# Preparation, Properties, and Reactions of Metal-Containing Heterocycles, 101[‡]

# Inclusion of Copper(I) into a Novel Bipyridine-Containing Tetraphosphadiplatinacyclophane

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*Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday*

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The 5,5′-bis(hydroxyalkyl)-2,2′-bipyridines **4a–c** (Scheme 1) were prepared either in one step (**4b**, **4c**) or in four steps (**4a**) starting with 5,5′-dimethyl-2,2′-bipyridine in each case. Reaction of **4a–c** with mesyl chloride afforded the bis(mesylates) $[-C_5H_3N-(CH_2)_n-CH_2-OSO_2Me]_2$ **5a–c** [$n$ = 1 (**a**), 2 (**b**), 3 (**c**)], which could easily be transformed into the diphosphanes **6a–c** by reaction with $LiPPh_2$. Treatment of **6c**, **6b** with $Cl_2Pt(NCPh)_2$ and $(RC_6H_4)_2Pt(COD)$ according to the high-dilution method resulted in the formation of the tetraphosphadiplatinacyclophanes $[-C_5H_3N-(CH_2)_4-PPh_2PtCl_2PPh_2-(CH_2)_4-C_5H_3N-]_2$ (**7c**) and $[-C_5H_3N-(CH_2)_3-PPh_2Pt(C_6H_4R)_2-PPh_2-(CH_2)_3-C_5H_3N-]_2$ (**8b**, **9b**) (**8b**: R = H, **9b**: R = *t*Bu), respectively (Scheme 2). The molecular structures of **8b** and **9b** were elucidated by X-ray structural analyses. The noncoordinated bipyridine moieties in **8b** were employed to encapsulate copper(I) to give the host/guest complex **10b** (Scheme 3), which was investigated by FAB-MS, NMR spectroscopy, and cyclovoltammetry. **10b** exhibited a quasi-reversible oxidation at $E_{1/2}$ = –0.31 V and an electrodeposition-redissolution redox system at $E_{1/2}$ = –0.79 V, owing to the formation of copper at the surface of the working electrode.

## Introduction

Since the systematic investigations of metal-containing macrocycles by Fujita et al.,[1] great interest emerged in the synthesis and design of such systems.[2] A couple of years later, the first synthesis of typical metallacyclophanes was published in the literature.[3] This kind of macrocycle presents the classically bridged cyclophane structure with aromatic units at the bottom and the top of the molecule, whereas the metals are located in the center of the aliphatic chain.[4] The introduction of transition metal fragments leads to a remarkable influence on the structure of the cyclophane framework.[3,5] Furthermore, a new potential reactive center is obtained, which can, for example, be used for the insertion of carbon monoxide into M–C σ bonds[3,5] or for catalysis.[6] Meanwhile several methods for the incorporation of transition metals into the cyclophane framework are known.[5,7,8] Most of these metallacyclophanes were obtained by reaction of metal-containing precursors with tertiary phosphanes or aliphatic and aromatic amines, in particular bipyridine.[9] Surprisingly, little attention has been paid to hybrid bipyridylphosphane ligands,[10] which combine the coordination chemistry of a remarkable chelator with that of a tertiary phosphane. Recently, Ziessel et al. described the generation of such a ligand and its employment in the formation of an interesting ruthenium(II)- and copper(I)-containing macrocycle.[10c,10d] In this case, the bipyridine core was provided with only one phosphane. Therefore, both donor types were needed to accomplish cyclization.

The present work deals with the construction of bipyridyldiphosphane ligands, which allows for the formation of metallacyclophanes by using only the P donors. Consequently, the resulting metallacyclophanes should have the capability to encapsulate metal ions by the formation of metal–nitrogen bonds, thus representing an important step in the design of organometallic analogues of the tris(bipyridine) cages published by Vögtle et al.[11] In this context, it was necessary to provide the macrocycle with sufficient flexibility. To achieve this goal, three novel PNNP ligands with methylene spacer units of different length between the phosphane and the bipyridine were made accessible. To prevent the formation of mononuclear species, less common 5,5′-substituted bipyridines were introduced.

## Results and Discussion

### Synthesis of Ligands

For the diols **4a–c** which are important intermediates in the synthesis of the bipyridyldiphosphane ligands **6a–c** (Scheme 1), three different approaches had to be investigated. The diol **4a** was obtained in a conventional four-step process, starting with 5,5′-dimethyl-2,2′-bipyridine.[11a] Chlorination with *N*-chlorosuccinimide afforded compound **1** in which both chlorides were subsequently exchanged by

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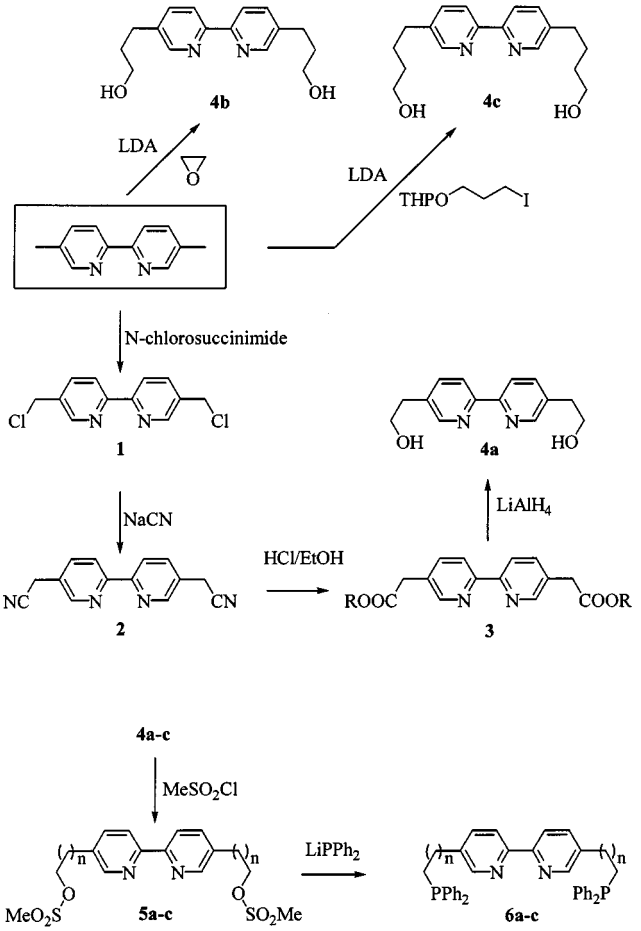
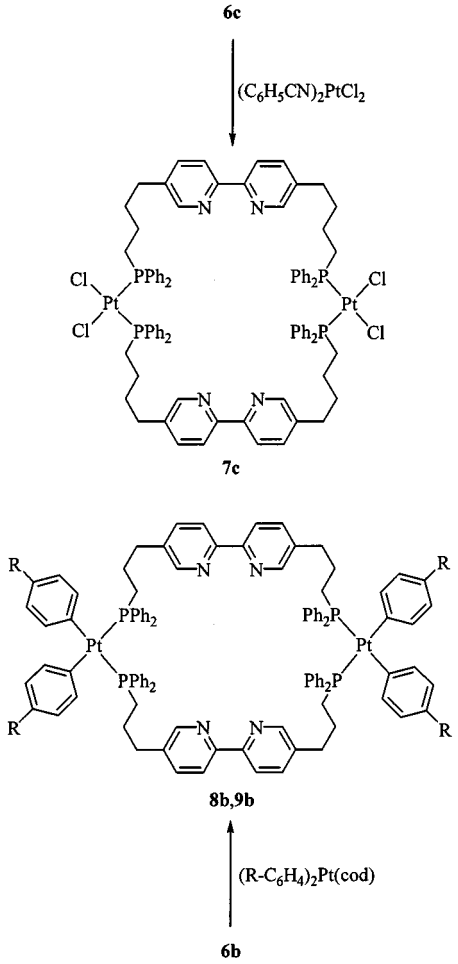



Scheme 1. Synthesis of the diols **4a–c** and their conversion into the bipyridyldiphosphanes **6a–c** [*n* = 1 (**a**), 2 (**b**), 3 (**c**); LDA = lithium diisopropylamide; THP = tetrahydropyran]




Scheme 2. Tetraphosphadiplatinacyclophanes **7c**, **8b**, and **9b** [R = H (**8b**), *t*Bu (**9b**)]

cyanides to achieve chain propagation. Acid catalyzed ethanolysis of **2** led to the bifunctionalized ester **3**, which was finally reduced with $LiAlH_4$ to form the target molecule **4a**. In contrast, the diols **4b**[12] and **4c** were made accessible in a one pot reaction. In both cases, 5,5′-dimethyl-2,2′-bipyridine was consecutively deprotonated with lithium diisopropylamide and reacted with oxirane and 1-tetrahydropyranyloxy-3-iodopropane,[13] respectively.

Treatment of the diols **4a–c** with mesyl chloride resulted in the formation of the corresponding dimesylates **5a–c**. This excellent leaving group was then replaced for phosphanes by the reaction of **5a–c** with $LiPPh_2$ to give the bipyridyldiphosphanes **6a–c**. The compounds **6a–c** were obtained as colorless, slightly air-sensitive solids, which were soluble in all common organic solvents with the exception of hydrocarbons and alcohols. Their molecular composition was corroborated by FAB mass spectra displaying in each case the expected molecular peak. Both phosphorus donors in **6a–c** are chemically equivalent, giving rise to a singlet each between δ = –15.1 and –15.5 in the $^{31}P\{^1H\}$-NMR spectra ($CDCl_3$).

