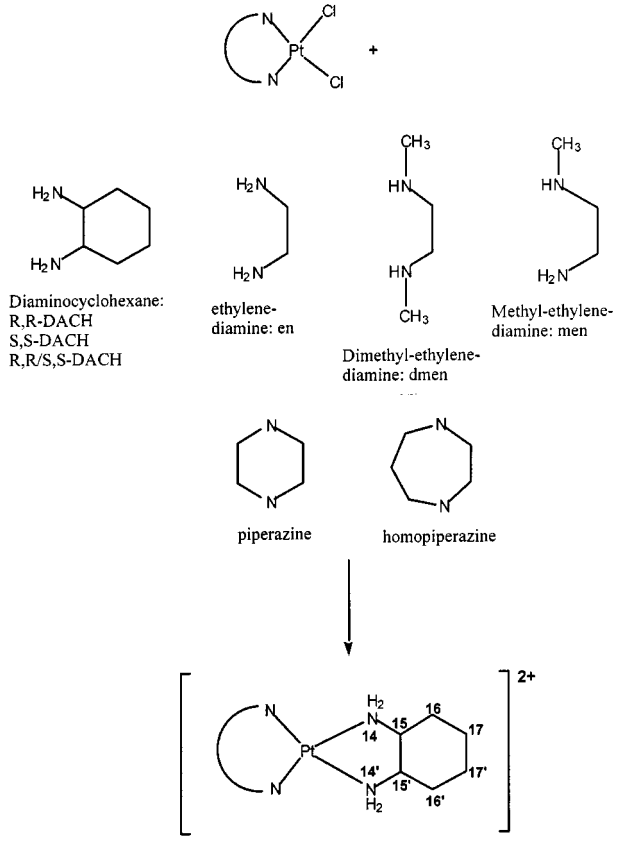


Figure 5. ORTEP[16] plot and Cerius2[17] packing representation of the crystal structure of **L4PtCl$_2$**

The substitution reactions with 'dmen', 'men', piperazine, and homopiperazine were successfully carried out only with **L1PtCl$_2$**. Complexation by replacing the two chlorine atoms with the achiral bidentate ligand 'dmen' with this compound creates stereogenic centers at the nitrogen atoms. The formation of four different diastereomers is possible, as represented in Scheme 6. In addition, the two conformers of the chelate ring, δ and λ, will now probably differ more in energy relative to 'en'. In the NMR spectrum of **51** (Fig-



Scheme 4. Bidentate ligands used for the substitution reactions and numbering scheme of the resulting complexes

Table 7. Matrix for the numbering scheme of the substitution reactions (en = ethylenediamine; R,R-DACH = (1*R*,2*R*)-(−)-1,2-diaminocyclohexane; S,S-DACH = (1*S*,2*S*)-(+)-1,2-diaminocyclohexane; dmen = *N*,*N*′-dimethylethylenediamine; men = *N*-methylethylenediamine)

	L1PtCl$_2$	L2PtCl$_2$	L3PtCl$_2$	L4PtCl$_2$	L5PtCl$_2$
en	**11**	**12**	**13**	**14**	**15**
R,R-DACH	**21**	**22**	-	**24**	-
S,S-DACH	**31**	**32**	-	-	**35**
S,S/R,R-DACH	**41**	**42**	-	**44**	**45**
dmen	**51**				
men	**61**				
piperazine	**71**	-	-	-	-
homopiperazine	**81**	-	-	-	-

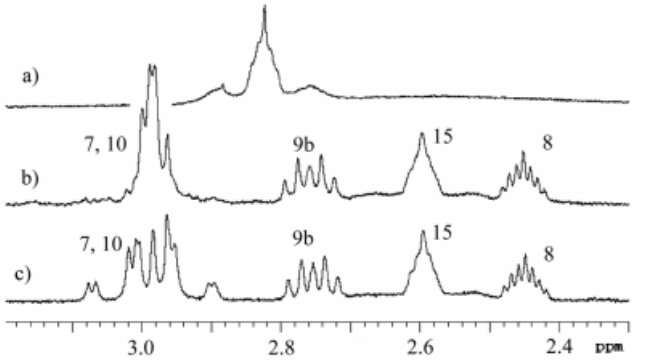
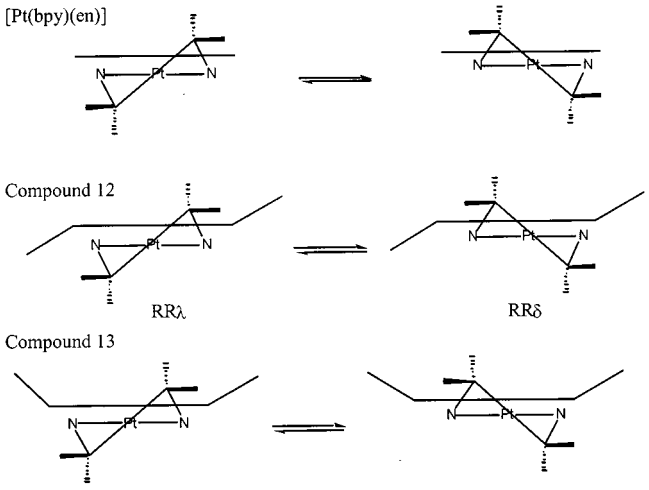


Figure 6. Part of the ^{1}H NMR aliphatic region of a) [Pt(bpy)(en)](PF$_6$)$_2$, b) compound **13**, c) compound **12**



Scheme 5

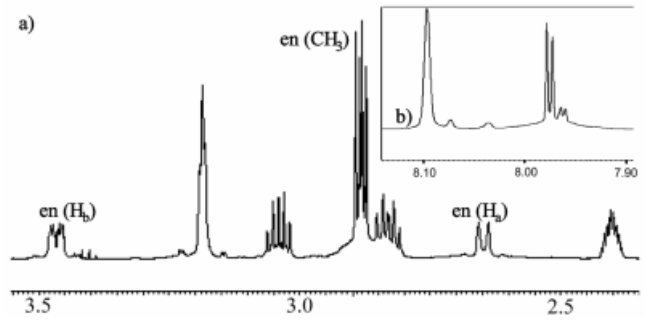


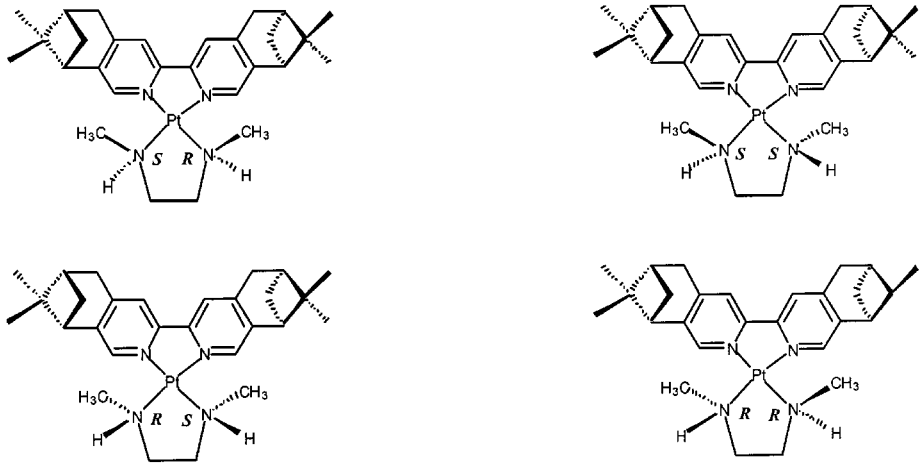
Figure 7. ^{1}H NMR spectrum (500 MHz) of compound **51**; a) aliphatic region, b) aromatic region

ure 7, a and b) most of the signals appear twice, with a ratio of 1:1. Small additional signals are observed in the region of the aromatic protons, as well as for the NH signal and the C(13)-methyl protons in an approximate ratio of 1:0.15. This indicates the formation of two main diastereomers, which are probably the two less constraining (*R,R*)- and (*S,S*)- forms. Furthermore, in this case we observed the expected nonequivalence (as discussed above) of the 'en'-methylene protons, which appear separated by 0.82 ppm as doublets with a coupling constant of 8.8 Hz. The diastereotopicity is much more pronounced owing to the new stereogenic centers located at the neighboring N-atoms.

In the case of 'men', the number of possible diastereomers is reduced to two since only one nitrogen atom becomes stereogenic and in addition a complete loss of symmetry occurs upon complexation with this unsymmetrical ligand. The NMR spectrum of compound **61** shows that both diastereomers, those with (*R*)- and (*S*)- configurations at the methylated N-atom, are formed in an approximate ratio of 1:1. Most of the signals of the ligands are quadrupled. Furthermore, the $H_2-C(15)$ ethylene protons appear as two separate doublets, whereas the $H_2-C(15')$ protons, which are not influenced by a close stereogenic center, gave rise to a singlet (the methyl-bearing nitrogen atom was assigned arbitrarily as N(14)]. The substitution of **L1PtCl$_2$** with piperazine yields only one possible isomer. Compound **71** shows the expected NMR pattern. The diastereotopic protons of the CH_2 groups of the piperazine ring are separated by 0.78 ppm, with a geminal coupling constant of 8.2 Hz.

In the case of homopiperazine, also only one isomer is possible, but the substitution results in a complete loss of symmetry owing to the absence of a C_2 axis of symmetry in the ligand. However, the influence of the unsymmetrical homopiperazine on the proton signals of the pinene group is small. The loss of symmetry could only be observed in the 500 MHz NMR spectra of compound **81**. All the proton signals of the pinene group show the same pattern as in the case of the symmetrical complexes, except that a doubling of the *exo*-oriented CH_3 groups and the *endo*-oriented $H-C(9)$ protons is also evident. Furthermore, two separate signals for the aromatic protons at the 6- and 6′-positions were observed. The signals for the protons of the CH_2 groups 15 and 15′, as well as 16 and 16′ are separated by 0.25 ppm and 0.51 ppm, respectively, in the latter case because of their diastereotopicity. The two protons at the C(17)-position do not show this phenomenon.

