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Preparation, properties, and reactions of metal-containing heterocycles☆

Part CVI. Three-dimensional water-soluble platinacyclophanes

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Dedicated to Professor Hans-Georg von Schnering on the occasion of his 70th birthday.

Abstract

Trifunctional primary phosphines of the type 1,3,5-$[PH_2(CH_2)_n]_3C_6H_3$ (**3b**–**d**) were obtained via an Arbusov reaction between the 1,3,5-tris(bromoalkyl)benzenes **1b**–**d** and $P(OEt)_3$ followed by a reaction of the trisphosphonates 1,3,5-$[(EtO)_2P(O)(CH_2)_n]_3C_6H_3$ (**2b**–**d**) with $LiAlH_4$. A straightforward conversion of these sensitive key phosphines **3b**–**d** to the corresponding water-soluble ligands 1,3,5-tris[bis(hydroxymethyl)phosphinylalkyl]benzenes **4b**–**d** and 1,3,5-tris[bis(2′-diethylphosphonatoethyl)phophinylalkyl]benzenes **5b**–**d** was achieved by formylation with formaldehyde and hydrophosphonation with diethyl vinylphosphonate, respectively. A five component self-assembly consisting of three equivalents of the platinum(II) complex $Cl_2Pt(NCPh)_2$ and two equivalents of the ligands **5b**–**d** under high dilution conditions resulted in the formation of the nanoscaled, water-soluble triplatinacyclophanes **6b**–**d** in high yields. However, comparable reactions with the ligands **4b**–**d** led only to polymeric materials, which are insoluble in all organic solvents and water. The structures of the metallacyclophanes **6b**–**d** were elucidated by $^{31}P\{^1H\}$-, $^{13}C\{^1H\}$-, and $^{195}Pt\{^1H\}$-NMR spectroscopic investigations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metallacyclophanes; Platinum; P ligands; Supramolecular chemistry; Water-soluble complexes

1. Introduction

Supramolecular chemistry has been rapidly expanding at the frontiers of chemical science with physical and biological phenomena [2–7,13,14]. 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 [5–7]. Host–guest interactions are established to mimic enzymes in their capability to bind substrates fast, selectively and reversibly and to catalyze chemical reactions [3,6,7]. 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 [3,7]. 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 [3,15,16]. This fact is due to interactions between the lipophilic cavity and the guest molecules [8].

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 [9,10]. 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 [11].

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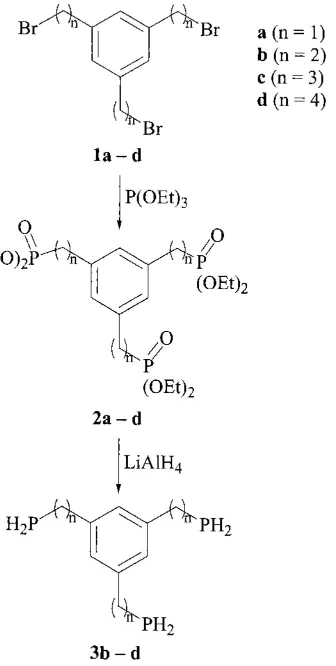
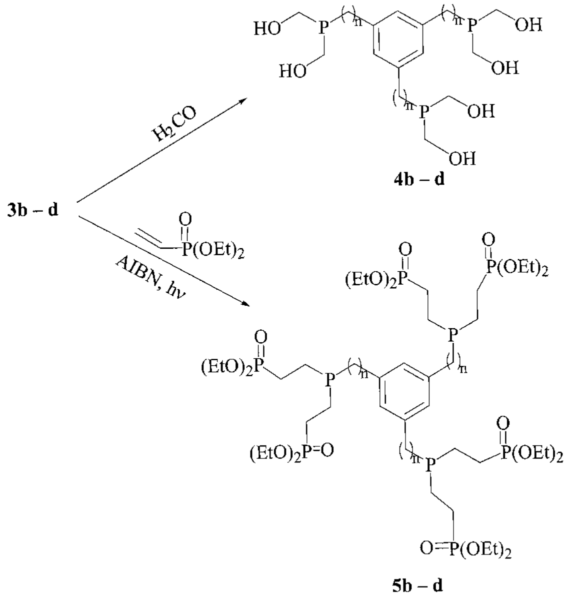
By introduction of suitable functional groups it should be possible to develop also water-soluble metallacyclophanes. Diederich et al. reported on the host–guest chemistry of a specific cyclophane, which displays solubility in solvents of all polarities [3,12,17]. To the best of our knowledge similar 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.



Scheme 1. Synthesis of the triprimary phosphines **3b**–**d**.



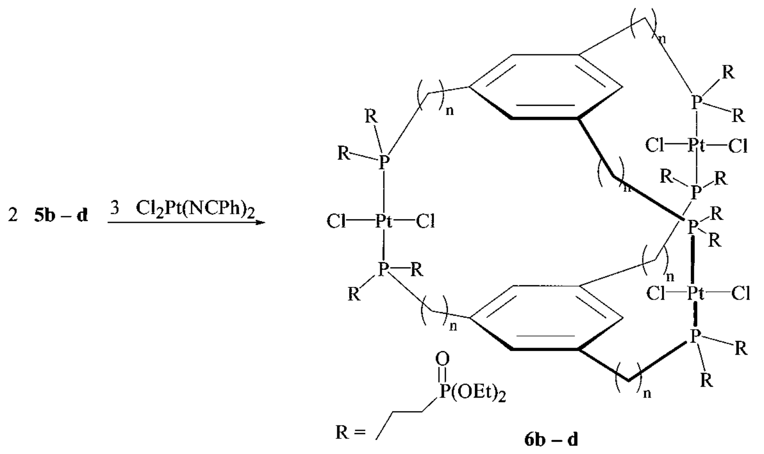
Scheme 2. Ligands synthesis.