### Platinacyclophanes

Under high-dilution conditions, the bipyridyldiphosphane ligand **6c** reacted with bis(benzonitrile)dichloroplatinum(II)[14] in $CH_2Cl_2$ to give the 38-membered macrocycle **7c** in remarkably good yields (Scheme 2). An ES mass spectrum confirmed the dinuclear assembly of this molecule. Owing to the 5,5′-substitution pattern in **6c**, the formation of the undesired mononuclear cyclophane was successfully prevented. From a dichloromethane solution **7c** precipitated as a colorless, thermally stable solid when this solvent was removed in vacuo. It is only slightly soluble in dichloromethane and hot chloroform.

The $^{31}P\{^1H\}$-NMR spectrum of **7c** (in $CD_2Cl_2$) displayed a singlet at δ = 8.4 which was assigned to the four chemically equivalent phosphorus atoms, and a doublet for the $^{195}Pt$ satellites. The coupling constant of 3646 Hz is typical for a *cis*-$PtCl_2$ arrangement.[15] In the downfield part of the $^{13}C\{^1H\}$-NMR spectrum of **7c** (in $CD_2Cl_2$), six singlets and three complex multiplets resulting from AXX′ spin systems were assigned to the five bipyridine- and *para*-substituted carbon atoms of the $P(C_6H_5)_2$ units and to the *ipso*-, *ortho*-, and *meta*-carbon atoms of the phosphorus-bound phenyl groups, respectively.[15] Two further AXX′ patterns at δ = 30.0 and 25.4 were ascribed to the α- and β-carbon atoms of the alkyl chain adjacent to the phosphorus atom.[15] Finally, a multiplet at δ = 32.5 consisted of overlapping peaks of the aliphatic γ- and δ-carbon atoms.

Analogous reactions of the bipyridyldiphosphanes **6a**,**b** with bis(benzonitrile) dichloroplatinum(II) afforded poorly soluble products of either polymers or platinacyclophanes, and hence no distinction or separation was possible. Since the solubility of platinacyclophanes of the above-mentioned type is strongly dependent on the kind of the ligands attached to platinum, for further reactions cyclooctadienediphenylplatinum(II)[16] was employed as a starting material. When (COD)Pt($C_6H_5$)$_2$ was allowed to react with the ligands **6a**–**c** under high-dilution conditions, soluble products could be obtained. However, only the tetraphosphadiplatinacyclophane **8b** was isolated in acceptable yields (Scheme 2). In the case of **8a**,**c** not only were the yields very low, but several by-products were also formed. The reasons for this behavior can be summarized as follows: (i) owing to the chelate effect of cyclooctadiene and the strengthening of the metal–carbon π back bond caused by the *trans*-positioned phenyl ligands which are strong σ donors, cyclooctadienediphenylplatinum(II) does not react as fast as bis(benzonitrile)dichloroplatinum(II).[16] This decrease in reaction rate exerts a negative impact on the effectiveness of the high dilution method.[17] (ii) In the case of the employment of cyclooctadienediphenylplatinum, the coordination of the bipyridine moiety in the ligands **6a**–**c** to platinum occurs as a side reaction. Although the ratio of coordinated bipyridine to phosphane is very low, this phenomenon upsets the exact stoichiometry of the starting compounds and favours an undesired polymerization. Nevertheless, the tetraphosphadiplatinacyclophane **8b** was obtained in more than 20% yield, while the isolation of the corresponding tetraphosphadiplatinacyclophanes **8a** and **8c** with shorter and longer alkyl chains failed. This suggested that the size of the 34-membered macrocycle **8b** represents an entropic maximum or enthalpic minimum with regard to the cyclization.[18]

By slow evaporation of the solvent, **8b** crystallized from a mixture of dichloromethane and methanol in the form of pale yellow plates, which were temperature-sensitive and dissolved readily in halogenated hydrocarbons and hot benzene. An FAB mass spectrum of **8b** displayed the expected molecular peak at *m*/*z* = 1915. The $^{31}P\{^1H\}$-NMR spectrum (in $CD_2Cl_2$) consisted of a singlet at δ = 8.8 along with a doublet for the $^{195}$Pt satellites with a coupling constant of 1773 Hz, typical for the *cis*-diphenyldiphosphaneplatinum(II) fragment.[19] The downfield part of the $^{13}C\{^1H\}$-NMR spectrum of **8b** revealed six singlets and three AXX′ spin systems[20] which could be assigned in the same way as in the corresponding spectrum of **7b**. Additionally, three singlets and one AXX′ pattern with platinum satellites were ascribed to the carbon atoms of the Pt($C_6H_5$)$_2$ unit.[19] In the upfield part of the spectrum, three AXX′ patterns were found, which were assigned to the three methylene groups of the alkyl chain.

The introduction of diareneplatinum(II) in the synthesis of metallacyclophanes creates a new possibility for tuning the properties of such compounds by varying the aromatic core. In the last years, a plethora of diareneplatinum(II) compounds with different properties with regard to crystallization, solubility, reactivity, and steric demand of the organometallic fragment was reported.[21] To investigate the practicability of these variations a bulky *tert*-butyl group was introduced in the *para*-position of the phenyl ligand. To achieve this goal, bis(*tert*-butylphenyl)cyclooctadieneplatinum(II)[19] was treated with the bipyridyldiphosphane **6b** under high-dilution conditions in $CH_2Cl_2$. The resulting macrocycle **9b** was obtained in a comparable yield to **8b**, but crystallized even better, which simplified the isolation of the compound. The $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectra of **9b** were similar to those of **8b**, but revealed two additional singlets, related to the *tert*-butyl group in the former case. The FAB mass spectrum displayed the expected molecular peak at *m*/*z* = 2138.

### X-ray Crystal Structures of 8b and 9b

Crystals of the tetraphosphadiplatinacyclophanes **8b** and **9b**, suitable for X-ray crystallography were obtained by slow concentration of a solution of **8b**, **9b** in dichloromethane/methanol. ORTEP diagrams of the molecular structures of **8b**, **9b** with atomic labeling are depicted in Figure 1 and Figure 2, respectively. Because of disordered solvent molecules, the diffraction data are of somewhat restricted quality which, however, is not unusual for macrocycles of the size presented in this investigation.[8,9,10b,22] Surprisingly, both structures are rather similar, despite the steric congestion of the bulky *tert*-butyl groups in **9b**. In both cases, the cavity has the shape of a parallelogram, with edges of lengths of 10.00(2)/11.83(2) Å and 9.92(4)/11.77(3) Å (C16–C3A/C16–C3) for **8b** and **9b**, respectively. The vertices of these parallelograms are occupied by the atoms C3, C3A and C16, C16A with distances of 15.84(3)/15.14(3) Å (**8b**) and 14.58(3)/16.18(6) Å (**9b**). The Pt1–Pt1A distances are 9.782(2) Å (**8b**) and 9.645(3) Å (**9b**). Owing to the center of inversion, the opposite pyridyl units are arranged face to face. The normals of the adjacent pyridyl rings form angles of 15.6(9)° (**8b**) and 14.8(9)° (**9b**). Also very similar are the distances of the bridging atoms of the opposite bipyridine groups (C7–C10A) with 12.08(2) Å (**8b**) and 12.07(3) Å (**9b**). In **8b** and **9b**, one P–phenyl and both Pt–phenyl substituents point to the interior of the macrocycle and exert a shielding effect on the access to the cavity. Nevertheless, a water molecule is encapsulated in **8b** which is not the case in **9b** containing additional bulky and hydrophobic *tert*-butyl groups. Remarkably, the water molecules in **8b** are located in the center of the macrocycle and simultaneously at the vertices of the triclinic unit cell (Figure 3). The two platinum atoms of each macrocycle and the encapsulated water molecule are arranged on an axis, which is indicated by dotted lines. Figure 3 demonstrates the appearance of tubes formed by the macrocycles along the *b* axis.