The ligand *trans*-1,2-diaminocyclohexane (DACH) is of special interest because of its configurations that are fixed by the six-membered ring. Substitution reactions were carried out with the pure (*S,S*) and (*R,R*)-forms, as well as with the racemic mixture (*S,S*)/(*R,R*) = 1:1. In the case of ligand **L1**, all the spectra of the substitution products **21**,



Scheme 6. The four possible diastereoisomers after the substitution reaction of **L1PtCl$_2$** with 'dmen'

31, and **41** are indistinguishable. Although this does not exclude a diastereoselective reaction, it is highly improbable that such selectivity occurs. In the case of the much bulkier ligand **L2**, complexes **22** and **32** can be distinguished by a difference in chemical shifts of one of the methyl groups and of one of the protons of the CH_2-group in the pinene part. From this, a diastereomeric ratio of (*RR*)/(*SS*) = 1:1.3 is calculated. The corresponding analysis for ligand **L4** yields a slightly higher diastereoselectivity for the (*R,R*)-form [(*R,R*)/(*S,S*) = 1.5:1].

Conclusions

Chiral bipyridine ligands induce significant distortions in square-planar platinum complexes if the 'substituents' of the pyridine are at the 6- and 6′-positions. However, C_2-symmetric, homochiral ligands yield molecules of low symmetry if the two other ligand positions are occupied by Cl^-. The distortions are not determined by the chiral nature of these ligands, since an overall achiral *meso*-form behaves in a very similar way. Consequently, substitution of these chlorides by amines proceeds in a nonstereoselective manner.

Experimental Section

Products: Solvents and reagents were purchased from Fluka and Aldrich. Iodine was sublimed before use. Pyridine was dried with KOH and freshly distilled prior to use. Ammonium acetate was dried for 5−6 h before use in a vacuum oven at 40 °C. Diethyl ether was distilled from sodium/benzophenone prior to use. The precursor platinum complex $K_2[PtCl_4]$ was prepared following procedures described by Livingstone.[13]

Measurements: NMR spectra were recorded on a 'Varian Gemini 300' (300.075 MHz) or on a 'Bruker Avance DRX500' (500.13 MHz) spectrometer. Chemical shifts are given in ppm using TMS or the solvent itself as internal standard, and coupling constants *J* are given in Hz. Assignment of the ^1H and ^{13}C NMR signals was performed by COSY, DEPT and HETCOR techniques. Diastereotopic protons are labeled as H_a for the *endo*-oriented protons and H_b for the *exo*-oriented protons. The *exo* methyl groups of the pinene moieties are assigned as 12 and 12′, the *exo*-oriented ones as 13 and 13′. The ^{195}Pt NMR spectra were recorded on the Varian Gemini 300 at 64.376 MHz. The signals were referenced to Na_2PtCl_6[14] (δ = 0.0). − UV/Vis spectra were measured on a Perkin−Elmer Lambda 40 spectrometer. − Mass spectral data were acquired on 'VG Instrument 7070E' equipped with a FAB inlet system. − Elemental analysis were obtained from CIBA Specialties, Marly (Switzerland) and 'Ecole d'ingéneurs de Fribourg' (Switzerland).

General: Compounds **3** and **4** (Scheme 2) were synthesized following a method described by M.Gianini.[7] The preparation of the appropriate Kröhnke salt **5** (Scheme 2) for condensation with **4** was described by Rupprecht.[7] The preparation of ligand **L5** was first described by Philippe Lainé in a private communication.[6]

L3: [2-{(−)-α-Pineno[2,3-*e*]pyridin-2-yl}acetyl]pyridinium iodide (2.27 g, 5.4 mmol, prepared as described in ref.[7]), pinocarvone (0.81 g, 5.40 mmol) prepared from (+)-α-pinene[7], and dry ammonium acetate (3.6 g) were dissolved in glacial acetic acid (7 mL) and stirred at 100 °C for 15 h. After cooling the dark brown reaction mixture to room temperature, water (100 mL) was added, followed by extraction of the water phase with hexane (at least 7 × 50 mL). The collected organic phases were washed with water (100 mL), dried with $MgSO_4$ and filtered. Evaporation of the solvent yielded **L3** (780 mg, 42%). The product was recrystallized from acetone. − ^1H NMR (300 MHz, $CDCl_3$): δ = 8.02 [d, ^3J = 7.9 Hz, 2 H, H−C(3,3′)], 7.30 [d, ^3J = 7.9 Hz, 2 H, H−C(4,4′)], 3.19 [d, ^3J = 2.6 Hz,4 H, H_2−C(7)], 2.78 [dd, ^3J = 5.6, 5.6 Hz, 2 H, H-(10,10′)], 2.68 [ddd, ^2J = 9.6 Hz, ^3J = 5.6, 5.6 Hz, 2 H, H_b−C(9,9′)], 2.37 [m, 2 H, H−C(8,8′)], 1.40 [s, 6 H, H_3−C(12,12′)], 1.28 [d, ^2J = 9.6 Hz, 2 H, H_a−C(9,9′)], 0.65 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2 [C(2,2′)], 141.8 [C(4,4′)], 133.9 [C(3,3′)], 117.9 [C(2,2′)], 112.8 [C(5,5′)], 46.5 [C(10,10′)], 40.3 [C(8,8′)], 39.5 [C(11,11′)], 36.6 [C(7,7′)], 31.9 [C(9,9′)], 26.1 [C(12,12′)], 21.3 (13,13′)]. − EI-MS: *m/z* (%) = 344 (100) [M^+], 329 (58) [$M^+ - CH_3$], 303 (59), 271 (22), 257 (42), 154 (10). − $C_{24}H_{28}N_2$ (344.5): calcd. C 83.68, H 8.19, N 8.13, found C 82.92, H 8.40, N 7.94.

(6*R*,8*R*)-2-(1′-Ethyloxime)-5,6,7,8-tetrahydro-9,9-dimethyl-6,8-metaquinoline (6): The Kröhnke salt **5** (6.90 g, 26.6 mmol), NH_4 acetate (17.7 g), glacial acetic acid (28 mL), and **4** (4.0 g, 26.6 mmol) were heated at reflux for 15 h. The reaction mixture was cooled to room temperature, diluted with water (100 mL) and extracted with hexane [7 × 50 mL). The combined organic phases were washed with water (100 mL), dried with $MgSO_4$ with active charcoal, and filtered. After evaporating the solvent a brown viscous liquid (3.84 g, 63%) was obtained. − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.51 [d, ^3J = 7.7 Hz, 1 H, H−C(3)], 7.40 [d, ^3J = 7.7 Hz, 1 H, H−C(4)], 3.09 [dd, ^3J = 5.8, 5.8 Hz, 1 H, H−C(8)], 2.93 [d, ^3J = 2.9 Hz, 2 H, H-(5)], 2.72 [ddd, ^2J = 9.8 Hz, ^3J = 5.8, 5.8 Hz, 1 H, H_a−C(7)], 2.35 [s, 3 H, H_3−C(11)], 1.28 [d, ^2J = 9.8 Hz, 1 H, H_b−C(7)], 0.65 [s, 3 H, H_3−C(10)].

1-{2-(Pineno[2,3-*e*]pyridin-2-yl)acetyl}pyridinium Iodide (7): Product **6** (3.80 g, 15 mmol) was reacted with HCl (70 mL, 25%) and heated at reflux for 8 h. After cooling the reaction mixture to room temperature, the black solution was brought to pH = 3 by the addition of NaOH (30%), and then carefully adjusted to pH = 7−8 with Na_2CO_3. This mixture was then extracted with hexane (7 × 50 mL). The organic phases were washed with water (100 mL), dried with $MgSO_4$ and filtered. Evaporation of the solvent gave a brown−yellow, viscous liquid (2.96 g). A portion of this product (2.70 g) was dissolved in pyridine (4 mL) in a 250-mL flask. Iodine (3.20 g, 12.5 mmol) dissolved in pyridine (10 mL) was added, and the mixture was heated at reflux for 3 h. After removing excess pyridine by vacuum distillation, dry diethyl ether (180 mL) was added to the black residue and kept at 4 °C overnight. The brown powder was filtered off, washed twice with diethyl ether and dried under high vacuum for 2 d. In order to obtain a good precipitate, it was essential to carry out this reaction with the exclusion of water, resulting in an hygroscopic product (7.05 g, 90%). The product was a mixture of the desired product **7** and pyridinium iodide. The ratio was determined to be 1:1. − ^1H NMR (300 MHz, [D_6]DMSO): (numbering see Scheme 2) δ = 9.00 [d, ^3J = 6.8 Hz, 2 H, H−C(15)], 8.70 [t, ^3J = 7.8 Hz, 1 H, H−C(13)], 8.25 [dd, ^3J = 7.8, 6.7 Hz, 2 H, H−C(14)], 7.89 [d, ^3J = 7.7 Hz, 1 H, H−C(3)], 7.86 [d, ^3J = 7.7 Hz, 1 H, H−C(4)], 6.48 [s, 2 H, H−C(16)], 3.05 [m, 3 H, H−C(8), H−C(5)], 2.80 [dd, ^2J = 9.8 Hz, ^3J = 5.8 Hz, 1 H, H_a−C(7)], 2.38 [m, 1 H, H−C(6)], 1.44 [s, 3 H, H_3−C(11)], 1.21 [d, ^2J = 9.8 Hz, 1 H, H_b−C(7)], 0.65 [s, 3 H, H_3−C(10)]. −

Pyridinium iodide: δ = 8.91 [d, ^3J = 6.5 Hz, 2 H, H−C(15)], 8.55 [t, ^3J = 7.8 Hz, 1 H, H−C(13)], 8.03 [dd, ^3J = 7.7, 6.6 Hz, 2 H, H−C(14)].

L4: Compound **7** (3.0 g, 4.78 mmol), ammonium acetate (3.1 g) and **4** (0.72 g, 4.78 mmol) were dissolved in glacial acetic acid (6 mL) and stirred at reflux for 15 h. The reaction temperature was gradually raised over a period of 4 h starting at 50 °C. After cooling the reaction mixture to ambient temperature, water (80 mL) was added. The mixture was extracted with hexane [7 × 50 mL). Washing, drying and evaporation of the solvent yielded a yellow powder (0.94 g, 57%). Recrystallization from hexane gave white crystals of **L4**. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 [d, ^3J = 7.7 Hz, 2 H, H−C(3,3′)], 7.49 [d, ^3J = 7.7 Hz, 2 H, H−C(4,4′)], 3.09 [dd, ^3J = 5.8, 5.8 Hz, 2 H, H−C(10,10′)], 2.94 [d, ^3J = 2.9 Hz, 4 H, H_2−C(7,7′)], 2.71 [ddd, ^2J = 9.8 Hz, ^3J = 5.8, 5.8 Hz, 2 H, H_b−C(9,9′)], 2.31 [m, 2 H, H−C(8,8′)], 1.40 [s, 6 H, H_3−C(12,12′)], 1.32 [d, ^2J = 9.8 Hz, 2 H, H_a−C(9,9′)], 0.65 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8 [C(2,2′)], 152.6 [C(6,6′)], 136.0 [C(4,4′)], 130.0 [C(5,5′)], 118.9 [C(3,3′)], 50.5 [C(10,10′)], 40.3 [C(8,8′)], 39.9 [C(11,11′)], 31.2 (C7,7′)], 30.9 [C(9,9′)], 26.0 [C(12,12′)], 21.5 [C(13,13′′)]. − EI-MS: *m*/*z* (%) = 344 (25) [M^+], 329 (10) [$M^+ - CH_3$], 315 (7) [$M^+ - 2\ CH_3$], 301 (100) [$M^+ - 3\ CH_3$]. − $C_{24}H_{28}N_2$ (344.5): calcd. C 83.7, H 8.2, N 8.1; found C 83.6, H 8.2, N 7.9.