2. Results and discussion

2.1. Ligand synthesis

A straightforward Arbosuv reaction between the corresponding 1,3,5-tris(bromoalkyl)benzenes **1a**–**d** and triethyl phosphite afforded the 1,3,5-tris[(diethoxyphosphinyl)alkyl]benzenes **2a**–**d** (Scheme 1). Reduction by $LiAlH_4$ in diethyl ether results in the formation of the respective triprimary phosphines **3a**–**d** (Scheme 1). With the exception of **3a**, which decomposed readily to the 3,5-bis(phosphinylmethyl)toluene and PH_3, **3b**–**d** were obtained in pure form. A similar decomposition was also observed in the case of tris(hydroxymethyl)phosphine [18]. 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 **2a**–**d** and **3b**–**d** represent hygroscopic viscous oils and colorless liquids, respectively, which are very sensitive to air, in particular in the case of **3b**–**d**. Therefore, **3b**–**d** were not further purified after extraction from the reaction mixture and they were directly used for the next step. The composition of **2a**–**d** and **3b**–**d** was corroborated by EI mass spectra showing the molecular peak in each case. As expected in the $^{31}P\{^{1}H\}$-NMR spectra of **2a**–**d** (in $CDCl_3$) a singlet each is observed ($\delta = 27.1-33.5$) which is markedly shifted to higher field ($\delta \approx -136$) by the reduction of **2b**–**d** to **3b**–**d**.

The trisphosphines **3b**–**d** are regarded as key synthons for the synthesis of the water-soluble phosphine ligands **4b**–**d** and **5b**–**d** (Scheme 2), because they can easily be converted to the related products by addition or substitution reactions with regard to the P–H functions [19]. Two examples were examined: (1) formylation of **3b**–**d** by an aqueous solution of formaldehyde in ethanol [18,20,21]; and (2) hydrophosphination of diethyl vinylphosphonate with **3b**–**d** [22–25] (Scheme 2). Both reactions proceeded quantitatively to afford **4b**–**d** and **5b**–**d** as viscous oils resistant to crystallization. These novel phosphine ligands show good solubility in water, however, **4c** and **d** need about 10% of additional methanol to be soluble. Furthermore **5b**–**d** are soluble in solvents of medium polarity. The compositions of **4b**–**d** and **5b**–**d** 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 3. Water-soluble cage-structured triplatinacyclophanes.

Scheme 2 and Section 4). It is characteristic for the $^{31}P\{^1H\}$-NMR spectra of **5b**–**d** that they display two signals in a 2:1 ratio representing an A_2X spin system with a coupling constant of about 50 Hz. It is assigned to the phosphonate ($\delta = 32$) and phosphine ($\delta \approx -20$) groups.

2.2. Self-assembly of the ligands 5b–d with $Cl_2Pt(NCPh)_2$

To obtain self-assembled cyclophane structures, a preorganization of the components is a necessary prerequisite. The trifunctionalized phosphines **4b**–**d** and **5b**–**d** 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 **6b**–**d**, the ligands **5b**–**d** were treated with $Cl_2Pt(NCPh)_2$ in a mixture of methanol and dichloromethane or only dichloromethane, respectively, according to the high dilution method [26] (Scheme 3). Corresponding reactions with **4b**–**d** as starting materials led only to colorless polymers, which were not further characterized. The self-assembled triplatinacyclophanes **6b**–**d** could be obtained in much higher yields (40–70%) than their nonwater-soluble counterparts [9,10]. The yields decreased by increasing the number of methylene groups in the sequence **6b** > **6c** > **6d**.

The pale yellow triplatinacyclophanes **6b–d** are soluble in water and organic solvents of medium polarity. Several experiments to grow single crystals of **6b–d** for an X-ray structural analysis failed.

An insight into structural facts of the platinacyclophanes **6b**–**d** is available by $^{31}P\{^1H\}$-NMR spectroscopic probes. ^{31}P chemical shifts and $^{195}Pt-^{31}P$ coupling constants allow an unambiguous distinction between *cis* and *trans* arrangement of the ligands at the platinum center. Corresponding coupling constants are in the range of 3500–2500 Hz, respectively [27–30]. In the spectra of **6b–d** occur two signals with a 2:1 ratio representing an $A_2XX'A'_2$ pattern. The A-part (pseudo-triplet) of this spin system is located at higher field ($\delta \approx 30$, m, $N = 58$ Hz [31a]) and ascribed to the phosphonate function, whereas the X-part (pseudo-pentet) at lower field ($\delta = 5$–13, m, $N = 58$ Hz [31b]) which is flanked by satellites at ± 1/2 ($^1J_{PtP}$) arising from scalar coupling to the 33% abundant ^{195}Pt nuclei [59] is attributed to the phosphine groups. This assignment is confirmed by $^{195}Pt\{^1H\}$-NMR spectra, which display a triplet each at $\delta \approx -3940$ ppm with coupling constants of about $^1J_{PtP} = 2450$ Hz. The size of these constants unequivocally points to a *trans*-P–Pt–P arrangement in the macrocycles **6b**–**d**, which is in contrast to the recently reported nonwater-soluble platinacyclophanes [9,10]. The different stereochemistry can be traced back to the greater steric demand of the phosphonate substituents at the phosphorus atoms compared to phenyl groups [32–37].

As the line patterns in the ^1H- and $^{13}C\{^1H\}$-NMR spectra of the methylene groups could not be resolved, a short discussion of the ^1H- and $^{13}C\{^1H\}$-NMR spectra of the triplatinacyclophanes **6b**–**d** refers to the central benzene rings. Only one ^1H 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 $^{13}C\{^1H\}$-NMR spectra, two resonances correspond to the methine ($\delta \approx 126$) and quaternary ($\delta \approx 141$) carbon atoms.

NMR spectroscopy is considered as the method of choice to study inclusion complexation in solution [3]. Extensive information is obtained on the structures of the complexes. Furthermore, the thermodynamics and kinetics of complexation can be evaluated. The metallacyclophanes **6b**–**d** 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 **6b**–**d** employing water or 10–30% (v/v) aqueous methanol as solvents. The amount of **6b**–**d** 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.