### Encapsulation of Copper(I)

The tetraphosphadimetallacyclophanes **7c**, **8b**, and **9b** are provided with bipyridine units, which are available to coordinate transition metals which prefer a tetrahedral envir-

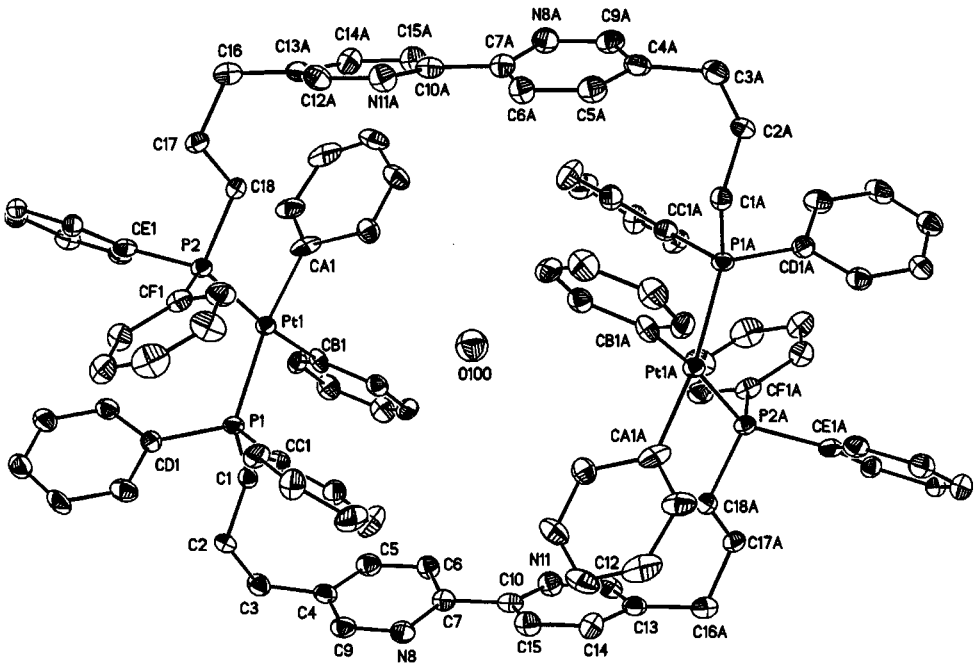



Figure 1. Molecular structure of **8b** · 3 $H_2O$ · 2 $CH_2Cl_2$ in the crystal; ORTEP plot with thermal ellipsoids at 20% probability; hydrogen atoms are omitted for clarity; selected distances [A]: Pt1–CA1 = Pt1A–CA1A = 2.01(2), Pt1–CB1 = Pt1A–CB1A = 2.02(1), Pt1–P1 = Pt1A–P1A = 2.313(3), Pt1–P2 = Pt1A–P2A = 2.330(3)

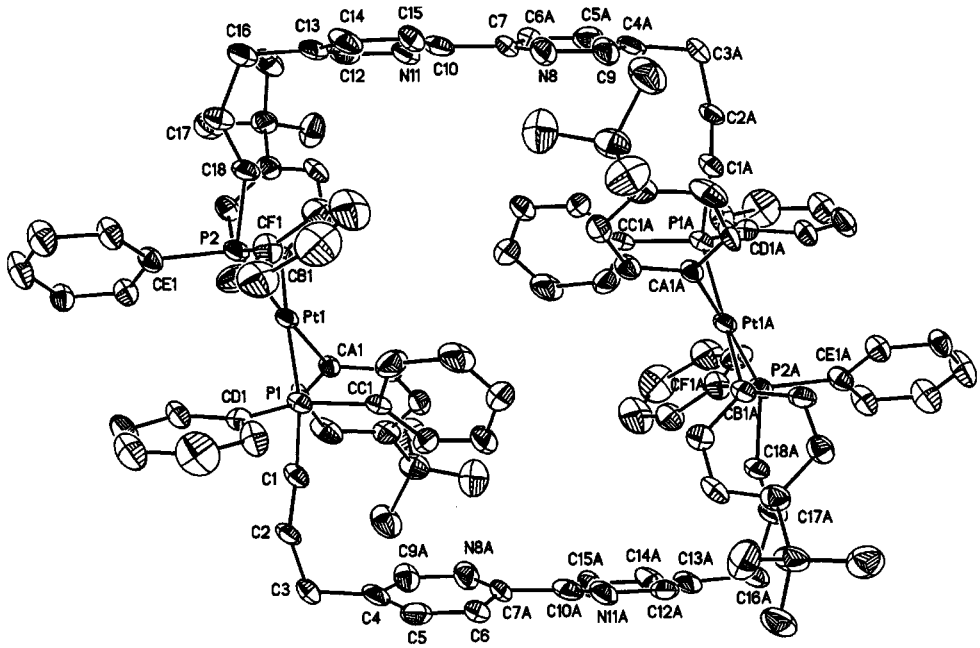



Figure 2. Molecular structure of **9b** · 2 $CH_2Cl_2$ in the crystal; ORTEP plot with thermal ellipsoids at 20% probability; hydrogen atoms are omitted for clarity; selected distances [A]: Pt1–CA1 = Pt1A–CA1A = 2.03(2), Pt1–CB1 = Pt1A–CB1A = 2.08(2), Pt1–P1 = Pt1A–P1A = 2.310(6), Pt1–P2 = Pt1A–P2A = 2.315(5)

onment. The incorporation of the bipyridine ligands into a macrocyclic framework should enhance the stability of such a complex. This phenomenon is known as the macrocyclic effect.[23] Owing to its better solubility, the macrocycle **8b** was chosen for encapsulation studies. Upon treatment of a solution of **8b** in dichloromethane with $[Cu(NCMe)_4][BF_4]$,[24] its color immediately turned from pale yellow to deep red, indicating the formation of a bis(bipyridine)copper(I) complex. Indeed, after purification the host/guest compound **10b** (Scheme 3) was obtained as a red–brown solid, which was air- and temperature-sensitive. An FAB mass spectrum confirmed the composition of **10b**. The $^{31}P\{^1H\}$-NMR spectrum of **10b** was still characterized by a singlet ($\delta$ = 9.8) along with two platinum satellites ($^1J_{PtP}$ = 1778 Hz). Only the $^{13}C$-NMR signals of the bipyridine framework show a difference in chemical shifts of up to

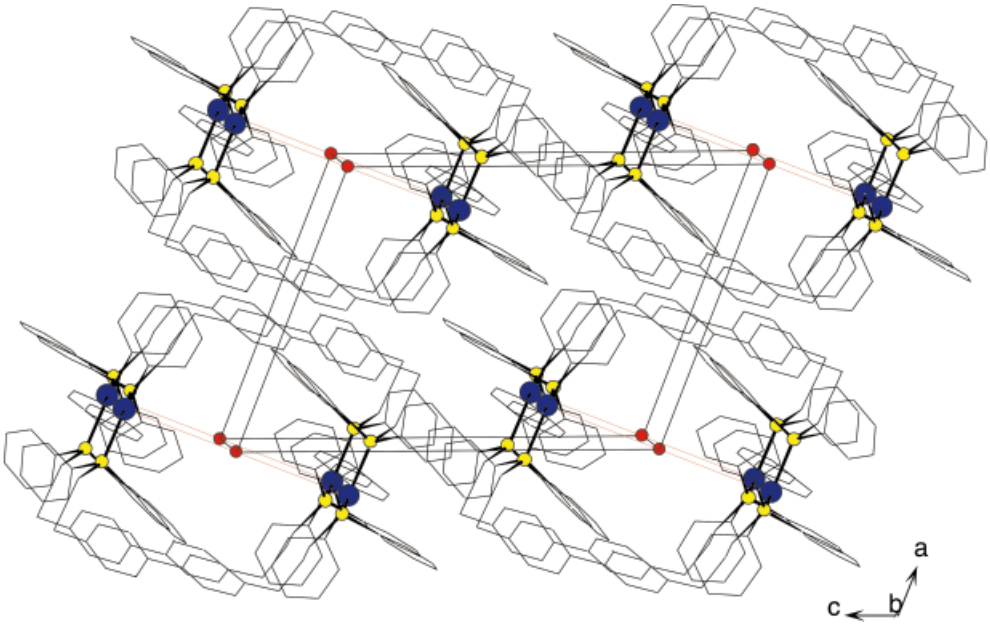
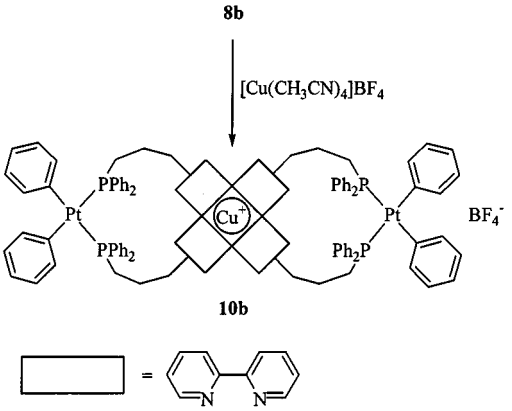



Figure 3. A view of the tubes formed by the macrocycle **8b** along the *b* axis of the crystal




Scheme 3. Encapsulation of copper(I) into the macrocycle **8b**

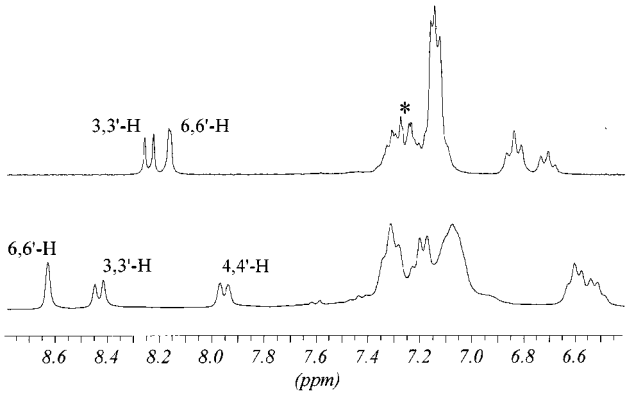



Figure 4. Comparison of the aromatic part of the $^1$H-NMR spectra of **8b** (top) and **10b** (bottom); resonances of protons of the bipyridine units are labeled; the asterisk marks the position of the 4,4′-H resonances of the bipyridine units in **8b** as determined by a 2D COSY NMR experiment

4.5 ppm, which was traced back to the coordination of copper(I); all other $^{13}$C resonances were similar to those of **8b**. A comparison of the downfield part of the $^1$H-NMR spectra of **10b** and **8b** showed that the resonances of the bipyridine protons also underwent remarkable shifts (Figure 4). The tetrahedral coordination of copper(I)[25] is responsible for a lowering of the symmetry causing a prochirality of the protons of the alkyl chain in **10b**.[26] Because of this prochirality, their $^1$H-NMR signals are broadened, which is rationalized by an ABCDEFXX′ spin system. In particular, the $^1$H-NMR signals of the γ-methylene groups adjacent to the bipyridine backbone were examined by a comparison of the HMQC spectra of **10b** and **8b**. As a result, the change of the splitting pattern from a triplet (**8b**) to *two* multiplets (**10b**) is observed, which is explained by the magnetic nonequivalence of the two protons, caused by their prochirality. Apart from a slight broadening of the $^1$H and $^{13}$C resonances, no chemical exchange effects[27] were observed, which is in agreement with the use of the non-coordinating counterion[27b,28] and solvent,[29] the chelate effect of the macrocyclic ligand,[23,30] the shielding of the copper center by the bulky organometallic units, and the rigidity of the host/guest complex **10b**. In the $^{19}$F-NMR spectrum of **10b**, the presence of the counterion $BF_4^-$ is confirmed by a singlet at $\delta = -153.0$. An intensive absorption at 1056 cm$^{-1}$ in the IR spectrum is assigned to the triply degenerate $BF_3$ vibration.