L5: [2-{(−)-α-Pineno[2,3-*e*]pyridin-2-yl}acetyl]pyridinium iodide (5.46 g, 13.0 mmol, prepared as described in ref.[7]) was suspended in formamide (50 mL). (1*R*)-(−)-Myrtenal (1.96 g, 13.0 mmol) and dry ammonium acetate (2.51 g) were added to this suspension and the reaction mixture was stirred at reflux for 15 h. After cooling the mixture to 0 °C, water (80 mL) was added and the mixture was stirred for 30 min. The black solution was extracted with diethyl ether (at least 8 × 70 mL). The collected organic phases were washed twice with water (80 mL), dried with $MgSO_4$ and filtered. Evaporation of the solvent yielded a brown powder (3.2 g). Recrystallization from acetone gave pure **L5** (2.50 g, 56%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 [s, 1 H, H−C(6′)], 8.14 [s, 1 H, H−C(3′)], 7.99 [d, ^3J = 7.8 Hz, 1 H, H−C(3)], 7.30 [d, ^3J = 7.8 Hz, 1 H, H−C(4)], 3.18 [d, ^3J = 2.6 Hz, 2 H, H_2−C(7)], 3.03 [d, ^3J = 2.7 Hz, 2 H, H_2−C(7′)], 2.84 [dd, ^3J = 5.5 Hz, 1 H, H−C(10′)], 2.78 [dd, ^3J = 5.7 Hz, 1 H, H−C(10)], 2.68 [m, 2 H, H_b−C(9,9′)], 2.38 [m, 1 H, H−C(8)], 2.28 [m, 1 H, H−C(8′)], 1.40 [s, 6 H, H_3−C(12,12′)], 1.30 [d, ^2J = 9.6 Hz, 1 H, H_a−C(9)], 1.22 [d, ^2J = 9.6 Hz, 1 H, H_a−C(9′)], 0.66 [s, 3 H, H_3−C(13)], 0.62 [s, 3 H, H_3−C(13′)]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.3 [C(2)], 154.8 [C(4′)], 154.2 [C(6)], 145.5 [C(2′)], 145.2 [C(6′)], 142.6 [C(5′)], 141.4 [C(5)], 133.8 [C(4)], 120.3 [C(3′)], 117.6 [C(3)], 46.4 [C(10)], 44.4 [C(10′)], 40.2 [C(8)], 40.1 [C(8′)], 39.5 [C(11)], 39.3 [C(11′)], 36.7 [C(7)], 32.9 [C(7′)], 31.9 [C(9)], 31.8 [C(9′)], 26.0 [C(12,12′)], 21.3 [C(13,13′)]. − EI-MS: *m*/*z* (%) = 345 (100) [M^+], 330 (44) [$M^+ - CH_3$], 301 (78), 271 (26), 257 (44), 154 (9).

L1PtCl$_2$: Compound **L1** (600 mg, 1.7 mmol) was added to a solution of K_2PtCl_4 (723 mg, 1.7 mmol) dissolved in HCl (0.2 M, 80 mL). After stirring for 3 h at reflux, the yellow precipitate was filtered off and washed with water. The crude product was dried at 50 °C in a vacuum oven. Recrystallization from chloroform/heptane gave bright yellow **L1PtCl$_2$** (1.02 g, 1.6 mmol, 96%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.20 [s, 2 H, H−C(6,6′)], 7.66 [s, 2 H, H−C(3,3′)]; 3.02 [d, ^3J = 2.5 Hz, 4 H, H_2−C(7,7′)], 2.95 [dd, ^3J = 5.4, 5.4 Hz, 2 H, H−C(10,10′)], 2.77 [m, 2 H, H_b−C(9,9′)], 2.36 [m, 2 H, H−C(8,8′)], 1.42 [s, 6 H, H_3−C(12,12′)], 1.19 [d, ^2J = 10.2 Hz, 2 H, H_a−C(9,9′)], 0.66 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 181.7 [C(2,2′)], 148.8 [C(4,4′)], 146.4 [C(5,5′)], 145.2 [C(6,6′)], 121.2 [C(3,3′)], 44.8 [C(10,10′)], 39.5 [C(8,8′)], 33.5 [C(11,11′)], 31.3 [C(7,7′)], 29.7 [C(9,9′)], 25.6 [C(12,12′)], 21.5 [C(13,13′)]. − ^{195}Pt NMR (64.376 MHz, $CDCl_3$): see Table 1. − FAB-MS: *m*/*z* (%) = 610 (25) [M^+]; 575 (86) [$M^+ - Cl$]; 537 (18) [$M^+ - 2\ Cl$]; 460 (20), 391 (43), 345 (98) [L1], − $C_{24}H_{28}Cl_2N_2Pt$ (610.5): calcd. C 47.20, H 4.62, N 4.59, found C 47.40, H 4.69, N 5.07.

[{Bis[(−)-pineno]−2,2′-bipyridine}(ethylenediamine)Pt^{II}](PF$_6$)$_3$ (11): To a suspension of **L1PtCl$_2$** (100 mg, 0.16 mmol) in water/acetone (1:1, 25 mL), ethylenediamine (10 μL) was added. After heating the reaction mixture at reflux for 8 h, the solution was cooled to room temperature and unreacted starting material was filtered off. The acetone was evaporated from the filtrate and solid NH_4PF_6 was added to the aqueous solution. The mixture was kept for 1 h at 4 °C. The white precipitate was filtered off, washed with water, and dried in vacuum. Purification by recrystallization from ethanol/diethyl ether gave **11** (90 mg, 62%). − ^{1}H NMR (300 MHz, [D_3]ACN): δ = 8.07 [s, 2 H, H−C(3,3′)], 7.97 [s, $J_{Pt\text{-}H}$ = 29.8 Hz, 2 H, H−C(6,6′)], 5.11 [b, 4 H, H_2−N(14,14′)], 3.17 [d, ^3J = 2.3 Hz, 4 H, H_2−C(7,7′)], 2.96 [dd, ^3J = 5.4, 5.4 Hz, 2 H, H−C(10,10′)], 2.80 [m, 6 H, H_b−C(9,9′), H_2−C(15,15′)], 2.40 [m, 2 H, H−C(8,8′)], 1.45 [s, 6 H, H_3−C(12,12′)], 1.23 [d, ^2J = 9.9 Hz, 2 H, H_a−C(9,9′)], 0.66 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (MHz, [D_3]ACN): δ = 147.0 [C(6,6′)], 124.3 [C(3,3′)], 47.9 (C15,15′)], 45.4 [C(10,10′)], 40.2 [C(8,8′)], 33.9 [C(7,7′)], 31.3 [C(9,9′)], 25.2 [C(12,12′)], 21.3[C(13,13′)], (the quaternary carbon atoms could not be detected). − FAB-MS: *m*/*z* (%) = 744 (12) [$M^+ - PF_6$], 598 (69) [$M^+ - 2\ PF_6$], 537 (13) [M^+ − en], 307 (29), 171 (57), 154 (100).

[{Bis[(−)-pineno]−2,2′-bipyridine}(R,R-DACH)Pt^{II}](PF$_6$)$_2$ (21): Compound **L1PtCl$_2$** (100 mg, 16 mmol) was suspended in water/acetone (1:1, 25 mL). (*R*,*R*)-diaminocyclohexane (30 mg, 26 mmol) was added. After the reaction mixture was heated at reflux for 10 h, unreacted starting materials were filtered off and the acetone was evaporated from the filtrate. To this solution, solid NH_4PF_6 was added and the solution was allowed to stand for 4 h at 4 °C. The white product was filtered off and washed with water. The product (95 mg, 61%), was recrystallized from ethanol/diethyl ether. − ^{1}H NMR (300 MHz, [D_3]acetonitrile): δ = 8.07 [s, 2 H, H−C(3,3′)], 8.00 [s, 2 H, H−C(6,6′)], 5.38 [b, 2 H, H_b−N(14,14′)], 4.77 [b, 2 H, H_a−N(14,14′)], 3.17 [d, ^3J = 3.4 Hz, 4 H, H_2−C(7,7′)], 2.96 [dd, ^3J = 5.3, 5.3 Hz, 2 H, H−C(10,10′)], 2.83 [ddd, ^2J = 10.0 Hz, ^3J = 5.8, 5.8 Hz, 2 H, Hb−C(9,9′)], 2.63 [m, 2 H, H−C(15,15′)], 2.40 [m, 2 H, H−C(8,8′)], 2.15 [d, ^2J = 12.0 Hz, 2 H, H_a−C(16,16′)], 1.65 [d, ^2J = 8.9 Hz, 2 H, H_a−C(17,17′)], 1.45 [s, 8 H, H_3−C(12,12′), H_b−C(16,16′)], 1.25 [d, ^2J = 8.9 Hz, 2 H, H_b−C(17,17′)], 1.24 [d, ^2J = 10.0 Hz, 2 H, H_a−C(9,9′)], 0.67 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, [D_3]acetonitrile): δ = 155.8; 154.5; 153.3; 148.9 [C(4,4′)], 146.9 [C(6,6′)], 124.2 [C(3,3′)], 62.5 [C(15,15′)], 45.3 [C(10,10′)], 40.4 [C(8,8′)], 36.7 [C(11,11′)], 34.2 [C(7,7′)], 33.2 (16,16′)], 31.6 [C(9,9′)], 25.8 [C(12,12′)], 24.8 [C(17,17′)], 21.5 [C(13,13′)]. − FAB-MS: *m*/*z* (%) = 799 (18) [$M^+ - PF_6$], 653 (11) [$M^+ - 2\ PF_6$], 327 (100).