3. Conclusions

Within the last 5–10 years, several new architectures of metallacyclophanes with interesting properties have been described in the literature [38–47]. This new variant of cyclophanes is available by the self-assembly of multifunctional ligands with suitable metal fragments. Recently, several metallacyclophanes were introduced which were formed by a template synthesis in aqueous media [48–51]. The solvent effect in self-assembly is also reported in the literature [52]. 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 and 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 **6b**–**d** 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 [3]. This drawback may be attributed to three effects: (i) external π–π stacking interactions leading to self-association of the hosts [3]; (ii) the host–guest association constants are too small to be measured; (iii) ethyl groups (24) at the phosphorus atoms may block the entrance of the cavities and hence prevent the encapsulation of guest molecules.

4. Experimental

4.1. General

All synthetic reactions and manipulations were performed under dry argon atmosphere using standard Schlenk techniques. Dichloromethane was freshly distilled from calcium hydride, and diethyl ether from sodium benzophenone ketyl. 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 F254, 0.5 mm (Merck). Elemental analysis, Elementar Vario EL analyzer. Mass spectra, EI-MS, Finnigan TSQ 70 eV (200 °C); FD and 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% $Na_2[PtCl_6] \cdot 6\ H_2O$. Triethylphosphite and 2,2′-azobis(2-methylpropionitrile) (AIBN) were obtained from commercial suppliers and used without further purification. Compounds **1a** [53], **1b** [54], **1c** [9], **1d** [55], diethyl vinylphosphonic ester [56], and $Cl_2Pt(NCPh)_2$ [57] were synthesized according to literature methods.

*4.2. Preparation of 1,3,5-tris[(diethoxyphosphinyl)-alkyl]benzenes **2a**–**d** [58]*

A mixture of **1a**–**d** (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 is 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 **2a**–**d**.

*4.2.1. 1,3,5-Tris[(diethoxyphosphinyl)methyl]benzene (**2a**)*

This compound was first reported in the literature by several authors [60] but **2a** was not properly characterized. Colorless oil (5.0 g, 95%). FAB-MS (NBA, 50 °C); *m*/*z* (%): 551 (4) $[M + Na]^+$, 529 (100) $[M + H]^+$, 392 (21) $[M - P(O)(OEt)_2]^+$. MS (FD, CH_2Cl_2, 30 °C); *m*/*z*: 528 $[M]^+$, 1057 $[2M + H]^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2982, 2908 (CH$_2$), 1603 (aromat. C=C), 1252 (P=O), 1028 (P–OEt). ^{31}P{^{1}H}-NMR (101.26 MHz, CDCl$_3$, 22 °C): δ = 27.1. ^{1}H-NMR (250.13 MHz, CDCl$_3$, 22 °C): δ = 1.10 (t, $^3J_{HH}$ = 7.1 Hz, 18H, OCH$_2$CH_3), 2.96 (d, $^2J_{PH}$ = 22.0 Hz, 6H, CH$_2$P), 3.87 (dq, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 7.4 Hz, 12H, OCH_2CH$_3$), 6.99 (d, $^4J_{PH}$ = 2.2 Hz, 3H, aromat. C$_6$H$_3$). ^{13}C{^{1}H}-NMR (62.90 MHz, CDCl$_3$, 22 °C): δ = 16.3 (d, $^3J_{PC}$ = 5.7 Hz, CH$_3$CH$_2$O), 33.3 (d, $^1J_{PC}$ = 138.0 Hz, CH$_2$P), 61.9 (d, $^2J_{PC}$ = 7.1 Hz, CH$_3$$CH_2$O), 129.7 (dt, $^3J_{PC}$ = 11.0 Hz, $^5J_{PC}$ = 5.7 Hz, aromat. CH), 132.1 (td, $^2J_{PC}$ = 12.1, $^4J_{PC}$ = 3.6 Hz, aromat. C).

4.2.2. 1,3,5-Tris[2′-(diethoxyphosphinyl)ethyl]benzene ***(2b)***

Colorless oil (5.6 g, 98%). FAB-MS (NBA, 50 °C); *m/z*: 571 [M + H]$^+$. Anal. Found: C, 50.86; H, 8.03. Calc. for C$_{24}$H$_{45}$O$_9$P$_3$ (570.5): C, 50.52; H, 7.95%. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2983, 2870 (CH$_2$), 1605 (aromat. C=C), 1234 (P=O), 1024 (P–OEt). ^{31}P{^{1}H}-NMR (101.26 MHz, CDCl$_3$, 22 °C): δ = 31.8. ^{1}H-NMR (250.13 MHz, CDCl$_3$, 22 °C): δ = 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 18H, OCH$_2$CH_3), 1.94 (td, $^2J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, CH$_2$P), 2.78 (dt, $^3J_{PH}$ = 9.3 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, CH_2CH$_2$P), 4.03 (dq, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 7.2 Hz, 12H, OCH_2CH$_3$), 6.82 (s, 3H, aromat. CH). ^{13}C{^{1}H}-NMR (62.90 MHz, CDCl$_3$, 22 °C): δ = 16.5 (d, $^3J_{PC}$ = 6.4 Hz, CH$_3$CH$_2$O), 27.6 (d, $^1J_{PC}$ = 139.4 Hz, CH$_2$P), 28.5 (d, $^2J_{PC}$ = 5.0 Hz, CH$_2$CH$_2$P), 61.9 (d, $^2J_{PC}$ = 6.4 Hz, CH$_3$$CH_2$O), 125.8 (s, aromat. CH), 141.7 (d, $^3J_{PC}$ = 17.8 Hz, aromat. C).

