Synthesis, Structure, and Host-Guest Investigations on Self-Assembled Nonwater-Soluble and Water-Soluble Multiple Bridged Platinacyclophanes

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Synthese, Struktur und Wirt-Gast-Untersuchungen an selbstorganisierten, wasserlöslichen und wasserunlöslichen mehrfach verbrückten Platinacyclophanen

DISSERTATION

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Im Namen Allahs, des Sich Erbarmenden, des Barmherzigen

In the Name of Allah, the Most Beneficent, the Most Merciful

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To my Parents
Sisters and Brothers
and to my developing country

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Contents

Abbreviations and Definitions

Å	Angstrom (10^{-10})
AIBN	2,2'-Azobis(2-methylpropionitrile)
aromat.	Aromatic
δ	Chemical shift
DMSO	Dimethylsulfoxide
EI	Electron ionization (mass spectroscopy)
eV	Electron volt
FAB	Fast atom bombardment (mass spectroscopy)
FD	Field desorption (mass spectrometry)
FT	Fourier transformation
g	Grams
h	Hour
HR	High resolution
Hz	Hertz
IR	Infrared spectroscopy
L	Liter
MHz	Megahertz
m.p.	Melting point
mL	Milliliter
mmol	Millimole
MS	Mass spectroscopy

n	Non-branched alkyl chain
$\tilde{\nu}$	Frequency
NBA	Nitrobenzyl alcohol
NBS	*N*-Bromosuccinimide
NMR	Nuclear magnetic resonance spectroscopy
ppm	Parts per million
quat	Quaternary
THF	Tetrahydrofuran
TMEDA	*N*′,*N*′,*N*′,*N*′-Tetramethylethylenediamine
TLC	Thin layer chromatography
TMS	Tetramethylsilane
tert	Tertiary

Introduction

Supramolecular chemistry is one of the most popular and fastest growing areas of experimental chemistry and it seems that this will remain in the foreseeable future. It is aesthetically appealing, readily visualized and lends itself to the translation of everyday concepts to the molecular level. It might also be fair to say that supramolecular chemistry is a very greedy topic. It is highly interdisciplinary in nature and, as a result, attracts not just chemists but biochemists, biologists, environmental scientists, engineers, physicists, theoreticians, mathematicians and a whole host of other researchers.[1] It seems that the term "supramolecular chemistry" was first used in 1978 by J.-M. Lehn with the statement: "*Just as there is a field of molecular chemistry based on the covalent bond, there is a field of supramolecular chemistry, the chemistry of molecular assemblies and of the intermolecular bond*"[2]. Today supramolecular chemistry is defined as "*the chemistry of molecular assemblies and of the intermolecular bond*".[3] It is the chemistry beyond the molecule and deals with organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces. The definition is very generous and covers a very broad area of chemical phenomena and structures and extends to biological molecules, coordination compounds, and new materials.[5] As currently defined, supramolecular chemistry may then be divided into two broad, partially overlapping areas concerning: (i) *supramolecules*, well-defined, discrete *oligo*molecular species that result from the intermolecular association of a few

components following an "Aufbau" scheme based on the principles of molecular recognition; (ii) *supramolecular assemblies*, *poly*molecular entities that result from the spontaneous association of a large undefined number of components into a specific phase having more or less well-defined microscopic organization and macroscopic characteristics depending on their nature (e.g. films, layers, micelles, ...etc.).[4] The formation of a supramolecular architecture through intermolecular interactions requires so-called *molecular recognition*.[5, 6] Molecular recognition is well illustrated by the complexation between crown ethers and alkali metal ions.[7] *Molecular receptors* are defined as "organic structures held by covalent bonds that are able to bind selectively ionic or molecular substrates (or both) by means of various intermolecular interactions, leading to an assembly of two or more species, a supramolecule".[5] The molecular receptor is a host and the bonded substrate is a guest.

Studies of recognition in designed supramolecular complexes may provide answers on a microscopic level to important open questions in biological sciences. However, a broader motivation for these investigations is the strong desire to generate a full understanding of week non-covalent interactions in ground and transition state complexes.[8]

Cyclophanes, which are defined as "*all molecular receptors with at least one aromatic ring bridged by at least one aliphatic n-membered bridge (n > 0)*",[8 – 11] represent the central class of synthetic receptors (hosts) in molecular recognition. All

types of substrates (guests), from inorganic and organic cations and anions to neutral molecules, have been complexed by cyclophanes.[8]

Most cyclophane hosts have been prepared to complex polar solutes in water rather than in organic media. Complexation in water has always attracted special interest since it can directly model molecular recognition events in biological systems. In addition earlier developments have shown that apolar complexation would be stronger in aqueous solution compared to organic solvents.[8, 12 – 14]

Attempts to construct such systems via three-fold carbon–carbon couplings are accompanied by multistep procedures, high dilution conditions and in the end low yields.[15 – 21] An attractive alternative however, is the dimerization of trifunctional molecular precursors.[22] By employment of this method several examples of three-dimensional cyclophanes could be verified.[8 – 11, 22]

A recent novel synthetic protocol in the construction of organized nanoscopic assemblies from multiple building blocks in a single step, namely *self-assembly*, relies on critical information about the shape and the properties of the resulting structure being preprogrammed into each individual building block. Self-assembly is described as "*a spontaneous association of molecules under equilibrium conditions into stable aggregates held together by non-covalent bonds*".[4] Although this approach was initiated by the artificial mimicking of natural receptors that utilize weak hydrogen bonds,

it has now resulted in an entirely different 'unnatural' strategy, molecular architecture, that employs transition metals and dative bonding to achieve structurally well defined, highly ordered assemblages. This approach relies on the fact that only a few metal–ligand bonds may be used in place of several hydrogen bonds owing to their greater strength. Another advantage lies in the existence of a large variety of transition metals with different co-ordination numbers, thus facilitating the building of diverse nanoscopic entities with tremendous variations in shapes and sizes.[23] A distinctive feature of using weak, non-covalent forces, or for that matter metal–donor bonds, in molecular assemblies is that such interactions are normally readily reversible so that the final product is in thermodynamic equilibrium with its components. This leads to an additional property of most supramolecular systems: they have an in-built capacity for *error correction* not normally available to fully covalent systems. Such a property is clearly of major importance for natural systems with their multitude of intermolecular contacts.[24]

The incorporation of transition metal centers into the structure of cyclophanes can confer new properties on these potential host molecules.[25] In particular, transition metal centers might introduce Lewis acidity,[26] magnetism,[27] redox activity,[28] or luminescence properties[29] into the macrocyclic structure. This may have important implications for the chemical reactivity or physical properties of a cyclophane host; for example optically driven charge transfer processes between the metal centers and ligands in the macrocyclic structure may lead to novel electro-optical properties.[25]

Although several interesting motifs have been reported in the literature, bonafide three-fold bridged metallacyclophanes, which respond to the classical cyclophane structure, are still rare till today. Recently Lindner et al.[30] created elastic three-dimensional molecular cages in which the kinetics is sufficiently fast for host/guest complexation and decomplexation. Furthermore, Fujita et al.[31] introduced remarkable template synthesis for pallada- and platinacyclophanes. The same group[32] as well as Steel[33], Lehn[34] and Stang[35], and others[36] reported also on multi-fold bridged metallacyclophanes with several symmetries.

This investigation refers to a synthetic route recently applied by Balch et al.[37] and expanded by Lindner et al.[30] to synthesize novel three-fold bridged platinacyclophanes. The object of this thesis is divided to two parts: (i) creation of a flexible tridentate phosphine ligand system based on a central benzene ring which is provided with three flexible aliphatic spacer units carrying a phosphine group each at their ends. These ligands are able to self-assemble via platinum fragments to form the desired triplatinacyclophanes with different cage size and to study the effect of the number of methylene groups which function as spacers in the self assembly; and (ii) functionalization of phosphines by water-soluble groups to perform water-soluble platinacyclophanes and test their inclusion behavior. It was achieved that two molecules of each ligand assemble via three molecules of platinum complexes to establish three-dimensional triplatinacyclophanes that are nonwater-soluble and water-soluble with different geometries. Several other motifs were performed for nonwater-soluble ligands

with four methylene groups as a spacer. Finally the inclusion behavior of the water-soluble triplatinacyclophanes was tested.

General Section

1. Nonwater-Soluble Studies

1.1. Introduction

Supramolecular chemistry, which may be regarded as a result of modern coordination chemistry,[38] is at the frontiers of molecular sciences as is evidenced by the fast growth of publications in this area in the last decade.[36, 39, 40] Cyclophanes and in particular metallacyclophanes are part of this chemistry.[8 – 11, 25] They contain cavities that have the capacity to include guest molecules of different kind.[8] The synthesis of these fascinating compounds was troublesome. However, studies in self-organization have provided a lot of interesting molecular architectures capable for host–guest chemistry, such as "cyclophane boxes",[41 – 52] squares and polygons,[53 – 65] cylinders,[66 – 70] rods[71 – 73] and many others.[74 – 76] Unlike two-dimensional metallacyclophane boxes, three-dimensional multicyclic species are still rare today.[31 – 35, 41 – 52]

Mono- and multidentate phosphines are attractive ligands for the generation of complexes with a great variety of transition metal fragments.[77 – 78] Recently van Koten *et al.*[79] synthesized a tetradentate ligand in which the phosphine arms are attached via methylene groups to a benzene ring in 1,2,4,5-position. The introduction of a

symmetrically 1,3,5-trisubstituted benzene ring with at least C_3 symmetry into phosphine chemistry has advantages for the synthetic design[80] of self-assembled supramolecular molecules[81, 82] and for chemical selectivity.[83] As it was demonstrated recently such tridentate phosphines are suitable to assemble via three platinum atoms to afford an elastic, three-dimensional molecular cage. By virtue of its size it was possible to reversibly encapsulate 1,2-dichloroethane in the triplatinacyclophane 1 (Figure 1).[30] In continuation of this work several triplatinacyclophanes were generated with different cage sizes to study the dependence of the number of methylene groups in the ligand system on the kind of self-assembly. For this purpose in this investigation novel tridentate phosphine ligands are introduced. They are based on a central benzene ring which is provided with three flexible aliphatic spacer units carrying a phosphine group each at their ends. Such ligands can be employed in catalysis and supramolecular chemistry.

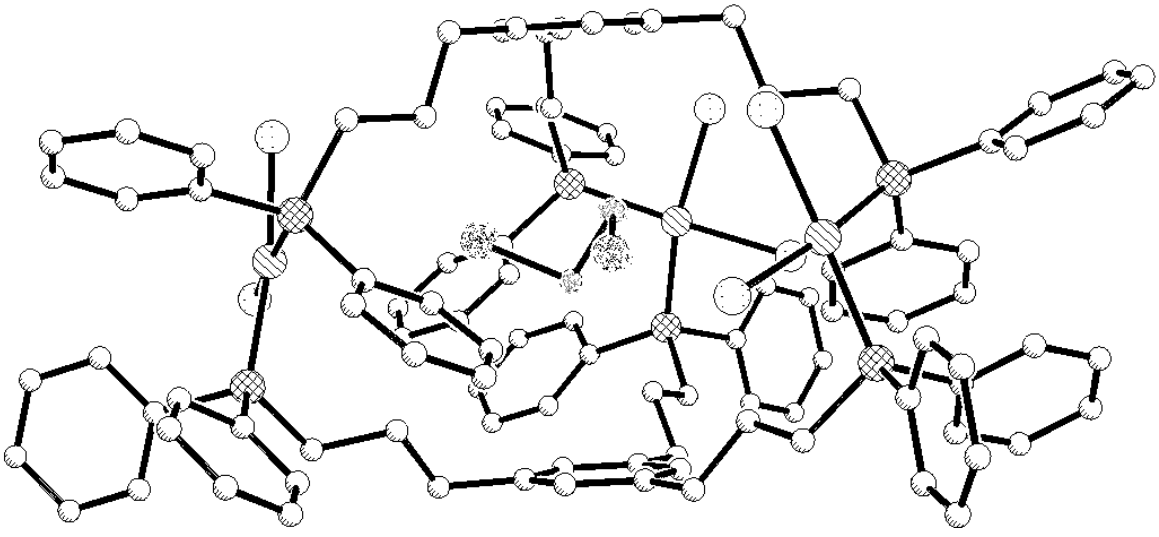
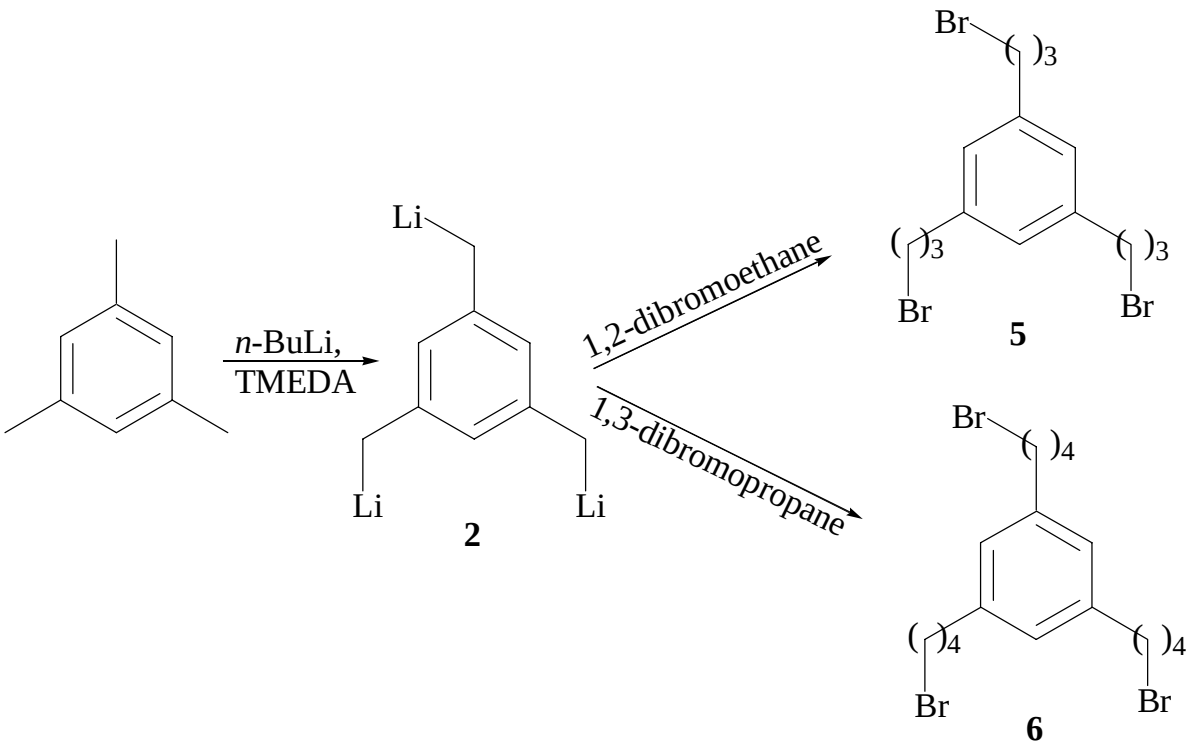


Figure 1. Inclusion of 1,2–dichloroethane into the three–dimensional triplatina-cyclophane **1**[30]

1.2. Ligand synthesis

*1.2.1. Synthesis of 1,3,5-tris(bromoalkyl)benzenes **3 – 6***

For the synthesis of the target ligands **11** – **14** the 1,3,5-tris(bromoalkyl)-benzenes **3** – **6** are used as starting materials. However, according to the literature 1,3,5-tris(bromopropyl)benzene (**5**) and 1,3,5-tris(4'-bromobutyl)benzene (**6**) are only available in a complicated eight–step[84] and twelve–step[85] reaction sequence, respectively. Therefore a much simpler access to **5** and **6** was developed. Lithiation of mesitylene with *n*BuLi / TMEDA in *n*-hexane afforded the trilithium derivative **2**. Subsequent addition of a suspension of **2** in *n*-pentane to a solution of 1,2-dibromoethane or 1,3-dibromopropane

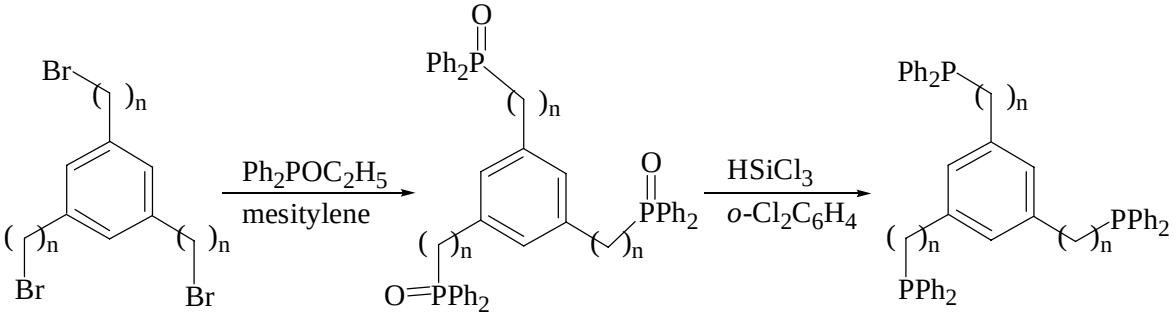


Scheme 1. Facile synthesis of **5** and **6**

in *n*-pentane at –85 °C resulted in the formation of **5** or **6**, respectively, in about 20 % yield (Scheme 1).

*1.2.2. Synthesis of 1,3,5-tris(diphenylphosphinoalkyl)benzenes **11** – **14***

Reactions of the trifunctionalized chloro- or bromoalkylbenzenes **3** – **6** with $MPPh_2$ (M = Li, Na) or $LiCH_2PPh_2$ were not successful. Also treatment of **2** with $ClPPh_2$ or $ClCH_2PPh_2$ did not result in the isolation of a defined product. Therefore a method of van Koten *et al*. was applied which was recently published in the literature.[79, 86, 87] According to this procedure an Arbusov reaction was carried out between **3** – **6** and $Ph_2POC_2H_5$ yielding quantitatively the phosphine oxides **7** – **10** (Scheme 2). In *o*-dichlorobenzene these phosphine oxides can easily be reduced with $HSiCl_3$ to the



3 (n = 1)
4 (n = 2)
5 (n = 3)
6 (n = 4)

7 (n = 1)
8 (n = 2)
9 (n = 3)
10 (n = 4)

11 (n = 1)
12 (n = 2)
13 (n = 3)
14 (n = 4)

Scheme 2. Synthesis of the ligands **11** – **14**

corresponding trifunctionalized phosphines **11** – **14** (Scheme 2). Whereas the phosphine oxides **7** – **10** represent colorless solids with rather high melting points which are soluble in all organic solvents of high and medium polarity, the colorless phosphines are obtained as waxy (**11**), crystalline (**12**), or gummy products (**13**, **14**). In contrast to **7** – **10** they are not soluble in polar solvents. The composition of **7** – **14** was corroborated by FAB and EI mass spectra, respectively, showing in each case the molecular peak. The IR spectra (in KBr) of **7** – **10** display a sharp absorption between 1197 and 1225 cm^{-1} being assigned to the P=O stretching vibration. Expectedly in the $^{31}P\{^{1}H\}$-NMR spectra (in $CDCl_3$) of the phosphine oxides **7** – **10** one singlet each is observed (δ = 31 to 34 ppm) which is shifted to higher field (δ = –9 to –15 ppm) on going from **7** – **10** to the phosphines **11** – **14** (Figure 2).

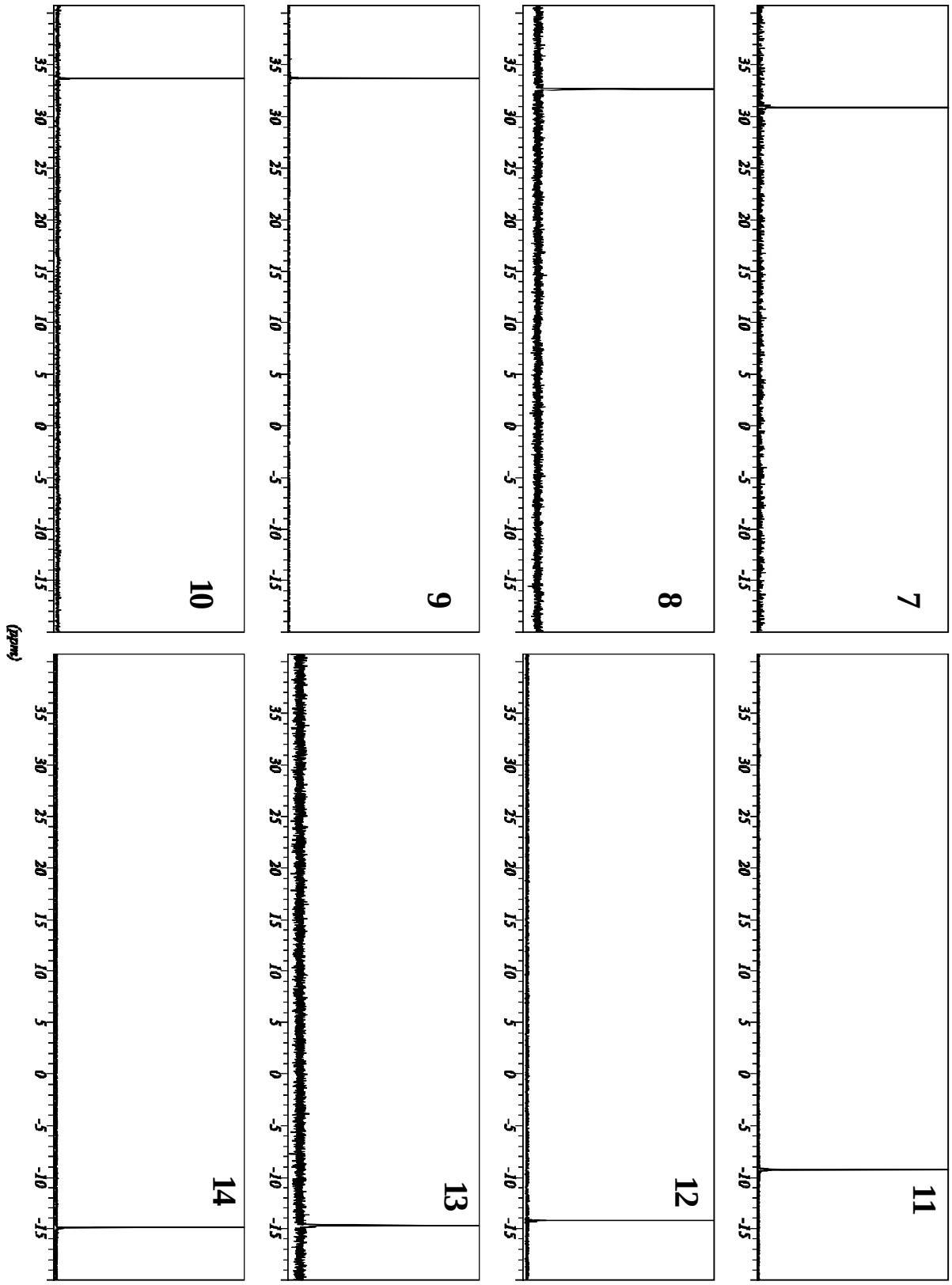


Figure 2. $^{31}P\{^{1}H\}$-NMR spectra of compounds **7** – **14**

*1.2.3. Crystal structures of **9** and **12***

To get a more detailed structural information about the trifunctional phosphine oxides and their oxygen free moieties X-ray structural analyses were performed by means of the examples **9** and **12** (Scheme 2). ORTEP drawings of their molecular structures with atom labeling are depicted in Figures 3 and 4. Although the crystal structure of **9** is of restricted quality, it can be used for a brief discussion. Because **9** has a C_3 axis of symmetry which is passing through the center of the benzene ring all three phosphine arms are equivalent. This fact gives rise to several structural implications. All distances between the phosphorus and carbon atoms of the central benzene ring are equal [5.307(5) Å] and the P1–C2, P1A–C2A, and P1B–C2B axes are bent toward the plane of the central benzene ring by an angle of 144.2(6)°. A further consequence is that the phosphorus atoms are located at the vertices of an equilateral triangle which is parallel to the benzene ring. The distance between the phosphorus atoms is 10.179(6) Å (Figure 3).

In the structure of the phosphine **12** such a C_3 axis of symmetry is not existent. Therefore the different distances between the phosphorus atoms and between these and the carbon atoms of the central benzene ring are not equal (Figure 4) and the unsymmetric triangle constituted by phosphorus atoms is not parallel toward the benzene ring. The P1–C1, P2–C3 and P3–C5 axes are bent to the plane of the benzene ring by angles of 154.9(3), 157.9(4), and 157.7(4)°, respectively.

