Trifunctional Phosphane Ligands and Their Application in the Synthesis of Novel Cage-Structured Platinacyclophanes and Trinuclear Chain-Like Platinacycles by Self-Assembly[‡]

Ekkehard Lindner,*[a] Monther Khanfar,[a] and Manfred Steimann[a]

Dedicated to Professor Dieter Sellmann on the occasion of his 60th birthday

Keywords: Cyclophanes / Platinum / P ligands / Supramolecular chemistry / Self assembly

The synthesis of the 1,3,5-tris[(diphenylphosphoryl)alkyl]-benzenes **7**–**10** succeeds by reaction of the corresponding 1,3,5-tris(bromoalkyl)benzenes **3**–**6** with ethyl diphenylphosphinite in an Arbusov-type reaction. Reduction of these phosphane oxides leads to the trifunctional phosphane ligands **11**–**14**. Their potency of self-assembly was examined by the employment of platinum(II) complex fragments. A five-component self-assembly consisting of 3 equiv. of the platinum complex $Cl_2Pt(NCPh)_2$ and 2 equiv. of the ligands **11**–**14** under high-dilution conditions led to the formation of the nanoscaled triplatinacyclophanes **1** and **15**–**17**. Polymers were formed as by-products from the reactions between **11**–**13** and $Cl_2Pt(NCPh)_2$, whereas in the case of **14** three other platinacyles **18**–**20** with a chain-like structure were formed. The structures of the metallacycles **1** and **15**–**17** as well as **18**–**20** were elucidated by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectroscopic investigations.

Introduction

Supramolecular chemistry, which may be regarded as a result of modern coordination chemistry,[1] is at the frontier of molecular sciences as is shown by the fast growth of publications in this area in the last decade.[2] Cyclophanes and in particular metallacyclophanes are part of this chemistry.[3,4] They contain cavities that have the capacity to include guest molecules of different kinds.[4] The synthesis of these fascinating compounds was troublesome. However, studies in self-organization have provided a lot of interesting molecular architectures capable of being used for host−guest chemistry, such as "cyclophane boxes",[5] squares and polygons,[6] cylinders,[7] rods[8] and many others.[9] Unlike two-dimensional metallacyclophane boxes, three-dimensional multicyclic species are still rare today.[5,10]

Mono- and multidentate phosphanes are attractive ligands for the generation of complexes with a great variety of transition metal fragments.[11] Recently, van Koten et al.[12] synthesized a tetradentate ligand in which the phosphane arms are attached via methylene groups to a benzene ring in the 1,2,4,5-positions. The introduction of a symmetrically 1,3,5-trisubstituted benzene ring with at least C_3 symmetry into phosphane chemistry has advantages for the synthetic design[13] of self-assembled supramolecular molecules[14] and for chemical selectivity.[15] As it was demonstrated recently such tridentate phosphanes are suitable for assembly via three platinum atoms to give an elastic, three-dimensional molecular cage. By virtue of its size it was possible to reversibly encapsulate 1,2-dichloroethane into the triplatinacyclophane **1** (Figure 1).[16] In continuation of this work several triplatinacyclophanes were generated with different cage sizes in order to study the dependence of the number of methylene groups in the ligand system on the type of self-assembly. Due to this novel tridentate phosphane ligands are introduced in this investigation. They are based on a central benzene ring which is provided with three flexible aliphatic spacer units, each carrying a phosphane group at their ends. Such ligands can be employed in catalysis and supramolecular chemistry.

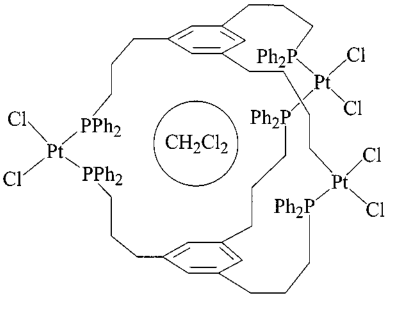


Figure 1. Inclusion of 1,2-dichloroethane into the three-dimensional triplatinacyclophane **1**

[‡] Preparation, Properties, and Reactions of Metal-Containing Heterocycles, 104. − Part 103: E. Lindner, R. Zong, K. Eichele, *Phosphorus Sulfur Silicon Relat. Elem.*, in press.