4.2.3. 1,3,5-Tris[3′-(diethoxyphosphinyl)propyl]benzene ***(2c)***

Colorless oil (6.0 g, 98%). MS (70 eV, EI, 200 °C); *m/z* (%): 612 (7) [M]$^+$, 475 (9) [M − P(O)(OEt)$_2$]$^+$, 461 (41) [M − CH$_2$P(O)(OEt)$_2$]$^+$. Anal. Found: C, 52.64; H, 8.19. Calc. for C$_{27}$H$_{51}$O$_9$P$_3$ (612.6): C, 52.94; H, 8.39%. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2981, 2938, 2865 (CH$_2$), 1602 (aromat. C=C), 1245 (P=O), 1042 (P–OEt). ^{31}P{^{1}H}-NMR (101.26 MHz, CDCl$_3$, 22 °C): δ = 33.2. ^{1}H-NMR (250.13 MHz, CDCl$_3$, 22 °C): δ = 1.22 (t, $^3J_{HH}$ = 7.1 Hz, 18H, OCH$_2$CH_3), 1.61 (m, 6H, CH_2CH$_2$P), 1.85 (m, 6H, CH$_2$P), 2.54 (t, $^3J_{HH}$ = 7.2 Hz, 6H, CH_2CH$_2$CH$_2$P), 3.99 (dq, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 7.3 Hz, 12H, OCH_2CH$_3$), 6.73 (s, 3H, aromat. CH). ^{13}C{^{1}H}-NMR (62.90 MHz, CDCl$_3$, 22 °C): δ = 16.4 (d, $^3J_{PC}$ = 5.7 Hz, CH$_3$CH$_2$O), 24.2 (d, $^2J_{PC}$ = 5.0 Hz, CH$_2$CH$_2$P), 25.2 (d, $^1J_{PC}$ = 140.9 Hz, CH$_2$P), 36.4 (d, $^3J_{PC}$ = 17.1 Hz, CH$_2$CH$_2$CH$_2$P), 61.4 (d, $^2J_{PC}$ = 6.4 Hz, CH$_3$$CH_2$O), 126.4 (s, aromat. CH), 141.3 (s, aromat. C).

4.2.4. 1,3,5-Tris[4′-(diethoxyphosphinyl)butyl]benzene ***(2d)***

Colorless oil (6.5 g, 99%). MS (70 eV, EI, 200 °C); *m/z* (%): 654 (18) [M]$^+$, 489 (100) [M − CH$_2$CH$_2$P(O)(OEt)$_2$]$^+$. Anal. Found: C, 55.24; H, 8.50. Calc. for C$_{30}$H$_{57}$O$_9$P$_3$ (654.7): C, 55.04; H, 8.78%. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2981, 2938, 2865 (CH$_2$), 1603 (aromat. C=C), 1245 (P=O), 1060 (P–OEt). ^{31}P{^{1}H}-NMR (101.26 MHz, CDCl$_3$, 22 °C): δ = 33.5. ^{1}H-NMR (250.13 MHz, CDCl$_3$, 22 °C): δ = 1.31 (t, $^3J_{HH}$ = 7.1 Hz, 18H, OCH$_2$CH_3), 1.72–1.80 (m, 18H, CH$_2$CH_2CH_2CH_2P), 2.55 (t, $^3J_{HH}$ = 7.2 Hz, 6H, CH_2CH$_2$CH$_2$CH$_2$P), 4.08 (dq, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 6.8 Hz, 12H, OCH_2CH$_3$), 6.78 (s, 3H, aromat. CH). ^{13}C{^{1}H}-NMR (62.90 MHz, CDCl$_3$, 22 °C): δ = 16.7 (d, $^3J_{PC}$ = 5.7 Hz, CH$_3$CH$_2$O), 22.5 (d, $^2J_{PC}$ = 5.0 Hz, CH$_2$CH$_2$P), 25.7 (d, $^1J_{PC}$ = 140.9 Hz, CH$_2$P), 32.7 (d, $^3J_{PC}$ = 17.1 Hz, CH$_2$CH$_2$CH$_2$P), 35.6 (s, CH$_2$CH$_2$CH$_2$CH$_2$P), 61.6 (d, $^2J_{PC}$ = 6.4 Hz, CH$_3$$CH_2$O), 126.1 (s, aromat. CH), 142.2 (s, aromat. C).

4.3. Preparation of the 1,3,5-tris(phosphinoalkyl)benzenes ***3b–d*** *[24]*

A diethyl ether (100 ml) solution of **2b–d** (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 (r.t.). After stirring for 48 h at r.t., 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$_2$SO$_4$) and removed under reduced pressure to give a clear residual liquid, which was identified as pure **3b–d**.

4.3.1. 1,3,5-Tris(2′-phosphinoethyl)benzene ***(3b)***

Colorless liquid (0.50 g, 64%). MS (70 eV, EI, 200 °C); *m/z* (%): 258 (1) [M]$^+$, 225 (100) [M − PH$_2$]$^+$. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2969, 2923 (CH$_2$), 2290 (P–H), 1603 (aromat. C=C). ^{31}P{^{1}H}-NMR (101.26 MHz, CDCl$_3$, 22 °C): δ = −136.8. ^{1}H-NMR (250.13 MHz, CDCl$_3$, 22 °C): δ = 1.72 (m, 6H, CH$_2$P), 2.62 (td, $^1J_{PH}$ = 195.3 Hz, $^3J_{HH}$ = 7.5 Hz, 6H, PH$_2$), 2.71 (dt, $^3J_{PH}$ = 7.9 Hz, $^3J_{HH}$ = 7.5 Hz, 6H, CH_2CH$_2$P), 6.76 (s, 3H, aromat. CH). ^{13}C{^{1}H}-NMR (62.90 MHz, CDCl$_3$, 22 °C): δ = 16.1 (d, $^1J_{PC}$ = 9.2 Hz, CH$_2$P), 39.2 (d, $^2J_{PC}$ = 2.9 Hz, CH$_2$CH$_2$P), 126.3 (s, aromat. CH), 142.4 (d, $^3J_{PC}$ = 5.0 Hz, aromat. C).

4.3.2. 1,3,5-Tris(3′-phosphinopropyl)benzene ***(3c)***

Colorless liquid (0.6 g, 67%). MS (70 eV, EI, 200 °C); *m/z* (%): 300 (1) [M]$^+$, 267 (100) [M − PH$_2$]$^+$. IR (KBr, cm^{-1}): = 2964, 2874 (CH$_2$), 2292 (P–H), 1603 (aromat. C=C). ^{31}P{^{1}H}-NMR (101.26 MHz, CDCl$_3$, 22 °C): δ = −136.1. ^{1}H-NMR (250.13 MHz, CDCl$_3$, 22 °C): δ = 1.53 (dt, $^3J_{HH}$ = 7.9 Hz, $^2J_{PH}$ = 6.9 Hz, 6H, CH_2P), 1.82 (dtt, $^3J_{PH}$ = 8.1 Hz, $^3J_{HH}$ = 6.9 Hz,

$^3J_{HH} = 7.5$ Hz, 6H, CH_2CH$_2$P), 2.62 (t, $^3J_{HH} = 7.5$ Hz, 6H, CH_2CH$_2$CH$_2$P), 2.71 (dt, $^1J_{PH} = 194.7$ Hz, $^3J_{HH} = 7.2$ Hz, 6H, PH$_2$), 6.80 (s, 3H, aromat. CH). ^{13}C{^{1}H}-NMR (62.90 MHz, CDCl$_3$, 22 °C): $\delta = 13.5$ (d, $^1J_{PC} = 8.5$ Hz, CH$_2$P), 34.8 (d, $^2J_{PC} = 2.9$ Hz, CH$_2$CH$_2$P), 36.7 (d, $^3J_{PC} = 5.7$ Hz, CH$_2$CH$_2$CH$_2$P), 126.2 (s, aromat. CH), 141.7 (s, aromat. C).