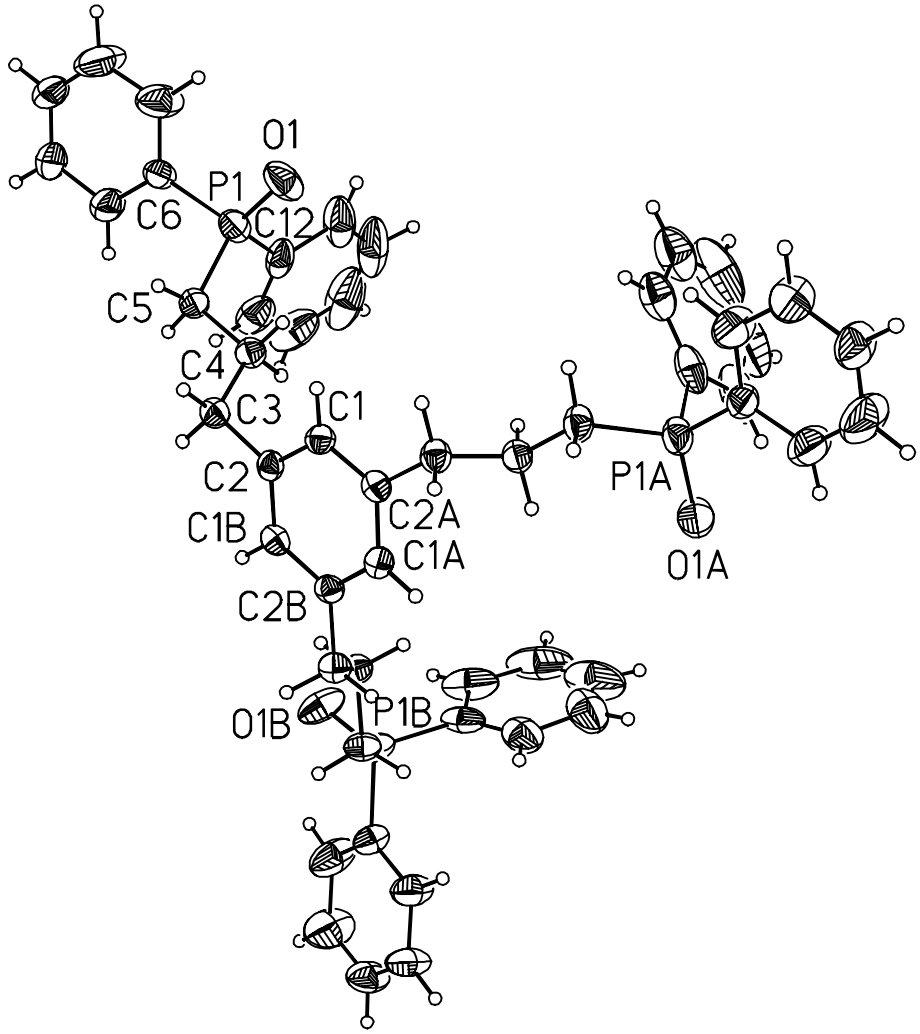


Figure 3. Molecular structure of **9** in the crystal; ORTEP plot with thermal ellipsoids at 20 % probability. Selected distances [Å]: P1–O1 = 1.487(4), P1–C6 = 1.800(5), P1–C5 = 1.809(4), P1–C12 = 1.809(8), P1–C2 = 5.307(5), P1–P1A = P1A–P1B = P1–P1B = 10.179. Selected angles [°]: C1A–C2–P1 = C1B–C2A–P1A = C1–C2B–P1B = 144.2(6)

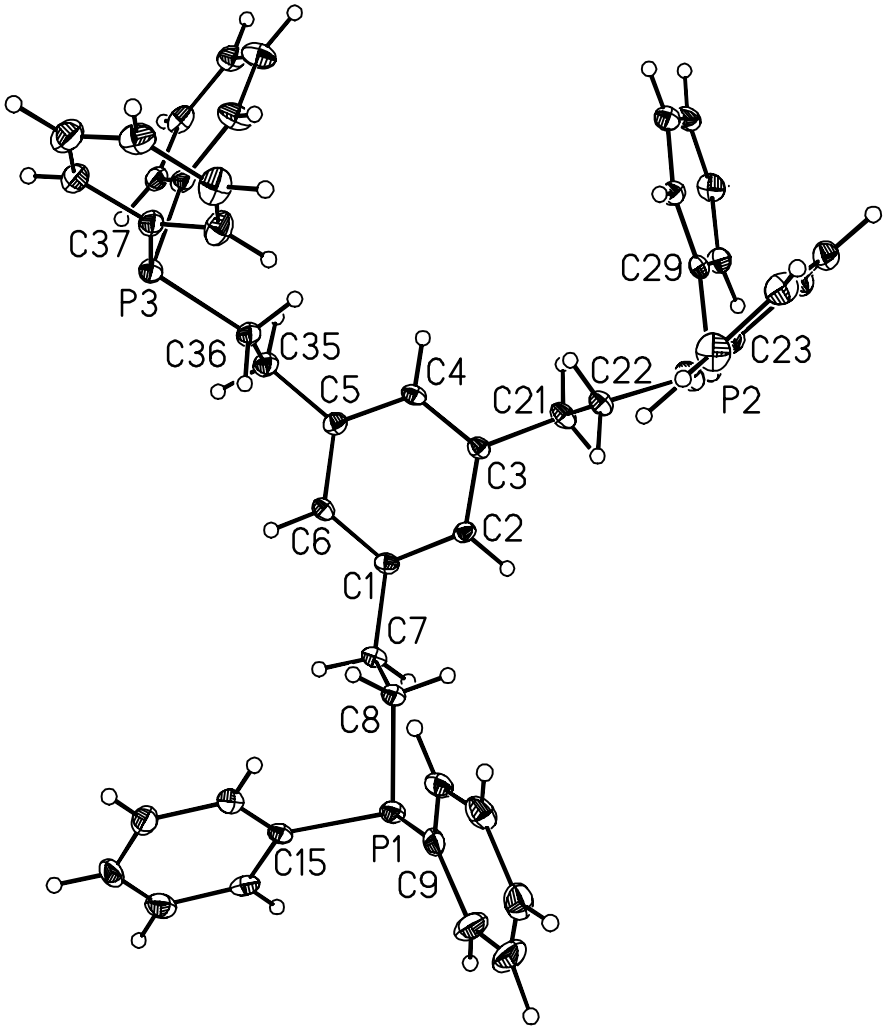
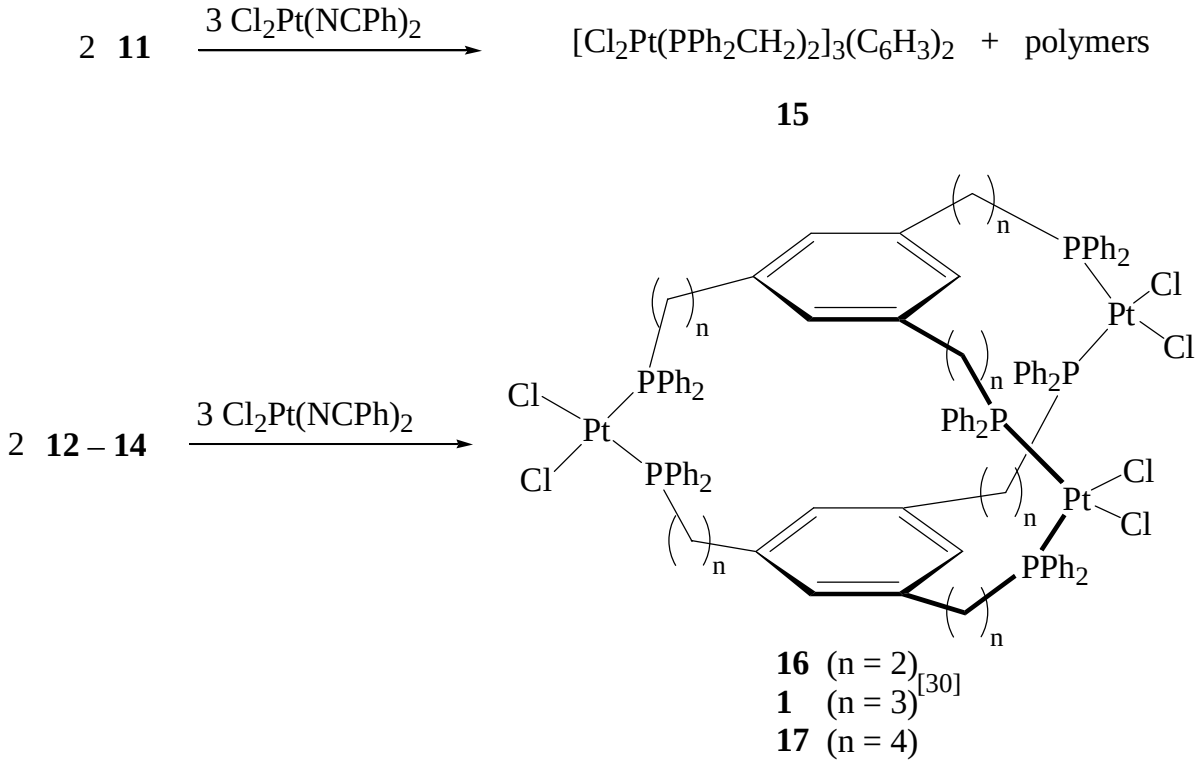


Figure 4. Molecular structure of **12** in the crystal; ORTEP plot with thermal ellipsoids at 20 % probability. Selected distances [Å]: P1–C9 = 1.831(7), P1–C8 = 1.834(5), P1–C15 = 1.849(5), P2–C23 = 1.809(6), P2–C29 = 1.833(5), P2–C22 = 1.847(5), P3–C36 = 1.854(5), P3–C37 = 1.811(7), P3–C43 = 1.839(5) P1–C1 = 4.180(3), P2–C3 = 4.166(3), P3–C5 = 4.169, P1–P2 = 8.672, P2–P3 = 9.292(4), P1–P3 = 9.329. Selected angles [°]: C4–C1–P1 = 154.9(3), C6–C3–P2 = 157.9(4), C2–C5–P3 = 157.7(4)

1.3. Motifs generated by self-assembly

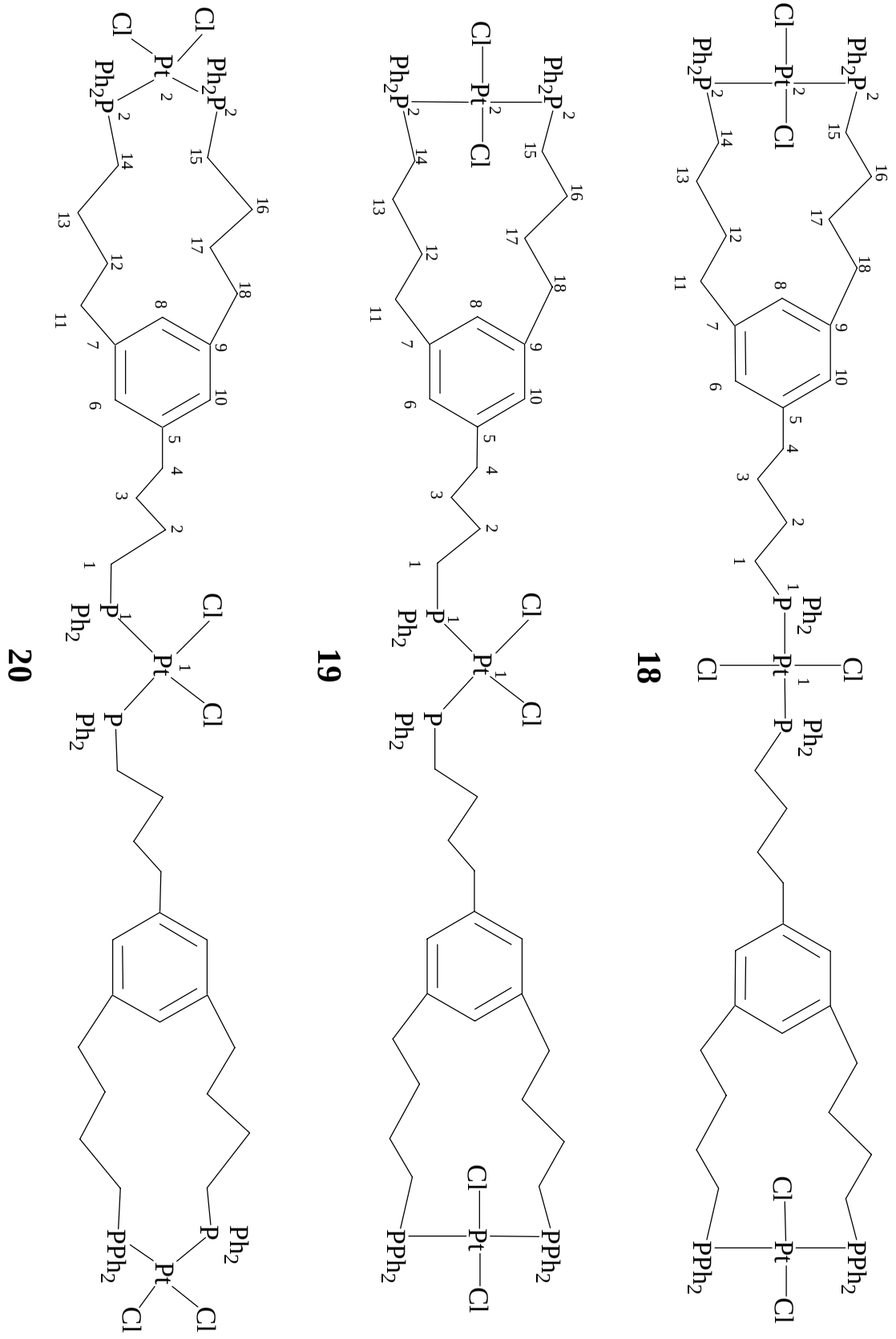
To obtain self-assembled cyclophane structures a preorganization of the components is a necessary prerequisite. Trifunctionalized phosphine ligands of the type **11** – **14** are provided with the necessary rigidity which is important to be preorganized. For the generation of the three-dimensional platinacyclophanes **15**, **16**, and **17** the ligands **11**, **12**, and **14** were treated with $Cl_2Pt(NCPh)_2$ in dichloromethane according to the high dilution method (Scheme 3).[88] In contrast to the platinacyclophane **1** which was recently described,[30] the smaller cages **15** and **16** were obtained in lower yields. In particular the platinacyclophane **15** could not be isolated in pure form, since polymers and oligomers



Scheme 3. Self-assembly of the ligands **11 – 14** with $Cl_2Pt(NCPh)_2$

were formed as by-products, an observation which was also made by Fujita *et al.* with comparable nitrogen ligands.[31] For a separation the solubility of **15** and these by-products is too low. This property prevented also a template synthesis to enhance the yield of **15**. Because of the better solubility **16** could be obtained as a pure compound by chromatography.

Compared to **11** and **12** the behavior of ligand **14** with four methylene units toward $Cl_2Pt(NCPh)_2$ was different. No oligomers or polymers were detected. In addition to the occurrence of the triplatinacyclophane **17** three other species **18** – **20** were isolated with increasing yields in the sequence **18** > **19** > **20** (Scheme 4). The separation of **17** – **20** succeeded by column chromatography. However, **17** was always impurified by **20**. According to their FAB mass spectra these compounds show the same molecular mass and it turned out that they are structural isomers (Figure 5). To optimize the yield of the triplatinacyclophane **17** the reaction between **14** and $Cl_2Pt(NCPh)_2$ was carried out at different temperatures (–70° to 40°C) in dichlormethane. At low temperatures the yields were around 10% and decrease with increasing temperature. At 40° C the structural isomer **18** is predominant (86%) and the formation of **17** is thermodynamically unfavorable.[89] Benzene is the best solvent for the generation of **17** and is superior to CCl_4 or $CHCl_3$.



Scheme 4. Trinuclear chain-like platinacycles

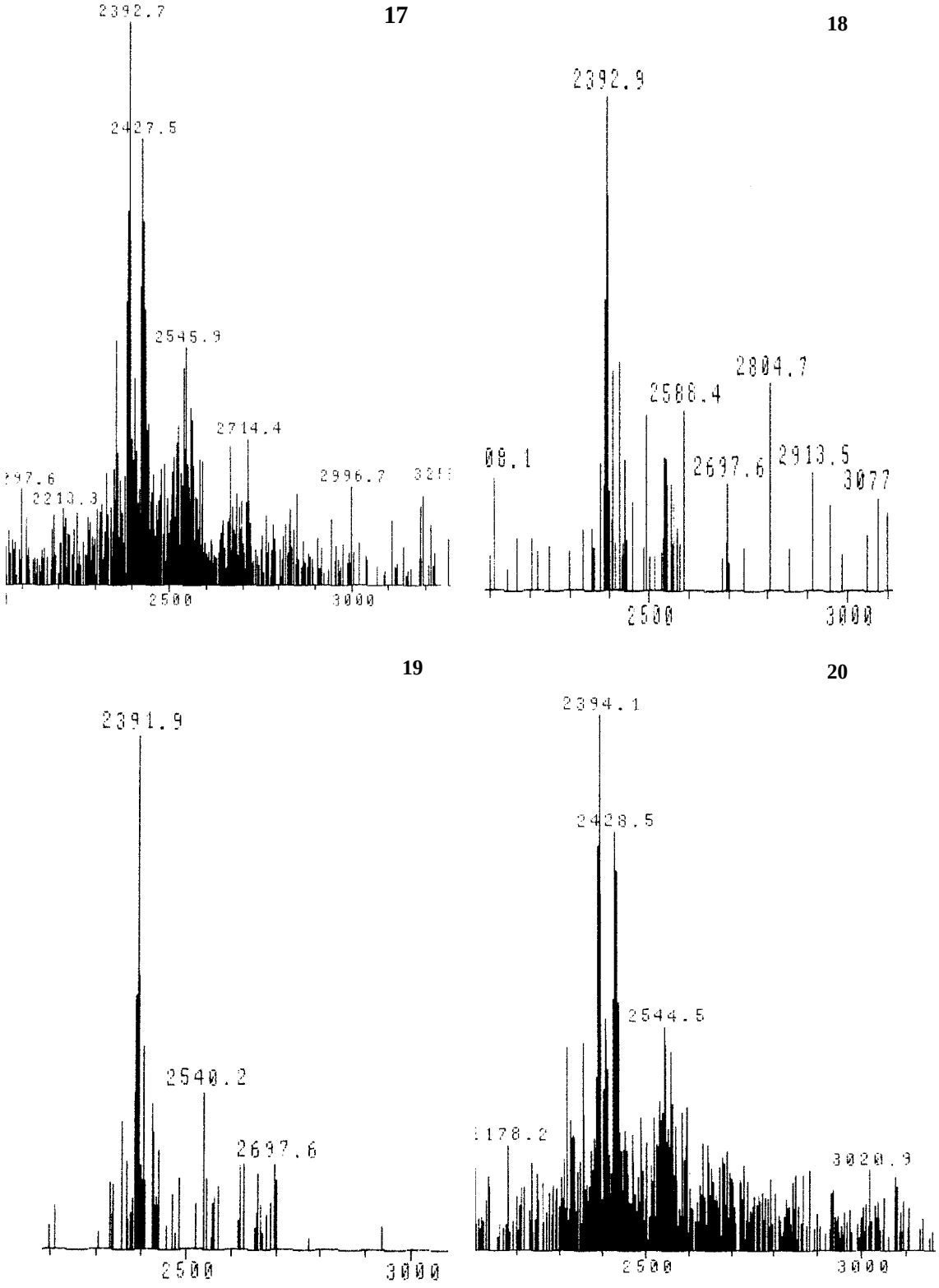


Figure 5. FAB-MS spectra of compounds **17** – **20**

The triplatinacyclophanes **1**, **15** – **17** and trinuclear platinacycles **18** – **20** represent colorless to pale yellow compounds which show a similar solubility behavior as their corresponding ligands **11** – **14**. However, **15** is nearly insoluble in all organic solvents. The *all-trans*- complex **18** transforms slowly to the *trans-cis-trans*-complex **19**.

Structural information about the motifs and geometry of the platinacyles **16** – **20** is available by $^{31}P\{^{1}H\}$-NMR spectroscopic investigations. ^{31}P chemical shifts and ^{195}Pt – ^{31}P coupling constants allow an unambiguous distinction between the architecture of the molecules and their stereoisomerism. Complexes with *cis*-geometry show coupling

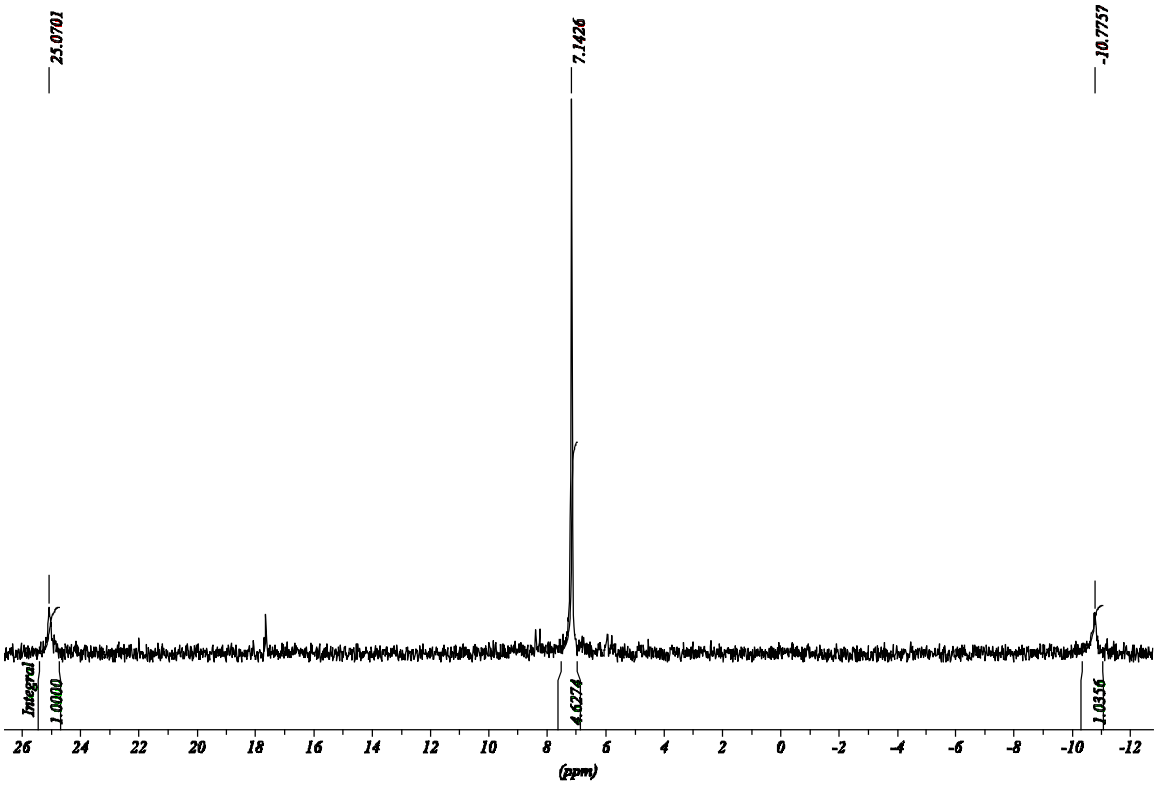


Figure 6. $^{31}P\{^{1}H\}$-NMR spectrum of **16**

constants of about 3500 Hz, whereas those with *trans*-environment reveal values of about 2500 Hz.[90 – 93] It is also well known that ^{31}P signals of *trans*-isomers are upfield shifted compared to *cis*-isomers.[90 – 93] The $^{31}P\{^{1}H\}$-NMR spectra of **16** (Figure 6) and **17** (Figure 7) show a singlet each for the six chemically equivalent phosphorus atoms at δ = 7.1 and 9.6 ppm, respectively, and a doublet for the ^{195}Pt satellites, which is typical for

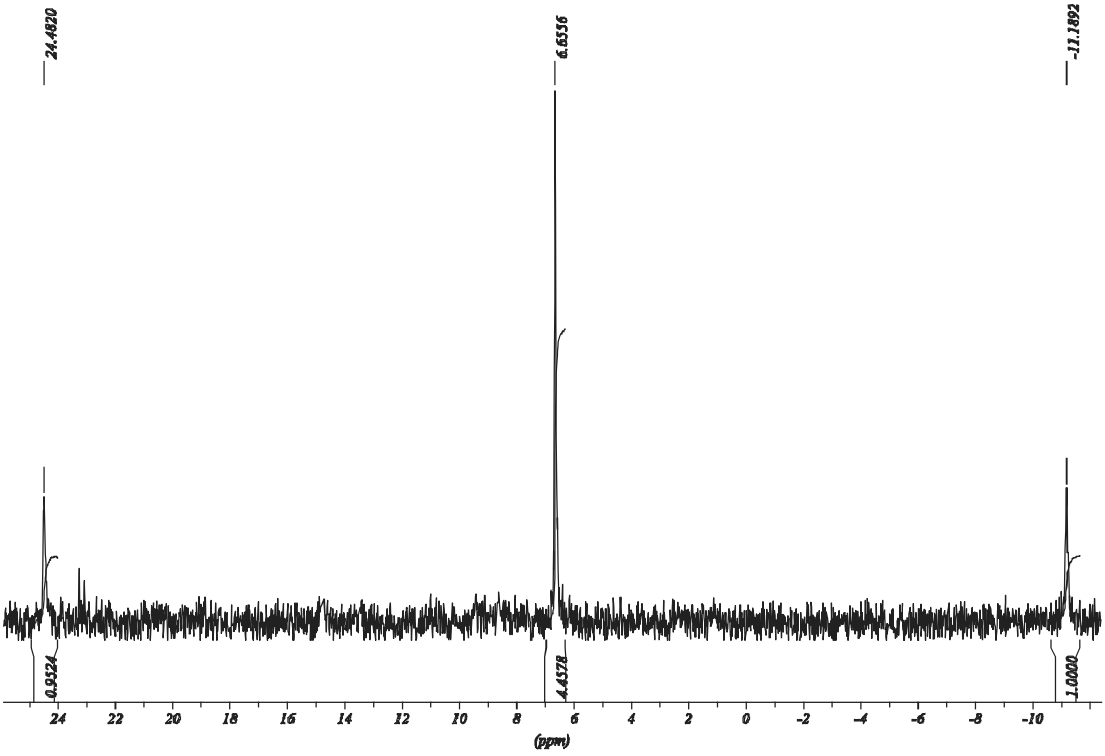


Figure 7. $^{31}P\{^{1}H\}$-NMR spectrum of **17**

cis-PtP_2 fragments. This assignment is confirmed by the $^{195}Pt\{^{1}H\}$-NMR spectra, which display a triplet each at δ = – 4423 and – 4413 with coupling constants of $^{1}J_{PtP}$ = 3600 and 3668 Hz, respectively (Figure 8). Moreover, the structure of **1** was recently confirmed by an X–ray structural analysis.[30] Because **15** was impurified by polymers

and because of its low solubility in all organic solvents, no exact NMR spectroscopic data were available.