The electrochemical behavior of the host/guest complex **10b** was investigated by cyclic voltammetry. A quasi-reversible wave at $E_{1/2} = -0.31$ V vs. fc/fc$^+$ in $CH_2Cl_2/CH_3CN$ was attributed to the $Cu^{I}/Cu^{II}$ redox system. The $E_{1/2}$ value was similar to that of $[Cu(bipy)_2]^+$ [31] and its derivatives which are not substituted at the 6-position.[32] Typical of the low $E_{1/2}$ value was the easy and fast oxidation of copper(I) to copper(II) when a solution of **10b** was exposed to air. This was accompanied by a change in color from deep red to green.[33] Obviously, the above-mentioned stabilization of the bis(bipyridine)copper(I) complex does not include inertness toward oxygen, which can only be achieved by the introduction of substituents at the 6-position.[34,35]

On the other hand, such air-sensitive bis(bipyridine)copper(I) systems have applications in the field of redox catalysis.[36,37]

A electrodeposition–redissolution peak system at $E_{1/2}$ = –0.79 V is traced back to the formation of copper(0) at the surface of the working electrode.[31] Finally, an irreversible peak was found at 0.92 V caused by the oxidation of the diphenyldiphosphaneplatinum(II) fragment.

## Conclusion

The incorporation of transition metals into the framework of cyclophanes has opened new perspectives in the field of macrocyclic chemistry.[5–9] Most of these systems were constructed using phosphorus or nitrogen donor functions and in particular they were provided with diphenylphosphane or bipyridine units.[9] However, surprisingly little attention has been paid to systems which combine both types of these ligand systems.[10] In the present investigation, the synthesis of new hybrid bipyridylphosphane ligands was introduced, enabling the formation of metallacyclophanes by the employment of P donors only. Major problems that had to be overcome to achieve the desired binuclear macrocycles were the formation of polymers, the premature complexation of bipyridine as a side reaction, and the poor solubility of the products. These drawbacks could largely be eliminated by variation of both the organometallic fragment and the length of the alkyl chain between the bipyridine and the phosphane units. As a result of these examinations, the tetraphosphadiplatinacyclophanes **8b** and **9b** were obtained, which exhibit satisfactory solubility and crystallization properties. At least two methylene groups between bipyridine and the phosphane were a prerequisite for sufficient flexibility to include tetrahedrally coordinated transition metals. The occurrence of undesirable mononuclear products was successfully prevented by the 5,5′-substitution pattern at the bipyridine cores. Owing to the presence of bipyridines which were still uncoordinated and the solubility of the macrocycle **8b** in solvents of medium polarity, it was possible to encapsulate copper(I) in **8b**. The resulting host/guest complex **10b** has three metal atoms with different coordination environments. The macrocycles described in this publication also represent an important step in the design of organometallic analogues of the tris(bipyridine) cages published by Vögtle et al.[11]

## Experimental Section

**General:** All reactions were carried out under dry argon. Solvents were dried with appropriate reagents and stored under dry argon. – Column chromatography was performed using activated silica gel, 0.063–0.200 mm (Merck); column dimensions are reported in the specific sections describing the synthesis of the respective compounds. – Elemental analyses were carried out with a Carlo Erba 1106 and an Elementar Vario EL analyzer. Cl and S analyses were carried out according to Schöniger.[38] Chlorine and sulphur were determined as described by Dirscherl and Erne[39] according to Brunisholz and Michot,[40] and Wagner,[41] respectively. Copper and platinum were quantitatively analyzed with a Varian AA20 spectrometer. – Mass spectra: EI-MS Finnigan TSQ 70 (200 °C). FD- and FAB-MS: Finnigan 711A (8 kV), modified by AMD. ESI spectra were recorded with a triple-quadrupole mass spectrometer API III (Sciex, Thornhill, Canada) equipped with a nebulizer-assisted electrospray source. – FT-IR: Bruker IFS 48. – $^{1}$H, $^{13}$C{$^{1}$H}, $^{31}$P{$^{1}$H}, and $^{19}$F{$^{1}$H} NMR: Bruker DRX 250 spectrometer operating at 250.13, 62.90, 101.26, and 235.33 MHz, respectively. $^{1}$H chemical shifts were referenced to the residual proton peaks of the solvent and are quoted in ppm downfield from TMS. $^{13}$C chemical shifts were calibrated against the deuterated solvent multiplets and referenced to TMS. $^{31}$P chemical shifts were measured relative to external 85% $H_3PO_4$ with downfield values being taken as positive. $^{19}$F chemical shifts were measured relative to external 0.05% 1,3,5-trifluorotoluene. The assignment of the signals has been supported by DEPT-135 (Distortionless Enhancement by Polarization Transfer), homonuclear, and heteronuclear correlation spectra, when necessary. – The electrochemical experiments were performed with a Bioanalytical Systems (BAS, West Lafayette, IN) CV-50 W electrochemical workstation controlled by a standard 80486 personal computer (control program version 2.0). For electroanalytical experiments a Metrohm Pt electrode tip (Filderstadt, Germany) was used as working electrode. The counter electrode was a Pt wire of 1 mm diameter. A single-unit Habber–Luggin double reference-electrode[42] was used. The resulting potential values refer to Ag/$Ag^+$ (0.01 M in $CH_3CN$/0.1 M $NBu_4PF_6$). Ferrocene was used as an external standard. Its potential was determined by separate cyclic voltammetric experiments in the respective solvent, and all potentials were rescaled to $E°$(fc/$fc^+$) (0.145 V in $CH_2Cl_2$/$CH_3CN$ vs Ag/$Ag^+$). All potentials in the present paper are reported relative to the fc/$fc^+$ standard.[43] For cyclic voltammetry, a gas-tight full-glass three-electrode cell was used: its assembly for the experiments has been described.[44] The cell was purged with argon before it was filled with the electrolyte. Background curves were recorded before adding the substrate to the solution. These were later subtracted from the experimental data with substrate. The automatic BAS CV-50 W *iR*-drop compensation facility was used for all experiments. – *N*-Chlorosuccinimide, lithium aluminum hydride, oxirane, ferrocene, and methanesulfonyl chloride were of commercial grade and used without further purification; the latter was stored under argon. 5,5′-Dimethyl-2,2′-bipyridine,[11] 1-tetrahydropyranyloxy-3-iodopropane,[13] lithium diphenylphosphide,[45] bis(benzonitrile)-dichloroplatinum(II),[14] cyclooctadienediphenylplatinum(II),[16] and bis(*tert*-butylphenyl)cyclooctadieneplatinum(II)[19] were synthesized according to literature methods.

**5,5′-Bis(chloromethyl)-2,2′-bipyridine (1):** 5,5′-Dimethyl-2,2′-bipyridine (30.0 g, 163.0 mmol), *N*-chlorosuccinimide (52.2 g, 391.2 mmol), and benzoyl peroxide (500 mg, 1.74 mmol) were suspended in $CCl_4$ (1300 mL). The suspension was heated at reflux for 48 h, and filtered hot (P3). The filtrate was concentrated to 200 mL under reduced pressure and the precipitated product was collected on a filter (P3). The crude product was purified by recrystallization from benzene. Yield 20.9 g (50.6%), colorless solid, m.p. 165 °C. – $^{1}$H NMR ($CDCl_3$): δ = 8.67 (d, $^{4}J_{HH}$ = 2.0 Hz, 2 H, 6,6′-H, bipy), 8.40 (d, $^{3}J_{HH}$ = 8.2 Hz, 2 H, 3,3′-H, bipy), 7.86 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 2.0 Hz, 2 H, 4,4′-H, bipy), 4.64 (s, 4 H, $CH_2Cl$). – $^{13}$C{$^{1}$H} NMR ($CDCl_3$): δ = 155.7 (s, C, bipy), 149.2 (s, CH, bipy), 137.4 (s, CH, bipy), 133.6 (s, C, bipy), 121.3 (s, CH, bipy), 43.2 (s, $CH_2Cl$). – MS (EI); *m/z*: 252.0 [$M^+$]. – $C_{12}H_{10}Cl_2N_2$ (253.1): calcd. C 56.94, H 3.98, Cl 28.01, N 11.07; found C 57.10, H 3.83, Cl 27.91, N 10.95.