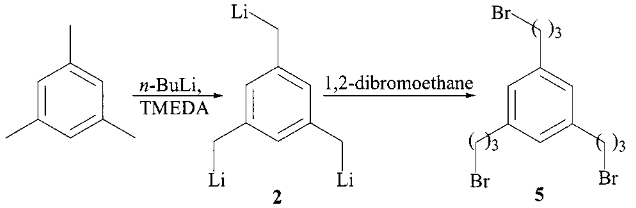
[a] Institut für Anorganische Chemie der Universität,
Auf der Morgenstelle 18, 72076 Tübingen, Germany
Fax: (internat.) + 49-(0)7071/295306
E-mail: ekkehard.lindner@uni-tuebingen.de

1434−1948/01/0909−2411 $ 17.50+.50/0

Results and Discussion

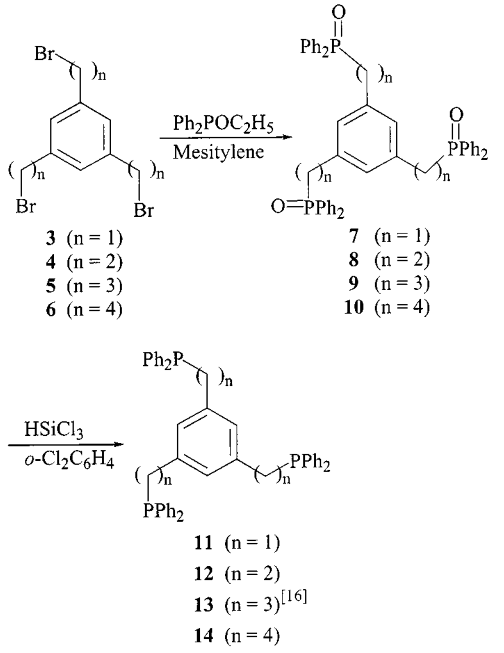
Ligand Synthesis

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**) is only available in a complicated eight-step reaction sequence.[17] Therefore a much simpler access to **5** 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 in *n*-pentane at −85 °C resulted in the formation of **5** in about 20% yield (Scheme 1).



Scheme 1

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.[12,18] According to this procedure an Arbusov reaction was carried out between **3−6** and $Ph_2POC_2H_5$ yielding quantitatively the phosphane oxides **7−10** (Scheme 2). In *o*-dichlorobenzene these phosphane oxides can easily be reduced with $HSiCl_3$ to the corresponding trifunctionalized phosphanes **11−14** (Scheme 2). Whereas the phosphane 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 phosphanes 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 confirmed by FAB and EI mass spectra, 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} which is assigned to the P=O stretching vibration. Expectedly, in the $^{31}P\{^1H\}$ NMR spectra (in $CDCl_3$) of the phosphane oxides **7−10** one singlet is observed for each of them (δ = 31 to 34) which is shifted to higher fields (δ = −9 to −15) on going from **7−10** to the phosphanes **11−14**.



Scheme 2

Crystal Structures of 9 and 12

To obtain more detailed structural information about the trifunctional phosphane oxides and their oxygen-free analogues, X-ray structural analyses were performed on compounds **9** and **12** (Scheme 2). ORTEP drawings of their molecular structures with atom labeling are depicted in Figures 2 and 3. 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 phosphane 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 towards 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 that is parallel to the benzene ring. The distance between the phosphorus atoms is 10.179(6) Å (Figure 2).

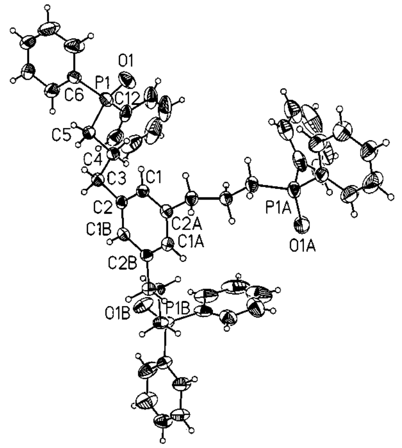


Figure 2. Molecular structure of **9** in the crystal; ORTEP plot with thermal ellipsoids at 20% probability; selected distances [Å] and angles [°]: P1−O1 1.487(4), P1−C6 1.800(5), P1−C5 1.809(4), P1−C12 1.809(8), P1−C2 5.307(5), P1−P1A = P1A−P1B = P1−P1B 10.179; C1A−C2−P1 = C1B−C2A−P1A = C1−C2B−P1B 144.2(6)