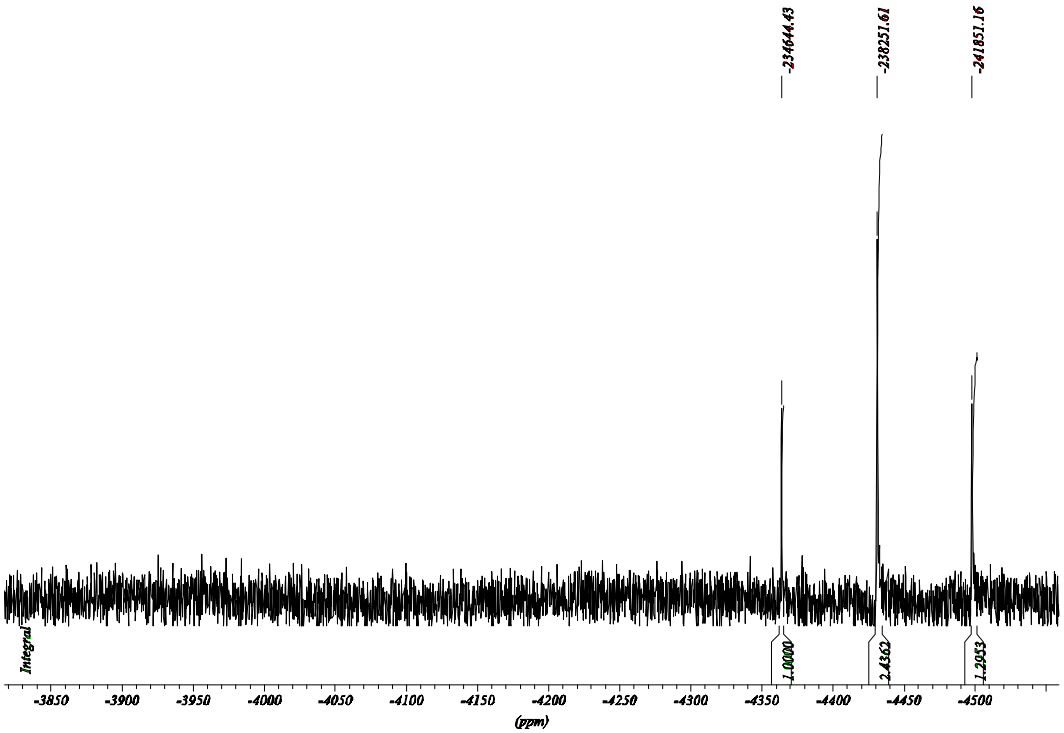


Figure 8. $^{195}Pt\{^{1}H\}$-NMR spectrum of **17**

In contrast to **16**, **17** (and **1**[30]) the $^{31}P\{^{1}H\}$-NMR spectra of the trinuclear platinacycles **18** – **20** show two ^{31}P singlets in a ratio of 2 : 1 (Figure 9). This is a clear indication that two different ^{31}P nuclei are present. Each singlet is accompanied by a doublet as satellites which is traced back by the ^{195}Pt – ^{31}P coupling (see Experimental Part). According to the chemical shifts and the size of the coupling constants, **18** is characterized by an *all-trans*-structure. In the case of the metallacycle **19** the central platinum atom (Pt^1, Scheme 4) has a *cis*-geometry, whereas both terminal platinum atoms

(Pt^2) have a *trans*-configuration. In compound **20** an *all-cis*-structure was established. The fact that the terminal platinum atoms in **18 – 20** are incorporated in a cycle was corroborated by the value of the $^{195}Pt - ^{31}P$ coupling constants which is higher than for the noncyclized central platinum atom (Figure 9 and 10). Moreover the terminal cyclized P_2Pt moieties show higher chemical shifts than the central *trans*-P_2Pt unit. A reverse observation was made in the case of **20**.

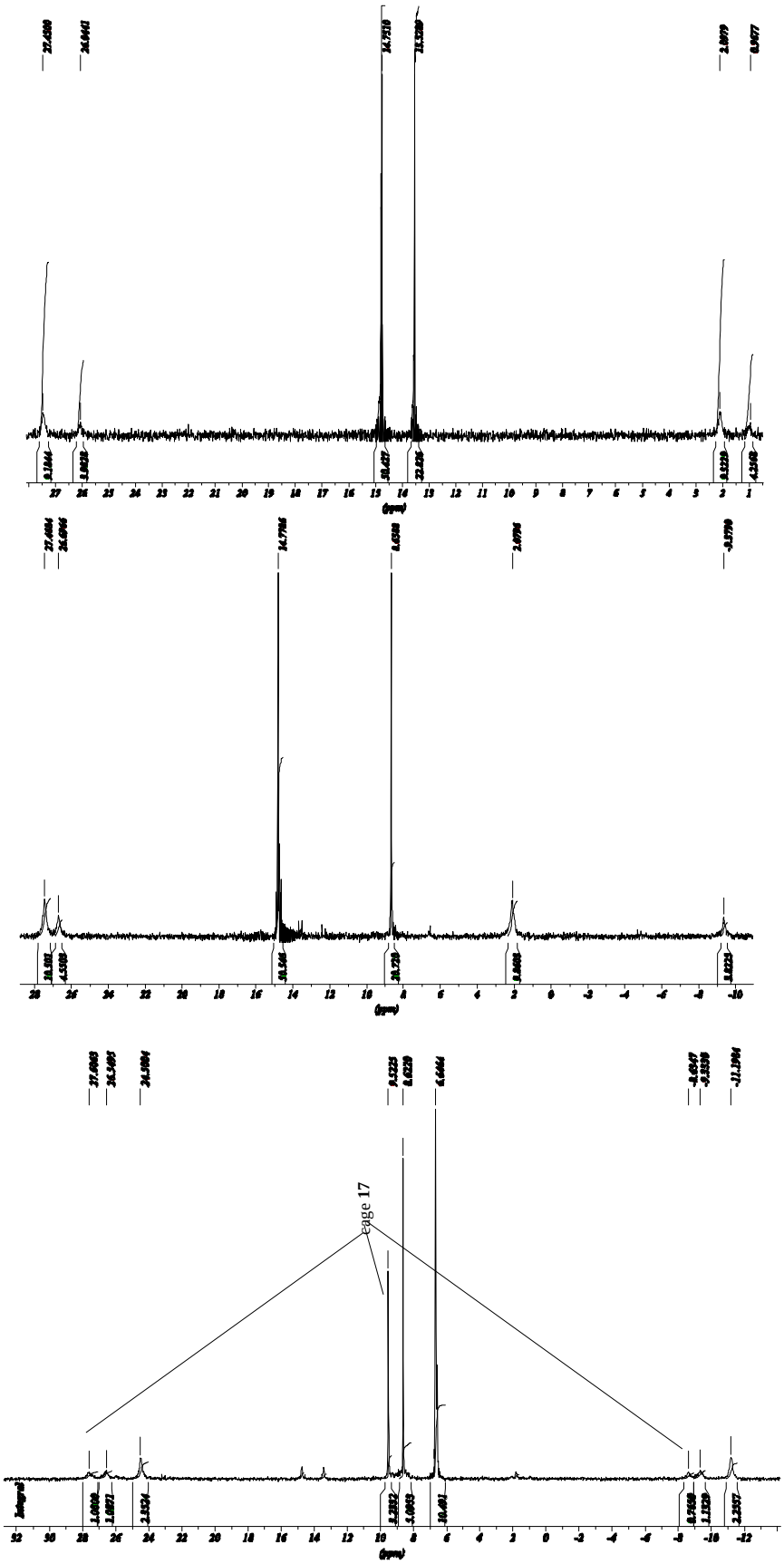


Figure 9. $^{31}P\{^{1}H\}$-NMR spectra of trinuclear platinacycles **18** – **20**

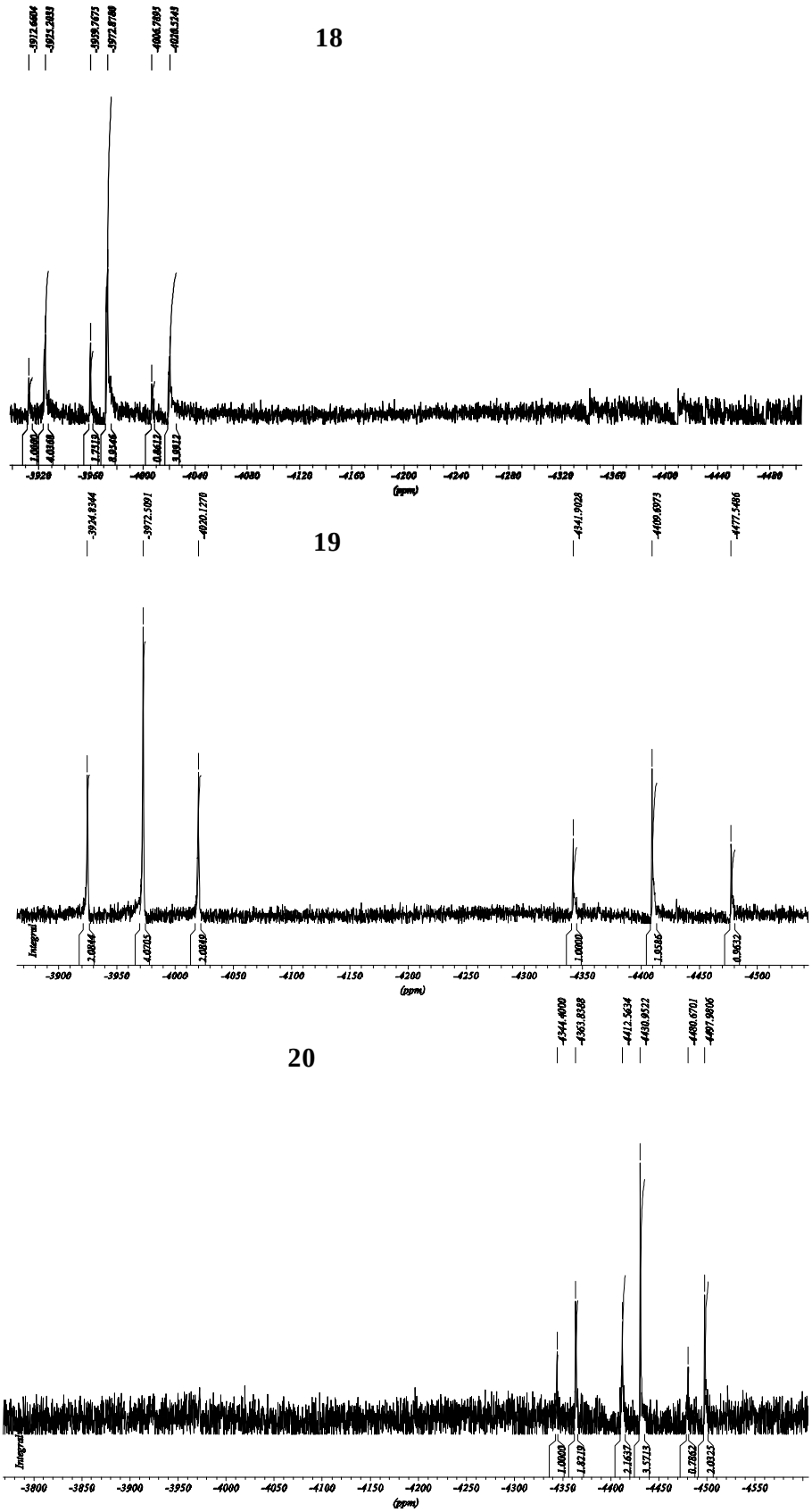


Figure 10. $^{195}Pt\{^{1}H\}$-NMR spectra of triplatinacycles **18** – **20**

A short discussion of the ^{1}H- and ^{13}C{^{1}H}-NMR spectra of the cycles **16** – **20** refers to the central benzene rings and the adjacent methylene groups. Only one ^{1}H signal is observed in the spectra of **16** (δ = 6.42) and **17** (δ = 6.86) for the aromatic protons. A different situation was found in the cases of **18** – **20**. Two singlets in a 2 : 1 ratio are assigned to H^{6} / H^{10} and H^{8}, which is in agreement with the proposed structure (Scheme 4). The methylene protons give rise only to broad unresolved signals. Two different ^{13}C resonances occur in the spectra of the cages **16** and **17** and they are ascribed to the methine (δ = 126.1) and quaternary carbon atoms [δ = 129.6 (**16**), 132.4 (**17**)] of the benzene rings. In the case of **16** the second one is split into a doublet, because of the ^{31}P – ^{13}C coupling [$^{3}J_{PC}$ = 7 Hz]. The corresponding signals for the aromatic methine and quaternary carbon atoms in the spectra of **18** – **20** are split in two peaks with an intensity of 2 : 1 (see Experimental Part). A doublet at δ = 28.6 [$^{2}J_{PC}$ = 47 Hz] in the spectrum of **16** and a singlet at δ = 35.8 in that of **17** are assigned to the methylene carbon atoms which are adjacent to the benzene rings. These resonances are split in two signals with an intensity of 2 : 1 in the spectra of **18** – **20**.

1.4. Conclusion

In contrast to metallacyclophanes the chemistry of organic cyclophanes is much more developed.[25] However, within the last five to ten years several new architectures of metallacyclophanes with interesting properties have been described in the literature.[23, 25, 38 – 65] This new variant of cyclophanes is available by self-assembly of multifunctional

ligands with suitable metal fragments. In the present investigation a simple strategy was introduced that allows a convenient access to trifunctional phosphines. They are provided with a central benzene ring which has three phosphine arms in a symmertrical 1,3,5-position. The distance of these phosphines from the benzene ring is controlled by methylene functions of different length. Ligands of this type cannot be used only for the generation of metallocyclophanes, but also as the first generation of dendrimers[37, 94, 95] and for the synthesis of catalytically active transition metal complexes.[81] It was demonstrated that these trifunctional phosphine ligands are capable to undergo self-assembly with adequate platinum complex fragments. Three items are observed to affect the formation of three–dimensional platinacyclophanes: 1) the rigidity of the ligand system; 2) steric factors; 3) intramolecular chelation. The first point is observed to be predominant in the formation of cages with a trisphosphine which contains no methylene groups between the central benzene ring and the phosphorus donors. Therefore the system appears to be rigid and it is not possible for the phosphines to avoid contact between each other to reduce the steric congestion caused by the phenyl substituents. Also the P–donors are too faraway from a metal center in order to give intramolecular chelation.[37] By the introduction of methylene groups and increasing their number, the ligand system becomes more flexible and the phosphine moieties are able to move away from each other to minimize the interactions and hence the steric demand. This was clearly observed in the crystallization patterns of these systems from triclinic (**7**, one phosphine group is in the opposite direction of the other two[96]), via monoclinic (**12**, this report) to cubic (**9**, this report) for trifunctional phosphines with one, two, and three methylene groups, respectively, as was shown from X-ray crystal structural analyses.

However, the introduction of only one methylene group is not enough to reduce the steric hindrance, which means that intermolecular chelation results in the favored formation of polymers. The flexibility of a phosphine system with four methylene bridges is accompanied by a release of the steric factor and thus enables intramolecular chelation. This is the reason why the formation of the chain–like platinacycles **18 – 20** is favored compared to the cage **17**. The optimum for self-assembly is obtained if the ligand contains three methylene groups.

2. Water-Soluble Studies

2.1. Introduction

Supramolecular chemistry has been rapidly expanding at the frontiers of chemical science with physical and biological phenomena.[4, 8, 10, 11, 22, 97 – 100] An important application in this field is constituted by molecular recognition. Cyclophanes belong to a special class in supramolecular chemistry and usually they are provided with cages suitable for the inclusion of guest molecules.[22, 97, 98] Host – guest interactions are established to mimic enzymes in their capability to bind substrates fast, selectively and reversibly and to catalyze chemical reactions.[8, 22, 98] Water is an essential biological fluid which promotes apolar aggregation and complexation processes necessary to sustain all functions of life. Therefore, complexation studies in aqueous media are of special interest since they can directly model molecular recognition in biologic systems.[8, 98] Cyclophanes are capable to form stable inclusion complexes with apolar organic molecules in water, because they possess accessible lipophilic cavities. It has been shown that apolar complexation is stronger in aqueous solutions compared to organic solvents.[8, 101, 102] This fact is due to interactions between the lipophilic cavity and the guest molecules. [103]

Recently, it was demonstrated that 1,3,5-tris(diphenylphosphinylalkyl)benzenes are able to undergo self-assembly with a suitable platinum complex to give three-dimensional metallacyclophanes (see Section 1).[30] The incorporation of a metal fragment into cyclophanes leads to a new type of macromolecules, with the ability to

alter, enhance, or create new properties for these systems.[25] By introduction of suitable functional groups it should be possible to develop also water-soluble metallacyclophanes. Diederich *et al.* reported on the host/guest chemistry of a specific cyclophane which displays solubility in solvents of all polarities.[8, 104, 105] To the best of our knowledge similar studies have not yet been carried out with metallacyclophanes. To achieve this goal, novel tridentate water-soluble phosphine ligands were generated. They are based on a central benzene ring which is provided with three flexible aliphatic spacer units carrying a phosphine substituent each at their ends. These phosphines are provided with hydroxy or phosphonate functions and are able to self-assemble with platinum precursor complexes. The inclusion behavior in water toward several guests was tested.

2.2. Ligand synthesis

*2.2.1. Synthesis of 1,3,5-tris(phosphinoalkyl)benzenes **25** – **28***

A straightforward Arbosuv reaction between the corresponding 1,3,5-tris(bromoalkyl)benzenes **3** – **6** and triethyl phosphite afforded the 1,3,5-tris[(diethoxy-phosphinyl)alkyl]benzenes **21** – **24** (Scheme 5). Reduction by $LiAlH_4$ in diethyl ether results in the formation of the respective triprimary phosphines **25** – **28** (Scheme 5). With the exception of **25**, which decomposed readily to the 3,5-bis(phosphinylmethyl)toluene and PH_3, **26** – **28** were obtained in pure form. A similar decomposition was also observed in the case of tris(hydroxymethyl)phosphine.[106] Several efforts were made to prevent decomposition by employing lower temperature and / or milder reducing agents

(e.g. $NaBH_4$), but they were unsuccessful and led to unreacted material or decomposition products. The phosphorus compounds **21** – **28** represent hygroscopic viscous oils and colorless liquids, respectively, which are very sensitive to air, in particular in the case of **26** – **28**. Therefore **26** – **28** were not further purified after extraction from the reaction mixture and they were directly used for the next step. The composition of **21** – **24** and **26** – **28** was corroborated by EI mass spectra showing the molecular peak in each case. Expectedly in the $^{31}P\{^1H\}$-NMR spectra of **21** – **24** (in $CDCl_3$) a singlet each is observed (δ = 27.1 – 33.5) which is markedly shifted to higher field ($\delta \approx -136$) by the reduction of **21** – **24** to **25** – **28** (Figure 11).

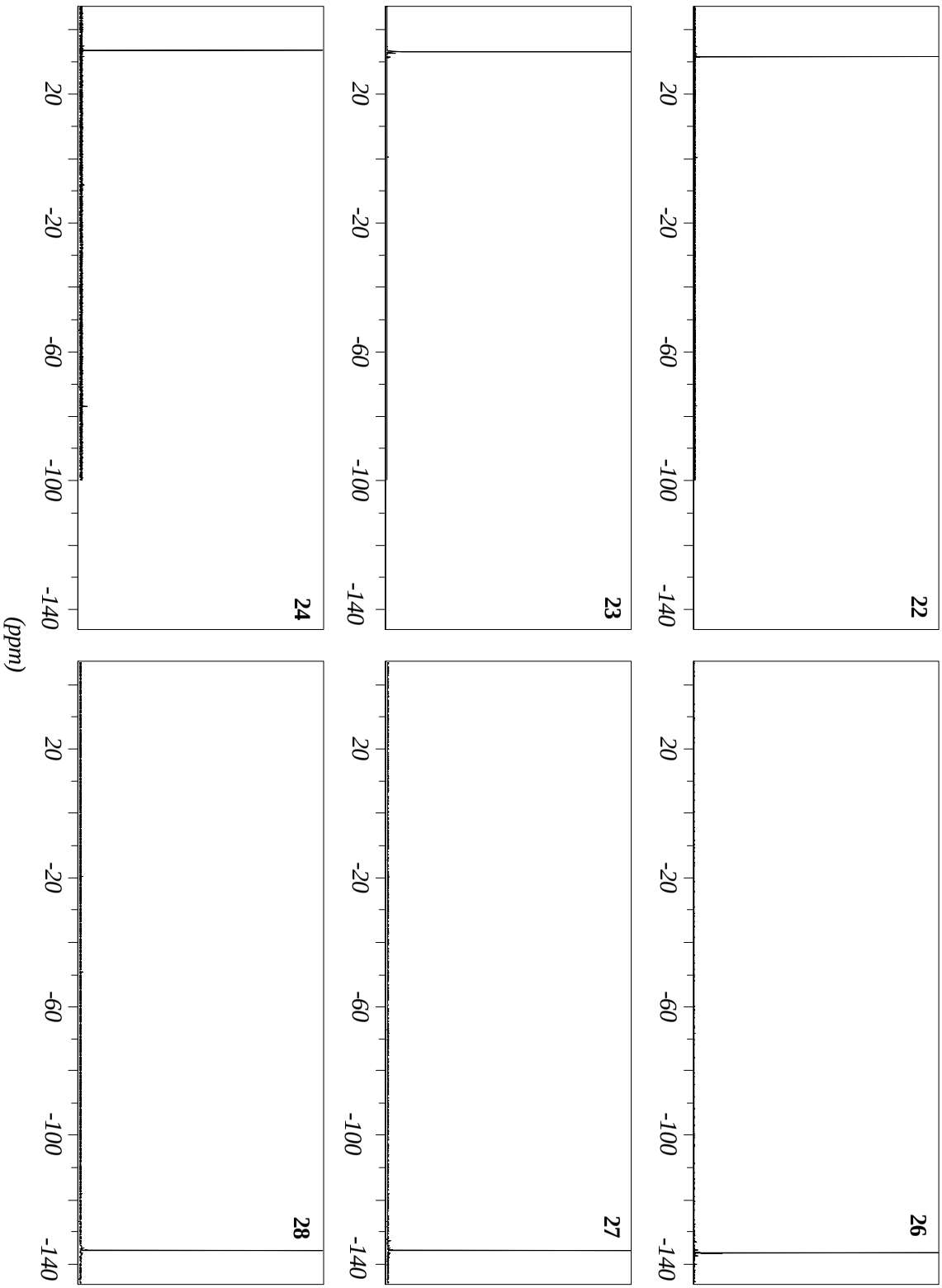
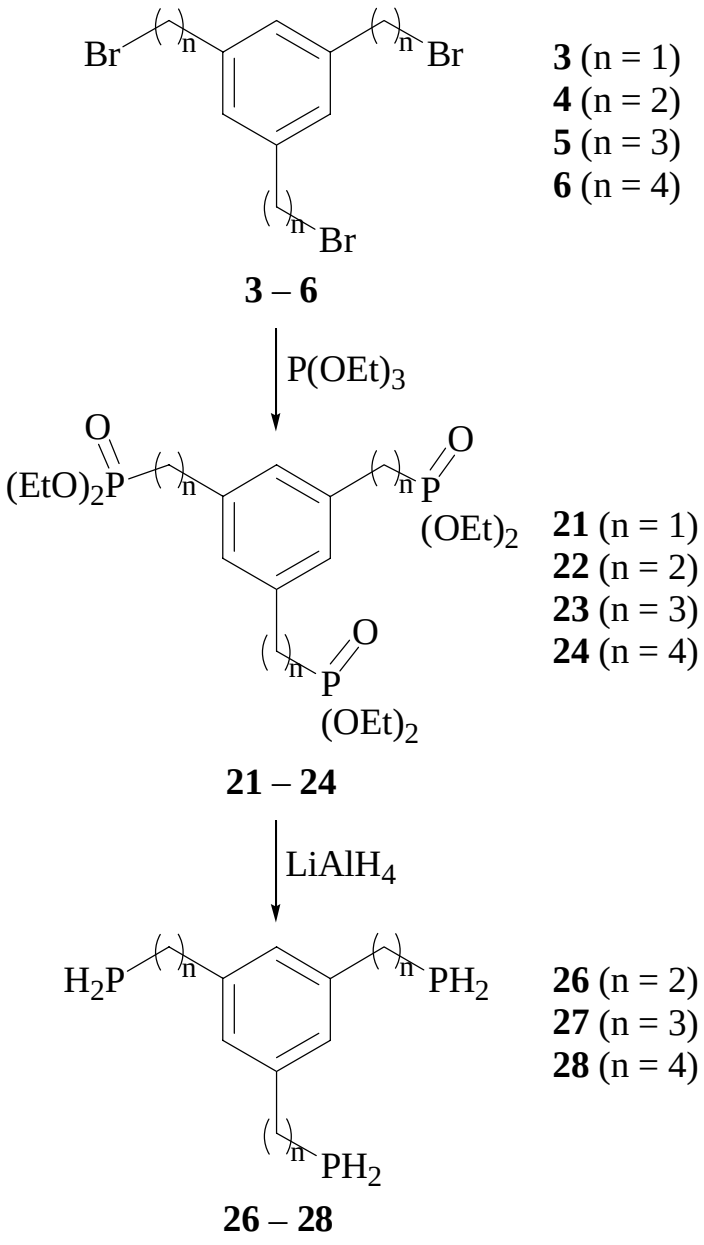


Figure 11. $^{31}P\{^{1}H\}$-NMR spectra of compounds **22** –**24** and **26** – **28**

*2.2.2 Reactions of **26** – **28***

The trisphosphines **26** – **28** are regarded as key synthons for the synthesis of the water-soluble phosphine ligands **29** – **31** and **32** – **34** (Scheme 6), because they can easily



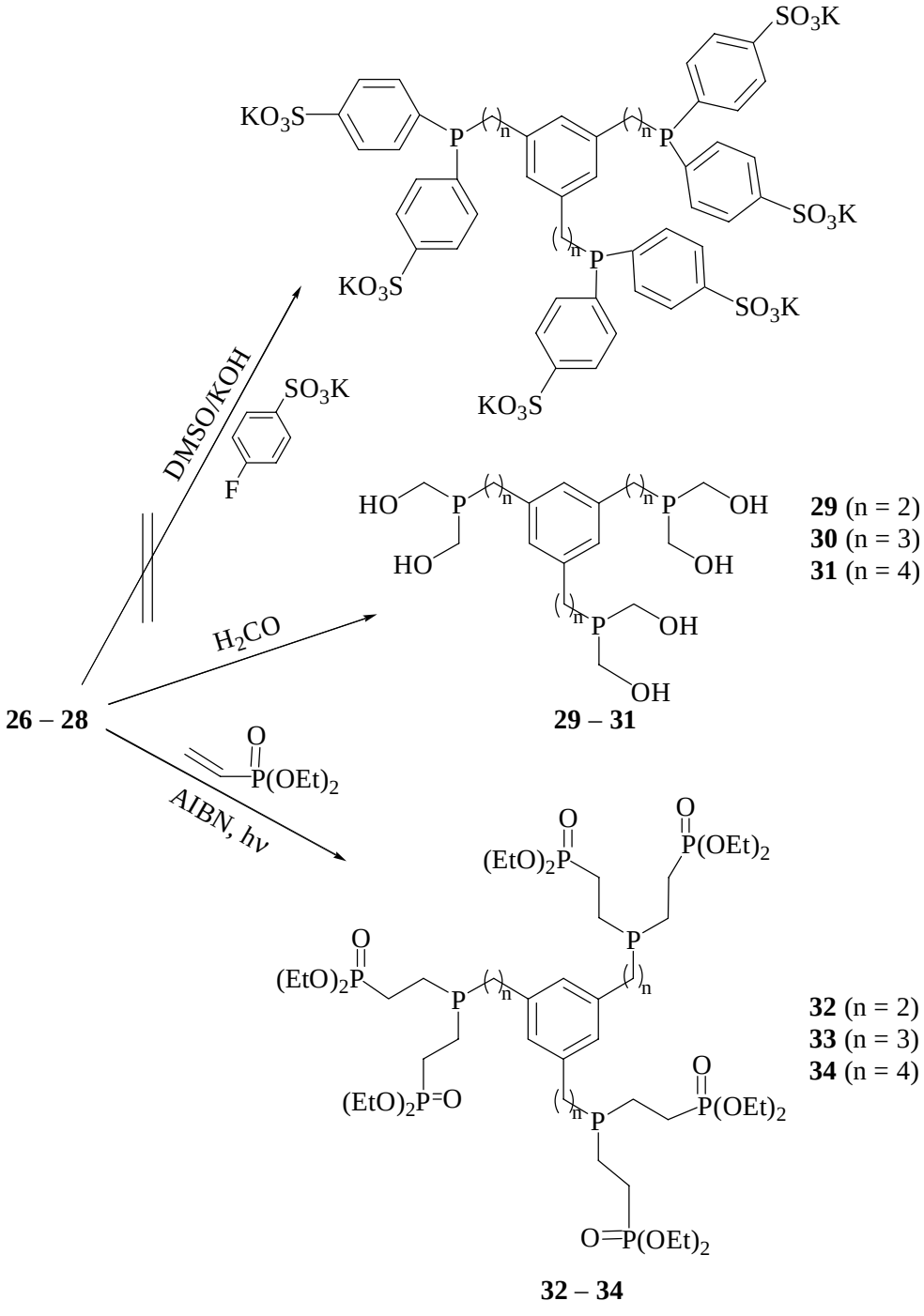
3 (n = 1)
4 (n = 2)
5 (n = 3)
6 (n = 4)

21 (n = 1)
22 (n = 2)
23 (n = 3)
24 (n = 4)

26 (n = 2)
27 (n = 3)
28 (n = 4)

Scheme 5. Synthesis of the triprimary phosphines **26** – **28**

be converted to related products by addition or substitution reactions with regard to the P–H functions.[107] Three examples were examined: 1) reaction of **26** – **28** with *p*-fluorobenzenesulfonate in DMSO[125, 126] 2) formylation of **26** – **28** by an aqueous solution of formaldehyde in ethanol[106, 108, 109] and 3) hydrophosphination of diethyl vinylphosphonate with **26** – **28**[110 – 113] (Scheme 6). Although the first reaction proceeds until a yield of 6%, the product seems to be unstable under the reaction conditions. This was confirmed by the isolation of trisulfonated triphenylphosphine from the reaction mixture instead of the product. The whole consumption of the primary phosphine was not achieved, even after 4 months, as controlled by $^{31}P\{^{1}H\}$-NMR. Both of the other reactions proceeded quantitatively to afford **29** – **34** as viscous oils resistant to crystallization. These novel phosphine ligands show good solubility in water, however **30** and **31** need about 10% of additional methanol to be soluble. Furthermore **32** – **34** are soluble in solvents of medium polarity. The compositions of **29** – **34** were corroborated by FD and FAB mass spectra showing the expected molecular peak in each case. ^{1}H-, $^{13}C\{^{1}H\}$-, and $^{31}P\{^{1}H\}$-NMR spectra are consistent with the given structures (see Scheme 2 and Experimental section). It is characteristic for the $^{31}P\{^{1}H\}$-NMR spectra of **32** – **34** that they display two signals in a 2 : 1 ratio representing an A_2X spin system with a coupling constant of about 50 Hz (Figure 12). It is assigned to the phosphonate (δ = 32) and phosphine ($\delta \approx -20$) groups.