**5,5′-Bis(cyanomethyl)-2,2′-bipyridine (2):** Compound **1** (15.0 g, 59.3 mmol) was dissolved in a mixture of ethanol (400 mL) and concentrated hydrochloric acid (7 mL). This solution was added dropwise over a period of 30 min to a refluxing solution of sodium cyanide (23.6 g, 480.6 mmol) in 500 mL of water and 500 mL of ethanol (***Caution: Generation of hydrogen cyanide!***). The solution was then heated at reflux for further 2 h and concentrated to a volume of 200 mL under reduced pressure. The remaining solution was diluted with 800 mL of water and the solution was stirred for 30 min. The precipitated product was filtered (P3) and washed with water (2 × 100 mL). The residue was dissolved in 300 mL of acetone and filtered (P3). The solvent of the filtrate was evaporated to dryness to give the crude product, which was used without further purification. Yield 8.3 g (59.3%), brown solid. For analytical data **2** was purified by sublimation and a colorless solid was obtained, m.p. 197 °C. – IR (KBr): $\tilde{\nu}$ = 2256 cm$^{-1}$ (CN). – $^1$H NMR ([D$_6$]acetone): δ = 8.72 (d, $^4J_{HH}$ = 1.9 Hz, 2 H, 6,6′-H, bipy), 8.51 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, 3,3′-H, bipy), 7.99 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, 4,4′-H, bipy), 4.14 (s, 4 H, $CH_2CN$). – $^{13}$C{$^1$H} NMR ([D$_6$]acetone): δ = 155.9 (s, C, bipy), 149.8 (s, CH, bipy), 137.7 (s, CH, bipy), 129.0 (s, C, bipy), 121.6 (s, CH, bipy), 118.6 (s, $CH_2CN$), 21.0 (s, $CH_2CN$). – MS (EI); *m*/*z*: 234.0 [M$^+$]. – $C_{14}H_{10}N_4$ (234.3): calcd. C 71.78, H 4.30, N 23.92; found C 71.80, H 4.14, N 23.37.

**Diester 3:** To a suspension of **2** (7.7 g, 32.9 mmol) in 500 mL of ethanol, at 0 °C dry hydrogen chloride was added until saturation was achieved. The solution was heated at reflux for 18 h and concentrated to dryness under reduced pressure. The residue was suspended in 200 mL of water, neutralized with $NaHCO_3$, and extracted with ethyl acetate (2 × 300 mL). The combined organic layers were dried with $Na_2SO_4$, filtered (P3), and the solution was concentrated to dryness under reduced pressure. The product was purified by column chromatography (ethyl acetate, diameter/length of column 7/50 cm). Yield 5.3 g (48.8%), colorless solid. – M.p. 76 °C. – IR (KBr): $\tilde{\nu}$ = 1736 cm$^{-1}$ (CO). – $^1$H NMR ($CDCl_3$): δ = 8.52 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, 6,6′-H, bipy), 8.30 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 3,3′-H, bipy), 7.69 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, 4,4′-H, bipy), 4.10 (q, $^3J_{HH}$ = 7.1 Hz, 4 H, $COOCH_2CH_3$), 3.61 (s, 4 H, $CH_2COOC_2H_5$), 1.18 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, $COOCH_2CH_3$). – $^{13}$C{$^1$H} NMR ($CDCl_3$): δ = 154.6 (s, C, bipy), 149.6 (s, CH, bipy), 137.6 (s, CH, bipy), 129.8 (s, C, bipy), 120.5 (s, CH, bipy) 61.0 (s, $COOCH_2CH_3$), 38.2 (s, $CH_2COOC_2H_5$), 14.0 (s, $COOCH_2CH_3$). – MS (EI); *m*/*z*: 328.1 [M$^+$]. – $C_{18}H_{20}N_2O_4$ (328.4): calcd. C 65.84, H 6.14, N 8.53; found C 65.52, H 6.14, N 8.56.

**Diol 4a:** Lithium aluminum hydride (1.18 g, 31.03 mmol) was suspended in 100 mL of THF and the suspension was added dropwise to an ice-cold solution of **3** (5.09 g, 15.50 mmol) in 200 mL of THF. The resulting suspension was stirred for 4 h at room temperature, then cautiously quenched with water and concentrated to dryness. The residue was dissolved in 120 mL of water and extracted continuously with diethyl ether for 48 h. The organic layer was dried with $Na_2SO_4$, filtered (P3), and concentrated. The crude product was purified using column chromatography (dichloromethane/methanol, 7:1, diameter/length of column 7/50). Yield 2.15 g (56.8%), colorless solid, m.p 146 °C. – $^1$H NMR ($CD_3OD$): δ = 8.49 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, 6,6′-H, bipy), 8.14 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, 3,3′-H, bipy), 7.79 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, 4,4′-H, bipy), 3.82 (t, $^3J_{HH}$ = 6.7 Hz, 4 H, $CH_2CH_2OH$), 2.90 (t, $^3J_{HH}$ = 6.7 Hz, 4 H, $CH_2CH_2OH$). – $^{13}$C{$^1$H} NMR ($CD_3OD$): δ = 154.7 (s, C, bipy), 150.3 (s, CH, bipy), 139.1 (s, CH, bipy), 136.4 (s, C, bipy), 122.1 (s, CH, bipy), 63.1 (s, $CH_2CH_2OH$), 36.7 (s, $CH_2CH_2OH$). – MS (EI); *m*/*z*: 244.1 [M$^+$]. – $C_{14}H_{16}N_2O_2$ (244.3): calcd. C 68.83, H 6.60, N 11.47; found C 68.31, H 6.11, N 11.27.

**Diol 4b:** A freshly prepared solution of 100.0 mmol of lithium diisopropylamide in 375 mL of a 1:2 mixture of *n*-hexane and THF was added dropwise to a solution of 5,5′-dimethyl-2,2′-bipyridine (18.4 g, 100.0 mmol) in 700 mL of THF at –50 °C. The solution was then allowed to warm to room temperature and stirred for 1 h. Then it was cooled to –50 °C and oxirane (4.9 g, 111.4 mmol) was added. Subsequently the solution was heated to 40 °C for 4 h, while the condenser was kept at –30 °C. The complete procedure had to be repeated. The solution was then quenched with a saturated aqueous $NH_4Cl$ solution until pH = 7 was achieved. THF was removed under reduced pressure and the resulting suspension was extracted seven times with a 2:1 mixture of dichloromethane and ethyl acetate. The combined organic layers were dried with $Na_2SO_4$, filtered (P3), and concentrated. The crude product was purified by column chromatography (dichloromethane/methanol, 10:1, diameter/length of column 7/50). Yield 6.32 g (23.2%), colorless solid, m.p. 119 °C. – $^1$H NMR ($CD_3OD$): δ = 8.47 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, 6,6′-H, bipy), 8.14 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, 3,3′-H, bipy), 7.75 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, 4,4′-H, bipy), 3.59 (t, $^3J_{HH}$ = 6.3 Hz, 4 H, $CH_2CH_2CH_2OH$), 2.76 (t, $^3J_{HH}$ = 7.8 Hz, 4 H, $CH_2CH_2CH_2OH$) 1.86 (m, 4 H, $CH_2CH_2CH_2OH$). – $^{13}$C{$^1$H} NMR ($CD_3OD$): δ = 155.0 (s, C, bipy), 150.3 (s, CH, bipy), 139.5 (s, CH, bipy), 138.7 (s, C, bipy), 122.3 (s, CH, bipy), 61.9 (s, $CH_2CH_2CH_2OH$), 35.0 (s, $CH_2CH_2CH_2OH$), 30.0 (s, $CH_2CH_2CH_2OH$). – MS (EI); *m*/*z*: 272.1 [M$^+$]. – $C_{16}H_{20}N_2O_2$ (272.3): calcd. C 70.56, H 7.40, N 10.29; found C 70.40, H 7.35, N 10.34.

**Diol 4c:** A freshly prepared solution of 100.0 mmol of lithium diisopropylamide in 375 mL of a 1:2 mixture of *n*-hexane and THF was added dropwise to a solution of 5,5′-dimethyl-2,2′-bipyridine (18.4 g, 100.0 mmol) in 700 mL of THF at –50 °C. The solution was allowed to warm to room temperature and stirred for 1 h. Then it was cooled to –78 °C and 1-iodo-3-(tetrahydropyranyloxy)propane (28.4 g, 105.2 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred for 30 min. The complete procedure was repeated. The solution was then quenched with 1 M hydrochloric acid until pH = 0 was achieved, stirred for an additional hour and neutralized with $NaHCO_3$. THF was removed under reduced pressure and the resulting suspension was extracted seven times with a 2:1 mixture of dichloromethane and ethyl acetate. The combined organic layers were dried with $Na_2SO_4$, filtered (P3), and concentrated. The crude product was purified by column chromatography (dichloromethane/methanol, 10:1, diameter/length of column 7/50). Yield 6.11 g (20.4%), colorless solid, m.p. 109 °C. – $^1$H NMR ($CD_3OD$): δ = 8.48 (d, $^4J_{HH}$ = 2.1 Hz, 2 H, 6,6′-H, bipy), 8.17 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 3,3′-H, bipy), 7.80 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, 4,4′-H, bipy), 3.57 (t, $^3J_{HH}$ = 6.3 Hz, 4 H, $CH_2CH_2CH_2CH_2OH$), 2.73 (t, $^3J_{HH}$ = 7.5 Hz, 4 H, $CH_2CH_2CH_2CH_2OH$) 1.74 (m, 4 H, $CH_2$), 1.59 (m, 4 H, $CH_2$). – $^{13}$C{$^1$H} NMR ($CD_3OD$): δ = 155.1 (s, C, bipy), 150.4 (s, CH, bipy), 140.0 (s, CH, bipy), 138.8 (s, C, bipy), 122.4 (s, CH, bipy), 62.8 (s, $CH_2CH_2CH_2CH_2OH$), 33.6 (s, $CH_2$), 33.3 (s, $CH_2$), 28.8 (s, $CH_2$). – MS (EI); *m*/*z*: 300.1 [M$^+$]. – $C_{18}H_{24}N_2O_2$ (300.4): calcd. C 71.96, H 8.06, N 9.32; found C 72.33, H 8.01, N 9.48.