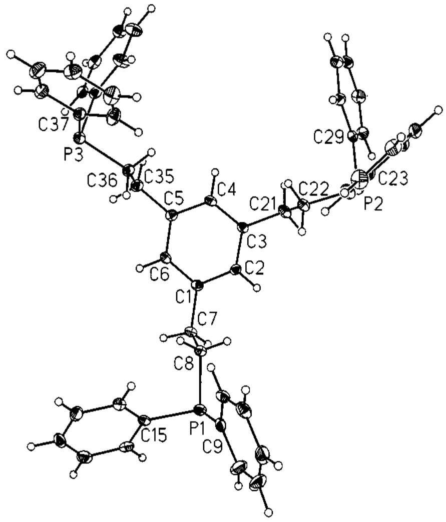


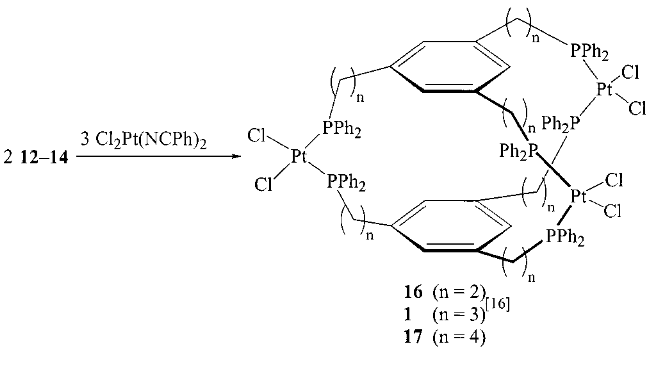
Figure 3. Molecular structure of **12** in the crystal; ORTEP plot with thermal ellipsoids at 20% probability; selected distances [Å] and angles [°]: P1−C9 1.831(7), P1−C8 1.834(5), P1−C15 1.849(5), P2−C23 1.809(6), P2−C29 1.833(5), P2−C22 1.847(5), P3−C36 1.854(5), P3−C37 1.811(7), P3−C43 1.839(5) P1−C1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

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

Motifs Generated by Self-Assembly

To obtain self-assembled cyclophane structures a pre-organization of the components is a necessary prerequisite. Trifunctionalized phosphane ligands of the type **11**−**14** provide the necessary rigidity that is important for this pre-organization. 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).[19] In contrast to the platinacyclophane **1**, which was recently described,[16] 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 were formed as by-products, an observation which was also made by Fujita et al. with comparable nitrogen ligands.[10c] The solubility of **15** as well as these by-products is too low for separation. This property also led to the prevention of a template synthesis being performed in order to enhance the yield of **15**. Because of its better solubility **16** could be obtained as a pure compound by chromatography.

$$2\ \mathbf{11} \xrightarrow{3\ Cl_2Pt(NCPh)_2} \underset{\mathbf{15}}{[Cl_2Pt(PPh_2CH_2)_2]_3(C_6H_3)_2} + \text{polymers}$$



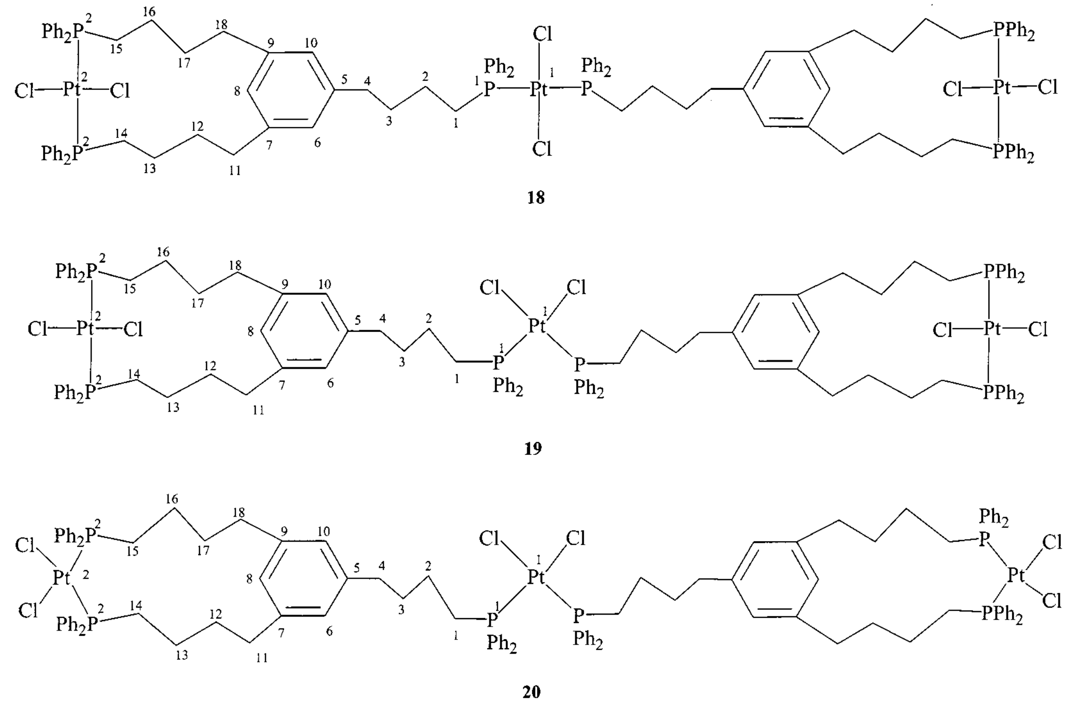
16 (n = 2)[16]
1 (n = 3)
17 (n = 4)