[{Bis[(−)-pineno]−2,2′-bipyridine}(S,S-DACH)Pt^{II}](PF$_6$)$_2$ (31): The synthesis, and purification of compound **31** was carried out as described for compound **21** with **L1PtCl$_2$** (53 mg, 0.086 mmol) in water/acetone (15 mL) and (*S*,*S*)-diaminocyclohexane (22 mg, (0.19 mmol). Yield: 54 mg (66%). − ^{1}H NMR (300 MHz, [D_3]acetonitrile): δ = 8.07 [s, 2 H, H−C(3,3′)], 8.00 [s, 2 H, H−C(6,6′)], 5.38 [b, 2 H, H_b−N(14,14′)], 4.77 [b, 2 H, H_a−N(14,14′)], 3.17 [d, ^3J = 3.4 Hz, 4 H, H_2−C(7,7′)], 2.96 [dd, ^3J = 5.3, 5.3 Hz, 2 H, H−C(10,10′)], 2.83 [ddd, ^2J = 10.0 Hz, ^3J = 5.8, 5.8 Hz, 2 H,

H_b−C(9,9′)], 2.63 [m, 2 H, H−C(15,15′)], 2.40 [m, 2 H, H−C(8,8′)], 2.15 [d, ^2J = 12.0 Hz, 2 H, H_a−C(16,16′)], 1.65 [d, ^2J = 8.9 Hz, 2 H, H_a−C(17,17′)], 1.45 [s, 8 H, H_3−C(12,12′), H_b−C(16,16′)]; 1.25 [d, ^2J = 8.9 Hz, 2 H, H_b−C(17,17′)]; 1.24 [d, ^2J = 10.0 Hz, 2 H, H_a−C(9,9′)]; 0.67 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): δ = 155.2; 154.3; 153.1; 149.0 [C(4,4′)], 146.8 [C(6,6′)], 124.6 [C(3,3′)], 62.5 [C(15,15′)], 45.4 [C(10,10′)], 40.8 [C(8,8′)], 36.6 [C(11,11′)], 34.3 [C(7,7′)], 33.4 [C(16,16′)], 31.7 [C(9,9′)], 25.9 [C(12,12′)], 24.6 [C(17,17′)], 21.5 [C(13,13′)], (the aromatic quaternary carbon atoms could not be assigned). − FAB-MS: *m*/*z* (%) = 799 (9) [M^+ − PF_6], 652 (13) [M^+ − 2 PF_6], 631 (14), 327 (100).

[{Bis[(−)-pineno]−2,2′-bipyridine}(S,S/R,R-DACH)Pt^{II}](PF$_6$)$_2$ (41): The synthesis, and purification of compound **41** was carried out as described for compound **21** with **L1PtCl$_2$** (105 mg, 0.17 mmol), (*S,S*)-diaminocyclohexane (23 mg, 0.20 mmol), and (*R,R*)-diaminocyclohexane (23 mg, 0.20 mmol) in water/acetone (25 mL). Yield: 115 mg (71%). − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 8.07 [s, 2 H, H−C(3,3′)], 8.00 [s, 2 H, H−C(6,6′)], 5.38 [b, 2 H, H_b−N(14,14′)], 4.77 [b, 2 H, H_a−N(14,14′)], 3.17 [d, ^3J = 3.4 Hz, 4 H, H_2−C(7,7′)], 2.96 [m, 2 H, H−C(10,10′)], 2.83 [ddd, ^2J = 11.2 Hz, ^3J = 5.2, 5.2 Hz, 2 H, H_b−C(9,9′)], 2.63 [m, 2 H, H−C(15,15′)], 2.40 [m, 2 H, H−C(8,8′)], 2.15 [d, ^2J = 12.0 Hz, 2 H, H_a−C(16,16′)], 1.65 [d, ^2J = 8.9 Hz, 2 H, H_a−C(17,17′)], 1.45 [s, 8 H, H_3−C(12,12′), Hb−C(16,16′)], 1.25 [d, ^2J = 8.9 Hz, 2 H, H_b−C(17,17′)], 1.24 [d, ^2J = 11.2 Hz, 2 H, H_a−C(9,9′)], 0.67 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): δ = 155.1, 154.4, 153.3, 148.9 [C(4,4′)], 146.7 [C(6,6′)], 124.1 [C(3,3′)], 62.5 [C(15,15′)], 45.2 [C(10,10′)], 40.3 [C(8,8′)], 36.7 [C(11,11′)], 34.2 [C(7,7′)], 33.2 [C(16,16′)], 31.6 [C(9,9′)], 25.8 [C(12,12′)], 24.8 [C(17,17′)], 21.5 [C(13,13′)]. − FAB-MS: *m*/*z* (%) = 798 (25) [M^+ − PF_6], 654 (75) [M^+ − 2 PF_6], 541 (19) [M^+ − DACH], 326 (21), 307 (83), 248 (30), 154 (100).

[{Bis[(−)-pineno]−2,2′-bipyridine}(*N*,*N*′-dimethylethylenediamine)-Pt^{II}](PF$_6$)$_2$ (51): The synthesis, and purification of compound **51** was carried out as described for compound **11** with **L1PtCl$_2$** (60 mg, 0.098 mmol) and dimethylethylenediamine (20 μL, 0.18 mmol) in water/acetone (20 mL). Yield: 55 mg (61%). − ^{1}H NMR (500 MHz, [D$_3$]acetonitrile): δ = 8.09 [s, 4 H, H−C(3,3′), H−C(3,3′)*], 8.06 [s, 0.30 H, H−C(3,3′)*], 8.03 [s, 0.30 H, H−C(3,3′)*], 7.97 [s, 2 H, H−C(6,6′)], 7.96 [s, 2 H, H−C(6,6′)*], 7.95 [s, 0.30 H, H−C(6,6′)*], 7.94 [s, 0.30 H, H−C(6,6′*), 5.78 [b, 0.30 H, H−N(14,14′)*], 5.60 [b, 4 H, H−N(14,14′)], 3.47 [d, ^2J = 8.8 Hz, 4 H, H_a−C(15,15′), H_a−C(15,15′)*], 3.19 [d, ^3J = 2.3 Hz, 8 H, H_2−C(7,7′), H_2−C(7,7′)*], 3.04 [dd, ^3J = 5.4, 5.4 Hz, 4 H, H−C(10,10′), H−C(10,10′)*], 2.89 [d, ^3J = 6.5 Hz, 6 H, H_3−C(N14,14′)], 2.88 [d, ^3J = 6.5 Hz, 6 H, H_3−C(N14,14′)*], 2.83 [dd, ^2J = 9.9 Hz, ^3J = 5.4 Hz, 4 H, H_b−C(9,9′), H_b−C(9,9′)*], 2.65 [d, ^2J = 8.8 Hz, 4 H, H_b−C(15,15′), H_b−C(15,15′)*], 2.40 [m, 4 H, H−C(8,8′), H−C(8,8′)*], 1.46 [s, 6 H, H_3−C(12,12′)], 1.45 [s, 6 H, H_3−C(12,12′)*], [1.25 [d, ^2J = 9.9 Hz, 2 H, H_a−C(9,9′)], 1.23 [d, ^2J = 9.9 Hz, 2 H, H_a−C(9,9′)*], 0.68 [s, 6 H, H_3−C(13,13′), 0.66 [s, 6 H, H_3−C(13,13′)*]. − ^{13}C NMR (125 MHz, [D$_3$]acetonitrile): δ = 155.7 [C(2, 4 or 5)*], 155.6 [C(2, 4 or 5)*], 153.6 [C(2, 4 or 5)], 153.5 [C(2, 4 or 5)*], 149.4 [C(2, 4 or 5)], 149.3 [C(2, 4 or 5)*], 146.1 [C(6,6′), 145.9 [C(6,6′)*], 124.8 [C(3,3′)], 54.1 [C(15,15′)], 45.5 [C(10,10′)], 45.3 [C(10,10′)*], 43.6 [C−N(14,14′)], 43.5 (C−N(14,14′)*], 40.2 [C(8,8′)], 40.1 [C(11,11′)*], 34.1 [C(7,7′)], 34.0 [C(7,7′)*], 31.5 [C(9,9′)], 31.4 [C(9,9′)*], 25.8 [C(12,12′)], 25.7 [C(12,12′)*], 21.5 [C(13,13′)], 21.4 [C(13,13′)*]. − FAB-MS: *m*/*z* (%) = 772 (10) [M^+ − PF_6], 627 (44) [M^+ − 2 PF_6], 598 (13) [M^+ − 2 CH_3], 537 (17), 460 (26), 307 (100). − The asterisk * denotes NMR signals of the other possible diastereomers.

[{Bis[(−)-pineno]−2,2′-bipyridine}(*N*-methylethylenediamine)-Pt^{II}](PF$_6$)$_2$ (61): The synthesis, and purification of compound **61** was carried out as described for compound **11** with **L1PtCl$_2$** (57 mg, 0.093 mmol) and methylethylenediamine (17 μL, 0.19 mmol) in water/acetone (15 mL). Yield: 50 mg (60%) of **61**. − ^{1}H NMR (500 MHz, [D$_3$]acetonitrile): δ = 8.08 [s, 2 H, H−C(3 or 3′), H−C(3 or 3′)*], 8.07 [s, 2 H, H−C(3 or 3′), H−C(3 or 3′)*], 8.00 [s, 1 H, H−C(6 or 6′)], 7.99 [s, 1 H, H−C(6 or 6′)*], 7.91 [s, 2 H, H−C(6 or 6′), H−C(6 or 6′)*], 5.64 [b, 2 H, H−N(14), H−N(14)*], 5.22 [b, 2 H, H_b−N(14′), H_b−N(14′)*], 5.13 [b, 2 H, H_a−N(14′), H_a−N(14′)*], 3.17 [d, ^3J = 2.5 Hz, 10 H, H_2−C(7,7′), H_2−C(7,7′)*, H_b−C(15), H_b−C(15)*], 3.06 [m, 6 H, H_2−C(15′), H_2−C(15′)*, H−C(10 or 10′), H−C(10 or 10′)*], 2.96 [dd, ^3J = 5.5, 5.5 Hz, 2 H, H−C(10 or 10′), H−C(10 or 10′)*], 2.86 [d, ^3J = 6.7 Hz, 3 H, H_3C−N(14)], 2.85 [d, ^3J = 6.7 Hz, 3 H, H_3C−N(14)*], 2.82 [m, 4 H, H_b−C(9), H_b−C(9′), H_b−C(9)*, H_b−C(9′)*], 2.68 [d, ^2J = 9.6 Hz, 2 H, H_a−C(15), H_a−C(15)*], 2.40 [m, 4 H, H−C(8), H−C(8′), H−C(8*), H−C(8′)*], 1.46 [s, 6 H, H_3−C(12 or12′), H_3−C(12 or12′)*], 1.44 [s, 3 H, H_3−C(12 or 12′)*], 1.43 [s, 3 H, H_3−C(12 or 12′)*], 1.24 [m, 4 H, H_a−C(9), H_a−C(9′), H_a−C(9)*, H_a−C(9′)*], 0.69 [s, 3 H, H_3−C(13 or 13′), 0.67 [s, 3 H, H_3−C(13 or 13′)*], 0.66 [s, 3 H, H_3−C(13 or 13′)*], 0.65 [s, 3 H, H_3−C(13 or 13′)*]. − ^{13}C NMR (125 MHz, [D$_3$]acetonitrile): δ = 155.6, 153.5, 149.4, 149.3, 148.8, 146.7, 146.3 [C(6 or 6′), 146.0 [C(6 or 6′)], 124.3 [C(3 or 3′)], 124.2 [C(3 or 3′)], 57.8 [C(15)], 45.5 [C(10 or 10′)], 45.3 [C(10 or 10′)], 43.9 [C-(15′)], 41.7 [C−N(14)], 41.6 [(C−N(14)*], 40.3 [C(8 or 8′)], 40.2 [C(8 or 8′)], 39.7 [C(11 or 11′)*], 39.6 [C(11 or 11′)*], 34.1 [C(7), C(7′)], 31.5 [C(9 or 9′)], 31.4 [C(9 or 9′)], 25.8 [C(12 or 12′)], 25.7 [C(12 or 12′)], 21.5 [C(13 or 13′)], 21.4 [C(13 or 13′)]. − FAB-MS: *m*/*z* (%) = 758 (12) [M^+ − PF_6], 612 (51) [M^+ − 2 PF_6], 598 (11) [M^+ − CH_3], 538 (21) [M^+ − en], 307 (100). − The asterisk * denotes NMR signals of the other possible diastereomers.