29 (n = 2)
30 (n = 3)
31 (n = 4)

32 (n = 2)
33 (n = 3)
34 (n = 4)

Scheme 6. Water-soluble ligands synthesis

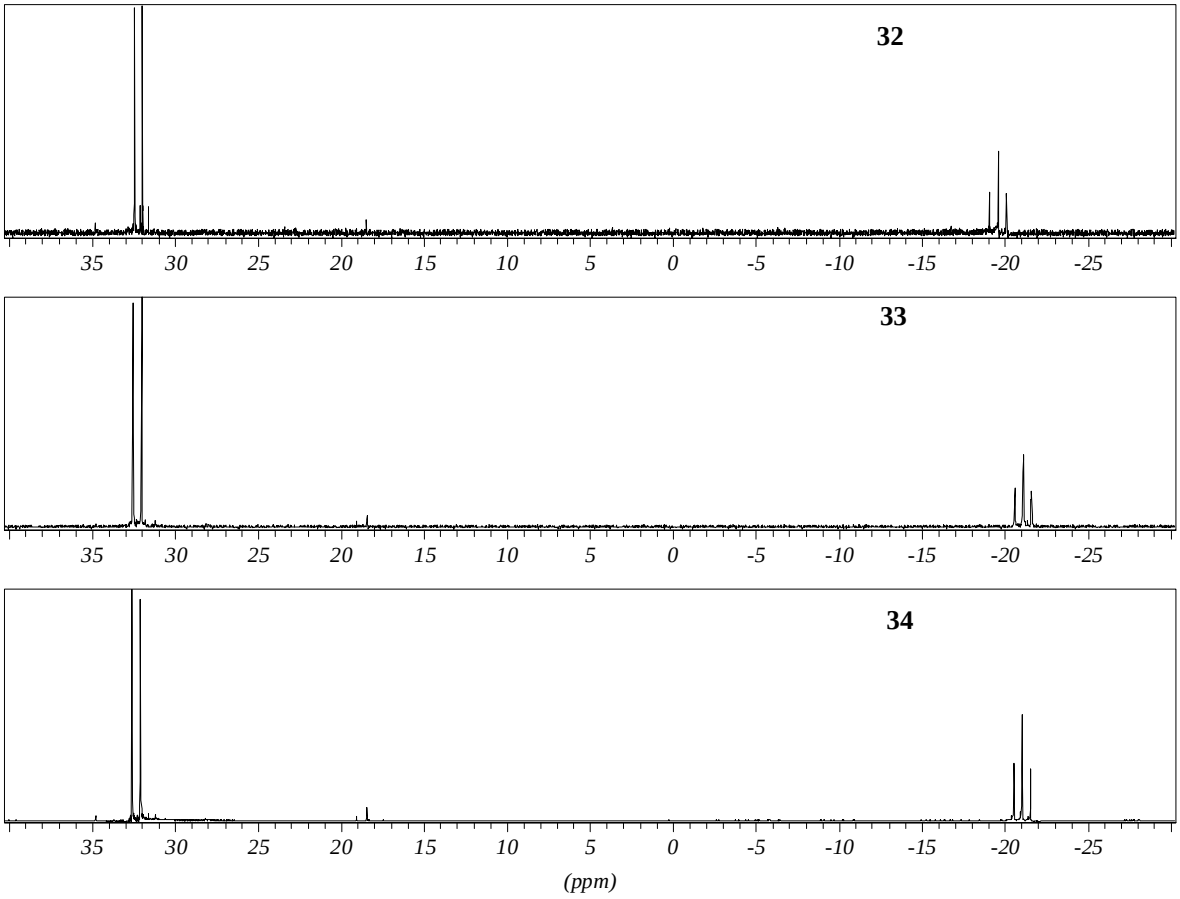
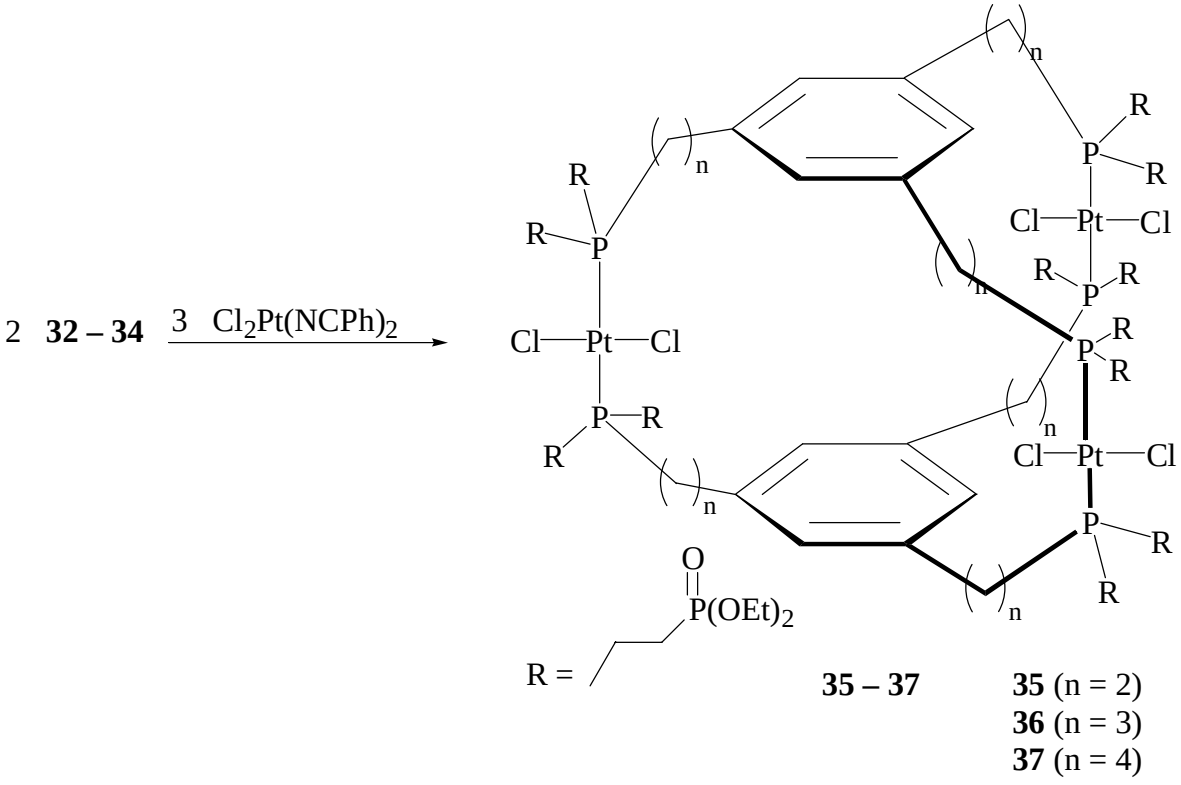


Figure 12. $^{31}P\{^{1}H\}$-NMR spectra of the ligands **32** – **34** showing an A_2X pattern

2.3. Self-assembly of the ligands 32 – 34 with $Cl_2Pt(NCPh)_2$

To obtain self-assembled cyclophane structures a preorganization of the components is a necessary prerequisite. The trifunctionalized phosphines **29** – **34** are provided with specific substituents that make them water-soluble. In addition they have the indispensable rigidity which is required to be preorganized. For the generation of the three-dimensional water-soluble platinacyclophanes **35** – **36**, the ligands **32** – **34** were treated with $Cl_2Pt(NCPh)_2$ in a mixture of methanol and dichloromethane or only

dichloromethane, respectively, according to the high dilution method[88] (Scheme 7). Corresponding reactions with **29 – 31** as starting materials led only to colorless polymers, which were not further characterized. The self-assembled triplatinacyclophanes **35 – 37** could be obtained in much higher yields (40 – 70%) than their nonwater-soluble counterparts (see Section 1). The yields decreased by increasing the number of methylene groups in the sequence **35** > **36** > **37**.



Scheme 7. Water-soluble cage-structured triplatinacyclophanes **35** – **37**

The pale yellow triplatinacyclophanes **35** – **37** are soluble in water and organic solvents of medium polarity. Several experiments to grow single crystals of **35** – **37** for an X-ray structural analysis failed.

An insight into structural facts of the platinacyclophanes **35** – **37** is available by $^{31}P\{^{1}H\}$-NMR spectroscopic probes. ^{31}P chemical shifts and ^{195}Pt – ^{31}P coupling constants allow an unambiguous distinction between *cis*- or *trans*- arrangement of the ligands at the platinum center. Corresponding coupling constants are in the range of 3500 and 2500 Hz, respectively.[90 – 93] In the spectra of **35** – **37** occur two signals with a 2 : 1 ratio representing an $A_2XX'A'_2$ pattern (Figure 13). The A-part of this spin system is located at higher field ($\delta \approx 30$, m = 58 Hz [114a]) and ascribed to the phosphonate function, whereas the X-part at lower field (δ = 5 to 13 , m = 58 Hz [114b]) which contains also a doublet for the ^{195}Pt satellites ($^{1}J_{PtP}$ = 2450 Hz) is attributed to the phosphine groups. This assignment is confirmed by $^{195}Pt\{^{1}H\}$-NMR spectra, which display a triplet each at $\delta \approx -3940$ ppm with coupling constants of about $^{1}J_{PtP}$ = 2450 Hz. The size of these constants unequivocally points to a *trans*-P–Pt–P arrangement in the macrocycles **35** – **37** which is in contrast to the recently reported nonwater-soluble platinacyclophanes (see Section 1). The different stereochemistry can be traced back to the greater steric demand of the phosphonate substituents at the phosphorus atoms compared to phenyl groups.[115 – 120]

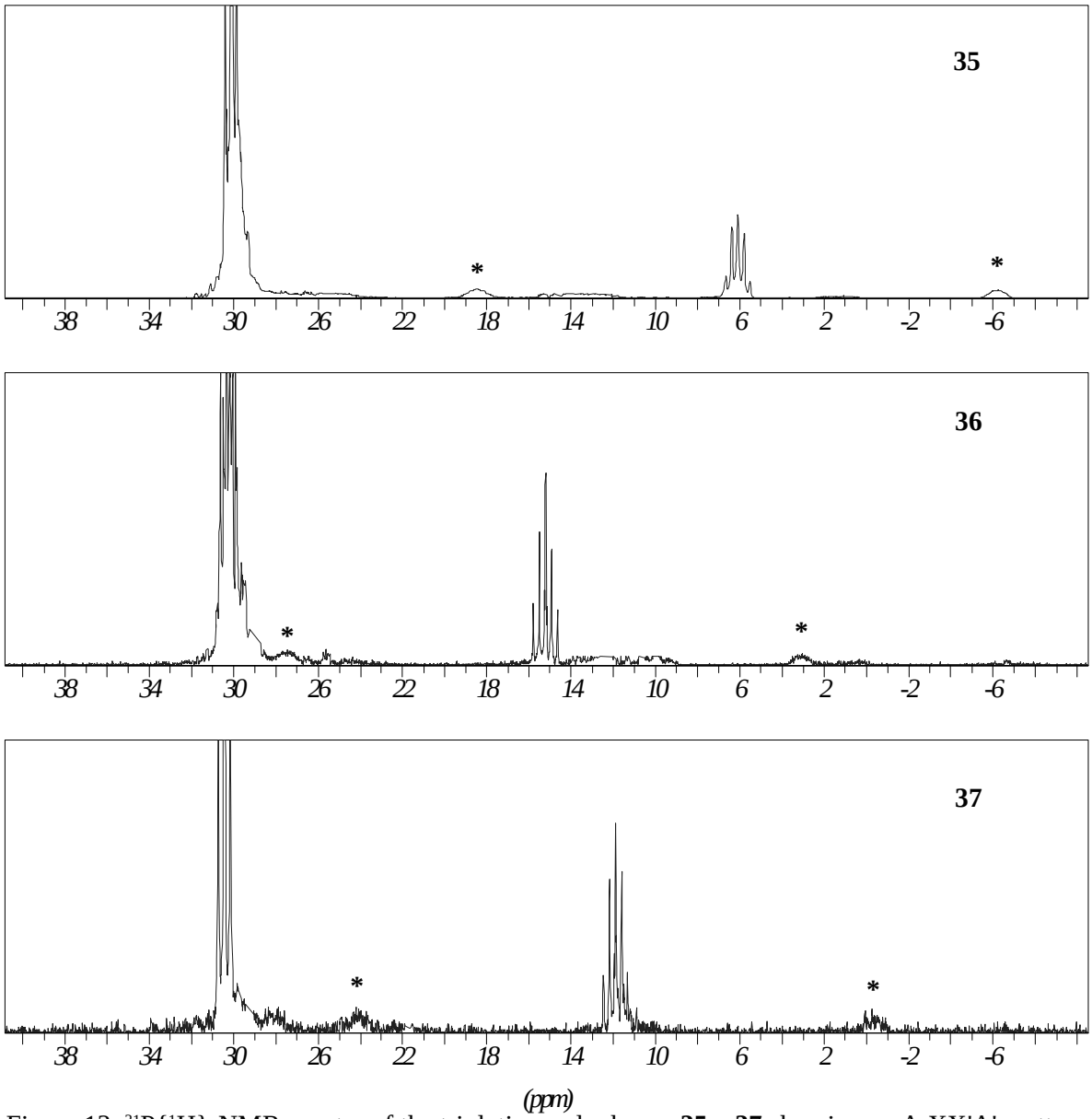


Figure 13. $^{31}P\{^{1}H\}$-NMR spectra of the triplatinacyclophanes **35** – **37** showing an $A_2XX'A'_2$ pattern. Asterisks denote ^{195}Pt satellites.

A short discussion of the ^{1}H- and ^{13}C{^{1}H}-NMR spectra of the triplatinacyclophanes **35** – **37** refers to the central benzene rings. Only one ^{1}H signal is observed at $\delta \approx 6.8$ which is an indication of the C_3 symmetry of these molecules. In the aromatic region of ^{13}C{^{1}H}-NMR spectra two resonances correspond to the methine ($\delta \approx 126$) and quaternary ($\delta \approx 141$) carbon atoms.

2.4. NMR investigations regarding host/guest chemistry

NMR spectroscopy is considered as the method of choice to study inclusion complexation in solution.[8] Extensive information is obtained on the structures of the complexes. Furthermore, the thermodynamics and kinetics of complexation can be evaluated. The metallacyclophanes **35** – **37** have the advantage to be soluble in many solvents of different polarity and the ^{31}P nucleus serves as a probe for NMR titrations. Several neutral organic guest (e.g. halogenated hydrocarbons, benzoic acid, potassium *p*-fluorobenzenesulfonate, fluorinated benzenes, toluene, 1,3,5-triacetylbenzene, and 1,3,5-trimesic acid) of different size were tested for the encapsulation into the cavities of **35** – **37** employing water or 10 to 30 %(v/v) aqueous methanol as solvents. The amount of **35** – **37** covered the accessible concentration range. However, no significant change of the chemical shifts for the ^{31}P or ^{1}H signals resulting from the phosphine and aromatic moiety, respectively, could be observed.

2.5. Conclusion

Within the last five to ten years several new architectures of metallacyclophanes with interesting properties have been described in the literature.[23, 32, 38 – 40 70 – 75, 121] This new variant of cyclophanes is available by self-assembly of multifunctional ligands with suitable metal fragments. Recently several metallacyclophanes were introduced which were formed by a template synthesis in aqueous media.[75] The solvent effect in self-assembly is also reported in the literature.[122 – 124] In the present investigation a simple strategy is presented that allows a convenient access to novel water-soluble trifunctional phosphines. They are provided with a central benzene ring which has three phosphine arms in a symmetrical 1,3,5-position. The distance of these phosphines from the benzene ring is controlled by methylene functions of different length. To these phosphines water-soluble functional groups are attached. It was demonstrated that these water-soluble trifunctional phosphine ligands are capable to undergo self-assembly with adequate platinum complex fragments to form triplatinacyclophanes. The tendency of self-organization is reduced by increasing the number of methylene groups. In that case the ligand system becomes more flexible and the phosphine moieties are able to move away from each other to minimize the interactions and hence the steric demand. Concomitant the production of polymers is enhanced.

The triplatinacyclophanes **35 – 37** are soluble in solvents of different polarity and even in water. Because of this favorable property they should be able to include guest molecules. However, experiments in this direction failed and did not lead to reproducible

or significant changes of the chemical shifts of ^{1}H or ^{31}P signals in the corresponding NMR spectra of these compounds.[8] This drawback may be attributed to three effects: (i) external $\pi - \pi$ stacking interactions leading to self-association of the hosts[8]; (ii) the host/guest association constants are too small to be measured; (iii) twenty-four ethyl groups at the phosphorus atoms may block the entrance of the cavities and hence prevent the encapsulation of guest molecules.

Experimental Section

1. General Considerations

1.1. Working procedures

All synthetic reactions and manipulations were performed under dry argon using standard Schlenk techniques. *n*-Pentane and TMEDA were freshly distilled from $LiAlH_4$, dichloromethane from calcium hydride, THF, diethyl ether, and benzene from sodium benzophenone ketyl, and mesitylene and *o*-dichlorbenzene from molecular sieves (5 Å). Column chromatography: activated silica gel, 0.063 – 0.200 mm or 0.04 – 0.063 (Merck); column dimensions are reported in the specific sections describing the synthesis of the compounds. Purifications by thin layer chromatography were carried out on preparative TLC glass plates (20 × 20 cm) using silica gel 60 F_{254}, 0.5 mm (Merck).

1.2. Characterization

Elemental analysis: Elementar Vario EL analyzer. Mass spectra: EI–MS: Finnigan TSQ 70 eV (200 °C); FD and pos. and neg. FAB-MS: Finnigan 711A (8 kV), modified by AMD. IR: Bruker IFS 48 FT-IR. ^{1}H-, ^{13}C{^{1}H}-, ^{31}P{^{1}H}-, and ^{195}Pt{^{1}H}-

NMR: Bruker DRX–250 spectrometer operating at 250.13, 62.90, 101.26, and 53.55 MHz, respectively. ^{1}H-NMR chemical shifts were referred to TMS as internal standard. $^{13}C\{^{1}H\}$-NMR chemical shifts were calibrated against the deuterated solvent multiplet and referenced to TMS. $^{31}P\{^{1}H\}$-NMR chemical shifts were measured relative to external 85% H_3PO_4 with downfield values being taken as positive. $^{195}Pt\{^{1}H\}$-NMR chemical shifts were measured relative to external 37.5% $Na_2[PtCl_6] \cdot 6\ H_2O$.

1.3. Starting Materials

Ethyl diphenylphosphonate[127], diethyl vinylphosphonate [127], $Cl_2Pt(NCPh)_2$[128] were synthesized according to literature methods. Chemicals from Aldrich: 1,3,5-benzenetricarboxylic acid; Fluka: triethylphosphite; Merck: lithiumaluminumhydride, 2,2'-azobis(2-methylpropionitrile) (AIBN), *N*-bromosuccinimide (NBS), potassium tetrachloroplatinate. Chemicals from Acros Organics: 1,3,5-triacetylbenzene. All these compounds were used without further purification.

2. Preparation of the Compounds

2.1. Preparation of 1,3,5-tris(bromoalkyl)benzenes 3 – 6

*2.1.1. 1,3,5-Tris(bromomethyl)benzene (**3**)*[129]

A suspension of mesitylene (15 mL, 108 mmol), *N*-bromosuccinimide (NBS, 55.6 g, 312 mmol), and 2,2'-azobis(2-methylpropionitrile) (AIBN, 100mg) in methylformate (300 mL) was placed in a 1.0 L round-bottom flask, equipped with a water-cooling condenser. The mixture was irradiated with a D 200 W (OSRAM) heating lamp placed at suitable distance to cause methyl formate to reflux (10 cm). After about 1 h, NBS is dissolved and a light red solution is formed. After additional irradiation (45 min), the solvent was removed by a rotation evaporator leaving a red oily residue. To this residue, water (40 mL) was added and the mixture was extracted with dichloromethane (4 × 200 mL). The combined organic extracts were washed with sodium carbonate (4%, 2 × 100 mL), and water (2 × 100 mL) and then dried (Na_2SO_4). Removal of dichloromethane leaves a pale yellow waxy material, which affords a colorless solid after crystallization from hot cyclohexane (four times). Yield: 12.9 g, 35%; m.p. 95 °C (m.p.[129] 96 °C). – ^{1}H-NMR ($CDCl_3$): δ = 4.38 (s, 6H; CH_2Br), 7.28 (s, 3H; aromat. H). – $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ = 32.6 (CH_2Br), 130.0 (aromat. CH), 139.4 (aromat. C). – MS (70 eV, EI, 200 °C); *m/z* (%): 360 (2), 358 (8), 356 (8), 354 (3) $[M]^+$, 279 (59), 277 (100), 275 (54) $[M – Br]^+$, 198 (47), 196 (43) $[M – 2\ Br]^+$.

*2.1.2. 1,3,5-Tris(2'-bromoethyl)benzene (**4**)*

2.1.2.1. 1,3,5-Benzenetriacetic acid[130]

A mixture of 1,3,5-triacetylbenzene (13.2 g, 75 mmol), morpholine (39.2 g, 450 mmol), and sulfur (14.4 g, 450mmol) was placed in a 100 mL round-bottom flask equipped with a condenser and refluxed for 20 h. The warm slurry was poured into water (300 mL) and the solid was collected on a frit (P2). The collected solid was hydrolyzed by refluxing for 12 h with water (50 mL), sulfuric acid (conc., 50 mL), and acetic acid (glacial, 50 mL). The solution was basified (NaOH, 50% solution, 100 mL), filtered (P2), and extracted with diethyl ether. After acidification with sulfuric acid, the solution was extracted with diethyl ether continuously until the aqueous phase became clear (five to six days). Removal of the ether left a pale yellow solid to afford a colorless solid by crystallization from glacial acetic acid. Yield: 14.9 g, 79%; m.p. 217 °C (m.p.[130] 215 – 216 °C). – ^{1}H-NMR (DMSO-d_6): δ = 3.51 (s, 6H; CH_2), 7.02 (s, 3H; aromat. C_6H_3). – $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): δ = 42.7 (CH_2), 130.8 (aromatic CH), 137.1 (aromatic C), 174.9 (COOH). – MS (70 eV, EI, 200 °C); *m/z* (%): 252 (7) $[M]^+$, 207 (14) $[M - CO_2]^+$, 162 (100) $[M - 2CO_2]^+$.

2.1.2.2. Triethyl 1,3,5-benzenetriacetate[131]

A solution of 1,3,5-benzenetriacetic acid (25.22 g, 100 mmol), ethanol (40 mL), sulfuric acid (conc., 4.5 mL), and 1,2-dichloroethane (90 mL) was refluxed until two layers were formed (20 h). The mixture was poured into water (300 mL) and the organic layer was separated. The aqueous phase was extracted with dichloromethane (3

× 150 mL). The combined extracts were washed with sodium bicarbonate (saturated, 100 mL) and water (100 mL). The volatile material was removed in vacuo to afford a pale yellow oil. Yield: 25.33 g, 86%. – ^{1}H-NMR ($CDCl_3$): δ = 1.12 (t, $^{3}J_{HH}$ = 7.0 Hz, 9H; C*H*$_3$CH$_2$O), 3.47 (s, 6H; CH_2CO), 4.02 (q, $^{3}J_{HH}$ = 7.0 Hz, 6H ; CH_3CH_2O), 7.02 (s, 3H; aromat. C_6H_3). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 14.3 (*C*H_3CH_2O), 41.2 (*C*H_2CO), 61.2 (OCH_2), 129.1 (aromat. CH), 134.8 (aromat. C), 171.4 (COO). – MS (70 eV, EI, 200 °C); *m/z* (%): 336 (19) $[M]^+$, 263 (88) $[M - CO_2Et]^+$, 190 (100) $[M - 2\ CO_2Et]^+$.