Scheme 3

Compared to **11** and **12** the behavior of ligand **14,** with four methylene units towards $Cl_2Pt(NCPh)_2$ 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** was performed by column chromatography. However, **17** always contained impurities of **20**. According to their FAB mass spectra these compounds show the same molecular mass and it turned out that they are structural isomers. 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 dichloromethane. At low temperatures the yields were around 10% and decreased with increasing temperature. At 40° C the structural isomer **18** is predominant (86%) and the formation of **17** is thermodynamically unfavorable.[20] Benzene is the best solvent for the generation of **17**; it is superior to CCl_4 or $CHCl_3$.

The triplatinacyclophanes **1**, **15**−**17** and trinuclear platinacycles **18**−**20** represent colorless to pale yellow compounds that show similar solubility behavior to 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 $^{31}P\{^1H\}$ 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 constants of about 3500 Hz, whereas those with a *trans* environment reveal values of about 2500 Hz.[21] It is also well known that ^{31}P signals of *trans* isomers are shifted upfield compared to those of *cis* isomers.[21] The $^{31}P\{^1H\}$ NMR spectra of **16** and **17** each show a singlet for the six chemical equivalent phosphorus atoms at $\delta = 7.1$ and 9.6, respectively, and a doublet for the ^{195}Pt satellites, which is typical for *cis*-PtP_2 fragments. This assignment is confirmed by $^{195}Pt\{^1H\}$ NMR spectra, which each display a triplet at $\delta = -4423$ and -4413 with coupling constants of $^1J_{PtP} = 3600$ and 3668 Hz, respectively. Moreover, the structure of **1** was recently confirmed by an X-ray structural analysis.[16] Because **15** was impurified by polymers and because of its low



Scheme 4

solubility in all organic solvents, no exact NMR spectroscopic data were available.

In contrast to **16**, **17** (and **1**[16]) the $^{31}P\{^1H\}$ NMR spectra of the trinuclear platinacycles **18−20** show two ^{31}P singlets in a ratio of 2:1. This is a clear indication that two different ^{31}P nuclei are present. Each singlet is accompanied by a doublet as satellites that is traced back by the $^{195}Pt-^{31}P$ coupling (see Exp. Sect.). 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 confirmed by the value of the $^{195}Pt-^{31}P$ coupling constants which is higher than that of the noncyclized central platinum atom. 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**.

A short discussion of the ^1H and $^{13}C\{^1H\}$ NMR spectra of the cycles **16−20** is with regards to the central benzene rings and the adjacent methylene groups. Only one ^1H 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 only give rise 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 ($^3J_{PC}$ = 7 Hz). The corresponding signals for the aromatic methine and quaternary carbon atoms in the spectra of **18−20** are split into two peaks with an intensity of 2:1 (see Exp. Sect.). A doublet at δ = 28.6 ($^2J_{PC}$ = 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 into two signals with an intensity of 2:1 in the spectra of **18−20**.