[{Bis[(−)-pineno]−2,2′-bipyridine}(piperazine)Pt^{II}](PF$_6$)$_2$ (71): The synthesis, and purification of compound **71** was carried out as described for compound **11** with **L1PtCl$_2$** (56 mg, 0.092 mmol) and piperazine (14 mg, 0.16 mmol) in water/acetone (20 mL). Yield: 30 mg (36%). − ^{1}H NMR (360 MHz, [D$_3$]acetonitrile): δ = 8.37 [s, ^{Pt-H}J = 33.5 Hz, 2 H, H−C(6,6′)], 8.04 [s, 2 H, H−C(3,3′)], 5.73 [b, 2 H, H−N(14,14′)], 3.78 [d, ^2J = 7.0 Hz, 4 H, H_b−C(15,15′), H_b−C(16,16′)], 3.19 [d, ^3J = 2.3 Hz, 4 H, H_2−C(7,7′)], 3.00 [d, ^2J = 7.0 Hz, 4 H, H_a−C(15,15′), H_a−C(16,16′)], 2.95 [dd, ^3J = 5.1, 5.1 Hz, 2 H, H−C(10,10′)], 2.84 [dd, ^2J = 10.0 Hz, ^3J = 5.1 Hz, 2 H, H_b−C(9,9′)], 2.41 [m, 2 H, H−C(8,8′)], 1.47 [s, 6 H, H_3−C(12,12′)], 1.25 [d, ^2J = 10.0 Hz, 2 H, H_a−C(9,9′)], 0.69 [s, 6 H, H_3−C(13,13′)].

[{Bis[(−)-pineno−2,2′-bipyridine}(homopiperazine)Pt^{II}](PF$_6$)$_2$ (81): The synthesis, and purification of compound **81** was carried out as described for compound **11** with **L1PtCl$_2$** (100 mg, 0.16 mmol) and homopiperazine (50 mg, 0.5 mmol) in water/acetone (30 mL). Yield: 110 mg (72%). − ^{1}H NMR (500 MHz, [D$_3$]acetonitrile): δ = 8.28 [s, 1 H, H−C(6 or 6′)], 8.27 [s, 1 H, H−C(6 or 6′)], 8.06 [s, 2 H, H−C(3,3′)], 6.06 (b, 1 H, H−N(14 or 14′)],)], 6.03 [b, 1 H, H−N(14 or 14′)], 3.61 [m, 2 H, H_b−C(16,16′)], 3.49 [m, 2 H, H_b−C(15,15′)], 3.36 [m, 2 H, H_a−C(16,16′)], 3.18 [d, ^3J = 2.4 Hz, 4 H, H_2−C(7,7′)], 2.98 [m, 4 H, H_a−C(15, 15′), H−C(10,10′)], 2.82 [dd, ^2J = 9.9 Hz, ^3J = 5.8 Hz, 2 H, H_b−C(9,9′)], 2.40 [m, 2 H, H−C(8,8′)], 2.14 [m, 2 H, H_2−C-(17)], 1.46 [s, 3 H, H_3−C(12 or 12′)], 1.45 [s, 3 H, H_3−C(12 or 12′)], 1.24 [d, ^2J = 9.9 Hz, 2 H, H_a−C(9,9′)], 0.68 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (125 MHz, [D$_3$]acetonitrile): δ = 153.9 [C(2,2′)], 151.9 [C(5 or 5′)], 151.8 [C(5′ or 5)], 147.4 [C(4 or 4′)], 147.3 [C(4′ or 4)], 146.2 [C(6 or 6′)], 146.1

[C(6′ or 6)], 122.6 [C(3,3′)], 50.9 [C(16, 16′)], 50.0 [C(15,15′)], 43.9 [C(10,10′)], 38.9 [C(8,8′)], 38.3 [C(11,11′)], 32.7 [C(7,7′)], 30.1 [C(9,9′)], 24.5 [C(12 or 12′)], 24.4 [C(12′ or 12)], 20.2 [C(13,13′)], 18.6[C(17)].

L2PtCl$_2$: K_2PtCl_4 (1.20 g, 2.90 mmol) was dissolved in HCl (0.2 M, 100 mL) and **L2** (1.0 g, 2.90 mmol) was added. The synthesis and purification was carried out in the same way as described for **L1PtCl$_2$** above, except that the reaction time was increased to 10 h. Yellow crystals (1.32 g, 75%) of **L2PtCl$_2$** were obtained. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 [d, ^3J = 7.7 Hz, 2 H, H−C(3,3′)], 7.39 [d, ^3J = 7.7 Hz, 2 H, H−C(4,4′)], 4.03 [dd, ^2J = 18.1 Hz, ^3J = 2.6 Hz, 2 H, H_b−C(7,7 ′)], 3.91 [dd, ^2J = 18.1 Hz, ^3J = 3.1 Hz, 2 H, H_a−C(7,7 ′)], 2.71 [dd, ^3J = 5.8, 5.8 Hz, 2 H, H−C(10,10,′)], 2.61 [ddd, ^2J = 9.8 Hz, ^3J = 5.8, 5.8 Hz, 2 H, H_b−C(9,9′)], 2.36 [m, 2 H, H−C(8,8′)], 1.35 [s, H_3−C(12,12′)], 1.16 [d, ^2J = 9.8 Hz, H_a−C(9,9′)], 0.62 [s, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6 [C(2,2′)], 156.8 [C(6,6′)], 145.9 [C(5,5′)], 135.9 [C(4,4′)], 119.8 [C(3,3′)], 46.8 [C(10,10′)], 40.0 [C(8,8′)], 39.1 [C(7,7′)], 36.4 [C(11,11′)], 30.9 [C(9,9′)], 25.6 [C(12,12′)], 21.9 [C(13,13′)]. − ^{195}Pt NMR (64.376 MHz, $CDCl_3$): see Table 1. − FAB-MS: *m/z* (%) = 1185 (80) [M_2^+ − Cl], 1112* (9), 1075* (4), 1015* (4), 919* (45), 882* (23), 841* (21), 575 (80) [M^+ − Cl], 537 (100) (* further dimer fragments). − $C_{24}H_{28}Cl_2N_2Pt$ (610.5): calcd. C 47.22, H 4.62, N 4.59, found C 49.0, H 4.71, N 4.49. − Crystal structure analysis see Tables 3 and 8, Figure 2.

[{Bis[(−)-pineno]−2,2′-bipyridine}(ethylenediamine)Pt^{II}](PF$_6$)$_2$ (12): The synthesis, and purification of compound **12** was carried out as described for compound **11** with **L2PtCl$_2$** (100 mg, 0.16 mmol) and ethylenediamine (13 μL, 0.19 mmol) in water/acetone (20 mL). Yield: 105 mg (72%). − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 7.96 [d, ^3J = 8.1 Hz, 2 H, H−C(3,3′)], 7.80 [d, ^3J = 8.1 Hz, 2 H, H−C(4,4′)], 5.24 [b, 4 H, H_2−N(14,14,′)], 2.98 [d, ^3J = 3.0 Hz, 4 H, H_2−C(7,7′)], 2.97 [dd, ^3J = 5.6, 5.6 Hz, 2 H, H−C(10,10′)], 2.75 [dd, ^2J = 10.1 Hz, ^3J = 5.6 Hz, 2 H, H_b−C(9,9′)], 2.60 [b, 4 H, H_2−C(15,15′)], 2.45 [m, 2 H, H−C(8,8′)], 1.43 [s, 6 H, H_3−C(12,12′)], 1.26 [d, ^2J = 10.1 Hz, 2 H, H_a−C(9,9′)], 0.66 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): δ = 161.1 [C(2,2′)], 157.3 [C(6,6′)], 148.0 [C(5,5′)]; 138.9 [C(4,4′)], 121.9 [C(3,3′)], 47.8 [C(15,15′)]; 47.4 [C(10,10′)], 40.6 [C(8,8′)], 39.7 [C(11,11′)], 37.1 [C(7,7′)], 31.0 [C(9,9′)], 25.4 [C(12,12′)], 21.3 [C(13,13′)]. − FAB-MS: *m/z* (%) = 744 (12) [M^+ − PF_6], 598 (70) [M^+ − 2 PF_6], 538 (33) [M^+ − en], 154 (100).