**General Procedure for the Preparation of the Dimesylates 5a–c:** Methanesulfonyl chloride (2.50 g, 22.0 mmol) in 20 mL of dichloromethane was added dropwise to a suspension of **5a–c** (10.0 mmol) and triethylamine (2.22 g, 22.0 mmol) in 200 mL of dichloromethane at 0 °C. The reaction mixture was allowed to

warm to room temperature, stirred for 1 h, and washed with 100 mL of a diluted aqueous $NaHCO_3$ solution. The aqueous layer was reextracted with 100 mL of dichloromethane and the combined organic layers were dried with $Na_2SO_4$, filtered (P3), and concentrated to dryness. The products were washed with 20 mL of cold methanol (0 °C) and dried in vacuo.

**Dimesylate 5a:** Yield 3.61 g (90.3%), colorless solid, m.p. >130 °C (dec.). – $^1$H NMR ($CDCl_3$): δ = 8.56 (d, $^4J_{HH}$ = 1.9 Hz, 2 H, 6,6′-H, bipy), 8.35 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, 3,3′-H, bipy), 7.72 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, 4,4′-H, bipy), 3.13 (t, $^3J_{HH}$ = 6.6 Hz, 4 H, $CH_2CH_2OSO_2CH_3$), 3.13 (t, $^3J_{HH}$ = 6.6 Hz, 4 H, $CH_2CH_2OSO_2CH_3$), 2.93 (s, 6 H, $CH_2CH_2OSO_2CH_3$). – $^{13}$C{$^1$H} NMR ($CDCl_3$): δ = 154.8 (s, C, bipy), 149.7 (s, CH, bipy), 137.7 (s, CH, bipy), 132.4 (s, C, bipy), 121.1 (s, CH, bipy), 69.3 (s, $CH_2CH_2OSO_2CH_3$), 37.7 (s, $CH_2CH_2OSO_2CH_3$), 32.9 (s, $CH_2CH_2OSO_2CH_3$). – MS (FD, 30 °C); *m/z*: 400.1 [M$^+$]. – $C_{16}H_{20}N_2O_6S_2$ (400.6): calcd. C 47.99, H 5.03, N 7.00, S 16.01; found C 47.98, H 5.08, N 6.93, S 15.73.

**Dimesylate 5b:** Yield 3.60 g (84.2%), colorless solid, m.p. >130 °C (dec.). – $^1$H NMR ($CDCl_3$): δ = 8.54 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, 6,6′-H, bipy), 8.32 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 3,3′-H, bipy), 7.67 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, 4,4′-H, bipy), 4.27 (t, $^3J_{HH}$ = 6.2 Hz, 4 H, $CH_2CH_2CH_2OSO_2CH_3$), 3.00 (s, 6 H, $CH_2CH_2CH_2OSO_2CH_3$), 2.84 (t, $^3J_{HH}$ = 7.6 Hz, 4 H, $CH_2CH_2CH_2OSO_2CH_3$), 2.13 (m, 4 H, $CH_2CH_2CH_2OSO_2CH_3$). – $^{13}$C{$^1$H} NMR ($CDCl_3$): δ = 154.1 (s, C, bipy), 149.2 (s, CH, bipy), 137.4 (s, CH, bipy), 136.1 (s, C, bipy), 121.1 (s, CH, bipy), 68.8 (s, $CH_2CH_2CH_2OSO_2CH_3$), 37.6 (s, $CH_2CH_2CH_2OSO_2CH_3$), 30.5 (s, $CH_2CH_2CH_2OSO_2CH_3$), 28.8 (s, $CH_2CH_2CH_2OSO_2CH_3$). – MS (FD, 30 °C); *m/z*: 428.0 [M$^+$]. – $C_{18}H_{24}N_2O_6S_2$ (428.6): calcd. C 50.45, H 5.64, N 6.54, S 14.97; found C 49.96, H 5.73, N 6.41, S 14.82.

**Dimesylate 5c:** Yield 3.71 g (81.4%), colorless solid, m.p. >130 °C (dec.). – $^1$H NMR ($CDCl_3$): δ = 8.45 (d, $^4J_{HH}$ = 2.1 Hz, 2 H, 6,6′-H, bipy), 8.24 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 3,3′-H, bipy), 7.59 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, 4,4′-H, bipy), 4.21 (t, $^3J_{HH}$ = 6.0 Hz, 4 H, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 2.96 (s, 6 H, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 2.68 (t, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 1.65–1.85 (m, 8 H, $CH_2CH_2CH_2CH_2OSO_2CH_3$). – $^{13}$C{$^1$H} NMR ($CDCl_3$): δ = 154.1 (s, C, bipy), 149.1 (s, CH, bipy), 137.0 (s, CH, bipy), 136.9 (s, C, bipy), 120.7 (s, CH, bipy), 69.7 (s, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 37.6 (s, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 30.5 (s, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 28.7 (s, $CH_2$), 27.0 (s, $CH_2$). – MS (FD, 30 °C); *m/z*: 456.0 [M$^+$]. – $C_{20}H_{28}N_2O_6S_2$ (456.6): calcd. C 52.61, H 6.18, N 6.13, S 14.04; found C 52.50, H 6.32, N 6.14, S 14.04.

**General Procedure for the Preparation of the Diphosphanes 6a–c:** A freshly prepared solution of lithium diphenylphosphide (1.69 g, 8.8 mmol) in 50 mL of THF was added dropwise to a solution of 8.0 mmol of **6a–c** in 200 mL of THF at –78 °C. The solution was allowed to warm to room temperature, stirred for 30 min and quenched with degassed water. The solvent was completly removed under reduced pressure and the residue was washed two times with 10 mL of cold methanol (0 °C). The remainder was dissolved in 50 mL of dichloromethane, and the solution was filtered (P4), and then concentrated in vacuo.

**Diphosphane 6a:** Yield 4.23 g (91.1%), colorless, slightly air-sensitive solid, m.p. 156 °C. – $^1$H NMR ($CDCl_3$): δ = 8.45 (d, $^4J_{HH}$ = 1.9 Hz, 2 H, 6,6′-H, bipy), 8.26 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, 3,3′-H, bipy), 7.59 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, 4,4′-H, bipy), 7.47–7.27 (m, 20 H, Ph), 2.75 (m, 4 H, $CH_2CH_2PPh_2$), 2.36 (m, 4 H, $CH_2CH_2PPh_2$). – $^{13}$C{$^1$H} NMR ($CDCl_3$): δ = 153.8 (s, C, bipy), 149.0 (s, CH, bipy), 138.3–138.0 (m, *ipso*-Ph and C, bipy), 136.9 (s, CH, bipy), 132.8 (d, $^2J_{PC}$ = 18.6 Hz, *ortho*-Ph), 128.9 (s, *para*-Ph), 128.7 (d, $^3J_{PC}$ = 6.4 Hz, *meta*-Ph), 121.1 (s, CH, bipy), 29.9 (d, $CH_2$), 29.3 (d, $CH_2$). – $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = –15.1 (s). – MS (FAB, 30 °C); *m/z*: 581.3 [M$^+$ + H]. – $C_{38}H_{34}N_2P_2$ (580.6): calcd. C 78.61, H 5.90, N 4.82; found C 78.29, H 5.51, N 4.69.

**Diphosphane 6b:** Yield 4.30 g (88.4%), colorless, slightly air sensitive solid, m.p. 163 °C. – $^1$H NMR ($CDCl_3$): δ = 8.45 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, 6,6′-H, bipy), 8.23 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 3,3′-H, bipy), 7.55 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, 4,4′-H, bipy), 7.42–7.28 (m, 20 H, Ph) 2.78 (t, $^3J_{HH}$ = 7.2 Hz, 4 H, $CH_2CH_2CH_2PPh_2$), 2.06 (m, 4 H, $CH_2CH_2CH_2PPh_2$), 1.73 (m, 4 H, $CH_2CH_2CH_2PPh_2$). – $^{13}$C{$^1$H} NMR ($CDCl_3$): δ = 154.3 (s, C, bipy), 149.6 (s, CH, bipy), 138.6 (d, $^1J_{PC}$ = 12.8 Hz, *ipso*-Ph), 137.1 (s, C, bipy), 137.0 (s, CH, bipy), 132.8 (d, $^2J_{PC}$ = 18.5 Hz, *ortho*-Ph), 128.8–128.5 (m, *meta*- and *para*-Ph), 120.6 (s, CH, bipy), 34.1 (d, $^3J_{PC}$ = 13.8 Hz, $CH_2CH_2CH_2PPh_2$), 27.7–27.3 (m, 8 H, $CH_2CH_2CH_2PPh_2$). – $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = –15.5 (s). – MS (FAB, 50 °C); *m/z*: 609.0 [M$^+$ + H]. – $C_{40}H_{38}N_2P_2$ (608.7): calcd. C 78.93, H 6.29, N 4.60; found C 79.06, H 6.44, N 4.45.