Conclusion

In contrast to metallacyclophanes, the chemistry of organic cyclophanes is much more developed.[3] However, within the last five to ten years several new architectures of metallacyclophanes with interesting properties have been described in the literature.[1−3,5,6] 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 phosphanes. They are provided with a central benzene ring with three phosphane arms in a symmetrical 1,3,5-position. The distance of these phosphanes 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[10b,22] and for the synthesis of catalytically active transition metal complexes.[14a] It was demonstrated that these trifunctional phosphane ligands are capable of undergoing self-assembly with adequate platinum complex fragments. Three items are observed that affect the formation of three-dimensional platinacyclophanes: 1) the rigidity of the ligand system, 2) steric factors, and 3) intramolecular chelation. The first point is predominant in the formation of cages with a trisphosphane that 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 phosphanes to avoid contact between each other to reduce the steric congestion caused by the phenyl substituents. Also the P-donors are too far away from a metal center to give intramolecular chelation.[10b] By the introduction of methylene groups and by increasing their number, the ligand system becomes more flexible and the phosphane 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 phosphane group is in the opposite direction of the other two[23]), via monoclinic (**12**, this report) to cubic (**9**, this report) for trifunctional phosphanes 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 intermolecular chelation results in the favored formation of polymers. The flexibility of a phosphane system with four methylene bridges is accompanied by a release of the steric factor and thus enables intramolecular chelation. This is the reason that the formation of the chain-like platinacycles **18−20** are favored compared with that of the cage **17**. The optimum for self-assembly is obtained if the ligand contains three methylene groups.

Experimental Section

General: 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, benzene from sodium benzophenone ketyl, and mesitylene and *o*-dichlorobenzene 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 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 referenced with TMS as the 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% $Na_2[PtCl_6]\cdot 6\ H_2O$. − Compounds **3**,[24] **4**,[25] **2**,[26] ethyl diphenylphosphinite,[27] $Cl_2Pt(NCPh)_2$,[28] and **14**[29] were synthesized according to the literature methods.

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 (quint, $^{3}J_{HH}$ = 7.0 Hz, 6 H, CH_2CH_2Br), 2.73 (t, $^{3}J_{HH}$ = 7.4 Hz, 6 H, $CH_2CH_2CH_2Br$), 3.40 (t, $^{3}J_{HH}$ = 6.6 Hz, 6 H, CH_2CH_2Br), 6.88 (s, 3 H, aromatic H). − $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 33.4 (CH_2Br), 34.0 (CH_2CH_2Br), 34.3 ($CH_2CH_2CH_2Br$), 126.8 (aromatic CH), 141.2 (aromatic 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].

1,3,5-Tris(diphenylphosphorylmethyl)benzene (7): A modification to the literature procedure was applied.[30] To a suspension of **3** (4.25 g, 12 mmol) in mesitylene (20 mL), Ph_2POEt (15.37 g, 67 mmol) was added. Heating of the reaction mixture to 110 °C afforded a colorless solution. After heating of 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.[30] 205−206 °C). − ^{1}H NMR ($CDCl_3$): δ = 3.44 (d, $^{3}J_{PH}$ = 13.8 Hz, 6 H, CH_2P), 6.96 (d, $^{4}J_{PH}$ = 1.9 Hz, 3 H, aromatic C_6H_3), 7.47−7.50 (m, 18 H, *ortho*- and *para*-P−C_6H_5), 7.59 (m, 12 H, *meta*-P−C_6H_5). − $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 37.7 (d, $^{1}J_{PC}$ = 66.9, CH_2P), 123.6 (s, *tert*-C_6H_3), 128.6 (d, $^{3}J_{PC}$ = 12.1 Hz, *meta*-C_6H_5), 130.6 (m, *quat*-C_6H_3), 131.1 (d, $^{2}J_{PC}$ = 9.3 Hz, *ortho*-C_6H_5), 131.8 (s, *para*-C_6H_3), 137.4 (d, $^{1}J_{PC}$ = 99.6 Hz, *ipso*-C_6H_5). − $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 30.9. − IR (KBr): $\tilde{\nu}$ = 3053, 3024 (aromatic CH), 2950, 2893 (CH_2), 1437 (P−Ph), 1198 (P=O) cm^{-1}. − 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) [$P(O)Ph_2^+$].

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 of the reaction mixture to 90 °C afforded a colorless solution. The procedure 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, 6 H, CH_2P), 2.82 (m, 6 H, CH_2CH_2P), 6.79 (s, 3 H, C_6H_3), 7.42−7.55 (m, 18 H, *ortho*- and *para*-P−C_6H_5), 7.75 (m, 12 H, *meta*-P−C_6H_5). − $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 27.5 (d, $^{3}J_{PC}$ = 2.14 Hz, CH_2CH_2P), 32.0 (d, $^{1}J_{PC}$ = 69.0, CH_2P), 126.1 (s, *tert*-C_6H_3), 128.9 (d, $^{3}J_{PC}$ = 11.4 Hz, *meta*-C_6H_5), 130.9 (d, $^{2}J_{PC}$ = 9.3 Hz, *ortho*-C_6H_5), 132.0 (d, $^{4}J_{PC}$ = 2.14 Hz, *para*-C_6H_5), 132.8 (d, $^{1}J_{PC}$ = 99.6 Hz, *ipso*-C_6H_5), 142.1 (d, $^{3}J_{PC}$ = 14.9 Hz, *quat*-C_6H_3). − $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 32.7. − IR (KBr): $\tilde{\nu}$ = 3052, 3022 (aromatic CH), 2935 (CH_2), 1438 (P−Ph), 1188 (P=O) cm^{-1}. − 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 (100) [M^+]. − $C_{48}H_{45}O_3P_3$ (762.8): MS (HR, pos. FAB, NBA, 50 °C): *m*/*z* = 763.25960 [M^+]; calcd. 763.26599. − $C_{48}H_{45}O_3P_3$ (762.8): calcd. C 75.58, H 5.95; found C 75.36, H 5.82.