2.1.2.3. 1,3,5-Tris(2'-hydroxyethyl)benzene[84, 132]

To a suspension of lithium aluminium hydride (8.6 g, 227 mmol) in THF (400 mL) was added a solution of triethyl 1,3,5-benzenetriacetate (25.33 g, 86 mmol) in THF (180 mL) at –10 °C (ice-salt bath). After stirring for 3 h at room temperature, water (8 mL), NaOH (15%, 8mL), and water (24 mL) were added respectively. The mixture was filtered (P2) and the filter cake was washed with THF. The combined washings and filtrates were evaporated to leave a pale yellow oil, which solidified on standing. Crystallization of this residue from ethyl acetate afforded a colorless solid. Yield: 17.4 g, 93%; m.p. 74 – 75 °C (m.p.[132] 75 °C). – ^{1}H-NMR (DMSO-d_6): δ = 2.65 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H; C*H*$_2$CH$_2$O), 3.58 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H; CH_2C*H*$_2$OH), 4.85 (br. s, 3H; OH), 6.85 (s, 3H; aromat. C_6H_3). – ^{13}C{^{1}H}-NMR (DMSO-d_6): δ = 39.7 (*C*H_2CH_2OH), 63.1 (CH_2CH_2OH), 127.9 (aromat. CH), 139.8 (aromat. C). – MS (70 eV, EI, 200 °C); *m/z* (%): 210 (1) $[M]^+$, 192 (43) $[M - H_2O]^+$, 180 (43) $[M - CH_2O]^+$, 162 (100) $[M - CH_2O - H_2O]^+$.

*2.1.2.4 1,3,5-Tris(2'-bromoethyl)benzene (**4**)*[133]

To a mixture of 1,3,5-tris(2'-hydroxyethyl)benzene (0.84 g, 4.0 mmol) and carbon tetrabromide (4.98 g, 15.0 mmol) in THF (50 mL) was added triphenylphosphine (3.93 g, 15.0 mmol) at room temperature under argon. After stirring for 1 h, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 150 mL). The combined extracts were dried (Na_2SO_4) and evaporated to dryness. The crude product was purified by column chromatography (15 × 5 cm, *n*-hexane) to afford a colorless solid. Yield: 1.5 g, 94%, m.p. 90 °C (m.p.[133] 89 °C). – ^{1}H-NMR ($CDCl_3$): δ = 3.07 (t, $^3J_{HH}$ = 7.0 Hz, 6H; C*H*$_2$CH$_2$Br), 3.50 (t, $^3J_{HH}$ = 7.0 Hz, 6H; CH_2Br), 6.89 (s, 3H; aromat. C_6H_3). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 31.8 (*C*H$_2$CH$_2$Br), 38.1 (CH_2Br), 126.6 (aromat. CH), 138.5 (aromat. C). – MS (70 eV, EI, 200 °C); *m/z* (%): 402 (11), 400 (40), 398 (38), 396 (9) $[M]^+$, 321 (32), 319 (54), 317 (29) $[M – Br]^+$, 307 (50), 305 (100), 303 (47) $[M – CH_2Br]^+$.

*2.1.3. 1,3,5-Tris(3'-bromopropyl)benzene (**5**)*

Pyrophoric **2**, prepared from *n*-butyllithium (500 mL, 15% in *n*-hexane), TMEDA (92.97 g, 800 mmol) and mesitylene (16.4 g, 136 mmol), was suspended in *n*-pentane (250 mL) and added in portions to a solution of 1,2-dibromoethane (150 g, 800 mmol) in *n*-pentane (200 mL) at –85 °C. After stirring for 2 h the resulting mixture was allowed to warm slowly to room temperature. After neutralization, the organic phase was separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and the volatile materials were distilled. The

residual material was subjected to column chromatography (30 × 7 cm, *n*-hexane) to afford a colorless oil. Yield: 12.0 g, 20%. – ^{1}H-NMR ($CDCl_3$): δ = 1.36 (p, $^3J_{HH}$ = 7.0 Hz, 6H; C*H*$_2$CH$_2$Br), 2.73 (t, $^3J_{HH}$ = 7.4 Hz, 6H; C*H*$_2$CH$_2$CH$_2$Br), 3.40 (t, $^3J_{HH}$ = 6.6 Hz, 6H; CH$_2$C*H*$_2$Br), 6.88 (s, 3H; aromat. H). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 33.4 (CH_2Br), 34.0 (*C*H$_2$CH$_2$Br), 34.3 (*C*H$_2$CH$_2$CH$_2$Br), 126.8 (aromat. CH), 141.2 (aromat. C). – MS (70 eV, EI, 200 °C); *m/z* (%): 438 (27), 440 (92), 442 (100), 444 (27) $[M]^+$, 363 (4), 361 (8), 359 (5) $[M – Br]^+$, 331 (41), 333 (69), 335 (40) $[M – CH_2CH_2Br]^+$.

*2.1.4. 1,3,5-Tris(4-bromobutyl)benzene (**6**)*

Pyrophoric 1,3,5-tris(lithiomethyl)benzene (**2**), prepared from 500 mL of a solution of *n*-butyl lithium (1.6 M in *n*-hexane), 92.97g (0.80 mol) of TMEDA, and 16.4 g (0.136 mol) of mesitylene, was filtered off from the reaction mixture (P3) and washed with *n*-pentane. After drying in vacuo, **2** was suspended in 200 mL of *n*-pentane and added to a solution of 123.6 g (0.614 mol) of 1,3-dibromopropane in 500 mL of *n*-pentane at –78 °C. The resulting mixture was stirred at –78 °C for 2 h and then allowed to warm slowly to room temperature. The reaction mixture was neutralized, the organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and the volatile materials were removed in vacuum. The product was purified by column chromatography (50 × 7 cm, 10% (*v/v*) CH_2Cl_2 / *n*-hexane) to afford a colorless oil. Yield 11.5 g, 18%. – ^{1}H-NMR ($CDCl_3$): δ = 1.68 (m, 6H; C*H*$_2$CH$_2$CH$_2$Br), 1.73 (m, 6H; C*H*$_2$CH$_2$Br), 2.50 (t, $^3J_{HH}$ = 7.4 Hz, 6H; C*H*$_2$CH$_2$CH$_2$CH$_2$Br), 3.33 (t, $^3J_{HH}$ = 6.6 Hz, 6H; CH_2Br), 6.74 (s, 3H;

aromat. CH). – ^{13}C{1H}-NMR ($CDCl_3$): δ = 28.6 (*C*$H_2CH_2CH_2Br$), 31.1 (CH_2Br), 32.5(*C*H_2CH_2Br), 33.6 (*C*$H_2CH_2CH_2CH_2Br$), 125.0 (s, aromat. CH), 140.5 (s, aromat. C). – MS (70 eV, EI, 200 °C); *m/z* (%): 480 (2), 482 (8), 484 (8), 486 (2) $[M]^+$.

2.2. Preparation of 1,3,5-tris(diphenylphosphorylalkyl)benzenes 7 – 10

2.2.1. 1,3,5-Tris(diphenylphosphorylmethyl)benzene (7)

To a suspension of **3** (4.25 g, 12 mmol) in mesitylene (20 mL), Ph_2POEt (15.37 g, 67 mmol) was added. Heating the reaction mixture to 110 °C afforded a colorless solution. After heating the reaction mixture to 150 °C for 2 h, a white precipitate was formed. The solid was collected and crystallized from hot benzene, to afford a colorless solid. Yield: 8.0 g, 93%, m.p. 210 – 211 °C (m.p.[134] 205 – 206 °C). – ^{1}H-NMR ($CDCl_3$): δ = 3.44 (d, $^3J_{PH}$ = 13.8 Hz, 6H; CH_2P), 6.96 (d, $^4J_{PH}$ = 1.9 Hz, 3H; aromat. C_6H_3), 7.47 – 7.50 (m, 18H; *ortho*- and *para*-P–C_6H_5), 7.59 (m, 12H; *meta*-P–C_6H_5). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 37.7 (d, $^1J_{PC}$ = 66.9 Hz; *C*H_2P), 123.6 (s; *tert*-C_6H_3), 128.6 (d, $^3J_{PC}$ = 12.1 Hz; *meta*-C_6H_5), 130.6 (m; *quat*-C_6H_3), 131.1 (d, $^2J_{PC}$ = 9.3 Hz; *ortho*-C_6H_5), 131.8 (s; *para*-C_6H_3), 137.4 (d, $^1J_{PC}$ = 99.6 Hz; *ipso*-C_6H_5). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 30.9. – IR (KBr): $\tilde{\nu}$ = 3053, 3024 (aromat. CH), 2950, 2893 (CH_2), 1437 (P – Ph), 1198 cm^{-1} (P = O). – MS (70 eV, EI, 200 °C); *m/z* (%): 720 (1) $[M]^+$, 596 (9) $[M – P(O)Ph]^+$, 519 (5) $[M – P(O)Ph_2]^+$, 201 (100) $[P(O)Ph_2]^+$.

*2.2.2. 1,3,5-Tris(2'-diphenylphosphorylethyl)benzene (**8**)*

To a suspension of **4** (3.99 g, 10 mmol) in mesitylene (20 mL), Ph_2POEt (14.0 g, 61 mmol) was added. Heating the reaction mixture to 90 °C afforded a colorless solution. The procedure was continued as outlined for **7** to afford a colorless solid. Yield: 7.0 g, 98%, m.p. 234 – 235 °C. – ^{1}H-NMR ($CDCl_3$): δ = 2.49 (m, 6H; C*H*$_2$P), 2.82 (m, 6H; C*H*$_2$CH$_2$P), 6.79 (s, 3H; aromat. C_6H_3), 7.42 – 7.55 (m, 18H; *ortho*- and *para*-P–C_6H_5), 7.75 (m, 12H; *meta*-P–C_6H_5). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 27.5 (d, $^3J_{PC}$ = 2.1 Hz; *C*H$_2$CH$_2$P), 32.0 (d, $^1J_{PC}$ = 69.0 Hz; *C*H$_2$P), 126.1 (s; *tert*-C_6H_3), 128.9 (d, $^3J_{PC}$ = 11.4 Hz; *meta*-C_6H_5), 130.9 (d, $^2J_{PC}$ = 9.3 Hz; *ortho*-C_6H_5), 132.0 (d, $^4J_{PC}$ = 2.1 Hz; *para*-C_6H_5), 132.8 (d, $^1J_{PC}$ = 99.6 Hz; *ipso*-C_6H_5), 142.1 (d, $^3J_{PC}$ = 14.9 Hz; *quat*-C_6H_3). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 32.7. – IR (KBr): $\tilde{\nu}$ = 3052, 3022 (aromat. CH), 2935 (CH_2), 1438 (P – Ph), 1188 cm^{-1} (P = O). – MS (70 eV, EI, 200 °C): *m/z* (%): 560 (37) [M – P(O)Ph_2]$^+$, 359 (100) [M – 2P(O)Ph_2]$^+$, 201 (56) [P(O)Ph_2]$^+$. – MS (FD, CH_2Cl_2, 30 °C); *m/z* : 763 [M + H]$^+$. – $C_{48}H_{45}O_3P_3$ (762.8): MS (HR, pos. FAB, NBA, 50 °C); *m/z*: 763.25960 [M + H]$^+$; Calc. 763.26599. – Anal. Calc. for $C_{48}H_{45}O_3P_3$ (762.8): C, 75.58; H, 5.95. Found C, 75.36; H, 5.82%.

*2.2.3. 1,3,5-Tris[3'-(diphenylphosphoryl)propyl]benzene (**9**)*

Ph_2POEt (4.70 g, 20.4 mmol) was added to a suspension of **5** (1.50 g, 3.4 mmol) in mesitylene (20 mL). Heating the reaction mixture to 70 °C afforded a colorless solution. After heating the reaction mixture to 150 °C for 4 h, the volatile materials were

removed under vacuum at 90 °C. The residue solidified after cooling. A colorless solid product was obtained upon crystallization from benzene / *n*-hexane. Yield: 2.54 g, 93 %, m.p. 115 °C. – ^{1}H-NMR ($CDCl_3$): δ = 1.90 (m, 6H; C*H*$_2$P), 2.24 (m, 6H; C*H*$_2$CH$_2$P), 2.61 (t, $^{3}J_{HH}$ = 7.4 Hz, 6H; C*H*$_2$CH$_2$CH$_2$P), 6.70 (s, 3H; C_6H_3), 7.39 – 7.51 (m, 18H; *ortho*- and *para*-P–C_6H_5), 7.68 (m, 12H; *meta*-P–C_6H_5). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 23.0 (d, $^{2}J_{PC}$ = 3.4 Hz; CH$_2$*C*H$_2$CH$_2$P), 29.2 (d, $^{1}J_{PC}$ = 71.4 Hz; *C*H$_2$P), 37.1 (d, $^{3}J_{PC}$ = 14.8 Hz; *C*H$_2$CH$_2$CH$_2$P), 126.5 (s; *tert*-C_6H_3), 129.1 (d, $^{3}J_{PC}$ = 12.1 Hz; *meta*-C_6H_5), 130.7 (d, $^{2}J_{PC}$ = 8.8 Hz; *ortho*-C_6H_5), 131.8 (d, $^{4}J_{PC}$ = 2.7 Hz; *para*-C_6H_5), 133.0 (d, $^{1}J_{PC}$ = 98.4 Hz; *ipso*-C_6H_5), 141.2 (s; *quat*-C_6H_3). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 33.8. – IR (KBr): $\tilde{\nu}$ = 3054, 3055 (CH_2), 2960, 2934 (aromat. CH), 1184 cm^{-1} (P = O). – MS (pos. FAB, NBA, 50 °C); *m/z* (%): 805 (37) [M^+ + H], 603 (9) [M^+ – P(O)Ph_2], 589 (15) [M – $CH_2P(O)Ph_2]^+$, 576 (2) [M – $C_2H_4P(O)Ph_2]^+$, 229 (16) [$C_2H_4P(O)Ph_2]^+$, 215 (100) [$CH_2P(O)Ph_2]^+$, 201 (55) [$P(O)Ph_2]^+$. – $C_{51}H_{51}O_3P_3$ (804.9); MS (HR, pos. FAB, NBA, 50 °C); *m/z*: 805.31829 [M + H]$^+$; Calc. 805.31294. – Anal. Calc. for $C_{51}H_{51}O_3P_3$ (804.9): C, 76.11; H, 6.39. Found C, 76.39; H, 6.40%.

*2.2.4. 1,3,5-Tris[4'-(diphenylphosphoryl)butyl]benzene (**10**)*

For the synthesis of **10** the same procedure was applied as mentioned in Section 2.2.3. Colorless solid. Yield 86%, m.p. 155 – 156 °C. – ^{1}H-NMR ($CDCl_3$): δ = 1.57 (br m, 12H; CH_2CH_2P), 2.19 (m, 6H; C*H*$_2$CH$_2$CH$_2$P), 2.39 (br s, 6H; C*H*$_2$CH$_2$CH$_2$CH$_2$P), 6.59 (s, 3H; C_6H_3), 7.23 (m, 6H; *para*-P–C_6H_5), 7.34 (m, 12H; *ortho*-P–C_6H_5), 7.62 (m, 12H; *meta*-P–C_6H_5). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 21.7 (d, $^{3}J_{PC}$ = 2.9 Hz; *C*H$_2$CH$_2$P),

29.9 (d, $^{1}J_{PC}$ = 73.3 Hz; *C*H_2P), 33.2 (d, $^{2}J_{PC}$ = 14.2 Hz; *C*H_2CH$_2$CH$_2$P), 35.7 (s; *C*H_2CH$_2$CH$_2$CH$_2$P), 126.0 (s; *tert*-C_6H_3), 129.0 (d, $^{2}J_{PC}$ = 11.4 Hz; *ortho*-P–C_6H_5), 131.1 (d, $^{3}J_{PC}$ = 9.3 Hz; *meta*-P–C_6H_5), 132.1 (d, $^{4}J_{PC}$ = 2.1 Hz; *para*-P–C_6H_5), 133.3 (d, $^{1}J_{PC}$ = 97 Hz; *ipso*-C_6H_5), 142.3 (s; *quat*-C_6H_3). – ^{31}P {^{1}H}-NMR ($CDCl_3$): δ = 34.1. – MS (70 eV, EI, 200 °C); *m/z* (%): 847 (4) $[M]^+$, 644 (6) $[M - P(O)Ph_2]^+$, 617 (44) $[M - C_2H_4P(O)Ph_2]^+$, 416 (24) $[M - C_2H_4P(O)Ph_2 - P(O)Ph_2]^+$, 229 (17) $[C_2H_4P(O)Ph_2]^+$, 201 (100) $[P(O)Ph_2]^+$. – $C_{54}H_{57}O_3P_3$ (846.9); MS (HR, pos. FAB, NBA, 50 °C); *m/z*: 847.36891 $[M + H]^+$; Calc. 847.35989. – Anal. Calc. for $C_{54}H_{57}O_3P_3$ (846.9): C, 76.58; H, 6.78. Found C, 76.71; H, 6.63%.

2.3. Preparation of the ligands 1,3,5-tris(diphenylphosphinylalkyl)benzenes 11 – 14

A suspension of **7** – **10** (1.6 mmol) in *o*-dichlorobenzene (10 mL) was heated in a three-necked 100 mL round-bottom flask, equipped with reflux condenser. The suspension became a clear solution between 80 – 110 °C. The reaction mixture was further heated to 120 °C. At this temperature trichlorosilane (2.00 g, 14.8 mmol) was added dropwise through a septum. After 2 h the reaction mixture was allowed to cool slowly to room temperature. The reaction mixture was neutralized with degassed sodium hydroxide (20 %, 40 mL) which was added through a dropping funnel at –10 °C (ice-salt bath). The organic layer was separated and the aqueous layer was extracted

with dichloromethane (3 × 30 mL). The combined organic extracts were dried (Na_2SO_4), filtered (P3), and dried in vacuum to give a colorless solid.

*2.3.1. 1,3,5-Tris(diphenylphosphinylmethyl)benzene (**11**)*

Colorless solid. Yield 1.0 g, 93 %, m.p. 58 °C. – ^{1}H-NMR ($CDCl_3$): δ = 3.08 (s, 6H; CH_2P), 6.50 (s, 3H; C_6H_3), 7.18 (s, 30H; P–C_6H_5). – $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ = 35.9 (d, $^1J_{PC}$ = 15.7 Hz; *C*H_2P), 128.4 (d, $^3J_{PC}$ = 6.4 Hz; *meta*-C_6H_5), 128.7 (s; *para*-C_6H_3), 130.7 (s; *tert*-C_6H_3), 133.0 (d, $^2J_{PC}$ = 18.5 Hz; *ortho*-C_6H_5), 137.4 (dt, $^2J_{PC}$ = 8.5, $^4J_{PC}$ = 1.4 Hz; *quat*-C_6H_3), 138.6 (d, $^1J_{PC}$ = 15.7 Hz; *quat*-C_6H_5). – $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ = –9.4. – IR (KBr): $\tilde{\nu}$ = 3070, 3050 (aromat. CH), 2925, 2904 (CH_2), 1432 cm^{-1} (P – Ph). – MS (70 eV, EI, 200 °C); *m/z* (%): 672 (37) $[M]^+$, 595 (3) $[M - Ph]^+$, 487 (37) $[M - Ph_2]^+$, 301 (25) $[M - 2\ PPh_2]^+$. – $C_{45}H_{39}P_3$ (672.7): MS (HR, 70 eV, EI, 210 °C); *m/z*: 672.230597 $[M]^+$; Calc. 672.226445. – Anal. Calc. for $C_{45}H_{39}P_3$ (672.7): C, 80.35; H, 5.84. Found C, 80.04; H, 5.85%.

*2.3.2. 1,3,5-Tris[(2'-diphenylphosphinyl)ethyl]benzene (**12**)*

Colorless solid was obtained. Yield 1.1g, 96 %, m.p. 108 – 109 °C. – ^{1}H-NMR ($CDCl_3$): δ = 2.32 (m, 6H; CH_2P), 2.66 (m, 6H; C$H_2$$CH_2P$), 6.78 (s, 3H; C_6H_3), 7.33 – 7.35 (m, 18H; *ortho*- and *para*-P–C_6H_5), 7.45 (m, 12H; *meta*-P–C_6H_5). – $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ = 30.3 (d, $^2J_{PC}$ = 12.8 Hz; *C*H_2CH_2P), 32.3 (d, $^1J_{PC}$ = 18.5 Hz; CH_2P), 125.9 (s; *tert*-C_6H_3), 128.6 (d, $^3J_{PC}$ = 7.1 Hz; *meta*-P–C_6H_5), 128.8 (s; *para*-P–C_6H_5), 132.9 (d,

$^{2}J_{PC}$ = 18.5 Hz; *ortho*-P–C_6H_5), 138.7 (d, $^{1}J_{PC}$ = 12.8 Hz; *ipso*-C_6H_5), 143.1 (d, $^{3}J_{PC}$ = 12.8 Hz; *quat*-C_6H_3). – $^{31}P\{^{1}H\}$-NMR ($CDCl_3$): δ = –14.3. – IR (KBr): $\tilde{\nu}$ = 3068, 3051 (aromat. CH), 2940, 2924 (CH_2), 1479 cm^{-1} (P – Ph). – MS (70 eV, EI, 200 °C); *m/z* (%): 714 (13) $[M]^+$, 637 (7) $[M – Ph]^+$, 529 (27) $[M – 2\ Ph]^+$. – $C_{48}H_{45}P_3$ (714.8): MS (HR, pos. FAB, NBA, 50 °C); *m/z*: 715.26919 $[M + H]^+$; Calc. 715.28142. – Anal. Calc. for $C_{48}H_{45}P_3$ (714.8): C, 80.66; H, 6.35. Found C, 80.56; H, 6.15%.

*2.3.3. 1,3,5-Tris[(3'-diphenylphosphinyl)propyl]benzene (**13**)*

Colorless oil obtained. Yield 1.10 g, 91%. – ^{1}H-NMR ($CDCl_3$): δ = 1.74 (m, 6H; C*H*$_2$CH$_2$P), 2.08 (m, 6H; CH_2P), 2.66 (t, $^{3}J_{HH}$ = 7.4 Hz, 6H; C*H*$_2$CH$_2$CH$_2$P), 6.73 (s, 3H; C_6H_3), 7.33 (m, 18H; *ortho*- and *para*-P–C_6H_5), 7.41 (m, 12H; *meta*-P–C_6H_5). – $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): δ = 27.6 (d, $^{2}J_{PC}$ = 6.1 Hz; *C*H$_2$CH$_2$P), 27.7 (d, $^{1}J_{PC}$ = 20.9 Hz; CH_2P), 37.2 (d, $^{3}J_{PC}$ = 14.2 Hz; *C*H$_2$CH$_2$CH$_2$P), 126.4 (s; *tert*-C_6H_3), 128.6 (d, $^{3}J_{PC}$ = 6.7 Hz; *meta*-C_6H_5), 128.9 (s; *para*-C_6H_5), 132.9 (d, $^{2}J_{PC}$ = 17.5 Hz; *ortho*-C_6H_5), 138.3 (d, $^{1}J_{PC}$ = 10.1 Hz; *ipso*-C_6H_5), 141.9 (s; *quat*-C_6H_3). – $^{31}P\{^{1}H\}$-NMR ($CDCl_3$): δ = –14.8. – MS (70 eV, EI, 200 °C); *m/z* (%): 756 (53) $[M]^+$, 571 (28) $[M – PPh_2]^+$, 557 (29) $[M – CH_2PPh_2]^+$, 543 (35) $[M – C_2H_4PPh_2]^+$, 199 (100) $[CH_2PPh_2]^+$. – MS (pos. FAB, NBA, 50 °C); *m/z* (%): 757 (16) $[M + H]^+$, 571 (7) $[M – PPh_2]^+$, 557 (7) $[M – CH_2PPh_2]^+$, 543 (5) $[M – C_2H_4PPh_2]^+$, 199 (100) $[CH_2PPh_2]^+$. – Anal. Calc. for $C_{51}H_{51}P_3$ (756.9): C, 80.93; H, 6.79. Found C, 80.77; H, 7.01%.

*2.3.4. 1,3,5-Tris[4'-(diphenylphosphanyl)butyl]benzene (**14**)*

Colorless oil. Yield 1.3g, 95%. – ^{1}H-NMR ($CDCl_3$): δ = 1.42 (m, 6H; C*H*$_2$CH$_2$P), 1.62 (m, 6H; C*H*$_2$CH$_2$CH$_2$P), 1.98 (m, 6H; CH$_2$P), 2.42 (t, $^{3}J_{HH}$ = 7.7 Hz; 6H; C*H*$_2$CH$_2$CH$_2$CH$_2$P), 6.64 (s, 3H; C$_6$H$_3$), 7.22 - 7.32 (m, 30H; P–C$_6$H$_5$). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 24.8 (d, $^{1}J_{PC}$ = 18.9 Hz; CH$_2$P), 26.9 (d, $^{3}J_{PC}$ = 6.3 Hz; *C*H$_2$CH$_2$CH$_2$P), 32.0 (d, $^{2}J_{PC}$ = 12.6 Hz; *C*H$_2$CH$_2$P), 34.4 (s; *C*H$_2$CH$_2$CH$_2$CH$_2$P), 124.8 (s; *tert*-C$_6$H$_3$), 127.3 (d, $^{3}J_{PC}$ = 6.3 Hz; *meta*-P–C$_6$H$_5$), 127.4 (s; *para*-P–C$_6$H$_5$), 131.7 (d, $^{2}J_{PC}$ = 18.9 Hz; *ortho*-P–C$_6$H$_5$), 137.8 (d, $^{1}J_{PC}$ = 12.6 Hz; *ipso*-P–C$_6$H$_5$), 141.2 (s; *quat*-C$_6$H$_3$). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = –15.0. MS (pos. FAB, NBA, 50 °C); *m/z*: 799 $[M + H]^+$. – MS (70 eV, EI, 200 °C); *m/z*: 798 (21) $[M]^+$, 721 (2) $[M – Ph]^+$, 613 (17) $[M – PPh_2]^+$, 585 (4) $[M – C_2H_4PPh_2]^+$, 427 (2) $[M – 2PPh_2]^+$, 399 (17) $[M – C_2H_4PPh_2 – PPh_2]^+$, 183 (83) $[PPh_2]^+$, 107 (100) $[PPh]^+$. – Anal. Calc. for $C_{54}H_{57}P_3$ (799.0): C, 81.18; H, 7.19. Found C, 80.97; H, 7.11%.