**Diphosphane 6c:** Yield 4.51 g (88.6%), colorless, slightly air sensitive solid, m.p. 132 °C. – $^1$H NMR ($CDCl_3$): δ = 8.41 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, 6,6′-H, bipy), 8.20 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, 3,3′-H, bipy), 7.50 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, 4,4′-H, bipy), 7.43–7.25 (m, 20 H, $PPh_2$), 2.60 (t, $^3J_{HH}$ = 7.6 Hz, 4 H, $CH_2CH_2CH_2CH_2PPh_2$), 2.06 (m, 4 H, $CH_2CH_2CH_2CH_2PPh_2$), 1.87–1.68 (m, 8 H, $CH_2CH_2CH_2CH_2PPh_2$). – $^{13}$C{$^1$H} NMR ($CDCl_3$): δ = 154.1 (s, C, bipy), 149.3 (s, CH, bipy), 138.8 (d, $^1J_{PC}$ = 13.0 Hz, *ipso*-Ph), 137.5 (s, C, bipy), 136.7 (s, CH, bipy), 132.8 (d, $^2J_{PC}$ = 18.5 Hz, *ortho*-Ph), 128.6 (s, *para*-Ph), 128.5 (d, $^3J_{PC}$ = 6.5 Hz, *meta*-Ph), 120.5 (s, CH, bipy), 32.5–32.2 (m, $CH_2CH_2CH_2CH_2PPh_2$ and $CH_2CH_2CH_2CH_2PPh_2$) 28.0 (d, $^1J_{PC}$ = 11.5 Hz, $CH_2CH_2CH_2CH_2PPh_2$), 25.7 (d, $^2J_{PC}$ = 16.2 Hz, $CH_2CH_2CH_2CH_2PPh_2$). – $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = –15.3 (s). – MS (FAB, 30 °C); *m/z*: 637.3 [M$^+$ + H]. – $C_{42}H_{42}N_2P_2$ (636.8): calcd. C 79.22, H 6.65, N 4.40; found C 78.83, H 6.70, N 4.21.

**Tetrachlorodiplatinacyclophane 7c:** Solutions of bis(benzonitrile)-dichloroplatinum(II) (1.35 g, 2.858 mmol) and of **6c** (1.82 g, 2.860 mmol) in 200 mL of dichloromethane each were simultaneously added dropwise within 2 h into 200 mL of dichloromethane. After the solution was stirred for 30 min and concentrated to 10 mL in vacuo, polymeric fractions precipitated. These were removed by filtration (P4) and the filtrate was concentrated to dryness. The residue was washed intensively with *n*-pentane, dissolved in 100 mL of hot chloroform, and the resulting solution was cooled to room temperature, filtered (P4), and concentrated to dryness. Yield: 1.52 g (58.9%), colorless solid, m.p. >290 °C (dec.). – $^1$H NMR ($CD_2Cl_2$): δ = 8.35 (d, 4 H, 6,6′-H, bipy), 8.24 (d, $^3J_{HH}$ = 8.1 Hz, 4 H, 3,3′-H, bipy), 7.53–7.18 (m, 44 H, $PPh_2$ and 4,4′-H, bipy), 2.54 (t, $^3J_{HH}$ = 7.6 Hz, 8 H, $CH_2CH_2CH_2CH_2PPh_2$), 2.12 (m, 8 H, $CH_2CH_2CH_2CH_2PPh_2$), 1.75–1.48 (m, 16 H, $CH_2CH_2CH_2CH_2PPh_2$). – $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 154.6 (s, C, bipy), 149.8 (s, CH, bipy), 137.9 (s, C, bipy), 137.1 (s, CH, bipy), 134.0 (m,[46] *N* = 9.5 Hz, *ortho*-Ph), 131.7 (s, *para*-Ph), 130.1 (m,[46] *N* = 58.8 Hz, *ipso*-Ph), 129.0 (m,[46] *N* = 10.2 Hz, *meta*-Ph), 120.8 (s, CH, bipy), 32.9–32.1 (m, $CH_2CH_2CH_2CH_2PPh_2$), 30.0 (m,[46] *N* = 39.5 Hz, $CH_2CH_2CH_2CH_2PPh_2$), 25.4 (s br,[14,46] $CH_2CH_2CH_2CH_2PPh_2$). – $^{31}$P{$^1$H} NMR ($CD_2Cl_2$): δ = 8.4 (s, d, $^1J_{PtP}$ = 3646 Hz). – MS (ES); *m/z*: 1769.4 [M$^+$ – Cl]. –

$C_{84}H_{84}Cl_4N_4P_4Pt_2$ (1805.5): calcd. C 55.88, H 4.69, Cl 7.85, N 3.10, Pt 21.61; found C 55.65, H 4.73, Cl 7.70, N 3.41, Pt 20.96.

**General Procedure for the Tetraaryldiplatinacyclophanes 8b and 9b:** Solutions of cyclooctadienediphenylplatinum(II) or bis(*tert*-butylphenyl)cyclooctadieneplatinum(II) (3.38 mmol) and of **6b** (2.06 g, 3.39 mmol) in 400 mL of dichloromethane each were simultaneously added dropwise during 5 h into 500 mL of dichloromethane. The solution was stirred overnight and concentrated. The residue was purified by column chromatography (dichloromethane/methanol, 50:1, diameter/length of column 7/50) and recrystallized twice from dichloromethane/methanol.

**Tetraphenyldiplatinacyclophane 8b:** Yield: 670 mg (20.7%), pale yellow plates, m.p. >150 °C (dec.). – $^1$H NMR ($CD_2Cl_2$): δ = 8.26 (d, $^3J_{HH}$ = 8.2 Hz, 4 H, 3,3′-H, bipy), 8.18 (d, $^4J_{HH}$ = 2.0 Hz, 4 H, 6,6′-H, bipy), 7.37–7.10 (m, 52 H, $Ph_2P$, $Ph_2Pt$ and 4,4′-H, bipy), 6.92–6.67 (m, 12 H, $Ph_2Pt$), 2.19 (t, $^3J_{HH}$ = 6.3 Hz, 8 H, $CH_2CH_2CH_2PPh_2$), 1.65–1.25 (m, 16 H, $CH_2CH_2CH_2PPh_2$). – $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 161.5 (m,[46] $^1J_{PtC}$ = 840.8 Hz, *ipso*-$Ph_2Pt$), 154.5 (s, C, bipy), 149.8 (s, CH, bipy), 137.7–136.8 (m, C, bipy, CH, bipy, *ortho*-$Ph_2Pt$), 133.5 (m,[46] *N* = 10.0 Hz, *ortho*-$Ph_2P$), 132.9 (m,[46] *N* = 41.3 Hz, *ipso*-$Ph_2P$), 130.1 (s, *para*-$Ph_2P$), 128.4 (m,[46] *N* = 8.5 Hz, *meta*-$Ph_2P$), 127.5 (s, d, $^3J_{PtC}$ = 65.5 Hz, *meta*-$Ph_2Pt$), 121.6 (s, *para*-$Ph_2Pt$), 120.4 (s, CH, bipy), 34.2 (m,[46] *N* = 13.5 Hz, $CH_2CH_2CH_2PPh_2$), 27.8 (m,[46] *N* = 33.4 Hz, $CH_2CH_2CH_2PPh_2$), 26.6 (s, br,[14,46] $CH_2CH_2CH_2PPh_2$). – $^{31}$P{$^1$H} NMR ($CD_2Cl_2$): δ = 8.8 (s, d, $^1J_{PtP}$ = 1773 Hz). – MS (FAB, 30 °C); *m/z*: 1915.6 [$M^+$], 1761.0 [$M^+$– 2 Ph], 1684.4 [$M^+$– 3 Ph], 1607.3 [$M^+$– 4 Ph]. – $C_{104}H_{96}N_4P_4Pt_2$ (1916.0): calcd. C 65.20, H 5.05, N 2.92, Pt 20.36; found C 65.16, H 5.28, N 2.97, Pt 19.95.