1,3,5-Tris[3′-(diphenylphosphoryl)propyl]benzene (9): Ph_2POEt (4.70 g, 20.4 mmol) was added to a suspension of **4** (1.50 g, 3.4 mmol) in mesitylene (20 mL). Heating of the reaction mixture to 70 °C afforded a colorless solution. After heating of the reaction mixture to 150 °C for 4 h, the volatile materials were removed under vacuum at 90 °C. The residue was solidified after cooling. A colorless solid product was obtained upon crystallization from benzene/*n*-hexane. Yield 2.54 gm, 93%, m.p. 115 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.90 (m, 6 H, C*H*$_2$P), 2.24 (m, 6 H, C*H*$_2$CH$_2$P), 2.61 (t, $^{3}J_{HH}$ = 7.4 Hz, 6 H, C*H*$_2$CH$_2$CH$_2$P), 6.70 (s, 3 H, C_6H_3), 7.39−7.51 (m, 18 H, *ortho*- and *para*-P−C_6H_5), 7.68 (m, 12 H, *meta*-P−C_6H_5). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 23.0 (d, $^{2}J_{PC}$ = 3.4, 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): ṽ = 3054, 3055 (CH_2), 2960, 2934 (aromatic CH), 1184 (P=O) cm^{-1}. − MS (pos. FAB, NBA, 50 °C): *m*/*z* (%) = 805 (37) [M^{+} + H], 603 (9) [M^{+} − P(O)Ph$_2$], 589 (15) [M^{+} − CH$_2$P(O)Ph$_2$], 576 (2) [M^{+} − CH$_2$CH$_2$P(O)Ph$_2$], 229 (16) [CH$_2$CH$_2$P(O)Ph$_2$$^{+}$], 215 (100) [CH$_2$P(O)Ph$_2$$^{+}$], 201 (55) [P(O)Ph$_2$$^{+}$]. − $C_{51}H_{51}O_3P_3$ (804.9). − MS (HR, pos. FAB, NBA, 50 °C): *m*/*z* = 805.31829 [M^{+}]; calcd. 805.31294. − $C_{51}H_{51}O_3P_3$ (804.9): calcd. C 76.11, H 6.39; found C 76.39, H 6.40.

1,3,5-Tris(diphenylphosphanylmethyl)benzene (11): A suspension of **3** (1.23 g, 1.7 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 at about 90 °C. The reaction mixture was further heated to 120 °C. At this temperature trichlorosilane (2.10 g, 15.5 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 by 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. Yield 1.1 g, 96%, m.p. 58 °C. − ^{1}H NMR ($CDCl_3$): δ = 3.08 (s, 6 H, CH_2P), 6.50 (s, 3 H, C_6H_3), 7.18 (s, 30 H, P−C_6H_5). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 35.9 (d, $^{1}J_{PC}$ = 15.7 Hz, *C*H$_2$P), 128.4 (d, $^{3}J_{PC}$ = 6.4 Hz, *meta*-C_6H_5), 128.7 (s, *para*-C_6H_3), 130.7 (s, *tert*-C_6H_3), 133.0 (d, $^{2}J_{PC}$ = 18.5 Hz, *ortho*-C_6H_5), 137.4 (dt, $^{2}J_{PC}$ = 8.5 Hz, $^{4}J_{PC}$ = 1.4 Hz, *quat*-C_6H_3), 138.6 (d, $^{1}J_{PC}$ = 15.7 Hz, *quat*-C_6H_5). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −9.4. − IR (KBr): ṽ = 3070, 3050 (aromatic CH), 2925, 2904 (CH_2), 1432 (P−Ph) cm^{-1}. − MS (70 eV, EI, 200 °C): *m*/*z* (%) = 672 (37) [M^{+}], 595 (3) [M^{+} − Ph], 487 (37) [M^{+} − Ph$_2$], 301 (25) [M^{+} − 2PPh$_2$]. − $C_{45}H_{39}P_3$ (672.7): MS (HR, 70 eV, EI, 210 °C): *m*/*z* = 672.230597 [M^{+}]; calcd. 672.226445. − $C_{45}H_{39}P_3$ (672.7): calcd. C 80.35, H 5.84; found C 80.04, H 5.85.