[{Bis[(−)-pineno]−2,2′-bipyridine}(R,R-DACH)Pt^{II}](PF$_6$)$_2$ (22): The synthesis, and purification of compound **22** was carried out as described for compound **21** with **L2PtCl$_2$** (112 mg, 0.18 mmol) and (*R,R*)-diaminocyclohexane (35 mg, 0.30 mmol) in water/acetone (25 mL). Yield: 120 mg (70%) white powder of **22**. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 7.95 [d, ^3J = 8.1 Hz, 2 H, H−C(3,3′)], 7.79 [d,^3J = 8.1 Hz, 2 H, H−C(4,4′)], 5.46 [b, 2 H, H_a−N(14,14′)], 4.80 [b, 2 H, H_b−N(14,14′)], 3.01 [dd, ^2J = 17.1 Hz, ^3J = 2.7 Hz, 4 H, H_a-H_b−C(7,7′)], 2.97 [dd, ^3J = 5.1, 5.1 Hz, 2 H, H−C(10,10′)], 2.74 [dd, ^2J = 10.1 Hz, ^3J = 5.1 Hz, 2 H, H_b−C(9,9′)], 2.46 [m, 4 H, H−C(8,8′), H−C(15,15′)], 2.19 [d, ^2J = 12.4 Hz, 2 H, H_a−C(16,16′)], 1.63 [d, ^2J = 8.8 Hz, 2 H, H_b−C(16,16′)], 1.42 [s, 6 H, H_3−C(12,12′)], 1.38 (b, 2 H, H_a−C17,17′)], 1.24 [d, ^2J = 10.1 Hz, 4 H, H_b−C(17,17′), H_a−C(9,9′)], 0.68 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): δ = 139.1, 122.2, 62.7, 47.7, 40.9, 37.4, 32.7, 31.5, 30.5, 25.6, 24.9, 21.7. − FAB-MS: *m/z* (%) = 798 (16) [M^+ − PF_6], 653 (73) [M^+ − 2 PF_6], 539 (51) [M^+ − DACH], 345 (26), 307 (31), 176 (32), 154 (100).

[{Bis[(−)-pineno]−2,2′-bipyridine}(S,S-DACH)Pt^{II}](PF$_6$)$_2$ (32): The synthesis, and purification of compound **32** was carried out as described for compound **21** with **L2PtCl$_2$** (106 mg, 0.17 mmol) and (*S,S*)-diaminocyclohexane (34 mg, 0.30 mmol) in water/acetone (25 mL). Yield: 112 mg (68%) white powder of **32**. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 7.95 [d, ^3J = 8.1 Hz, 2 H, H−C(3,3′)], 7.79 [d,^3J = 8.1 Hz, 2 H, H−C(4,4′)], 5.48 [b, 2 H, H_a−N(14,14′)], 4.83 [b, 2 H, H_b−N(14,14′)], 3.01 [dd, ^2J = 17.1 Hz, ^3J = 2.7 Hz, 4 H, H_a-H_b−C(7,7′)], 2.97 [dd, ^3J = 5.8, 5.8 Hz, 2 H, H−C(10,10′)], 2.74 [dd, ^2J = 10.1 Hz, ^3J = 5.1 Hz, 2 H, H_b−C(9,9′)]; 2.46 [m, 6 H, H−C(8,8′), H_2−C(15,15′)], 2.19 [d, ^2J = 12.4 Hz, 2 H, H_a−C(16,16′)], 1.63 [d, ^2J = 8.8 Hz, 2 H, H_b−C(16,16′)], 1.42 [s, 6 H, H_3−C(12,12′)], 1.38 (b, 2 H, H_a−C17,17′)], 1.30 [d, ^2J = 10.1 Hz, 2 H, H_a−C(9,9′)], 1.22 [d, ^2J = 10.1 Hz, 2 H, H_b−C(17,17′)], 0.64 [s, 6 H, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): δ = 139.1, 122.2, 62.7, 47.7, 40.9, 37.4, 32.7, 31.5, 30.5, 25.6, 24.9, 21.7. − FAB-MS: *m/z* (%) = 798 (11) [M^+ − PF_6], 652 (54) [M^+ − 2 PF_6], 538 (41) [M^+ − DACH], 439 (12), 345 (18), 307 (20), 154 (100).

[{Bis[(−)-pineno]−2,2′-bipyridine}(S,S/R,R-DACH)Pt^{II}](PF$_6$)$_2$ (42): The synthesis, and purification of compound **32** was carried out as described for compound **21** with **L2PtCl$_2$** (92 mg, 0.15 mmol), (*S,S*)-diaminocyclohexane (32 mg, 0.28 mmol) and (*R,R*)-diaminocyclohexane (32 mg, 0.28 mmol) in water/acetone (25 mL). Yield: 108 mg (76%) white powder of **42**. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 7.95 [d, ^3J = 8.1 Hz, 2 H, H−C(3,3′)], 7.79 [d, ^3J = 8.1 Hz, 2 H, H−C(4,4′)], 5.48 [b, 2 H, H_a−N(14,14′)], 4.82 [b, 2 H, H_b−N(14,14′)], 3.01 [dd, ^2J = 17.1 Hz, ^3J = 2.7 Hz, 4 H, H_a-H_b−C(7,7′)], 2.97 [dd, ^3J = 5.8 Hz, 2 H, H−C(10,10′)], 2.74 [dd, ^2J = 10.1 Hz, ^3J = 5.1 Hz, 2 H, H_b−C(9,9′)], 2.46 [m, 4 H, H−C(8,8′), H−C(15,15′)], 2.19 [d, ^2J = 12.4 Hz, 2 H, H_a−C(16,16′)], 1.63 [d, ^2J = 8.8 Hz, 2 H, H_b−C(16,16′)], 1.42 [s, 6 H, H_3−C(12,12′)], 1.38 (b, 2 H, H_a−C17,17′)], 1.30 [d, ^2J = 10.1 Hz, 2 H, H_a−C(9,9′)-(*S,S*-DACH), 1.24 [d, ^2J = 10.1 Hz, 2 H, H_a−C(9,9′)-(*R,R*-DACH)], 1.22 [d, ^2J = 10.1 Hz, 2 H, H_b−C(17,17′)], 0.68 [s, 6 H, H_3−C(13,13′)-(*R,R*-DACH)], 0.64 [s, 6 H, H_3−C(13,13′)-(*S,S*-DACH)]. − ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): δ = 139.1, 122.2, 62.7, 47.7, 40.9, 37.4, 32.7, 31.5, 30.5, 25.6, 24.9, 21.7. − FAB-MS: *m/z* (%) = 798 (12) [M^+ − PF_6], 652 (38) [M^+ − 2 PF_6], 538 (20) [M^+ − DACH], 345 (11), 307 (73), 154 (100).

L3PtCl$_2$: K_2PtCl_4 (240.7 mg, 0.58 mmol) was dissolved in HCl (0.2 M, 33 mL) and **L3** (200 mg, 0.58 mmol) was added. The synthesis and purification was carried the same way as described for **L2PtCl$_2$** above. Yellow crystals (260 mg, 73%) of **L3PtCl$_2$** were obtained. −^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 [d, ^3J = 8.1 Hz, 2 H, H−C(3,3′)], 7.37 [d, ^3J = 8.1 Hz, 2 H, H−C(4,4′)], 4.03 [dd, ^2J = 18.7 Hz, ^3J = 2.6 Hz, 2 H, H_b−C(7,7 ′)], 3.91 [dd, ^2J = 18.7 Hz, ^3J = 3.1 Hz, 2 H, H_a−C(7,7 ′)], 2.72 [dd, ^3J = 5.4, 5.4 Hz, 2 H, H−C(10,10,′)], 2.61 [ddd, ^2J = 9.6 Hz, ^3J = 5.6 Hz, 2 H, H_b−C(9,9′)], 2.38 [m, 2 H, H−C(8,8′)], 1.37 [s, H_3−C(12,12′)], 1.13 [d, ^2J = 9.6 Hz, H_a−C(9,9′)], 0.66 [s, H_3−C(13,13′)]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6 [C(2,2′)], 156.8 [C(6,6′)], 145.9 (5,5′)], 135.9 [C(4,4′)], 119.8 [C(3,3′)], 46.8 [C(10,10′)], 40.0 [C(8,8′)], 39.1 [C(11,11′)], 36.4 [C(9,9′)], 25.6 [C(12,12′)], 21.9 [C(13,13′)]. − ^{195}Pt NMR (64.376 MHz, $CDCl_3$): see Table 1. − FAB-MS: *m/z* (%) = 609 (13) [M^+], 578 (80) [M^+ − Cl], 539 (48) [M^+ − 2 Cl], 506 (18), 462 (12), 345 (40), 307 (78), 289 (68), 154 (100). − $C_{24}H_{28}Cl_2N_2Pt$ (610.5): calcd. C 47.22, H 4.62, N 4.59, found C 45.77, H 4.74, N 4.70. − Crystal structure analysis see Tables 4 and 8, Figure 3.

[{Bis[(−)-(+)-pineno]−2,2′-bipyridine}(ethylenediamine)Pt^{II}](PF$_6$)$_2$ (13): The synthesis, and purification of compound **13** was carried out as described for compound **11** with **L3PtCl$_2$** (50 mg, 0.081 mmol) and ethylenediamine (10 μL, 0.15 mmol) in water/acetone (15 mL). Yield: 51 mg (70%). − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 7.96 [d, ^3J = 8.1 Hz, 2 H, H−C(3,3′)], 7.80 [d, ^3J = 8.1 Hz, 2 H, H−C(4,4′)], 5.26 [b, 4 H, H$_2$−N(14,14′)], 2.98 [d, ^3J = 2.4 Hz, 6 H, H$_2$−C(7,7′), H−C(10,10′)], 2.76 [dd, ^2J = 10.1 Hz, ^3J = 5.2 Hz, 2 H, H$_b$−C(9,9′)]; 2.60 [b, 4 H, H$_2$−C(15,15′)], 2.45 [m, 2 H, H−C(8,8′)], 1.42 [s, 6 H, H$_3$−C(12,12′)], 1.32 [d, ^2J = 10.1 Hz, H$_a$−C(9,9′)], 0.63 [s, 6 H, H$_3$−C(13,13′)]. − ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): δ = 161.3 [C(2,2′)], 157.4 [C(6,6′)], 148.2 [C(5,5′)]; 139.0 [C(4,4′)], 121.9 [C(3,3′)], 47.7 [C(15,15′)]; 47.5 [C(10,10′)], 40.6 [C(8,8′)], 39.7 [C(11,11′)], 37.1 [C(7,7′)]; 31.2 [C(9,9′)], 25.4 [C(12,12′)]; 21.2 [C(13,13′)]. − FAB-MS: *m/z* (%) = 744 (14) [M$^+$ − PF$_6$], 600 (66) [M$^+$ − 2 PF$_6$], 541 (42) [M$^+$ − en], 345 (16), 165 (28), 154 (100).