2.4. Preparation of 1,3,5-tris[(diethoxyphosphinyl)alkyl]benzenes 21 – 24[135]

A mixture of **3** – **6** (10 mmol) and triethylphosphite (20 ml, 117 mmol) was heated in a two-necked 50 mL round-bottomed flask equipped with a distillation condenser. The temperature was maintained at 145 – 150 °C. After the distillation of ethylbromide was finished, the reaction mixture was further heated for 2 h at the same

temperature. Excess triethylphosphite was removed in vacuo to leave the pure products **21** – **24**.

*2.4.1. 1,3,5-Tris[(diethoxyphosphinyl)methyl]benzene (**21**)*

Colorless oil. Yield 5.0 g, 95%. – ^{1}H-NMR ($CDCl_3$): δ = 1.10 (t, $^{3}J_{HH}$ = 7.1 Hz, 18H; OCH_2CH_3), 2.96 (d, $^{2}J_{PH}$ = 22.0 Hz, 6H; CH_2P), 3.87 (dq, $^{3}J_{HH}$ = 7.4, $^{3}J_{PH}$ = 7.4 Hz, 12H; OCH_2CH_3), 6.99 (d, $^{4}J_{PH}$ = 2.2 Hz, 3H; aromat. C_6H_3). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): δ = 16.3 (d, $^{3}J_{PC}$ = 5.7 Hz; CH_3CH_2O), 33.3 (d, $^{1}J_{PC}$ = 138.0 Hz; CH_2P), 61.9 (d, $^{2}J_{PC}$ = 7.1 Hz; CH_3CH_2O), 129.7 (dt, $^{3}J_{PC}$ = 11.0, $^{5}J_{PC}$ = 5.7 Hz; aromat. CH), 132.1 (td, $^{2}J_{PC}$ = 12.1, $^{4}J_{PC}$ = 3.6 Hz; aromat. C). – $^{31}P\{^{1}H\}$-NMR ($CDCl_3$): δ = 27.1. – IR (KBr): $\tilde{\nu}$ = 2982, 2908 (CH_2), 1603 (aromat. C = C), 1252 (P = O), 1028 cm^{-1} (P – OEt). – MS (pos. FAB, NBA, 50 °C); *m/z* (%): 551 (4) $[M + Na]^+$, 529 (100) $[M + H]^+$, 501 (20) $[M – CH_2CH_2]^+$, 392 (21) $[M – P(O)(OEt)_2]^+$. – MS (FD, CH_2Cl_2, 30 °C); *m/z*: 528 $[M]^+$, 1057 $[2 M + H]^+$.

*2.4.2. 1,3,5-Tris[2'-(diethoxyphosphinyl)ethyl]benzene (**22**)*

Colorless oil. Yield 5.6 g, 98%. – ^{1}H-NMR ($CDCl_3$): δ = 1.25 (t, $^{3}J_{HH}$ = 7.1 Hz, 18H; OCH_2CH_3), 1.94 (td, $^{2}J_{PH}$ = 17.3, $^{3}J_{HH}$ = 7.1 Hz, 6H; CH_2P), 2.78 (dt, $^{3}J_{PH}$ = 9.3, $^{3}J_{HH}$ = 7.1 Hz, 6H; CH_2CH_2P), 4.03 (dq, $^{3}J_{HH}$ = 7.2, $^{3}J_{PH}$ = 7.2 Hz, 12H; OCH_2CH_3), 6.82 (s, 3H; aromat. CH). – $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): δ = 16.5 (d, $^{3}J_{PC}$ = 6.4 Hz;

CH_3CH_2O), 27.6 (d, $^1J_{PC}$ = 139.4 Hz; CH_2P), 28.5 (d, $^2J_{PC}$ = 5.0 Hz; *C*H_2CH_2P), 61.9 (d, $^2J_{PC}$ = 6.4 Hz; CH_3CH_2O), 125.8 (s; aromat. CH), 141.7 (d, $^3J_{PC}$ = 17.8 Hz; aromat. C). – $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ = 31.8. – IR (KBr): $\tilde{\nu}$ = 2983, 2870 (CH_2), 1605 (aromat. C = C), 1234 (P = O), 1024 cm^{-1} (P – OEt). – MS (pos. FAB, NBA, 50 °C); *m/z*: 571 $[M + H]^+$. – Anal. Calc. for $C_{24}H_{45}O_9P_3$ (570.5): C, 50.53; H; 7.95. Found C, 50.86; H, 8.03%.

*2.4.3. 1,3,5-Tris[3'-(diethoxyphosphinyl)propyl]benzene (**23**)*

Colorless oil. Yield 6.0 g, 98%. – ^{1}H-NMR ($CDCl_3$): δ = 1.22 (t, $^3J_{HH}$ = 7.1 Hz, 18H; OCH_2CH_3), 1.61 (m, 6H; C*H*$_2CH_2P$), 1.85 (m, 6H; CH_2P), 2.54 (t, $^3J_{HH}$ = 7.2 Hz, 6H; C*H*$_2CH_2CH_2P$), 3.99 (dq, $^3J_{HH}$ = 7.4, $^3J_{PH}$ = 7.3 Hz, 12H; OCH_2CH_3), 6.73 (s, 3H; aromat. CH). – $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ = 16.4 (d, $^3J_{PC}$ = 5.7 Hz; *C*H_3CH_2O), 24.2 (d, $^2J_{PC}$ = 5.0 Hz; *C*H_2CH_2P), 25.2 (d, $^1J_{PC}$ = 140.9 Hz; CH_2P), 36.4 (d, $^3J_{PC}$ = 17.1 Hz; *C*$H_2CH_2CH_2P$), 61.4 (d, $^2J_{PC}$ = 6.4 Hz; CH_3CH_2O), 126.4 (s; aromat. CH), 141.3 (s; aromat. C). – $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ = 33.2. – IR (KBr): $\tilde{\nu}$ = 2981, 2938, 2865 (CH_2), 1602 (aromat. C = C), 1245 (P = O), 1042 cm^{-1} (P – OEt). – MS (70 eV, EI, 200 °C); *m/z* (%): 612 (7) $[M]^+$, 475 (9) $[M - P(O)(OEt)_2]^+$, 461 (41) $[M - CH_2P(O)(OEt)_2]^+$, 165 (100) $[C_2H_4P(O)(OEt)_2]^+$. – Anal. Calc. for $C_{27}H_{51}O_9P_3$ (612.6): C, 52.94; H, 8.39. Found C, 52.64; H, 8.19%.

*2.4.4. 1,3,5-Tris[4'-(diethoxyphosphinyl)butyl]benzene (**24**)*

Colorless oil. Yield 6.5 g, 99%. – ^{1}H-NMR ($CDCl_3$): δ = 1.31 (t, $^{3}J_{HH}$ = 7.1 Hz, 18H; OCH_2CH_3), 1.72 – 1.80 (m, 18H; $CH_2CH_2CH_2CH_2P$), 2.55 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H; CH_2CH_2 CH_2CH_2P), 4.08 (dq, $^{3}J_{HH}$ = 6.8, $^{3}J_{PH}$ = 6.8 Hz, 12H; OCH_2CH_3), 6.78 (s, 3H; aromat. CH). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 16.7 (d, $^{3}J_{PC}$ = 5.7 Hz; CH_3CH_2O), 22.5 (d, $^{2}J_{PC}$ = 5.0 Hz; CH_2CH_2P), 25.7 (d, $^{1}J_{PC}$ = 140.9 Hz; CH_2P), 32.7 (d, $^{3}J_{PC}$ = 17.1 Hz; $CH_2CH_2CH_2P$), 35.6 (s; $CH_2CH_2CH_2CH_2P$), 61.6 (d, $^{2}J_{PC}$ = 6.4 Hz; CH_3CH_2O), 126.1 (s; aromat. CH), 142.2 (s; aromat. C). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 33.5. – IR (KBr): $\tilde{\nu}$ = 2981, 2938, 2865 (CH_2), 1603 (aromat. C=C), 1245 (P=O), 1060 cm^{-1} (P – OEt). – MS (70 eV, EI, 200 °C): *m/z* (%) 654 (18) $[M]^+$, 517 (3) $[M - P(O)(OEt)_2]^+$, 503 (4) $[M - CH_2P(O)(OEt)_2]^+$, 489 (100) $[M - C_2H_4P(O)(OEt)_2]^+$, 179 (5) $[M - C_3H_6P(O)(OEt)_2]^+$, 165 (18) $[M - C_2H_4P(O)(OEt)_2]^+$, 137 (32) $[P(O)(OEt)_2]^+$. – Anal. Calc. for $C_{30}H_{57}O_9P_3$ (654.7): C, 55.04; H, 8.78. Found C, 55.24; H, 8.50%.

2.5. Preparation of the 1,3,5-tris(phosphinoalkyl)benzenes 26 – 28[136]

A diethyl ether (100 mL) solution of **22** – **24** (3 mmol) in a pressure-equalizing dropping funnel was added slowly within 3 h to a stirred suspension of powdered $LiAlH_4$ (0.96 g, 27 mmol) in diethyl ether (150 mL) at –10 °C (ice-salt bath). The reaction mixture was allowed to warm slowly to room temperature. After stirring for 48 h at room temperature, the reaction was hydrolyzed slowly with aqueous hydrochloric acid

(6M, 50 mL) at –10 °C (ice-salt bath). The ether layer was separated and the aqueous phase was extracted with diethyl ether (2 × 100 mL). The combined ether extracts were dried (Na_2SO_4) and the solvent removed under reduced pressure to give a clear residual liquid which was identified as pure **26** – **28**.

*2.5.1. 1,3,5-Tris(2'-phosphinoethyl)benzene (**26**)*

Colorless liquid. Yield 0.50 g, 64 %. – ^{1}H-NMR ($CDCl_3$): δ = 1.72 (m, 6H; CH_2P), 2.62 (td, $^1J_{PH}$ = 195.3, $^3J_{HH}$ = 7.5 Hz, 6H; PH_2), 2.71 (dt, $^3J_{PH}$ = 7.9, $^3J_{HH}$ = 7.5 Hz, 6H; C*H*$_2$CH$_2$P), 6.76 (s, 3H; aromat. CH). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 16.1 (d, $^1J_{PC}$ = 9.2 Hz; *C*H$_2$P), 39.2 (d, $^2J_{PC}$ = 2.9 Hz; *C*H$_2$CH$_2$P), 126.3 (s; aromat. CH), 142.4 (d, $^3J_{PC}$ = 5.0 Hz; aromat. C). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = –136.8. – IR (KBr): $\tilde{\nu}$ = 2969, 2923 (CH_2), 2290 (P – H), 1603 cm^{-1} (aromat. C = C). – MS (70 eV, EI, 200 °C); *m/z* (%): 258 (1) $[M]^+$, 225 (100) $[M - PH_2]^+$.

*2.5.2. 1,3,5-Tris(3'-phosphinopropyl)benzene (**27**)*

Colorless liquid. Yield 0.6 g, 67%. – ^{1}H-NMR ($CDCl_3$): δ = 1.53 (dt, $^3J_{HH}$ = 7.9, $^2J_{PH}$ = 6.9 Hz, 6H; C*H*$_2$P), 1.82 (dtt, $^3J_{PH}$ = 8.1, $^3J_{HH}$ = 6.9, $^3J_{HH}$ = 7.5 Hz, 6H; C*H*$_2$CH$_2$P), 2.62 (t, $^3J_{HH}$ = 7.5 Hz, 6H; C*H*$_2$CH$_2$CH$_2$P), 2.71 (dt, $^1J_{PH}$ = 194.7, $^3J_{HH}$ = 7.2 Hz, 6H; PH_2), 6.80 (s, 3H; aromat. CH). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 13.5 (d, $^1J_{PC}$ = 8.5 Hz; CH_2P), 34.8 (d, $^2J_{PC}$ = 2.9 Hz; *C*H$_2$CH$_2$P), 36.7 (d, $^3J_{PC}$ = 5.7 Hz; *C*H$_2$CH$_2$CH$_2$P), 126.2 (s; aromat. CH), 141.7 (s; aromat. C). – ^{31}P{^{1}H}-NMR (101.26

MHz, $CDCl_3$, 22 °C): δ = –136.1. – IR (KBr): $\tilde{\nu}$ = 2964, 2874 (CH_2), 2292 (P – H), 1603 cm^{-1} (aromat. C = C). – MS (70 eV, EI, 200 °C); *m/z* (%): 300 (1) $[M]^+$, 267 (100) $[M – PH_2]^+$, 234 (30) $[M – 2\ PH_2]^+$, 205 (15) $[M – C_2H_4PH_2 – PH_2]^+$.

*2.5.3. 1,3,5-Tris(4'-phosphinobutyl)benzene (**28**)*

Colorless liquid. Yield 0.7 g, 68%. – ^{1}H-NMR ($CDCl_3$): δ = 1.55 (m, 12H; C*H*$_2$CH$_3$C*H*$_2$P), 1.67 (m, 6H; C*H*$_2$CH$_2$P), 2.56 (t, $^3J_{HH}$ = 7.4 Hz, 6H; C*H*$_2$CH$_2$CH$_2$CH$_2$P), 2.69 (dt, $^1J_{PH}$ = 194.7, $^3J_{HH}$ = 6.9 Hz, 6H; PH_2), 6.80 (s, 3H; aromat. CH). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 13.8 (d, $^1J_{PC}$ = 7.4 Hz; CH_2P), 32.6 (d, $^3J_{PC}$ = 5.4 Hz; *C*H$_2$CH$_2$CH$_2$P), 32.7 (d, $^2J_{PC}$ = 2.7 Hz; *C*H$_2$CH$_2$P), 35.6 (s; *C*H$_2$CH$_2$CH$_2$CH$_2$P), 126.1 (s; aromat. CH), 142.5 (s; aromat. C). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = –136.0. – IR (KBr): $\tilde{\nu}$ = 2963, 2925, 2853 (CH_2), 2290 (P – H), 1602 cm^{-1} (aromat. C = C). – MS (70 eV, EI, 200 °C); *m/z* (%): 341 (1) $[M – H]^+$, 309 (100) $[M – PH_2]^+$, 275 (8) $[M – 2\ PH_2]^+$, 233 (4) $[M – C_3H_6PH_2 – PH_2]^+$.

2.6. Preparation of the 1,3,5-tris[bis(hydroxymethyl)phosphinoalkyl]benzenes 29 – 31

To a vigorously stirred solution of compounds **26** – **28** (2 mmol) in ethanol (20 mL) a degassed solution of aqueous formaldehyde (37%, 1.0 g, 12 mmol) in ethanol (5

mL) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 12 h. Removal of volatile materials in vacuo afforded the pure compounds **29** – **31**.

*2.6.1. 1,3,5-Tris[2'-bis(hydroxymethyl)phosphinoethyl]benzene (**29**)*

Clear gummy material. Yield 0.85 g, 97%. – ^{1}H-NMR (D_2O): δ = 1.86 (dd, $^{2}J_{PH}$ = 7.2, $^{3}J_{HH}$ = 7.2 Hz, 6H; CH_2P), 2.76 (dt, $^{3}J_{PH}$ = 9.5, $^{3}J_{HH}$ = 7.6 Hz, 6H; C*H*$_2$CH$_2$P), 3.98 (m, 12H; OC*H*$_2$P), 7.02 (s, 3H; aromat. CH); ^{1}H-NMR (acetone-d_6): δ = 2.06 (m, 6H; CH_2P), 2.82 (m, 6H; C*H*$_2$CH$_2$P), 4.13 (m, 12H; OC*H*$_2$P), 7.07 (s, 3H; aromat. CH). – ^{13}C{^{1}H}-NMR (D_2O): δ = 20.0 (d, $^{1}J_{PC}$ = 8.6 Hz; CH_2P), 29.1 (d, $^{2}J_{PC}$ = 15.3 Hz; *C*H$_2$CH$_2$P), 55.8 (d, $^{1}J_{PC}$ = 9.53 Hz; PCH$_2$O), 123.8 (s; aromat. CH), 140.7 (d, $^{3}J_{PC}$ = 9.5 Hz; aromat. C); ^{13}C{^{1}H}-NMR (acetone-d_6): δ = 20.2 (d, $^{1}J_{PC}$ = 11.4 Hz; CH_2P), 31.8 (d, $^{2}J_{PC}$ = 17.1 Hz; *C*H$_2$CH$_2$P), 59.3 (d, $^{1}J_{PC}$ = 15.7; PCH$_2$O), 125.3 (s; aromat. CH), 142.7 (d, $^{3}J_{PC}$ = 12.8 Hz; aromat. C). – ^{31}P{^{1}H}-NMR (D_2O): δ = –24.5; ^{31}P{^{1}H}-NMR (acetone-d_6): δ = –22.9. – IR (KBr): $\tilde{\nu}$ = 3346 (O – H), 2899 (CH_2), 1600 (aromat. C = C), 1012 cm^{-1} (C – O). – MS (pos. FAB, NBA, 50 °C); *m/z* (%): 439 (41) [M + H]$^{+}$, 408 (42) [M – CH_2O]$^{+}$, 378 (41) [M – 2CH_2O]$^{+}$, 346 (29) [M – P(CH$_2$O)$_2$]$^{+}$, 334 (63) [M – CH_2P(CH$_2$O)$_2$]$^{+}$. – Anal. Calc. for $C_{18}H_{33}O_6P_3$ (438.4): C, 49.32; H, 7.59. Found C, 49.45; H, 7.76%.

*2.6.2. 1,3,5-Tris[3'-bis(hydroxymethyl)phosphinopropyl]benzene (**30**)*

Clear gummy material. Yield 0.90 g, 94%. – ^{1}H-NMR (D_2O): δ = 1.86 (dd, $^{2}J_{PH}$ = 7.2, $^{3}J_{HH}$ = 7.2 Hz, 6H; CH_2P), 2.76 (dt, $^{3}J_{PH}$ = 9.5, $^{3}J_{HH}$ = 7.6 Hz, 6H; C*H*$_2$CH$_2$P), 3.98 (m, 12H; OC*H*$_2$P), 7.02 (s, 3H; aromat. CH); ^{1}H-NMR (acetone-d_6): δ = 2.06 (m, 6H; CH_2P), 2.82 (m, 6H; C*H*$_2$CH$_2$P), 4.13 (m, 12H; OC*H*$_2$P), 7.07 (s, 3H; aromat. CH). – ^{13}C{^{1}H}-NMR (D_2O): δ = 20.0 (d, $^{1}J_{PC}$ = 8.6 Hz; CH_2P), 29.1 (d, $^{2}J_{PC}$ = 15.3 Hz; *C*H$_2$CH$_2$P), 55.8 (d, $^{1}J_{PC}$ = 9.53 Hz; PCH$_2$O), 123.8 (s; aromat. CH), 140.7 (d, $^{3}J_{PC}$ = 9.5 Hz; aromat. C); ^{13}C{^{1}H}-NMR (acetone-d_6): δ = 20.2 (d, $^{1}J_{PC}$ = 11.4 Hz; CH_2P), 31.8 (d, $^{2}J_{PC}$ = 17.1 Hz; *C*H$_2$CH$_2$P), 59.3 (d, $^{1}J_{PC}$ = 15.7 Hz; PCH$_2$O), 125.3 (s; aromat. CH), 142.7 (d, $^{3}J_{PC}$ = 12.8 Hz; aromat. C). – ^{31}P{^{1}H}-NMR (D_2O): δ = –24.5; ^{31}P{^{1}H}-NMR (acetone-d_6): δ = –22.9. – IR (KBr): $\tilde{\nu}$ = 3346 (O – H), 2899 (CH_2), 1600 (aromat. C = C), 1012 cm^{-1} (C – O). – MS (FD, EtOH, 30 °C); *m/z*: 481 [M + H]$^{+}$, 961 [2 M + H]$^{+}$. – MS (pos. FAB, NBA, 50 °C); *m/z* (%): 481 (20) [M + H]$^{+}$, 449 (28) [M – CH_2OH]$^{+}$, 420 (33) [M – 2 CH_2O]$^{+}$. – Anal. Calc. for $C_{21}H_{39}O_6P_3$ (480.5): C, 52.50; H, 8.18. Found C, 52.31; H, 8.50%.

*2.6.3. 1,3,5-Tris[4'-bis(hydroxymethyl)phosphinobutyl]benzene (**31**)*

Clear gummy material. Yield 1.0 g, 96%. – ^{1}H-NMR (acetone-d_6): δ = 1.50 – 1.72 (m, 18H; $CH_2CH_2CH_2P$), 2.58 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H; C*H*$_2$CH$_2$CH$_2$CH$_2$P), 4.01 (m, 12H; OC*H*$_2$P), 6.86 (s, 3H; aromat. CH). – ^{13}C{^{1}H}-NMR (acetone-d_6): δ = 18.9 (d, $^{1}J_{PC}$ = 10.1 Hz; CH_2P), 26.5 (d, $^{2}J_{PC}$ = 15.5 Hz; *C*H$_2$CH$_2$P), 34.1 (d, $^{3}J_{PC}$ = 11.5 Hz;

C$H_2CH_2CH_2P$), 36.2 (s; *C*$H_2CH_2CH_2CH_2P$), 60.6 (d, $^3J_{PC}$ = 16.2 Hz; PCH_2OH), 126.8 (s; aromat. CH), 143.2 (s; aromat. C). – $^{31}P\{^1H\}$-NMR (acetone-d_6): δ = –24.0. – IR (KBr): $\tilde{\nu}$ = 3346 (O – H), 2899 (CH_2), 1600 (aromat. C = C), 1012 cm^{-1} (C – O). – MS (pos. FAB, NBA, 50 °C); *m/z* (%): 523 (20) $[M + H]^+$, 491 (15) $[M – CH_2OH]^+$, 462 (28) $[M – 2\ CH_2O]^+$. – Anal. Calc. for $C_{24}H_{45}O_6P_3$ (522.5): C, 55.17; H, 8.68. Found C, 54.97; H, 8.88%.

2.7. Preparation of the 1,3,5-tris{bis[(2'-diethylphosphonatoethyl)phosphino-alkyl]}benzenes 32 – 34

A mixture of **26** – **28** (2.0 mmol), diethyl vinylphosphonate (2.17 g, 13.2 mmol), and AIBN (50 mg) was irradiated in a closed quartz Schlenk tube for 24 h. The volatile materials were removed under vacuum at 80 °C to leave the pure products **32** – **34**.

*2.7.1. 1,3,5-Tris{2'-bis[(2'-diethylphosphonatoethyl)phosphinoethyl]}benzene (**32**)*

Clear gummy material. Yield 2.4 g, 96%. – ^{1}H-NMR ($CDCl_3$): δ = 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 36H; OCH_2CH_3), 1.63 – 1.86 (m, 30H; $CH_2P(CH_2CH_2)_2$), 2.64 (dt, $^3J_{PH}$ = 4.4, $^3J_{HH}$ = 7.4 Hz, 6H; C*H*$_2CH_2P$), 4.07 (dq, $^3J_{HH}$ = 7.2, $^3J_{PH}$ = 7.2 Hz, 24H; OCH_2CH_3), 6.82 (s, 3H; aromat. CH). – $^{13}C\{^1H\}$-NMR ($CDCl_3$, 22 °C): δ = 16.2 (d, $^3J_{PC}$ = 5.7 Hz;

*C*H$_3$CH$_2$O), 18.3 (dd, $^1J_{PC}$ = 17.4, $^2J_{PC}$ = 6.8 Hz; O=PCH$_2$*C*H$_2$P), 21.5 (dd, $^1J_{PC}$ = 140.5, $^2J_{PC}$ = 13.9 Hz; O=P*C*H$_2$CH$_2$P) 28.2 (d, $^1J_{PC}$ = 15.7 Hz; CH$_2$P), 31.6 (d, $^2J_{PC}$ = 14.9 Hz; *C*H$_2$CH$_2$P), 61.4 (d, $^2J_{PC}$ = 6.4 Hz; CH$_3$*C*H$_2$O), 125.4 (s; aromat. CH), 142.6 (d, $^3J_{PC}$ = 11.4 Hz; aromat. C). – ^{31}P{^{1}H}-NMR (CDCl$_3$): δ = –19.6 (t, $^3J_{PP}$ = 51.2 Hz, 3P; PC$_3$), 32.2 (d, $^3J_{PP}$ = 51.2 Hz, 6P; CP(O)(OEt)$_2$). – IR (KBr): $\tilde{\nu}$ = 2983, 2908 (CH$_2$), 1602 (aromat. C = C), 1237 (P = O), 1055 cm^{-1} (P – OEt). – MS (FD, CH$_2$Cl$_2$, 35 °C); *m/z*: 1243 [M]$^+$. – Anal. Calc. for C$_{48}$H$_{99}$O$_{18}$P$_9$ (1243.1): C, 46.38; H, 8.03. Found C, 46.24, H, 8.18%.