4.3.3. 1,3,5-Tris(4′-phosphinobutyl)benzene (3d)

Colorless liquid (0.7 g, 68%). MS (70 eV, EI, 200 °C); *m/z* (%): 341 (1) [M − H]$^+$, 309 (100) [M − PH$_2$]$^+$. IR (KBr, cm^{-1}): $\tilde{\nu} = 2963$, 2925, 2853 (CH$_2$), 2290 (P–H), 1602 (aromat. C=C). ^{31}P{^{1}H}-NMR (101.26 MHz, CDCl$_3$, 22 °C): $\delta = -136.0$. ^{1}H-NMR (250.13 MHz, CDCl$_3$, 22 °C): $\delta = 1.55$ (m, 12H, CH_2CH$_3$CH_2P), 1.67 (m, 6H, CH_2CH$_2$P), 2.56 (t, $^3J_{HH} = 7.4$ Hz, 6H, CH_2CH$_2$CH$_2$CH$_2$P), 2.69 (dt, $^1J_{PH} = 194.7$ Hz, $^3J_{HH} = 6.9$ Hz, 6H, PH$_2$), 6.80 (s, 3H, aromat. CH). ^{13}C{^{1}H}-NMR (62.90 MHz, CDCl$_3$, 22 °C): $\delta = 13.8$ (d, $^1J_{PC} = 7.4$ Hz, CH$_2$P), 32.6 (d, $^3J_{PC} = 5.4$ Hz, CH$_2$CH$_2$CH$_2$P), 32.7 (d, $^2J_{PC} = 2.7$ Hz, CH$_2$CH$_2$P), 35.6 (s, CH$_2$CH$_2$CH$_2$CH$_2$P), 126.1 (s, aromat. CH), 142.5 (s, aromat. C).

4.4. Preparation of the 1,3,5-tris[bis(hydroxymethyl)-phosphinoalkyl]benzenes **4b**–**d**

To a vigorously stirred solution of compounds **3b**–**d** (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 r.t. The reaction mixture was allowed to stir at r.t. for 12 h. Removal of volatile materials in vacuo afforded the pure compounds **4b**–**d**.

4.4.1. 1,3,5-Tris[2′-bis(hydroxymethyl)-phosphinoethyl]benzene (4b)

Clear gummy material (0.85 g, 97%). FAB-MS (NBA, 50 °C); *m/z* (%): 439 (41) [M + H]$^+$, 408 (42) [M − CH$_2$O]$^+$, 378 (41) [M − 2CH$_2$O]$^+$. Anal. Found: C, 49.45; H, 7.76. Calc. for $C_{18}H_{33}O_6P_3$ (438.4): C, 49.32; H, 7.59%. IR (KBr, cm^{-1}): $\tilde{\nu} = 3346$ (O–H), 2899 (CH$_2$), 1600 (aromat. C=C), 1012 (C–O). ^{31}P{^{1}H}-NMR (101.26 MHz, D$_2$O, 22 °C): $\delta = -24.5$. ^{31}P{^{1}H}-NMR (101.26 MHz, acetone-d_6, 22 °C): $\delta = -22.9$. ^{1}H-NMR (250.13 MHz, D$_2$O, 22 °C): $\delta = 1.86$ (dd, $^2J_{PH} = 7.2$ Hz, $^3J_{HH} = 7.2$ Hz, 6H, CH$_2$P), 2.76 (dt, $^3J_{PH} = 9.5$ Hz, $^3J_{HH} = 7.6$ Hz, 6H, CH_2CH$_2$P), 3.98 (m, 12H, OCH_2P), 7.02 (s, 3H, aromat. CH). ^{1}H-NMR (250.13 MHz, acetone-d_6, 22 °C): $\delta = 2.06$ (m, 6H, CH$_2$P), 2.82 (m, 6H, CH_2CH$_2$P), 4.13 (m, 12H, OCH_2P), 7.07 (s, 3H, aromat. CH). ^{13}C{^{1}H}-NMR (62.90 MHz, D$_2$O, 22 °C): $\delta = 20.0$ (d, $^1J_{PC} = 8.6$ Hz, CH$_2$P), 29.1 (d, $^2J_{PC} = 15.3$ Hz, CH$_2$CH$_2$P), 55.8 (d, $^1J_{PC} = 9.53$ Hz, PCH$_2$O), 123.8 (s, aromat. CH), 140.7 (d, $^3J_{PC} = 9.5$ Hz, aromat. C). ^{13}C{^{1}H}-NMR (62.90 MHz, acetone-d_6, 22 °C): $\delta = 20.2$ (d, $^1J_{PC} = 11.4$ Hz, CH$_2$P), 31.8 (d, $^2J_{PC} = 17.1$ Hz, CH$_2$CH$_2$P), 59.3 (d, $^1J_{PC} = 15.7$, PCH$_2$O), 125.3 (s, aromat. CH), 142.7 (d, $^3J_{PC} = 12.8$ Hz, aromat. C).