**Tetrakis(*tert*-butylphenyl)diplatinacyclophane 9b:** Yield: 840 mg (23.2%), pale yellow plates, m.p. >145 °C (dec.). – $^1$H NMR ($CD_2Cl_2$): δ = 8.25 (d, $^3J_{HH}$ = 8.2 Hz, 4 H, 3,3′-H, bipy), 8.15 (d, $^4J_{HH}$ = 2.0 Hz, 4 H, 6,6′-H, bipy), 7.36–7.12 (m, 52 H, $Ph_2P$, $Ph_2Pt$ and 4,4′-H, bipy), 6.98–6.89 (m, 8 H, $PtPh_2$), 2.14 (t, $^3J_{HH}$ = 6.3 Hz, 8 H, $CH_2CH_2CH_2PPh_2$), 1.58–1.22 [m, 52 H, $CH_2CH_2CH_2PPh_2$, and $C(CH_3)_3$]. – $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 157.4 [m,[46] *ipso*-(*tert*-butylPh)$_2$Pt], 154.5 (s, C, bipy), 149.8 (s, CH, bipy), 144.0 [s, *para*-(*tert*-butylPh)$_2$Pt], 137.2 (s, C, bipy) 137.1 (s, CH, bipy), 136.6 [s, d, $^2J_{PtC}$ = 34.8 Hz, *ortho*-(*tert*-butylPh)$_2$Pt], 133.5 (m,[46] *N* = 10.7 Hz, *ortho*-$Ph_2P$), 133.0 (m,[46] *N* = 41.3 Hz, *ipso*-$Ph_2P$), 130.0 (s, *para*-$Ph_2P$), 128.4 (m,[46] *N* = 9.3 Hz, *meta*–$Ph_2P$), 124.4 [s, d, $^3J_{PtC}$ = 64.0 Hz, *meta*-(*tert*-butylPh)$_2$Pt], 120.6 (s, CH, bipy), 34.3–34.0 [m, $CH_2CH_2CH_2PPh_2$ and $C(CH_3)_3$],

Table 1. Crystal data, data collection and structure refinement for compounds **8b** and **9b**

| | **8b** | **9b** |
|---|---|---|
| *Crystal data* | | |
| Empirical formula | $C_{106}H_{106}Cl_4N_4O_3P_4Pt_2$ | $C_{122}H_{132}Cl_4N_4P_4Pt_2$ |
| Formula weight | 2139.81 | 2310.18 |
| Crystal system | Triclinic | Orthorhombic |
| Space group | $P\bar{1}$ | *Pbcn* |
| *Z* | 1 | 4 |
| $d_{calcd.}$[g/cm$^3$] | 1.444 | 1.307 |
| *a* [Å] | 12.422(2) | 19.769(6) |
| *b* [Å] | 12.970(1) | 23.409(5) |
| *c* [Å] | 16.723(2) | 25.374(8) |
| α [°] | 90.11(1) | 90 |
| β [°] | 110.29(1) | 90 |
| γ [°] | 102.26(1) | 90 |
| *V* [Å$^3$] | 2461(1) | 11742(6) |
| μ [mm$^{-1}$] | 7.252 | 2.572 |
| *F*(000) | 1078 | 4704 |
| *Data Collection* | | |
| Radiation | Cu-$K_\alpha$ | Mo-$K_\alpha$ |
| Monochromator | graphite | graphite |
| Crystal size [mm] | 0.25 × 0.25 × 0.15 | 0.20 × 0.30 × 0.40 |
| Temperature [K] | 213 | 173 |
| Scan mode | ω | ω |
| $\theta_{min/max}$ [°] | 2.77/32.52 | 2.06/27.60 |
| *hkl* range | *h* –1/14 | *h* –1/25 |
| | *k* –15/14 | *k* –30/1 |
| | *l* –19/18 | *l* –33/1 |
| Measured reflections | 9619 | 15388 |
| Unique reflections | 8352 | 13356 |
| Absorption correction | Ψ scans | none |
| $T_{max}/T_{min}$ | 0.9715/0.6456 | |
| *Refinement* | | |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 8352/2/573 | 13356/0/598 |
| Hydrogen treatment | Calculated except solvent molecules | calculated |
| Final *R* Values [$I > 2\sigma(I)$] | | |
| *R*1[a] | 0.0891 | 0.1154 |
| *wR*2[b] | 0.2333 | 0.3174 |
| $\rho_{residual}$(max/min) [eÅ$^{-3}$] | 3.465/–5.865 | 4.393/–2.292 |

[a] $R1 = \Sigma||F_o| - |Fc||/\Sigma|F_o|$. – [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/[\Sigma[w(F_o^2)]\}^{1/2}$; $w = 1/[\delta^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0946$; $b = 8.58$. – $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

31.9 [s, C($CH_3$)$_3$], 27.7 (m,[46] $N$ = 32.7 Hz, $CH_2CH_2CH_2PPh_2$), 26.5 (s, br,[14,46] $CH_2CH_2CH_2PPh_2$). – $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): δ = 9.1 (s, d, $^1J_{PtP}$ = 1763 Hz). – MS (FAB, 30 °C); *m/z*: 2138.8 [$M^+$ – H], 1873.5 [$M^+$ – 2 *tert*-butylPh], 1740.2 [$M^+$ – 3 *tert*-butylPh], 1607.2 [$M^+$ – 4 *tert*-butylPh]. – $C_{120}H_{128}N_4P_4Pt_2$ (2140.4): calcd. C 67.34, H 6.03, N 2.62, Pt 18.23; found C 67.11, H 6.06, N 2.44, Pt 17.88.

**Copper Complex 10b:** $[Cu(CH_3CN)_4][BF_4]$ (47.2 mg, 0.15 mmol) in 4 mL of acetonitrile was added to a solution of **8b** (287.4 mg, 0.15 mmol) in 10 mL of dichloromethane. The solution was stirred for 15 min and concentrated. The residue was dissolved in 10 mL of dichloromethane, precipitated with 40 mL of *n*-pentane, filtered (P4), and washed with benzene/dichlormethane (1:1). Yield: 257.6 mg (83.1%), red-brown, air-sensitive solid. – IR (KBr): $\tilde{\nu}$ = 1056 $cm^{-1}$ ($BF_4$). – UV/Vis ($CD_2Cl_2$): $\chi_{max}$ = 300.9, 314.2, 433.0 nm. – $^1H$ NMR ($CD_2Cl_2$): δ = 8.64 (s, 4 H, 6,6′-H, bipy), 8.44 (d, $^3J_{HH}$ = 8.1 Hz, 4 H, 3,3′-H, bipy), 7.96 (d, $^3J_{HH}$ = 8.1 Hz, 4 H, 4,4′-H, bipy), 7.39–6.98 (m, 48 H, $Ph_2P$ and $Ph_2Pt$), 6.66–6.47 (m, 12 H, $Ph_2Pt$), 3.02–1.08 (m, 24 H, $CH_2CH_2CH_2PPh_2$). – $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): δ = 161.0 (m,[46] *ipso*-$Ph_2Pt$), 151.0 (s, C, bipy), 148.4 (s, CH, bipy), 141.7 (s, C, bipy), 139.1 (s, CH, bipy), 137.0 (s, d, $^2J_{PtC}$ = 29.9 Hz, *ortho*-$Ph_2Pt$), 134.2–132.3 (m, *ipso*- and *ortho*-$Ph_2P$), 130.0 (s, *para*-$Ph_2P$), 128.5 (m,[46] $N$ = 8.8 Hz, *meta*-$Ph_2P$), 127.3 (s, d, $^3J_{PtC}$ = 64.0 Hz, *meta*-$Ph_2Pt$), 122.3 (s, CH, bipy), 121.5 (s, *para*-$Ph_2Pt$), 35.0 (m,[46] $N$ = 16.8 Hz, $CH_2CH_2CH_2PPh_2$), 28.6 (s, br,[14,46] $CH_2CH_2CH_2PPh_2$), 26.3 (m,[46] $N$ = 34.9 Hz $CH_2CH_2CH_2PPh_2$). – $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): δ = 9.8 (s, d, $^1J_{PtP}$ = 1778 Hz). – $^{19}F\{^1H\}$ NMR ($CD_2Cl_2$): δ = –153.0 (s, br). – MS (FAB, 30 °C); *m/z*: 1979.4 [$M^+$ – $BF_4$], 1670.4 [$M^+$ – $BF_4$ – 4 Ph]. – $C_{104}H_{96}BCuF_4N_4P_4Pt_2 \cdot 2\ CH_2Cl_2$ (2236.2): calcd. C 56.93, H 4.51, Cu 2.84, N 2.51, Pt 17.45; found C 56.59, H 4.32, Cu 2.32, N 2.44, Pt 16.67.

**X-ray Structural Determination of the Diplatinacyclophanes 8b · 3 $H_2O$ · 2 $CH_2Cl_2$ and 9b · 2 $CH_2Cl_2$:** Crystallographic data for both compounds are summarized in Table 1. Single crystals of **8b** and **9b** were obtained from a dichloromethane/methanol solution. Each crystal was mounted on a goniometer head and transferred to a Siemens P4 diffractometer (Mo-$K_\alpha$ radiation, graphite monochromator) and to an Enraf Nonius CAD4 diffractometer (Cu-$K_\alpha$, graphite monochromator), respectively. Accurate unit cell parameters and orientation matrices were determined by least-squares refinement of setting angles of a set of well-centered reflections. Reduced cell calculations did not indicate higher lattice symmetry for **8b** than $P\bar{1}$, while **9b** crystallizes in the orthorhombic space group *Pbcn*. Data were corrected for LP effects and for observed linear decay. An empirical absorption correction via Ψ-scan was applied for **8b**. The structures were solved by direct methods (SHELXS)[47] and refined by least-squares methods based on $F^2$ using SHELXL 97.[48] All non-hydrogen atoms except the solvent molecules were refined anisotropically. All hydrogen atoms were located in calculated positions, with the exception of those of the solvent molecules in **8b**. Crystallographic data for both structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-131421 for **8b** and CCDC-131420 for **9b**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int. code) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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