L4PtCl$_2$: Compound **L4** (700 mg, 2.03 mmol) was added to a solution of K$_2$PtCl$_4$ (843.5 mg, 2.03 mmol) dissolved in HCl (0.2 M, 80 mL). After stirring for 10 h at reflux, the yellow precipitate was filtered off and washed with water. The crude product was dried at 50 °C in the vacuum oven. Recrystallization from chloroform/heptane gave yellow crystals (786 mg, 63%) of **L4PtCl$_2$**. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 8.15 [d, ^3J = 7.7 Hz, 2 H, H−C(3,3′)], 7.50 [d, ^3J = 7.7 Hz, 2 H, H−C(4,4′)], 4.23 [dd, ^3J = 5.8, 5.8 Hz, 2 H, H−C(10,10′)], 2.86 [d, ^3J = 2.6 Hz, 4 H, H$_2$−C(7,7′)], 2.79 [dd, ^3J = 5.8 Hz, ^2J = 9.8 Hz, 2 H, H$_b$−C(9,9′)], 2.25 [m, 2 H, H−C(8,8′)], 1.42 [s, 6 H, H$_3$−C(12,12′)], 1.27 [d, ^2J = 9.8 Hz, 2 H, H$_a$−C(9,9′)], 0.64 [s, 6 H, H$_3$−C(13,13′)]. − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 171.3 [C(2,2′)], 154.2 [C(6,6′)], 137.0 [C(4,4′)], 134.0 [C(5,5′)], 120.5 [C(3,3′)], 51.4 [C(10,10′)], 39.3 [C(11,11′)], 39.1 [C(8,8′)], 31.7 [C(7,7′)], 31.2 [C(9,9′)], 24.8[C(13,13′)], 21.6 [C(12,12′)]. − ^{195}Pt NMR (64.376 MHz, CDCl$_3$): see Table 1. − FAB-MS: *m/z* (%) = 1186 (6) [M$_2^+$ − Cl], 920 (20) and 883 (8) further dimer fragments, 610 (7) [M$^+$], 575 (54) [M$^+$ − Cl], 536 (87) [M$^+$ − 2 Cl], 522 (26), 345 (100). − C$_{24}$H$_{28}$Cl$_2$N$_2$Pt (610.5): calcd. C 47.22, H 4.62, N 4.59; found C 47.00, H 4.62, N 4.44. − Crystal structure analysis see Tables 5 and 8, Figure 4.

[{Bis[(−)-β-pineno]−2,2′-bipyridine}(ethylenediamine)Pt^{II}](PF$_6$)$_2$ (14): The synthesis, and purification of compound **14** was carried out as described for compound **11** with **L4PtCl$_2$** (100 mg, 0.16 mmol) and ethylenediamine (12 μL, 0.18 mmol) in water/acetone (20 mL). Yield: 85 mg (58%) white powder of **14**. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 8.02 [s, 4 H, H−C(3,3′), H−C(4,4′)], 4.61 [b, 4 H, H$_2$−N(14,14′)], 3.10 [m, 6 H, H$_2$−C(7,7′), H−C(10,10′)], 2.87 [dd, ^2J = 10.0 Hz, ^3J = 5.7 Hz, 2 H, H$_b$−C(9,9′)], 2.65 [b, 4 H, H$_2$−C(15,15′)], 2.40 [m, 2 H, H−C(8,8′)], 1.50 [s, 6 H, H$_3$−C(12,12′)], 1.36 [d, ^2J = 10.0 Hz, 2 H, H$_a$−C(9,9′)], 0.70 [s, 6 H, H$_3$−C(13,13′)]. − ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): δ = 141.1, 136.2, 121.6, 51.3, 48.3, 40.6, 40.3, 31.8, 30.8, 25.6, 21.8, (two carbon atoms could not be observed). − FAB-MS: *m/z* (%) = 744 (36) [M$^+$ − PF$_6$], 599 (80) [M$^+$ − 2 PF$_6$], 536 (25) [M$^+$ − en], 345 (100), 307 (81), 154 (100).

[{Bis[(−)-β-pineno]−2,2′-bipyridine}(R,R-DACH)Pt^{II}](PF$_6$)$_2$ (24): The synthesis, and purification of compound **24** was carried out as described for compound **21** with **L4PtCl$_2$** (50 mg, 0.082 mmol) and (*R,R*)-diaminocyclohexane (15 mg, 0.13 mmol) in water/acetone (15 mL). Yield: 43 mg (55%) white powder of **24**. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 8.03 [s, 4 H, H−C(3,3′), H−C(4,4′)], 4.58 [b, 4 H, H$_2$−N(14,14′)], 3.11 [m, 6 H, H$_2$−C(7,7′), H−C(10,10′)], 2.86 [dd, ^2J = 10.4 Hz, ^3J = 5.6 Hz, 2 H, H$_b$−C(9,9′)], 2.44 (b, 2 H, DACH), 2.42 [m, 2 H, H−C(8,8′)], 2.04 (b, 2 H, DACH), 1.61 (b, 2 H, DACH), 1.50 [s, 6 H, H$_3$−C(12,12′)], 1.39 [d, ^2J = 10.4 Hz, 2 H, H$_a$−C(9,9′)], 1.19 (b, 2 H, DACH), 0.68 [s, 6 H, H$_3$−C(13,13′)]. − FAB-MS: *m/z* (%) = 799 (12) [M$^+$ − PF$_6$], 652 (70) [M$^+$ − 2 PF$_6$], 537 (34) [M$^+$ − DACH], 345 (11), 307 (14), 154 (100).

[{Bis[(−)-β-pineno]−2,2′-bipyridine}(R,R/S,S-DACH)Pt^{II}](PF$_6$)$_2$ (44): The synthesis, and purification of compound **44** was carried out as described for compound **21** with **L4PtCl$_2$** (87 mg, 0.14 mmol), (*R,R*)-diaminocyclohexane (20 mg, 0.18 mmol), and (*S,S*)-diaminocyclohexane (20 mg, 0.18 mmol) in water/acetone (15 mL). Yield: 70 mg (52%) white powder of **44**. − ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): δ = 8.02 [s, 4 H, H−C(3,3′), H−C(4,4′)], 4.58 [b, 4 H, H$_2$−N(14,14′)], 3.11 [m, 6 H, H$_2$−C(7,7′), H−C(10,10′)], 2.87 [dd, ^2J = 10.7 Hz, ^3J = 5.7 Hz 2 H, H$_b$−C(9,9′)], 2.44 (b, 2 H, DACH), 2.42 [m, 2 H, H−C(8,8′)], 2.03 (b, 2 H, DACH), 1.60 (b, 2 H, DACH), 1.50 [s, 6 H, H$_3$−C(12,12′)-*R,R*-DACH], 1.49 [s, H$_3$−C(12,12′)-*S,S*-DACH, ratio see discussion], 1.39 [d, ^2J = 10.7 Hz, 2 H, H$_a$−C(9,9′)], 1.37 (b, 2 H, DACH), 1.19 (b, 2 H, DACH), 0.72 [s, 6 H, H$_3$−C(13,13′)-*S,S*-DACH, ratio see discussion], 0.68 [s, 6 H, H$_3$−C(13,13′)-*R,R*-DACH]. − FAB-MS: *m/z* (%) = 798 (16) [M$^+$ − PF$_6$], 653 (63) [M$^+$ − 2 PF$_6$], 539 (34) [M$^+$ − DACH], 307 (28), 154 (100).

L5PtCl$_2$: Compound **L5** (437 mg, 1.26 mmol) was added to a solution of K$_2$PtCl$_4$ (524 mg, 1.26 mmol) dissolved in HCl (0.2 M, 50 mL). After stirring for 10 h at reflux, the yellow precipitate was filtered off and washed with water. The crude product was dried at 50 °C in a vacuum oven. Recrystallization from chloroform/heptane gave a yellow powder (560 mg, 72%) of **L4PtCl$_2$**. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.15 [s, 1 H, H−C(6′)], 7.85 [d, ^3J = 7.9 Hz, 1 H, H−C(3)], 7.75 [s, 1 H, H−C(3′)], 7.50 [d, ^3J = 7.9 Hz, 1 H, H−C(4)], 4.39 [dd, ^2J = 18.8 Hz, ^3J = 3.2 Hz, 1 H, H$_b$−C(7)], 3.60 [dd, ^2J = 18.8 Hz, ^3J = 2.8 Hz, 1 H, H$_a$−C(7)], 3.15 [dd, ^2J = 17.7 Hz, ^3J = 3.3 Hz, 1 H, H$_b$−C(7′)], 2.94 [dd, ^2J = 17.7 Hz, ^3J = 2.6 Hz, 1 H, H$_a$−C(7′)], 2.87 [dd, ^3J = 5.8, 5.8 Hz, 1 H, H−C(10′)], 2.79 [dd, ^3J = 5.8, 5.8 Hz, 1 H, H−C(10)], 2.71 [dd, ^2J = 9.9 Hz, ^3J = 5.8 Hz, 1 H, H$_b$−C(9′)], 2.62 [dd, ^2J = 9.9 Hz, ^3J = 5.8 Hz, 1 H, H$_b$−C(9)], 2.42 [m, 1 H, H−C(8)], 2.34 [m, 1 H, H−C(8′)], 1.39 [s, 3 H, H$_3$−C(12′)], 1.36 [s, 3 H, H$_3$−C(12)], 1.15 [d, ^2J = 9.9 Hz, 2 H, H$_a$−C(9,9′)], 0.59 [s, 3 H, H$_3$−C(13 or 13′)], 0.55 [s, 3 H, H$_3$−C(13′ or 13)]. − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 164.7 [C(2′)], 156.1 [C(2)], 155.9 [C(6)], 149.3 [C(4′)], 147.5 [C(5)], 145.3 [C(5′)], 144.2 (6′)], 135.2 [C(4)], 122.4 (3′)], 120.3 (3)], 47.2 (10)], 44.7 [C(10′)], 39.9 [C(8)], 39.4 [C(8′)], 39.1 [C(11)], 38.9 [C(7)], 38.6 [C(9)], 33.4 [C(11′)], 31.1 [C(7′)], 30.3 [C(9′)], 25.6 [C(12)], 25.2 [C(12′)], 21.3 [C(13)], 21.2 [C(13′)]. − FAB-MS: *m/z* (%) = 1186 (8) [M$_2^+$ − Cl], 920 (9) and 842 (10) [further dimer fragments], 574 (80) [M$^+$ − Cl], 537 (54) [M$^+$ − 2 Cl], 493 (20), 345 (66), 154 (100). − C$_{24}$H$_{28}$Cl$_2$N$_2$Pt (610.5): calcd. C 47.22, H 4.62, N 4.59, found C 47.37, H 4.70, N 4.59.