4.4.2. 1,3,5-Tris[3′-bis(hydroxymethyl)phosphinopropyl]-benzene (4c)

Clear gummy material (0.90 g, 94%). FAB-MS (NBA, 50 °C); *m/z* (%): 481 (20) [M + H]$^+$, 449 (28) [M − CH$_2$OH]$^+$, 420 (33) [M − 2CH$_2$O]$^+$. Anal. Found: C, 52.31; H, 8.50. Calc. for $C_{21}H_{39}O_6P_3$ (480.5): C, 52.50; H, 8.18%. IR (KBr, cm^{-1}): $\tilde{\nu} = 3346$ (O–H), 2899 (CH$_2$), 1600 (aromat. C=C), 1012 (C–O). ^{31}P{^{1}H}-NMR (101.26 MHz, D$_2$O, 22 °C): $\delta = -24.5$. ^{31}P{^{1}H}-NMR (101.26 MHz, acetone-d_6, 22 °C): $\delta = -22.9$. ^{1}H-NMR (250.13 MHz, D$_2$O, 22 °C): $\delta = 1.86$ (dd, $^2J_{PH} = 7.2$ Hz, $^3J_{HH} = 7.2$ Hz, 6H, CH$_2$P), 2.76 (dt, $^3J_{PH} = 9.5$ Hz, $^3J_{HH} = 7.6$ Hz, 6H, CH_2CH$_2$P), 3.98 (m, 12H, OCH_2P), 7.02 (s, 3H, aromat. CH). ^{1}H-NMR (250.13 MHz, acetone-d_6, 22 °C): $\delta = 2.06$ (m, 6H, CH$_2$P), 2.82 (m, 6H, CH_2CH$_2$P), 4.13 (m, 12H, OCH_2P), 7.07 (s, 3H, aromat. CH). ^{13}C{^{1}H}-NMR (62.90 MHz, D$_2$O, 22 °C): $\delta = 20.0$ (d, $^1J_{PC} = 8.6$ Hz, CH$_2$P), 29.1 (d, $^2J_{PC} = 15.3$ Hz, CH$_2$CH$_2$P), 55.8 (d, $^1J_{PC} = 9.53$ Hz, PCH$_2$O), 123.8 (s, aromat. CH), 140.7 (d, $^3J_{PC} = 9.5$ Hz, aromat. C). ^{13}C{^{1}H}-NMR (62.90 MHz, acetone-d_6, 22 °C): $\delta = 20.2$ (d, $^1J_{PC} = 11.4$ Hz, CH$_2$P), 31.8 (d, $^2J_{PC} = 17.1$ Hz, CH$_2$CH$_2$P), 59.3 (d, $^1J_{PC} = 15.7$ Hz, PCH$_2$O), 125.3 (s, aromat. CH), 142.7 (d, $^3J_{PC} = 12.8$ Hz, aromat. C).

4.4.3. 1,3,5-Tris[4′-bis(hydroxymethyl)phosphinobutyl]-benzene (4d)

Clear gummy material (1.0 g, 96%). FAB-MS (NBA, 50 °C); *m/z* (%): 523 (20) [M + H]$^+$, 491 (15) [M − CH$_2$OH]$^+$, 462 (28) [M − 2CH$_2$O]$^+$. Anal. Found: C, 54.97; H, 8.88. Calc. for $C_{24}H_{45}O_6P_3$ (522.5): C, 55.17; H, 8.68%. IR (KBr, cm^{-1}): = 3346 (O–H), 2899 (CH$_2$), 1600 (aromat. C=C), 1012 (C–O). ^{31}P{^{1}H}-NMR (101.26 MHz, acetone-d_6, 22 °C): $\delta = -24.0$. ^{1}H-NMR (250.13 MHz, acetone-d_6, 22 °C): $\delta = 1.50$–1.72 (m, 18H, CH$_2$CH$_2$CH$_2$P), 2.58 (t, $^3J_{HH} = 7.2$ Hz, 6H, CH_2CH$_2$CH$_2$CH$_2$P), 4.01 (m, 12H, OCH_2P), 6.86 (s, 3H, aromat. CH). ^{13}C{^{1}H}-NMR (62.90 MHz, acetone-d_6, 22 °C): $\delta = 18.9$ (d, $^1J_{PC} = 10.1$ Hz, CH$_2$P), 26.5 (d, $^2J_{PC} = 15.5$ Hz, CH$_2$CH$_2$P), 34.1 (d, $^3J_{PC} = 11.5$ Hz, CH$_2$CH$_2$CH$_2$P), 36.2 (s, CH$_2$CH$_2$CH$_2$CH$_2$P), 60.6 (d, $^3J_{PC} = 16.2$ Hz, PCH$_2$OH), 126.8 (s, aromat. CH), 143.2 (s, aromat. C).

4.5. Preparation of the 1,3,5-tris{bis[(2′-diethylphosphonatoethyl)phosphinolkyl]}benzenes **5b**–**d**

A mixture of **3b**–**d** (2.0 mmol), diethyl vinylphosphonate (2.17 g, 13.2 mmol), and AIBN (50 mg) was irradiated with ultraviolet light of a mercury high pressure lamp at 20 °C in a closed quartz Schlenk tube for

24 h. The volatile materials were removed under vacuum at 80 °C to leave the pure products **5b**–**d**.

4.5.1. *1,3,5-Tris{2′-bis[(2′-diethylphosphonatoethyl)phosphinoethyl]}benzene* (***5b***)

Clear gummy material (2.4 g, 96%). MS (FD, CH_2Cl_2, 35 °C); *m*/*z*: 1243 $[M]^+$. Anal. Found: C, 46.24; H, 8.18. Calc. for $C_{48}H_{99}O_{18}P_9$ (1243.1): C, 46.38; H, 8.03%. IR (KBr, cm^{-1}): $\tilde{\nu} = 2983$, 2908 (CH_2), 1602 (aromat. C=C), 1237 (P=O), 1055 (P–OEt). $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$, 22 °C): $\delta = -19.6$ (t, $^3J_{PP} = 51.2$ Hz, 3P, PC_3), 32.2 (d, $^3J_{PP} = 51.2$ Hz, 6P, $CP(O)(OEt)_2$). ^1H-NMR (250.13 MHz, $CDCl_3$, 22 °C): $\delta = 1.29$ (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, $^3J_{PH} = 4.4$ Hz, $^3J_{HH} = 7.4$ Hz, 6H, CH_2CH_2P), 4.07 (dq, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 7.2$ Hz, 24H, OCH_2CH_3), 6.82 (s, 3H, aromat. CH). $^{13}C\{^1H\}$-NMR (62.90 MHz, $CDCl_3$, 22 °C): $\delta = 16.2$ (d, $^3J_{PC} = 5.7$ Hz, CH_3CH_2O), 18.3 (dd, $^1J_{PC} = 17.4$ Hz, $^2J_{PC} = 6.8$ Hz, $O{=}PCH_2CH_2P$), 21.5 (dd, $^1J_{PC} = 140.5$ Hz, $^2J_{PC} = 13.9$ Hz, $O{=}PCH_2CH_2P$) 28.2 (d, $^1J_{PC} = 15.7$ Hz, CH_2P), 31.6 (d, $^2J_{PC} = 14.9$ Hz, CH_2CH_2P), 61.4 (d, $^2J_{PC} = 6.4$ Hz, CH_3CH_2O), 125.4 (s, aromat. CH), 142.6 (d, $^3J_{PC} = 11.4$ Hz, aromat. C).