1,3,5-Tris[(2′-diphenylphosphanyl)ethyl]benzene (12): The same procedure outlined for **11** was applied for the synthesis of **12**. A suspension of compound **8** (3.05 g, 4.0 mmol) in *o*-dichlorobenzene (10 mL) became a colorless solution at 110 °C. After reduction with trichlorosilane (4.94 g, 36.5 mmol) and work-up, a white solid was obtained. Yield 2.80 g, 98%, m.p. 108−109 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.32 (m, 6 H, CH_2P), 2.66 (m, 6 H, C*H*$_2$CH$_2$P), 6.78 (s, 3 H, C_6H_3), 7.33−7.35 (m, 18 H, *ortho*- and *para*-P−C_6H_5), 7.45 (m, 12 H, *meta*-P−C_6H_5). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 30.3 (d, $^{2}J_{PC}$ = 12.8 Hz, *C*H$_2$CH$_2$P), 32.3 (d, $^{1}J_{PC}$ = 18.5 Hz, CH_2P), 125.9 (s, *tert*-C_6H_3), 128.6 (d, $^{3}J_{PC}$ = 7.1 Hz, *meta*-C_6H_5), 128.8 (s, *para*-C_6H_5), 132.9 (d, $^{2}J_{PC}$ = 18.5 Hz, *ortho*-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): ṽ = 3068, 3051 (aromatic CH), 2940, 2924 (CH_2), 1479 (P−Ph) cm^{-1}. − MS (70 eV, EI, 200 °C): *m*/*z* (%) = 714 (13) [M^{+}], 637 (7) [M^{+} − Ph], 529 (27) [M^{+} − Ph$_2$]. − $C_{48}H_{45}P_3$ (714.8): MS (HR, pos. FAB, NBA, 50 °C): *m*/*z* = 715.26919; found 715.26919. − $C_{48}H_{45}P_3$ (714.8): calcd. C 80.66, H 6.35; found C 80.56, H 6.15.

1,3,5-Tris[(3′-diphenylphosphanyl)propyl]benzene (13): The same procedure outlined for **11** was applied for the synthesis of **13**. A suspension of compound **9** (1.29 g, 1.6 mmol) in *o*-dichlorobenzene (10 mL) became a colorless solution at 80 °C. After reduction with trichlorosilane (2.0 g, 14.8 mmol) and work-up, a colorless oil was obtained. Yield 1.10 g, 91%. − ^{1}H NMR ($CDCl_3$): δ = 1.74 (m, 6 H, C*H*$_2$CH$_2$P), 2.08 (m, 6 H, CH$_2$C*H*$_2$P), 2.66 (t, $^{3}J_{HH}$ = 7.4 Hz, 6 H, C*H*$_2$CH$_2$CH$_2$P), 6.73 (s, 3 H, *tert*-C_6H_3), 7.33 (m, 18 H, *ortho*- and *para*-P−C_6H_5), 7.41 (m, 12 H, *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$_2$PPh$_2$], 543 (35) [M^{+} − CH$_2$CH$_2$PPh$_2$], 199 (100) [CH$_2$PPh$_2$]$^{+}$. − MS (pos. FAB, NBA, 50 °C): *m*/*z* (%) = 757 (16) [M^{+} + H], 571 (7) [M^{+} − PPh$_2$], 557 (7) [M^{+} − CH$_2$PPh$_2$], 543 (5) [M^{+} − CH$_2$CH$_2$PPh$_2$], 199 (100) [CH$_2$PPh$_2$$^{+}$].

Preparation of the Triplatinacyclophanes 15−17 and the Trinuclear Platinacycles 18−20: 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 stirred for 24 h at room temperature. The solvent was then removed under vacuum and the resulting residue was subjected to column chromatography.