[{Bis[(−)-pineno]−2,2′-bipyridine}(ethylenediamine)Pt^{II}](PF$_6$)$_2$ (15): The synthesis and purification of compound **15** was carried out as described for compound **11** with **L5PtCl$_2$** (70 mg, 0.11 mmol) and ethylenediamine (10 μL, 0.15 mmol) in water/acetone (20 mL). Yield: 65 mg (63%) white powder of **14**. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.08 [s, 1 H, H−C(6′)], 8.01 [d, ^3J = 7.8 Hz, 1 H, H−C(3)], 7.86 [s, 1 H, H−C(3′)], 7.84 [d, ^3J = 7.9 Hz, 1 H, H−C(4)], 5.30 [b, 2 H, H$_b$−N(14,14′)], 5.18 [b, 2 H, H$_a$−N(14,14′)], 3.16 [d, ^3J = 2.7 Hz, 2 H, H$_2$−C(7′)], 3.03 [dd, ^3J = 5.6, 5.6 Hz, 1 H, H−C(10′)], 2.95 [m, 3 H, H−C(10), H$_2$−C(7)], 2.84−2.61 [m, 6 H, H$_2$−C(15), H$_2$−C(15′), H$_b$−C(9), H$_a$−C(9′)], 2.47 [m, 1 H, H−C(8)], 2.40 [m, 1 H, H−C(8′)], 1.46

[s, 3 H, H_3−C(12′)], 1.44 [s, 3 H, H_3−C(12)], 1.27 [d, ^2J = 9.9 Hz, 1 H, H_a−C(9 or 9′)], 1.22 [d, ^2J = 9.9 Hz, 1 H, H_a−C(9 or 9′)], 0.69 [s, 3 H, H_3−C(13)], 0.67 [s, 3 H, H_3−C(13′)]. − FAB-MS: *m/z* (%) = 744 (21) [$M^+ - PF_6$], 600 (95) [$M^+ - 2\,PF_6$], 543 (58) [M^+ -en], 345 (40), 289 (82), 165 (42), 154 (100).

[{Bis[(−)-pineno]−2,2′-bipyridine}(S,S-DACH)Pt^{II}](PF$_6$)$_2$ (35): The synthesis and purification of compound **35** was carried out as described for compound **31** with **L5PtCl$_2$** (50 mg, 0.082 mmol) and (*S,S*)-diaminocyclohexane (15 mg, 0.13 mmol) in water/acetone (20 mL). Yield: 55 mg (71%) white powder of **35.** − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 [s, 1 H, H−C(6′)], 8.01 [d, ^3J = 7.9 Hz, 1 H, H−C(3)], 7.86 [s, 1 H, H−C(3′)], 7.85 [d, ^3J = 7.9 Hz, 1 H, H−C(4)], 5.44 [b, 2 H, H_b−N(14,14′)], 4.86 [b, 2 H, H_a−N(14,14′)], 3.16 [d, ^3J = 2.6 Hz, 2 H, H_2−C(7′)], 3.07−2.73 [m, 6 H, H−C(10′), H−C(10′), H_2−C(7), H_b−C(9), H_b−C(9′)], 2.54 (b, 2 H, DACH), 2.48 (b, 2 H, DACH), 2.40 [m, 1 H, H−C(8 or 8′)], 2.21 [m, 1 H, H−C(8 or 8′)], 1.66 (b, 2 H, DACH), 1.46 [s, 3 H, H_3−C(12′)], 1.44 [s, 3 H, H_3−C(12)], 1.43 (b, 2 H, DACH), 1.27−1.23 [m, 4 H, H_a−C(9), H_a−C(9′), DACH], 0.67 [s, 3 H, H_3−C(13)], 0.65 [s, 3 H, H_3−C(13)].

[{Bis[(−)-pineno]−2,2′-bipyridine}(S,S/R,R-DACH)Pt^{II}](PF$_6$)$_2$ (45): The synthesis and purification of compound **45** was carried out as described for compound **41** with **L5PtCl$_2$** (50 mg, 0.082 mmol), (*R,R*)-diaminocyclohexane (15 mg, 0.13 mmol) and (*S,S*)-diaminocyclohexane (15 mg, 0.13 mmol) in water/acetone (20 mL). Yield: 55 mg (70%) white powder of **44**. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 [s, 1 H, H−C(6′)], 8.02 [d, ^3J = 8.0 Hz, 1 H, H−C(3)], 7.88 (s, 1 H, H−C(3′)], 7.85 [d, ^3J = 8.0 Hz, 1 H, H−C(4)], 5.45 [b, 2 H, H_b−N(14,14′)], 4.86 [b, 2 H, H_a−N(14,14′)], 3.16 [d, ^3J = 2.8 Hz, 2 H, H_2−C(7′)], 3.07−2.72 [m, 6 H, H−C(10′), H−C(10′), H_2−C(7), H_b−C(9), H_b−C(9′)], 2.54 (b, 2 H, DACH), 2.49 (b, 2 H, DACH), 2.40 (m, 1 H, H−C(8 or 8′)], 2.22 (m, 1 H, H−C(8 or 8′)], 1.66 (b, 2 H, DACH), 1.46 [s, 3 H, H_3−C(12′)], 1.44 [s, 3 H, H_3−C(12)], 1.43 (b, 2 H, DACH), 1.27−1.23 [m, 4 H, H_a−C(9), H_a−C(9′), DACH], 0.67 [s, 3 H, H_3−C(13)], 0.65 [s, 3 H, H_3−C(13)].

Crystallographic Measurements and Structure Solution:[13] Suitable crystals of **L2** were grown from acetone as pale yellow rods. Intensity data were collected at room temperature on a Stoe AED2 4-circle diffractometer using Mo-K_α graphite-monochromated radiation (λ = 0.71073 Å) with ω/2Θ scans in the 2Θ range 5−51°. The structure was solved by direct methods using the program SHELXS-97[14]. The refinement and all further calculations were carried out using SHELXL-97[15]. H-atoms were located from difference Fourier maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares method on F^2. The absolute structure was assigned with reference to the absolute structure of the ligand.

Crystallographic details are given in Table 8 and significant bond lengths and bond angles are listed in Table 3.

Suitable crystals for the platinum complexes were grown by diffusion of heptane into a chloroform solution. The data for **L2PtCl$_2$** and **L4PtCl$_2$** were collected on a 'Siemens SMART CCD′ System, whereas a 'STOE Image Plate Diffraction System′ was used to collect data for **L3PtCl$_2$**. Determinations of the crystal class, orientation matrix, and unit-cell dimensions were performed in a standard fashion. The data were collected using monochromated Mo-K_α

Table 8. Crystallographic data

Compound	L2	**L2PtCl$_2$**	**L3PtCl$_2$**	**L4PtCl$_2$**
Empirical formula	$C_{24}H_{28}N_2$	$C_{24}H_{28}Cl_2N_2Pt{\cdot}2CHCl_3$	$C_{24}H_{28}Cl_2N_2Pt{\cdot}2CHCl_3$	$C_{24}H_{28}Cl_2N_2Pt{\cdot}1.25CHCl_3$
Mol. wt.	344.48	849.21	849.21	759.68
Temperature [K]	293 (2)	133 (2)	223 (2)	133 (2)
Radiation, λ [Å]	Mo-K_α, 0.71073	Mo-K_α, 0.71073	Mo-K_α, 0.71073	Mo-K_α, 0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1$ (No.4)	$P\bar{1}$ (No.1)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.1)
a [Å]	6.1105 (7)	11.1430 (3)	11.2775 (11)	11.1789 (2)
b [Å]	10.9121 (18)	12.2591 (3)	12.2377 (12)	13.4606 (2)
c [Å]	14.5203 (12)	12.9160 (3)	12.8743 (13)	19.4045 (3)
α [°]	90.0	95.9000 (10)	95.475 (12)	74.6130 (10)
β [°]	94.383 (9)	114.4540 (10)	114.540 (11)	87.3960 (10)
γ [°]	90.0	97.8210 (10)	98.311 (12)	83.63
V [Å^3]	965.4 (2)	1566.19 (7)	1575.3 (3)	2797.47 (8)
Z	2	2	2	4
Density (calculated) [g cm^{-3}]	1.185	1.801	1.790	1.804
Absorption coefficient [mm^{-1}]	0.069	5.182	5.152	5.583
F [000]	372	828	828	1482
Crystal size [mm]	0.46 × 0.23 × 0.11	0.45 × 0.29 × 0.22	0.60 × 0.30 × 0.10	0.34 × 0.28 × 0.11
θ min. and max. [°]	2.34 to 25.47	2.05 to 27.28	2.23 to 25.80	1.58 to 26.70
Reflections collected/unique	3802/1901	13528/10833	12237/5604	23429/18354
Absorpt. correct.	none	ψ-scan	Emp.-DIFABS	ψ-scan
T min/*T* max		0.196/0.308	0.230/0.693	0.197/0.514
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1901/1/348	10833/3/679	5604/4/339	18354/172/1259
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0551 *wR*2 = 0.0925	*R*1 = 0.0280 *wR*2 = 0.0703	*R*1 = 0.0670 *wR*2 = 0.1733	*R*1 = 0.0384 *wR*2 = 0.0880
R indices all data	*R*1 = 0.0979 *wR*2 = 0.1067	*R*1 = 0.0303 *wR*2 = 0.0718	*R*1 = 0.0732 *wR*2 = 0.1787	*R*1 = 0.0430 *wR*2 = 0.0909
Absolute structure parameter	−1.00 (6)	0.034 (5)	−	0.000 (5)
Largest diff. peak and hole [e.Å^{-3}]	0.143 and −0.125	0.945 and −0.738	3.056 (near Pt-atom) and −4.470	1.352 and −2.309

graphite-monochromated radiation (λ = 0.71073 Å). Absorption correction for all three compounds were applied. The structures were solved by direct methods using SHELXS-97[14] and refined on F^2 against all reflections with anisotropic thermal parameters by full-matrix least-squares method using SHELXL-97.[15] Crystal data and further details of structure refinement are summarized in Table 8 and significant bond lengths and bond angles are listed in Tables 3, 4, 5, and 6.

The molecular structures and crystallographic numbering schemes for these compounds are illustrated in the PLATON[16] and Cerius2[17] drawings in Figures 2, 3, 4, and 5.

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[13] 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-117441 (**L2**), CCDC-115332 (**L2PtCl$_2$**), CCDC-115333 (**L4PtCl$_2$**), and CCDC-115334 (**L3PtCl$_2$**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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