*2.7.2. 1,3,5-Tris{3'-bis[(2'-diethylphosphonatoethyl)phosphinopropyl]}benzene (**33**)*

Clear gummy material. Yield 2.5 g, 97%. – ^{1}H-NMR (CDCl$_3$): δ = 1.22 (t, $^3J_{HH}$ = 7.1 Hz, 36H; OCH$_2$C*H*$_3$), 1.35 (m, 6H; C*H*$_2$P), 1.43 – 1.75 (m, 30H; O=PC*H*$_2$C*H*$_2$P and C*H*$_2$CH$_2$P), 2.52 (t, $^3J_{HH}$ = 7.4 Hz, 6H; C*H*$_2$CH$_2$CH$_2$P), 3.99 (dq, $^3J_{HH}$ = 7.2, $^3J_{PH}$ = 7.2 Hz, 24H; OC*H*$_2$CH$_3$), 6.70 (s, 3H; aromat. CH). – ^{13}C{^{1}H}-NMR (CDCl$_3$): δ = 16.4 (d, $^3J_{PC}$ = 5.7 Hz; *C*H$_3$CH$_2$O), 18.5 (dd, $^1J_{PC}$ = 16.4, $^2J_{PC}$ = 6.4 Hz; O=PCH$_2$*C*H$_2$P), 21.7 (dd, $^1J_{PC}$ = 140.1, $^2J_{PC}$ = 13.5 Hz; O=P*C*H$_2$CH$_2$P), 26.1 (d, $^2J_{PC}$ = 14.2 Hz; *C*H$_2$CH$_2$P), 27.5 (d, $^1J_{PC}$ = 14.2 Hz; CH$_2$P), 37.3 (d, $^3J_{PC}$ = 11.4 Hz; *C*H$_2$CH$_2$CH$_2$P), 61.6 (d, $^2J_{PC}$ = 6.4 Hz; CH$_3$*C*H$_2$O), 126.1 (s; aromat. CH), 141.8 (s; aromat. C). – ^{31}P{^{1}H}-NMR (CDCl$_3$): δ = –21.2 (t, $^3J_{PP}$ = 51.2 Hz, 3P; PC$_3$), 32.3 (d, $^3J_{PP}$ = 51.2 Hz, 6P; CP(O)(OEt)$_2$). – IR (KBr): $\tilde{\nu}$ = 2984, 2932, 2929 (CH$_2$), 1603 (aromat. C = C), 1237 (P = O), 1026 cm^{-1} (P – OEt). – MS (FD, CH$_2$Cl$_2$, 35 °C); *m/z* (%): 1285 [M]$^+$. – Anal. Calc. for C$_{51}$H$_{105}$O$_{18}$P$_9$ (1285.1): C, 47.67; H, 8.23. Found, C, 47.23, H, 7.97%.

*2.7.3. 1,3,5-Tris{4'-bis[(2'-diethylphosphonatoethyl)phosphinobutyl]}benzene (**34**)*

Clear gummy material. Yield 2.55 g, 96%. – ^{1}H-NMR ($CDCl_3$): δ = 1.28 (t, $^{3}J_{HH}$ = 7.1 Hz, 36H; OCH_2CH_3), 1.41 (br. s, 12H; CH_2CH_2P), 1.49 – 1.64 (m, 24H; $O{=}PCH_2CH_2P$), 1.77 (m, 6H; $CH_2CH_2CH_2P$), 2.50 (t, $^{3}J_{HH}$ = 7.5 Hz, 6H; $CH_2CH_2CH_2P$), 4.05 (dq, $^{3}J_{HH}$ = 7.2, $^{3}J_{PH}$ = 7.2 Hz, 24H; OCH_2CH_3), 6.74 (s, 3H; aromat. CH). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 16.6 (d, $^{3}J_{PC}$ = 6.1 Hz; CH_3CH_2O), 18.7 (dd, $^{1}J_{PC}$ = 16.5, $^{2}J_{PC}$ = 6.4 Hz; $O{=}PCH_2CH_2P$), 21.9 (dd, $^{1}J_{PC}$ = 140.5, $^{2}J_{PC}$ = 13.9 Hz; $O{=}PCH_2CH_2P$), 25.8 (d, $^{3}J_{PC}$ = 10.8 Hz; $CH_2CH_2CH_2P$), 26.4 (d, $^{1}J_{PC}$ = 13.5 Hz; CH_2P), 33.5 (d, $^{3}J_{PC}$ = 13.5 Hz, CH_2CH_2P), 35.8 (s; $CH_2CH_2CH_2CH_2P$), 61.8 (d, $^{2}J_{PC}$ = 6.7 Hz; CH_3CH_2O), 125.0 (s; aromat. CH), 142.4 (s; aromat. C). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = –21.1 (t, $^{3}J_{PP}$ = 51.2 Hz, 3P; PC_3), 32.4 (d, $^{3}J_{PP}$ = 51.2 Hz, 6P; $CP(O)(OEt)_2$). – IR (KBr): $\tilde{\nu}$ = 2983, 2933, 2857 (CH_2), 1603 (aromat. C = C), 1240 (P = O), 1066 cm^{-1} (P – OEt). – MS (pos. FAB, NBA, 50 °C); *m/z* (%): 1327 (23) $[M]^+$, 1161 (13) $[M - C_2H_4P(O)(OEt)_2]^+$, 995 (4) $[M - 2\ C_2H_4P(O)(OEt)_2]^+$, 967 (15) $[M - P(C_2H_4P(O)(OEt)_2)_2]^+$, 801 (16) $[M - C_2H_4P(O)(OEt)_2)_2 - P(C_2H_4P(O)(OEt)_2)_2]^+$, 361 $[P(C_2H_4P(O)(OEt)_2)_2]^+$, – Anal. Calc. for $C_{54}H_{111}O_{18}P_9$ (1327): C, 48.87; H, 8.43. Found C, 48.70, H, 8.64%.

2.8. Preparation of the triplatinacyclophanes 15 – 17, the trinuclear platinacycles 18 – 20, and the water-soluble triplatinacyclophanes 35 - 37

Solutions of $Cl_2Pt(NCPh)_2$ (708 mg, 1.5 mmol) and the corresponding ligand (1.0 mmol) in dichloromethane (250 mL each) were simultaneously added dropwise during 36 h into stirred dichloromethane (600 mL). After the addition was complete, the reaction mixture was allowed to stir for 24 h at room temperature. Then the solvent was removed in vacuum and the resulting residue was subjected to column chromatography.

*2.8.1. 3,3,14,14,25,25–Hexachloro–2,2,4,4,13,13,15,15,24,24,26,26–dodecaphenyl–2,4, 13,15,24,26–hexaphospha–3,14,25–triplatina [5$_3$] (1,3,5)–cyclophane (**15**)*

Colorless solid. Yield: 5 %, m.p. 273 – 275 °C. – ^{1}H-NMR ($CDCl_3$): δ = 3.9 (br. s; CH_2P), 6.68 (s; C_6H_3), 7.31 – 7.65 (m; P–C_6H_5). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 15.8 (t, $^1J_{PtP}$ = 2548 Hz). – IR (KBr): $\tilde{\nu}$ = 3050 (aromat. CH), 2928 (CH_2), 1435 cm^{-1} (P – Ph). – MS (neg. FAB, NBA, 50 °C); *m/z*: 2180 $[M + Cl]^-$. – Anal. Calc. for $C_{90}H_{78}Cl_6P_6Pt_3$ (2143.3): C, 50.43; H, 3.67; Cl, 11.35. Found C, 49.98; H, 3.40; Cl, 10.97%.

*2.8.2. 4,4,17,17,30,30-Hexachloro-3,3,5,5,16,16,18,18,29,29,31,31-dodecaphenyl-3,5,16,18,29,31-hexaphospha-4,17,30-triplatina [7$_3$] (1,3,5)-cyclophane (**16**)*

Colorless solid. Yield: 15 %, m.p. 241 – 242 °C. – ^{1}H-NMR ($CDCl_3$): δ = 2.64, 2.36 (br. s, 24H; CH_2CH_2P), 6.42 (s, 6H; C_6H_3), 7.11 – 7.49 (m, 60H; P–C_6H_5). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 22.2 (d, $^1J_{PC}$ = 90 Hz; CH_2P), 28.6 (d, $^2J_{PC}$ = 47 Hz; *C*H_2CH_2P), 126.1(s; *tert*-C_6H_3), 128.1 (d, $^3J_{PC}$ = 20 Hz; *meta*-P–C_6H_5), 129.6 (m; *ipso*-P–C_6H_5), 129.9 (s; *para*-P–C_6H_5), 131.6 (d, $^2J_{PC}$ = 23 Hz; *ortho*-P–C_6H_5), 140.3 (m; *quat*-C_6H_3). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 7.14 (sd, $^1J_{PtP}$ = 3600 Hz). – ^{195}Pt NMR ($CDCl_3$): δ = – 4423 (t, $^1J_{PtP}$ = 3600 Hz). – IR (KBr): $\tilde{\nu}$ = 3051 (aromat. CH), 2923 (CH_2), 1434 (P – Ph) cm^{-1}. – MS (neg. FAB, NBA, 50 °C); *m/z*: 2262 $[M + Cl]^-$. – Anal. Calc. for $C_{96}H_{90}Cl_6P_6Pt_3$ (2227.5): C, 51.76; H, 4.07; Cl, 9.55. Found C 51.34, H 4.10; Cl, 9.72%.

*2.8.3. 6,6,29,29,40,40-Hexachloro-5,5,7,7,22,22,24,24,39,39,41,41-dodecaphenyl-5,7,22,24,39,41-hexaphospha-6,23,40-triplatina [11$_3$] (1,3,5)-cyclophane (**17**)*

Colorless amorphous solid. Yield: 9%, m.p. 230 °C. – ^{1}H-NMR ($CDCl_3$): δ = 1.65 (br. s, 24H; C*H*$_2$C*H*$_2$CH$_2$P), 2.37 (s, 12H; CH_2P), 2.55 (s, 12H; C*H*$_2$CH$_2$CH$_2$CH$_2$P), 6.86 (s, 6H; *tert*-C_6H_3), 7.1 – 7.7 (m, 60H; P-C_6H_5). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 24.4 (s; *C*$H_2CH_2CH_2P$), 25.9 (d, $^2J_{PC}$ = 45 Hz; *C*H_2CH_2P), 32.9 (d, $^1J_{PC}$ = 16 Hz; CH_2P), 35.8 (s; *C*$H_2CH_2CH_2CH_2P$), 126.1 (s; *tert*-C_6H_3), 128.3 (t, $^3J_{PC}$ = 5.7 Hz; *meta*-P–C_6H_5), 131.1 (s; *para*-P–C_6H_5), 132.4 (m; *ipso*-P–C_6H_5), 133.5 (t, $^2J_{PC}$ = 6.3 Hz; *ortho*-P–C_6H_5), 143.4

(s; *quat*-C_6H_3). – $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ = 9.6 (sd, $^1J_{PtP}$ = 3668 Hz). – ^{195}Pt NMR ($CDCl_3$): δ = – 4413 (t, $^1J_{PtP}$ = 3668 Hz). – IR (KBr): $\tilde{\nu}$ = 3051 (aromat. CH), 2925, 2853 (CH_2), 1435 (P – Ph) cm^{-1}. – MS (neg. FAB, NBA, 50 °C); *m/z*: 2393 $[M]^-$. – (pos. FAB, NBA, 50 °C): *m/z*: 2359 $[M - Cl]^+$. – Anal. Calc. for $C_{108}H_{114}Cl_6P_6Pt_3$ (2395.9): C, 54.14; H, 4.80; Cl, 8.88. Found C, 54.40; H, 4.71; Cl, 9.16%.

*2.8.4. Compound **18***

Colorless amorphous solid. Yield: 5%, m.p. 158 °C. – ^1H-NMR ($CDCl_3$): δ = 1.51, 1.71 (br. s; 24H; H2,3,12,13,16,17, for labeling see Scheme 4), 2.23 (m, 4H; H1), 2.37 (m, 12H; H4,11,18), 2.51 (br. s, 8H; H14,15), 6.65 (s, 4H; H6,10), 6.98 (s, 2H; H8), 7.2 – 7.7 (m, 60H; P–C_6H_5). – $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ = 21.7 (s; C12,17), 22.0 (s; C3), 22.8 (d, $^2J_{PC}$ = 41 Hz; C2), 23.1 (d, $^2J_{PC}$ = 46 Hz; C13,16), 30.9 (t, $^1J_{PC}$ = 16 Hz; C14,15), 32.0 (t, $^1J_{PC}$ = 13 Hz; C1), 33.7 (s; C11,18), 34.4 (s; C4), 125.5 (s; C6,10), 126.0 (s; C8), 127.1 (t, $^3J_{PC}$ = 5 Hz; *meta*-P–C_6H_5), 129.3 (s; *para*-P–C_6H_5), 129.7 (m; *ipso*-P^2–C_6H_5), 129.9 (m; *ipso*-P^1–C_6H_5), 132.4 (t, $^2J_{PC}$ = 6 Hz; *ortho*-P^2–C_6H_5), 132.7 (t, $^2J_{PC}$ = 6 Hz; *ortho*-P^1–C_6H_5), 140.3 (s; C7,9), 141.2 (s; C5). – $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ = 13.6 (sd, $^1J_{PtP}$ = 2534 Hz, 2P; P^1), 14.8 (sd, $^1J_{PtP}$ = 2566 Hz, 4P; P^2). – $^{195}Pt\{^1H\}$-NMR ($CDCl_3$): δ = –3973 (t, $^1J_{PtP}$ = 2566 Hz, 2Pt; Pt^2), –3960 (t, $^1J_{PtP}$ = 2534 Hz, 1Pt, Pt^1). – IR (KBr): $\tilde{\nu}$ = 3053, 3006 (aromat. CH), 2926, 2854 (CH_2), 1434 (P – Ph) cm^{-1}. – MS (neg. FAB, NBA, 50 °C); *m/z*: 2393 $[M]^-$. – Anal. Calc. for $C_{108}H_{114}Cl_6P_6Pt_3$ (2395.9): C, 54.14; H, 4.80; Cl, 8.88. Found C, 54.32; H, 4.81; Cl, 8.96%.

*2.8.5. Compound **19***

Pale yellow amorphous solid. Yield: 20%, m.p. 171 °C. – ^{1}H-NMR ($CDCl_3$): δ = 1.50, 1.70 (br. s, 24H; H2,3,12,13,16,17), 2.23 (m, 4H; H1), 2.37 (m,12H; H4,11,18), 2.54 (br. s, 8H; H14,15), 6.60 (s, 4H; H6,10), 6.98 (s, 2H; H8), 7.1 – 7.6 (m, 60H; P–C_6H_5). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 22.0 (s; C3,12,17), 23.4 (s, $^{2}J_{PC}$ = 37 Hz; C13,16), 23.8 (d, $^{2}J_{PC}$ = 38 Hz; C2), 30.9 (t, $^{1}J_{PC}$ = 17 Hz; C14,15), 31.6 (t, $^{1}J_{PC}$ = 16 Hz; C1), 33.7 (s; C11,18), 34.2 (s; C4), 125.4 (s; C6,10), 126.1 (s; C8), 127.0 (t, $^{3}J_{PC}$ = 5 Hz; *meta*-P–C_6H_5), 129.3 (s; *para*-P–C_6H_5), 129.7 (m; *ipso*-P^1–C_6H_5), 129.9 (m; *ipso*-P^2–C_6H_5), 132.4(t, $^{2}J_{PC}$ = 6 Hz; *ortho*-P–C_6H_5), 140.4 (s; C7,9), 140.9 (s; C5). –^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 8.7 (sd, $^{1}J_{PtP}$ = 3648 Hz, 2P; P^1), 14.7 (sd, $^{1}J_{PtP}$ = 2565 Hz, 4P; P^2). – ^{195}Pt NMR ($CDCl_3$): δ = –3973 (t, $^{1}J_{PtP}$ = 2565 Hz, 2Pt; Pt^2), – 4410 (t, $^{1}J_{PtP}$ = 3648 Hz, 1Pt, Pt^1); IR (KBr): $\tilde{\nu}$ = 3052 (aromat. CH), 2925, 2854 (CH_2), 1434 cm^{-1} (P – Ph). – MS (neg. FAB, NBA, 50 °C); *m/z*: 2392 $[M]^-$. – Anal. Calc. for $C_{108}H_{114}Cl_6P_6Pt_3$ (2395.9): C, 54.14; H, 4.80; Cl, 8.88. Found C, 54.28; H, 4.76; Cl, 8.73%.

*2.8.6. Compound **20***

Pale yellow amorphous solid. Yield 60%, m.p. 191 – 193 °C. – ^{1}H-NMR ($CDCl_3$): δ = 1.47, 1.85 (br. s, 24H; H2,3,12,13,16,17), 2.13 (m, 8H; H14,15), 2.37 (m, 4H; H1), 2.55 (br. s, 12H; H4,11,18), 6.82 (s, 4H; H6,10), 6.92 (s, 2H; H8), 7.1 – 7.7 (m, 60H; P–C_6H_5). – ^{13}C{^{1}H}-NMR ($CDCl_3$, 25 °C): δ = 24.4 (s; C3), 24.6 (s; C12,17), 25.9 (d, $^{2}J_{PC}$ = 45 Hz; C2), 27.5 (d, $^{2}J_{PC}$ = 48 Hz; C13,16), 32.9 (t, $^{1}J_{PC}$ = 16 Hz;

C14,15), 33.6 (t, $^{1}J_{PC}$ = 13 Hz; C1), 35.5 (s; C11,18), 36.0 (s; C4), 126.1 (s; C8), 126.6 (s; C6,10), 128.1 (t, $^{3}J_{PC}$ = 5 Hz; *meta*-P^{2}–C_6H_5), 128.3 (s, $^{3}J_{PC}$ = 5 Hz; *meta*-P^{1}–C_6H_5), 130.9 (s; *para*-P^{2}–C_6H_5), 131.1 (s; *para*-P^{1}–C_6H_5), 131.2 (m; *ipso*-P–C_6H_5), 133.1(t, $^{2}J_{PC}$ = 5 Hz; *ortho*-P^{2}–C_6H_5), 133.5 (t, $^{2}J_{PC}$ = 5 Hz; *ortho*-P^{1}–C_6H_5), 141.8 (s; C7,9), 142.3 (s; C5). – $^{31}P\{^{1}H\}$-NMR ($CDCl_3$): δ = 6.7 (sd, $^{1}J_{PtP}$ = 3610 Hz, 4P; P^{2}), 8.7 (sd, $^{1}J_{PtP}$ = 3635 Hz, 2P; P^{1}). – ^{195}Pt NMR ($CDCl_3$): δ = – 4431 (t, $^{1}J_{PtP}$ = 3610 Hz, 2Pt; Pt^{2}), – 4413 (t, $^{1}J_{PtP}$ = 3635 Hz, 1Pt; Pt^{1}). – IR (KBr): $\tilde{\nu}$ = 3051 (aromat. CH), 2925, 2853 (CH_2), 1435 (P – Ph) cm^{-1}. – MS (neg. FAB, NBA, 50 °C); *m/z*: 2394 $[M]^{-}$. – Anal. Calc. for $C_{108}H_{114}Cl_6P_6Pt_3$ (2395.9): C, 54.14; H, 4.80; Cl, 8.88. Found C, 54.50; H, 4.91; Cl, 8.43%.

*2.8.7. 4,4,17,17,30,30-Hexachloro-3,3,5,5,16,16,18,18,29,29,31,31–dodeca(2'-diethyl-phosphonatoethyl)3,5,16,18,29,31–hexaphospha–4,17,30–triplatina[7₃](1,3,5)-cyclophane (**35**)*

Pale yellow gummy material. Yield 68 %. – ^{1}H-NMR (CD_2Cl_2): δ = 1.27 (t, $^{3}J_{HH}$ = 7.1 Hz, 72H; CH_3), 1.52 – 2.28 (m, 60H; $(O{=}PCH_2CH_2)_2PCH_2$), 2.80 (br. s, 12H; CH_2CH_2P), 4.05 (m, 48H; OCH_2), 6.82 (s, 3H; C_6H_3). – $^{13}C\{^{1}H\}$-NMR (CD_2Cl_2): δ = 13.1 (m; $O{=}PCH_2CH_2P$), 16.7 (d, $^{2}J_{PC}$ = 5.7 Hz; CH_3), 20.1 (d, $^{1}J_{PC}$ = 140.1 Hz; $O{=}PCH_2CH_2P$), 27.3 (m; CH_2P), 29.5 (br. s; CH_2CH_2P), 127.6 (s; aromat. CH), 140.5 (s; aromat. C). – $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2): δ = 6.1 ($m^{[114b]}$ d, *N* = 58.1, $^{1}J_{PtP}$ = 2478 Hz, 6P, $PtPC_3$), 30.1 ($m^{[114a]}$, *N* = 58.1 Hz, 12P, $CP(O)(OEt)_2$). – $^{195}Pt\{^{1}H\}$-NMR ($CDCl_3$): δ = –3940 (t, $^{1}J_{PtP}$ = 2478 Hz). – IR (KBr): $\tilde{\nu}$ = 2981, 2930, 2910 (CH_2), 1604 (aromat.

C = C), 1239 (P = O), 1023 cm^{-1} (P – OEt). – MS (pos. FAB, NBA, 50 °C): *m/z* 3288 $[M]^+$, 3247 $[M - Cl]^+$. – Anal. Calc. for $C_{96}H_{198}Cl_6O_{36}P_{18}Pt_3$ (3284.1): C, 35.11; H, 6.08; Cl, 6.48. Found C, 34.91; H, 6.05; Cl, 6.60%.

*2.8.8. 5,5,20,20,35,35-Hexachloro-4,4,6,6,19,19,21,21,34,34,36,36-dodeca-(2'-diethyl-phosphonatoethyl)-4,6,19,21,34,36-hexaphospha-5,20,35-triplatina[9$_3$](1,3,5)-cyclophane (**36**)*

Pale yellow gummy material. Yield: 55 %. – ^{1}H-NMR ($CDCl_3$): δ = 1.33 (m, 72H; CH_3), 1.74 – 2.06 (m, 72H; $(O{=}PCH_2CH_2)_2PCH_2CH_2$), 2.59 (br. s, 12H; C*H*$_2$$CH_2CH_2P$), 4.11 (m, 48H; OCH_2), 6.76 (s, 3H; C_6H_3). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 12.1 (m; $O{=}PCH_2$*C*H_2P), 16.5 (d, $^2J_{PC}$ = 5.4 Hz; CH_3), 19.6 (d, $^1J_{PC}$ = 141.5 Hz; $O{=}P$*C*H_2CH_2P), 24.4 (m; *C*H_2CH_2P), 35.1 (m; CH_2P), 36.8 (s; *C*$H_2CH_2CH_2P$), 128.2 (s; aromat. CH), 141.0 (s; aromat. C). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 15.2 (m[114a] d, *N* = 58.2, $^1J_{PtP}$ = 2465 Hz, 6P, $PtPC_3$), 30.3 (m[114b], *N* = 58.2 Hz, 12P, $CP(O)(OEt)_2$). – ^{195}Pt{^{1}H}-NMR ($CDCl_3$): δ = –3966 (t, $^1J_{PtP}$ = 2465 Hz). – IR (KBr): $\tilde{\nu}$ = 2981, 2930 (CH_2), 1603 (aromat. C = C), 1242 (P = O), 1028 cm^{-1} (P – OEt). – MS (pos. FAB, NBA, 50 °C); *m/z*: 3448 $[M]^+$. – Anal. Calc. for $C_{102}H_{210}Cl_6O_{36}P_{18}Pt_3$ (3368.2): C, 36.37; H, 6.28; Cl, 6.32. Found C, 35.98; H, 6.06; Cl, 6.40%.

*2.8.9. 6,6,29,29,40,40–Hexachloro–5,5,7,7,22,22,24,24,39,39,41,41–dodec(2'-diethyl-phosphonatoethyl)-5,7,22,24,39,41-hexaphospha-6,23,40-triplatina[11$_3$](1,3,5)-cyclophane (**37**)*

Pale yellow gummy material. Yield: 37 %. – ^{1}H-NMR ($CDCl_3$): δ = 1.34 (m, 72H; CH_3), 1.59 – 2.23 (m, 72H; $(O{=}PCH_2CH_2)_2PCH_2CH_2CH_2$), 2.61 (br. s, 12H; $CH_2CH_2CH_2CH_2P$), 4.11 (m, 48H; OCH_2), 6.76 (s, 3H; C_6H_3). – ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 13.8 (m; $O{=}PCH_2CH_2P$), 16.5 (d, $^2J_{PC}$ = 6.1 Hz; CH_3), 18.9 (s; $CH_2CH_2CH_2P$), 19.6 (d, $^1J_{PC}$ = 141.5 Hz; $O{=}PCH_2CH_2P$), 22.8 (s; $CH_2CH_2CH_2P$), 32.4 (m; CH_2CH_2P), 34.6 (s; $CH_2CH_2CH_2CH_2P$), 126.3 (s; aromat. CH), 141.1 (s; aromat. C). – ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 12.9 (m [114b] d, *N* = 58.2, $^1J_{PtP}$ = 2460 Hz, 6P, $PtPC_3$), 30.5 (m [114a], *N* = 58.2 Hz, 12P, $CP(O)(OEt)_2$). – ^{195}Pt{^{1}H}-NMR ($CDCl_3$): δ = –3933 (t, $^1J_{PtP}$ = 2460 Hz). – IR (KBr): $\tilde{\nu}$ = 2981, 2930, 2860 (CH_2), 1603 (aromat. C = C), 1242 (P = O), 1046 cm^{-1} (P – OEt). – MS (pos. FAB, NBA, 50 °C); *m/z*: 3364 $[M]^+$, 3329 $[M - Cl]^+$. – Anal. Calc. for $C_{108}H_{222}Cl_6O_{36}P_{18}Pt_3$ (3452.4): C, 37.57; H, 6.48; Cl, 6.16. Found C, 37.65; H, 6.54; Cl, 6.38%.

3. Dosing Apparatus

The dosing apparatus consists of two 50 mL Hamilton gastight syringe barrels mounted on a carrier. The plungers are precisely and simultaneously moved by a step motor via a spindle. Each of the syringes is connected via a teflon pipe to a magnetic valve with three entries that controls the direction of the flow of the solutions of the reactants. Further two entries of the magnetic valves are connected to storing vessels which can be cooled. Another set of entries is connected to cannulas which are penetrating compact teflon blocks. These teflon blocks fit into ground joins of the reaction vessel. The step motor and the magnetic valves are computer controlled.

4. Host/Guest Chemistry Investigations by NMR

4.1. Pre-experiments

Prior to a NMR titration the expected maximum shift ($\Delta\delta_{max}$) was determined. Hereby the chemical shifts (δ) at the first point of an NMR titration curve (pure triplatinacyclophanes in solution, p = 0) and last point (triplatinacyclophane + tenfold excess of guest, p = 1) were measured. A complete NMR titration was performed when

the shift difference ($\Delta\delta_{max}$) was larger than the spectral resolution of the NMR spectrometer ($\Delta\delta_{max} \geq 0.01$ ppm).

4.2. NMR titration procedure

The titration experiments were performed in a NMR tube (diameter/length = 5/160 mm) containing 500 μL of the NMR spectroscopically observed component: 5.0×10^{-3} or 1.0×10^{-3} mol/L of the triplatinacyclophanes **35** – **37** in D_2O or 30% (v/v) CD_3OD/D_2O. An initial spectrum of these starting solutions (**35** – **37**) was taken and the initial chemical shift of the aromatic CH protons or ^{31}P signals in the ^{1}H- or $^{31}P\{^{1}H\}$-NMR spectra, respectively, was determined. Control studies indicated that in the absence of the guest, the chemical shifts of the observed nuclei were not dependent on the concentration. The titration solutions of $CHCl_3$, CCl_4, benzoic acid, potassium *p*-fluorobenzenesulfonate, fluorobenzene, 1,3,5-trifluorobenzene, benzene, toluene, 1,3,5-triacetylbenzene, and 1,3,5-trimesic acid (0.5 mol/L) were added via a calibrated Eppendorf pipette. Initially 2 μL portions were added, and the chemical shift of the respective nucleus was recorded after each addition. After one equivalent of the titrant component was added, the aliquot amount was increased to 10 μL. After a total of 100 μL was added, the aliquot amount was increased to 40 μL until a total of 300 μL was achieved. Then a 100 μL aliquot was added until a total of 500 μL of the titrant was achieved.