4.5.2. *1,3,5-Tris{3′-bis[(2′-diethylphosphonatoethyl)phosphinopropyl]}benzene* (***5c***)

Clear gummy material (2.5 g, 97%). MS (FD, CH_2Cl_2, 35 °C); *m*/*z*: 1285 $[M]^+$. Anal. Found: C, 47.23; H, 7.97. Calc. for $C_{51}H_{105}O_{18}P_9$ (1285.1): C, 47.67; H, 8.23%. IR (KBr, cm^{-1}): $\tilde{\nu} = 2984$, 2932, 2929 (CH_2), 1603 (aromat. C=C), 1237 (P=O), 1026 (P–OEt). $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$, 22 °C): $\delta = -21.2$ (t, $^3J_{PP} = 51.2$ Hz, 3P, PC_3), 32.3 (d, $^3J_{PP} = 51.2$ Hz, 6P, $CP(O)(OEt)_2$). ^1H-NMR (250.13 MHz, $CDCl_3$, 22 °C): $\delta = 1.22$ (t, $^3J_{HH} = 7.1$ Hz, 36H, OCH_2CH_3), 1.35 (m, 6H, CH_2P), 1.43–1.75 (m, 30H, $O{=}PCH_2CH_2P$ and CH_2CH_2P), 2.52 (t, $^3J_{HH} = 7.4$ Hz, 6H, $CH_2CH_2CH_2P$), 3.99 (dq, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 7.2$ Hz, 24H, OCH_2CH_3), 6.70 (s, 3H, aromat. CH). $^{13}C\{^1H\}$-NMR (62.90 MHz, $CDCl_3$, 22 °C): $\delta = 16.4$ (d, $^3J_{PC} = 5.7$ Hz, CH_3CH_2O), 18.5 (dd, $^1J_{PC} = 16.4$ Hz, $^2J_{PC} = 6.4$ Hz, $O{=}PCH_2CH_2P$), 21.7 (dd, $^1J_{PC} = 140.1$ Hz, $^2J_{PC} = 13.5$ Hz, $O{=}PCH_2CH_2P$), 26.1 (d, $^2J_{PC} = 14.2$ Hz, CH_2CH_2P), 27.5 (d, $^1J_{PC} = 14.2$ Hz, CH_2P), 37.3 (d, $^3J_{PC} = 11.4$ Hz, $CH_2CH_2CH_2P$), 61.6 (d, $^2J_{PC} = 6.4$ Hz, CH_3CH_2O), 126.1 (s, aromat. CH), 141.8 (s, aromat. C).

4.5.3. *1,3,5-Tris{4′-bis[(2′-diethylphosphonatoethyl)phosphinobutyl]}benzene* (***5d***)

Clear gummy material (2.55 g, 96%). FAB-MS (NBA, 50 °C); *m*/*z* (%): 1327 (23) $[M]^+$, 1161 (13) $[M - CH_2CH_2P(O)(OEt)_2]^+$. Anal. Found: C, 48.70; H, 8.64. Calc. for $C_{54}H_{111}O_{18}P_9$ (1327.2): C, 48.87; H, 8.43%. IR (KBr, cm^{-1}): $\tilde{\nu} = 2983$, 2933, 2857 (CH_2), 1603 (aromat. C=C), 1240 (P=O), 1066 (P–OEt). $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$, 22 °C): $\delta = -21.1$ (t, $^3J_{PP} = 51.2$ Hz, 3P, PC_3), 32.4 (d, $^3J_{PP} = 51.2$ Hz, 6P, $CP(O)(OEt)_2$). ^1H-NMR (250.13 MHz, $CDCl_3$, 22 °C): $\delta = 1.28$ (t, $^3J_{HH} = 7.1$ 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, $^3J_{HH} = 7.5$ Hz, 6H, $CH_2CH_2CH_2P$), 4.05 (dq, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 7.2$ Hz, 24H, OCH_2CH_3), 6.74 (s, 3H, aromat. CH). $^{13}C\{^1H\}$-NMR (62.90 MHz, $CDCl_3$, 22 °C): $\delta = 16.6$ (d, $^3J_{PC} = 6.1$ Hz, CH_3CH_2O), 18.7 (dd, $^1J_{PC} = 16.5$ Hz, $^2J_{PC} = 6.4$ Hz, $O{=}PCH_2CH_2P$), 21.9 (dd, $^1J_{PC} = 140.5$ Hz, $^2J_{PC} = 13.9$ Hz, $O{=}PCH_2CH_2P$), 25.8 (d, $^3J_{PC} = 10.8$ Hz, $CH_2CH_2CH_2P$), 26.4 (d, $^1J_{PC} = 13.5$ Hz, CH_2P), 33.5 (d, $^3J_{PC} = 13.5$ Hz, CH_2CH_2P), 35.8 (s, $CH_2CH_2CH_2CH_2P$), 61.8 (d, $^2J_{PC} = 6.7$ Hz, CH_3CH_2O), 125.0 (s, aromat. CH), 142.4 (s, aromat. C).

4.6. *Preparation of the triplatinacyclophanes* ***6b***–***d***

Solutions of $Cl_2Pt(NCPh)_2$ (708 mg, 1.5 mmol) and the corresponding ligand (1.0 mmol) in dichloromethane (250 ml) 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 r.t. Then the solvent was removed in vacuo and the resulting residue was subjected to column chromatography (30 × 3 cm, 15% MeOH–CH_2Cl_2). TLC purifications were performed for analysis.

4.6.1. *4,4,17,17,30,30-Hexachloro-3,3,5,5,16,16,18,18,29,29,31,31-dodeca(2′-diethylphos-phonatoethyl)-3,5,16,18,29,31-hexaphospha-4,17,30-triplatina[7_3](1,3,5)-cyclophane* (***6b***)

Pale yellow gummy material (68 %). MS (pos. FAB, NBA, 50 °C); *m*/*z*: 3288 $[M]^+$, 3239 $[M - OEt]^+$, 3202 $[M - Cl - EtO]^+$. Anal. Found: C, 34.91; H, 6.05; Cl, 6.60. Calc. for $C_{96}H_{198}Cl_6O_{36}P_{18}Pt_3$ (3284.1): C, 35.11; H, 6.08; Cl, 6.48%. IR (KBr, cm^{-1}): $\tilde{\nu} = 2981$, 2930, 2910 (CH_2), 1604 (aromat. C=C), 1239 (P=O), 1023 (P–OEt). $^{195}Pt\{^1H\}$-NMR ($CDCl_3$): $\delta = -3940$ (t, $^1J_{PtP} = 2478$ Hz). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): $\delta = 6.1$ (m [31b] d, $N = 58.1$, $^1J_{PtP} = 2478$ Hz, 6P, $PtPC_3$), 30.1 (m 31a, $N = 58.1$ Hz, 12P, $CP(O)(OEt)_2$). ^1H-NMR (250.13 MHz, CD_2Cl_2, 22 °C): $\delta = 1.27$ (t, $^3J_{HH} = 7.1$ 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). $^{13}C\{^1H\}$-NMR (62.90 MHz, CD_2Cl_2, 22 °C): $\delta = 13.1$ (m, $O{=}PCH_2CH_2P$), 16.7 (d, $^2J_{PC} = 5.7$ Hz, CH_3), 20.1 (d, $^1J_{PC} = 140.1$ 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).

4.6.2. 5,5,20,20,35,35-Hexachloro-4,4,6,6,19,19,21,21,34,34,36,36-dodeca-(2′-diethylphos-phonatoethyl)-4,6,19,21,34,36-hexaphospha-5,20,35-triplatina[9_3]-(1,3,5)-cyclophane ***(6c)***

Pale yellow gummy material (55%). MS (pos. FAB, NBA, 50 °C); *m/z*: 3365 $[M]^+$, 3233 $[M-3EtO]^+$. Anal. Found: C, 35.98; H, 6.06; Cl, 6.40. Calc. for $C_{102}H_{210}Cl_6O_{36}P_{18}Pt_3$ (3368.2): C, 36.37; H, 6.28; Cl, 6.32%. IR (KBr, cm^{-1}): $\tilde{\nu}=2981$, 2930 (CH_2), 1603 (aromat. C=C), 1242 (P=O), 1028 (P–OEt). $^{195}Pt\{^1H\}$-NMR ($CDCl_3$): $\delta=-3966$ (t, $^1J_{PtP}=2465$ Hz). $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$, 22 °C): $\delta=15.2$ (m [31b] d, $N=58.2$, $^1J_{PtP}=2465$ Hz, 6P, $PtPC_3$), 30.3 (m [31a], $N=58.2$ Hz, 12P, $CP(O)(OEt)_2$). ^1H-NMR (250.13 MHz, $CDCl_3$, 22 °C): $\delta=1.33$ (m, 72H, CH_3), 1.74–2.06 (m, 72H, $(O{=}PCH_2CH_2)_2PCH_2CH_2$), 2.59 (br. s, 12H, $CH_2CH_2CH_2P$), 4.11 (m, 48H, OCH_2), 6.76 (s, 3H, C_6H_3). $^{13}C\{^1H\}$-NMR (62.90 MHz, $CDCl_3$, 22 °C): $\delta=12.1$ (m, $O{=}PCH_2CH_2P$), 16.5 (d, $^2J_{PC}=5.4$ Hz, CH_3), 19.6 (d, $^1J_{PC}=141.5$ Hz, $O{=}PCH_2CH_2P$), 24.4 (m, CH_2CH_2P), 35.1 (m, CH_2P), 36.8 (s, $CH_2CH_2CH_2P$), 128.2 (s, aromat. CH), 141.0 (s, aromat. C).

4.6.3. 6,6,29,29,40,40-Hexachloro-5,5,7,7,22,22,24,24,39,39,41,41-dodec(2′-diethylphos-phonatoethyl)-5,7,22,24,39,41-hexaphospha-6,23,40-triplatina[11_3]-(1,3,5)-cyclophane ***(6d)***

Pale yellow gummy material (37%). MS (pos. FAB, NBA, 50 °C); *m/z*: 3450 $[M]^+$, 3417 $[M-Cl]^+$. Anal. Found: C, 37.65; H, 6.54, 6.38. Calc. for $C_{108}H_{222}Cl_6O_{36}P_{18}Pt_3$ (3452.4): C, 37.57; H, 6.48; Cl, 6.16%. IR (KBr, cm^{-1}): $\tilde{\nu}=2981$, 2930, 2860 (CH_2), 1603 (aromat. C=C), 1242 (P=O), 1046 (P–OEt). $^{195}Pt\{^1H\}$-NMR ($CDCl_3$): $\delta=-3933$ (t, $^1J_{PtP}=2460$ Hz). $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$, 22 °C): $\delta=12.9$ (m [31b] d, $N=58.2$, $^1J_{PtP}=2460$ Hz, 6P, $PtPC_3$), 30.5 (m [31a], $N=58.2$ Hz, 12P, $CP(O)(OEt)_2$). ^1H-NMR (250.13 MHz, $CDCl_3$, 22 °C): $\delta=1.34$ (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). $^{13}C\{^1H\}$-NMR (62.90 MHz, $CDCl_3$, 22 °C): $\delta=13.8$ (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).

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