5. X–ray Crystal Determination of 9 and 12

Crystallographic data for both compounds are summarized in Table 1. Colorless single crystals were obtained from slow cooling of a benzene / *n*-hexane solution of **9** and slow diffusion of *n*-pentane into a solution of **12**, respectively. Each crystal was mounted on a glass fiber with the aid of perfluoropolyether RS 3000 and transferred to a Siemens P4 diffractometer (Mo-K_α radiation, graphite monochromator). The lattice constants for both compounds were determined by 25 precisely centered high-angle reflections and refined by least-square methods. Accurate unit cell parameters and orientation matrices were formed by least-squares refinement of setting angles of a set of well-centered reflections, which were found by random search. Intensities were collected via the ω–scan technique. No absorption correction was made. While **12** crystallizes in the monoclinic space group $P2_1/n$ (Z = 4), **9** crystallizes in the cubic space group $Pa\bar{3}$ (Z = 8), and no solvent molecules were detected in the crystal lattice. The structures were solved by direct methods with ShelXTL V5.1 (NT-Version)[137] and refined by least squares using the same program with anisotropic thermal parameters for all non–hydrogen atoms. All hydrogen atoms were located in calculated positions (riding mode). Maximum and minimum peaks in the final difference synthesis were 1.076 and –0.275 (**9**), and 0.907 and –0.867 (**12**) e $Å^{-3}$, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-

158457 for **9** and CCDC-158456 for **12**. 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: deposite@ccdc.cam.ac.uk).

Table 1. Crystal data, data collection and structure refinement for compounds **9** and **12**.

	9	**12**
Crystal data		
Empirical formula	$C_{51}H_{51}O_3P_3$	$C_{48}H_{45}P_3$
Formula weight	804.83	714.75
Crystal system	Cubic	Monoclinic
Space group	$Pa\bar{3}$	$P2_1/n$
Z	8	4
$d_{Calc.}$ [g / cm^3]	0.964	1.192
a [Å]	22.303(4)	16.112(4)
b [Å]	22.303(4)	10.602(17)
c [Å]	22.303(4)	23.607(6)
α [°]	90	90
β [°]	90	99.118(14)
γ [°]	90	90
V *[A^3]*	11094(4)	3982(6)
μ [mm^{-1}]	0.140	0.182
F(000)	3408	1512
Data collection		
Radiation		Mo–K_α
Monochromator		Graphite
Wave length [Å]		0.71073
Crystal size [mm^3]	0.35 x 0.35 x 0.35	0.15 x 0.55 x 0.15
Temperature [K]	298(2)	293(2)
Scan mode		ω
$\theta_{min/max}$ [°]	2.04 / 27.50	2.11 / 27.52
hkl range	$-1 \le h \le 28$ $-1 \le k \le 28$ $-28 \le l \le 1$	$-20 \le h \le 2$ $-13 \le k \le 13$ $-30 \le l \le 30$

Table 1. continue

Measured reflections	14521	20325
Independent reflections	4248 (R_{int} = 0.0680)	9147 (R_{int} = 0.1798)
Absorption correction	None	
Refinement		
Refinement Method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4248 / 0 / 173	9147 / 0 / 461
Hydrogen treatment	Calculated	
Final R Values [$I > 2\sigma(I)$]		
$R1$[a]	0.1358	0.0879
$wR2$[b]	0.3171	0.1920
$\rho_{residual}$(max/min) [e $Å^{-3}$]	1.060 / –0.291	0.907 / –0.867

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

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	Y	z	U(eq)
P(1)	941(1)	3588(1)	2975(1)	96(1)
O(1)	1452(2)	4016(2)	2998(2)	134(2)
C(1)	–139(2)	5679(2)	3998(2)	67(1)
C(2)	–532(2)	5199(2)	3922(2)	64(1)
C(3)	–434(2)	4757(2)	3419(2)	75(1)
C(4)	134(2)	4398(2)	3482(2)	75(1)
C(5)	214(2)	3947(2)	2971(2)	82(1)
C(6)	955(2)	3140(2)	2304(3)	89(2)
C(7)	509(3)	2750(3)	2166(3)	128(2)
C(8)	554(3)	2392(3)	1630(3)	132(2)
C(9)	1027(4)	2429(4)	1289(3)	131(3)
C(10)	1460(4)	2805(5)	1417(4)	199(5)
C(11)	1454(3)	3152(3)	1954(4)	162(3)
C(12)	961(3)	3058(3)	3589(3)	110(2)
C(13)	456(4)	2732(3)	3775(3)	131(2)
C(14)	551(6)	2327(4)	4247(5)	175(4)
C(15)	1037(10)	2223(8)	4495(8)	245(10)
C(16)	1528(7)	2542(7)	4351(8)	228(10)
C(17)	1513(4)	2976(4)	3860(4)	171(4)

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **12**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
P(1)	8034(1)	318(2)	1523(1)	40(1)
P(2)	3455(1)	3774(2)	–222(1)	35(1)
P(3)	3563(1)	1456(2)	3545(1)	39(1)
C(1)	5447(3)	–24(5)	1513(2)	32(1)
C(2)	5016(3)	509(5)	1011(2)	32(1)
C(3)	4204(3)	969(5)	987(2)	31(1)
C(4)	3827(3)	874(5)	1475(2)	34(1)
C(5)	4240(3)	353(5)	1985(2)	34(1)
C(6)	5053(3)	–116(5)	1989(2)	32(1)
C(7)	6359(3)	–450(5)	1530(2)	36(1)
C(8)	6943(3)	696(6)	1589(2)	39(1)
C(9)	8510(3)	1884(6)	1508(2)	42(1)
C(10)	8174(3)	3008(6)	1686(2)	45(2)
C(11)	8551(4)	4164(6)	1615(3)	52(2)
C(12)	9274(4)	4202(8)	1363(3)	64(2)
C(13)	9608(4)	3107(9)	1207(3)	77(2)
C(14)	9237(4)	1971(8)	1256(3)	63(2)
C(15)	8437(3)	–198(6)	2264(2)	37(1)
C(16)	8376(3)	505(6)	2743(2)	47(2)
C(17)	8693(4)	77(7)	3283(3)	56(2)
C(18)	9089(4)	–1068(7)	3348(3)	56(2)
C(19)	9180(4)	–1781(6)	2885(3)	54(2)
C(20)	8845(3)	–1336(6)	2336(3)	44(2)
C(21)	3759(3)	1579(5)	447(2)	42(1)
C(22)	3918(3)	2978(5)	450(2)	41(1)

Table 3. continue

C(23)	3611(3)	5407(5)	–10(2)	34(1)
C(24)	3089(3)	6334(6)	–312(2)	40(1)
C(25)	3179(4)	7573(6)	–178(2)	45(2)
C(26)	3796(4)	7978(6)	266(3)	51(2)
C(27)	4329(4)	7092(7)	554(3)	59(2)
C(28)	4239(3)	5843(6)	431(2)	45(2)
C(29)	2328(3)	3569(5)	–209(2)	34(1)
C(30)	1878(3)	4261(6)	147(2)	38(1)
C(31)	1024(3)	4068(6)	137(2)	43(1)
C(32)	608(3)	3186(6)	–238(3)	45(2)
C(33)	1029(4)	2502(6)	–582(2)	46(2)
C(34)	1890(3)	2717(5)	–579(2)	39(1)
C(35)	3837(3)	332(6)	2516(2)	42(1)
C(36)	3929(3)	1556(5)	2841(2)	38(1)
C(37)	3577(3)	3083(6)	3780(2)	39(1)
C(38)	3733(4)	4112(6)	3462(3)	53(2)
C(39)	3730(4)	5335(7)	3677(3)	58(2)
C(40)	3585(4)	5536(7)	4227(3)	55(2)
C(41)	3446(4)	4516(7)	4555(3)	61(2)
C(42)	3449(4)	3324(6)	4343(2)	46(2)
C(43)	2437(3)	1187(6)	3294(2)	39(1)
C(44)	1890(3)	2132(6)	3062(3)	52(2)
C(45)	1054(4)	1850(7)	2850(3)	59(2)
C(46)	759(4)	659(6)	2873(3)	46(2)
C(47)	1290(4)	–296(6)	3106(2)	43(1)
C(48)	2121(3)	–2(6)	3318(2)	38(1)

Table 4. Bond lengths [Å] and angles [°] for **9**

P(1)–O(1)	1.487(4)	C(6)–C(11)	1.361(8)
P(1)–C(6)	1.800(5)	C(7)–C(8)	1.442(7)
P(1)–C(5)	1.809(4)	C(8)–C(9)	1.303(8)
P(1)–C(12)	1.809(8)	C(9)–C(10)	1.312(10)
C(1)–C(2)[a]	1.382(5)	C(10)–C(11)	1.427(9)
C(1)–C(2)	1.394(5)	C(12)–C(17)	1.382(9)
C(2)–C(1)[b]	1.382(5)	C(12)–C(13)	1.404(9)
C(2)–C(3)	1.509(6)	C(13)–C(14)	1.404(11)
C(3)–C(4)	1.506(5)	C(14)–C(15)	1.238(15)
C(4)–C(5)	1.531(5)	C(15)–C(16)	1.34(2)
C(6)–C(7)	1.356(7)	C(16)–C(17)	1.463(18)
O(1)–P(1)–C(6)	111.8(3)	C(11)–C(6)–P(1)	118.7(4)
O(1)–P(1)–C(5)	113.8(2)	C(6)–C(7)–C(8)	119.6(6)
C(6)–P(1)–C(5)	104.9(2)	C(9)–C(8)–C(7)	120.3(6)
O(1)–P(1)–C(12)	112.0(3)	C(8)–C(9)–C(10)	120.7(7)
C(6)–P(1)–C(12)	105.4(3)	C(9)–C(10)–C(11)	121.5(7)
C(5)–P(1)–C(12)	108.4(3)	C(6)–C(11)–C(10)	118.6(7)
C(2)[a] –C(1)–C(2)	121.7(4)	C(17)–C(12)–C(13)	121.1(8)
C(1)[b]–C(2)–C(1)	118.3(4)	C(17)–C(12)–P(1)	116.0(8)
C(1)[b]–C(2)–C(3)	121.6(4)	C(13)–C(12)–P(1)	122.9(5)
C(1)–C(2)–C(3)	120.1(4)	C(12)–C(13)–C(14)	115.7(9)
C(4)–C(3)–C(2)	113.6(3)	C(15)–C(14)–C(13)	126.0(15)
C(3)–C(4)–C(5)	112.2(4)	C(14)–C(15)–C(16)	120(2)
C(4)–C(5)–P(1)	113.0(3)	C(15)–C(16)–C(17)	120.7(15)
C(7)–C(6)–C(11)	118.9(5)	C(12)–C(17)–C(16)	115.8(10)
C(7)–C(6)–P(1)	122.1(4)		

[a] –y+1/2, –z+1, x+1/2. [b] z–1/2, –x+1/2, –y+1

Table 5. Bond lengths [Å] and angles [°] for **12**

P(1)–C(9)	1.831(7)	C(18)–C(19)	1.355(9)
P(1)–C(8)	1.834(5)	C(19)–C(20)	1.406(8)
P(1)–C(15)	1.849(5)	C(21)–C(22)	1.506(8)
P(2)–C(23)	1.809(6)	C(23)–C(28)	1.411(7)
P(2)–C(29)	1.833(5)	C(23)–C(24)	1.411(7)
P(2)–C(22)	1.847(5)	C(24)–C(25)	1.353(8)
P(3)–C(37)	1.811(7)	C(25)–C(26)	1.394(8)
P(3)–C(43)	1.839(5)	C(26)–C(27)	1.378(9)
P(3)–C(36)	1.854(5)	C(27)–C(28)	1.359(9)
C(1)–C(6)	1.379(7)	C(29)–C(34)	1.372(7)
C(1)–C(2)	1.394(7)	C(29)–C(30)	1.402(7)
C(1)–C(7)	1.530(7)	C(30)–C(31)	1.387(7)
C(2)–C(3)	1.390(7)	C(31)–C(32)	1.384(8)
C(3)–C(4)	1.388(7)	C(32)–C(33)	1.349(8)
C(3)–C(21)	1.505(7)	C(33)–C(34)	1.405(7)
C(4)–C(5)	1.395(7)	C(35)–C(36)	1.502(8)
C(5)–C(6)	1.400(7)	C(37)–C(38)	1.370(8)
C(5)–C(35)	1.500(7)	C(37)–C(42)	1.401(7)
C(7)–C(8)	1.530(8)	C(38)–C(39)	1.391(9)
C(9)–C(14)	1.398(8)	C(39)–C(40)	1.373(8)
C(9)–C(10)	1.400(8)	C(40)–C(41)	1.368(9)
C(10)–C(11)	1.390(8)	C(41)–C(42)	1.361(9)
C(11)–C(12)	1.391(9)	C(43)–C(48)	1.365(8)
C(12)–C(13)	1.354(10)	C(43)–C(44)	1.388(8)
C(13)–C(14)	1.358(10)	C(44)–C(45)	1.393(8)
C(15)–C(20)	1.371(8)	C(45)–C(46)	1.353(9)
C(15)–C(16)	1.371(8)	C(46)–C(47)	1.382(8)
C(16)–C(17)	1.374(8)	C(47)–C(48)	1.388(7)
C(17)–C(18)	1.369(9)		

Table 5. continue

C(9)–P(1)–C(8)	102.4(3)	C(3)–C(21)–C(22)	111.2(4)
C(9)–P(1)–C(15)	101.6(2)	C(21)–C(22)–P(2)	113.6(4)
C(8)–P(1)–C(15)	100.5(2)	C(15)–C(20)–C(19)	121.1(6)
C(23)–P(2)–C(29)	101.7(2)	C(28)–C(23)–C(24)	116.4(5)
C(23)–P(2)–C(22)	100.4(3)	C(28)–C(23)–P(2)	124.7(4)
C(29)–P(2)–C(22)	101.4(2)	C(24)–C(23)–P(2)	118.8(4)
C(37)–P(3)–C(43)	102.1(3)	C(25)–C(24)–C(23)	121.7(5)
C(37)–P(3)–C(36)	103.3(3)	C(24)–C(25)–C(26)	120.8(6)
C(43)–P(3)–C(36)	99.0(2)	C(27)–C(26)–C(25)	118.4(6)
C(6)–C(1)–C(2)	119.3(5)	C(28)–C(27)–C(26)	121.5(6)
C(6)–C(1)–C(7)	121.4(5)	C(27)–C(28)–C(23)	121.2(6)
C(2)–C(1)–C(7)	119.3(5)	C(34)–C(29)–C(30)	117.6(5)
C(3)–C(2)–C(1)	121.1(5)	C(34)–C(29)–P(2)	118.6(4)
C(4)–C(3)–C(2)	118.3(5)	C(30)–C(29)–P(2)	123.8(4)
C(4)–C(3)–C(21)	121.4(5)	C(31)–C(30)–C(29)	121.2(5)
C(2)–C(3)–C(21)	120.3(5)	C(30)–C(31)–C(32)	119.3(6)
C(3)–C(4)–C(5)	122.3(5)	C(33)–C(32)–C(31)	120.7(5)
C(4)–C(5)–C(6)	117.6(5)	C(32)–C(33)–C(34)	119.9(5)
C(4)–C(5)–C(35)	121.1(5)	C(29)–C(34)–C(33)	121.3(5)
C(6)–C(5)–C(35)	121.3(5)	C(5)–C(35)–C(36)	113.1(5)
C(1)–C(6)–C(5)	121.4(5)	C(35)–C(36)–P(3)	112.8(4)
C(8)–C(7)–C(1)	110.0(4)	C(38)–C(37)–C(42)	116.2(6)
C(7)–C(8)–P(1)	113.8(4)	C(38)–C(37)–P(3)	125.9(5)
C(14)–C(9)–C(10)	117.5(6)	C(42)–C(37)–P(3)	117.9(5)
C(14)–C(9)–P(1)	116.7(5)	C(37)–C(38)–C(39)	122.1(6)
C(10)–C(9)–P(1)	125.6(4)	C(40)–C(39)–C(38)	120.0(6)
C(11)–C(10)–C(9)	121.1(6)	C(41)–C(40)–C(39)	118.7(7)
C(12)–C(11)–C(10)	119.3(7)	C(42)–C(41)–C(40)	121.0(6)
C(13)–C(12)–C(11)	119.1(7)	C(41)–C(42)–C(37)	121.9(6)

Table 5. continue

C(14)–C(13)–C(12)	122.6(7)	C(48)–C(43)–C(44)	117.7(5)
C(13)–C(14)–C(9)	120.3(7)	C(48)–C(43)–P(3)	119.1(4)
C(20)–C(15)–C(16)	118.1(5)	C(44)–C(43)–P(3)	123.2(5)
C(20)–C(15)–P(1)	117.9(4)	C(43)–C(44)–C(45)	120.3(6)
C(16)–C(15)–P(1)	123.9(5)	C(46)–C(45)–C(44)	120.7(6)
C(15)–C(16)–C(17)	121.4(6)	C(45)–C(46)–C(47)	120.0(5)
C(18)–C(17)–C(16)	119.7(6)	C(46)–C(47)–C(48)	118.7(6)
C(19)–C(18)–C(17)	120.9(6)	C(43)–C(48)–C(47)	122.5(6)
C(18)–C(19)–C(20)	118.8(6)		

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Summary

Supramolecular chemistry has become a vivid interface between chemistry, biology, physics, and materials science. Although still a relatively young field of research, termini such as molecular recognition, host/guest chemistry, or self-assembly are now common knowledge, and this research has already been honored with the Nobel price. The pioneering work of Pedersen, Lehn, and Cram on various cyclic structures acting as hosts and their interactions with cationic species, is considered as the start of modern supramolecular chemistry – the chemistry of week forces and non-covalent interactions. Clearly, thirty years ago transition metals and their complexes were not regarded as important components in such structures and the field of host/guest recognition and coordination chemistry was very distinct with almost nothing to share. Things have changed dramatically! It suffices to wander through the nearly exponential growth of contributions in the literature to realize that transition metal complexes are nowadays used almost routinely to build large multicomponent architectures. Transition metals utilized to construct fascinating structures such as metal-containing cyclophanes, the receptors which play a central role in the development of host/guest chemistry, since they contain molecular cavities. Water-soluble cyclophanes have a lot of interest since they contain a lipophilic cage to capture organic guests in water– a mimic of several natural phenomena. Stepwise synthesis of these molecules is troublesome, therefore, molecular self-assembly represent a useful alternative to classical strategies. One major factor in

self-assembly is the symmetry of molecular components. Ligands with C_3 symmetry could form several interesting architectures with different metals.

Objective of the present work is the synthesis of different types of self-assembled metallacyclophanes. These molecules should be flexible enough to include lipophilic guest molecules. The way of self-assembly of these molecules is controlled by the ligands. These ligands should be rigid enough for preorganization, a precondition for self-assembly, as well flexible to form the desired metallacyclophanes. To secure these properties ligand systems have to be created with an aromatic nucleus having 1,3,5-trisubstitueted patterns consisting of methylene groups as spacers provided with functional phosphine units at their ends.

In the first part of this work, the synthesis and characterization of 1,3,5-tris(bromoalkyl)benzenes were described, which were used as starting materials for the access of the ligands. Synthetic methods for these compounds are known in the literature. However, 1,3,5-tris(3'-bromopropyl)benzene and 1,3,5-tris(4'-bromobutyl)-benzene are only accessible with eight and twelve multistep reaction sequences, respectively. A much more versatile method for the generation of these *trisbromides* was verified by a two stage reaction sequence starting with mesitylene and followed by the "dibromoalkane method". These syntheses employ the substitution of the bromide by nucleophilic reagents. Precondition in this connection is the isolation of 1,3,5-tri(lithiomethyl)benzene. By conversion of this trilithio compound with 1,2-

dibromoethane and 1,3-dibromopropane, 1,3,5-tris(3'-bromopropyl)benzene and 1,3,5-tris(4'-bromobutyl)benzene were obtained, respectively.

In the following part the 1,3,5-tris(diphenylphosphorylalkyl)benzenes 1,3,5-$C_6H_3[(CH_2)_nP(O)Ph_2]_3$ (n = 1 – 4), which are basically necessary for the nonwater-soluble ligands discussed in this work, are described. There syntheses succeeded by an Arbusov type reaction of ethyl diphenylphosphonate, $Ph_2P(OEt)$, with 1,3,5-$C_6H_3[(CH_2)_nBr]_3$ (n = 1 – 4) at 150 °C. These compounds represent hygroscopic colorless solids. The structure of 1,3,5-tris(diphenylphosphorylpropyl)benzene was confirmed by X-ray crystallographic investigations. It shows a C_3 axis of symmetry passing through the central benzene ring. The compound crystallizes in the cubic crystal system $Pa\bar{3}$.

The reduction of 1,3,5-tris(diphenylphosphorylalkyl)benzenes by $HSiCl_3$ in *o*-dichlorobenzene at 120 °C led to the expected nonwater-soluble ligands 1,3,5-tris(diphenylphosphinylalkyl)benzenes 1,3,5-$C_6H_3[(CH_2)_nP(O)Ph_2]_3$ (n = 1 – 4). These compounds are solid (n = 1, 2) or gummy (n = 3, 4) materials which are soluble in organic solvents of moderate polarity. Suitable crystals for an X-ray structural analysis were obtained in *n*-pentane. In the structure of 1,3,5-tris(diphenylphosphinylethyl)-benzene a C_3 axis of symmetry is absent, the crystal system is monoclinic ($P2_1/n$).

On the way to synthesize water-soluble ligands an Arbusov reaction of triethylphosphite with 1,3,5-$C_6H_3[(CH_2)_nBr]_3$ (n = 1 – 4) at 150 °C affords the

corresponding hygroscopic oily compounds 1,3,5-$C_6H_3[(CH_2)_nP(O)(OEt)_2]_3$ (n = 1 – 4). They can be regarded as the first generation of dendrimers.

Reduction of $C_6H_3[(CH_2)_nP(O)(OEt)_2]_3$ (n = 1 – 4) with $LiAlH_4$ in diethyl ether afforded the triprimary phosphines 1,3,5-$C_6H_3[(CH_2)_nPH_2]_3$ (n = 1 – 4). However, 1,3,5-tris(phosphinomethyl)benzene (n = 1) is unstable and decomposed readily to 3,5-bis(phosphinomethyl)toluene. The phosphines 1,3,5-$C_6H_3[(CH_2)_nPH_2]_3$ (n = 2 – 4) are regarded as key synthons for water-soluble ligands, are very sensitive to air, and were directly employed after extraction from the reaction mixture without further purification. Their characterization was performed by NMR experiments in addition to mass and IR spectroscopy.

Water-soluble ligands are available by reaction of the phosphines 1,3,5-$C_6H_3[(CH_2)_nPH_2]_3$ (n = 2 – 4) with either (i) aqueous formaldehyde in ethanol to afford 1,3,5-$C_6H_3[(CH_2)_nP(CH_2OH)_2]_3$ (n = 2 – 4) or with (ii) diethyl vinylphosphonate in the presence of AIBN to achieve 1,3,5-$C_6H_3\{(CH_2)_nP[CH_2CH_2P(O)(OEt)_2]_2\}_3$ (n = 2 – 4), which can regarded as the second generation of a dendrimer. However, the reaction of the triprimary phosphines with potassium *p*-fluorobenzenesulfonate failed to get the corresponding sulfonated water-soluble ligands. 1,3,5-$C_6H_3[(CH_2)_nP(CH_2OH)_2]_3$ and 1,3,5-$C_6H_3\{(CH_2)_nP[CH_2CH_2P(O)(OEt)_2]_2\}_3$ (n = 2 – 4) represent gummy materials and their structures were fully characterized by spectroscopic techniques.

To realize the generation of three-dimensional, triply bridged metallacyclophanes, a cage which is provided with metal-phosphorus instead of metal-carbon σ bonds has been taken into consideration. The above-mentioned ligands are suitable starting materials for the reaction with substitution labile platinum complexes for the access of cage-like molecules. By employment of the high dilution method and with the aid of a dosing apparatus, two equivalents of these ligands were assembled via three equivalents of $Cl_2Pt(NCPh)_2$ to give triplatinacyclophanes. However, 1,3,5-$C_6H_3[(CH_2)_nP(CH_2OH)_2]_3$ (n = 2 – 4) is not able to form a cyclophane. Only a colorless solid was obtained which was not further characterized. The structure of the self-assembled complexes was elucidated by several NMR experiments in addition to FAB-MS techniques.

In the case of the self-assembly of the nonwater-soluble ligands 1,3,5-$C_6H_3[(CH_2)_nPPh_2]_3$ (n = 2 – 4) the best cyclophane yields were observed for n = 3. However, the ligand with n = 1 brought the lowest yield and polymers were obtained. For the ligand with n = 4 the cyclophane yield is low. However, chain-like trinuclear platinacycles were formed in stead of polymers. The cage compounds show a *cis*-P_2Pt configuration whereas in the case of the chain-like trinuclear cycles several *cis*-/*trans*-isomers were formed. Three factors are discussed to affect these trends in self-assembly: (i) the rigidity of the ligand system, (ii) steric factors, and (iii) intramolecular chelation.

For the self-assembly of the water-soluble ligands 1,3,5-$C_6H_3\{(CH_2)_nP[CH_2CH_2P(O)(OEt)_2]_2\}_3$ (n = 2 – 4) the best cyclophane yields were

obtained for n = 2. The yield decreased by increasing n as a consequence of the higher ability of the phosphine groups to move far away from each other. The water-soluble cages prefer a *trans*-P_2Pt configuration.

Phosphonated triplatinacyclophanes are soluble in solvents of different polarity and even in water. However, NMR titration experiments failed to give reproducible or significant changes of the chemical shifts of ^{1}H or ^{31}P signals in the corresponding NMR spectra of these compounds. This drawback is attributed to three effects: (i) external π – π interactions, (ii) too small association constants to be measured, and (iii) blocking of the cavity by twenty-four ethyl groups at the phosphorus atoms.

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