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): Yield 54 mg, 5%, white solid, 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, C_6H_5). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 15.8 (t, $^{1}J_{PtP}$ = 2548 Hz). − IR (KBr): ṽ = 3050 (aromatic CH), 2928 (CH_2), 1435 cm^{-1} (P−Ph). − MS (neg. FAB, NBA, 50 °C): *m*/*z* = 2180 [M^{-} + Cl]. − $C_{90}H_{78}Cl_6P_6Pt_3$ (2143.3): calcd. C 50.43, H 3.67; found C 49.98, H 3.40.

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): Yield 56 mg, 15%, white solid, m.p. 241−242 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.64, 2.36 (br. s, 24 H, C*H*$_2$P, C*H*$_2$CH$_2$P), 6.42 (s, 6 H, C_6H_3), 7.11−7.49 (m, 60 H, C_6H_5). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$, 25 °C): δ = 22.2 (d, $^{1}J_{PC}$ = 90 Hz, *C*H$_2$P), 28.6 (d, $^{2}J_{PC}$ = 47 Hz, *C*H$_2$CH$_2$P), 126.1(s, *tert*-C_6H_3), 128.1 (d, $^{3}J_{PC}$ = 20 Hz, *meta*-C_6H_5), 129.6 (m, *ipso*-C_6H_5), 129.9 (s, *para*-C_6H_5), 131.6 (d, $^{2}J_{PC}$ = 23 Hz, *ortho*-C_6H_5), 140.3 (m, *quat*-C_6H_3). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 7.14 (sd, $^{1}J_{PtP}$ = 3600 Hz). − ^{195}Pt NMR ($CDCl_3$): δ = −4423 (t, $^{1}J_{PtP}$ = 3600 Hz). − IR (KBr): ṽ = 3051 (aromatic CH), 2923 (CH_2), 1434 (P−Ph) cm^{-1}. − MS (neg. FAB, NBA, 50 °C): *m*/*z* = 2262 [M^{-} + Cl]. − $C_{96}H_{90}Cl_6P_6Pt_3$ (2227.5): calcd. C 51.76, H 4.07; found C 51.53, H 4.10.

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): Yield 108 mg, 9%, colorless amorphous solid, m.p. 230 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.65 (br. s, 24 H,

$CH_2CH_2CH_2P$), 2.37 (s, 12 H, CH_2P), 2.55 (s, 12 H, $CH_2CH_2CH_2CH_2P$), 6.86 (s, 6 H, *tert*-C_6H_3), 7.1−7.7 (m, 60 H, $P-C_6H_5$). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.4 (s, $CH_2CH_2CH_2CH_2P$), 25.9 (d, $^2J_{PC}$ = 45 Hz, CH_2CH_2P), 32.9 (d, $^1J_{PC}$ = 16 Hz, CH_2P), 35.8 (s, $CH_2CH_2CH_2CH_2P$), 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 (aromatic CH), 2925, 2853 (CH_2), 1435 (P−Ph) cm^{-1}. − MS (neg. FAB, NBA, 50 °C): *m*/*z* = 2395 [M$^-$]. − (pos. FAB, NBA, 50 °C): *m*/*z*: 2359 [M$^+$ − Cl]. − $C_{108}H_{114}Cl_6P_6Pt_3$ (2395.9): calcd. C 54.14, H 4.80; found C 54.40, H 4.71.1

Compound 18: Yield 60 mg, 5%, colorless amorphous solid, m.p. 158 °C. − ^1H NMR ($CDCl_3$): δ = 1.51, 1.71 (br. s, 24 H, H2,3,12,13,16,17, for labeling see Scheme 4), 2.23 (m, 4 H, H-1), 2.37 (m, 12 H, H-4,-11,-18), 2.51 (br. s, 8 H, H-14,-15), 6.65 (s, 4 H, H-6, -10), 6.98 (s, 2 H, H-8), 7.2−7.7 (m, 60 H, $P-C_6H_5$). − $^{13}C\{^1H\}$ 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 (aromatic CH), 2926, 2854 (CH_2), 1434 (P−Ph) cm^{-1}. − MS (neg. FAB, NBA, 50 °C): *m*/*z* = 2395 [M$^-$]. − $C_{108}H_{114}Cl_6P_6Pt_3$ (2395.9): calcd. C 54.14, H 4.80, found C 54.32, H 4.81.

Compound 19: Yield 240 mg, 20%, pale yellow amorphous solid, m.p. 171 °C. − ^1H NMR ($CDCl_3$): δ = 1.50, 1.70 (br. s, 24 H, H-2,3,12,13,16,17), 2.23 (m, 4 H, H-1), 2.37 (m,12 H, H-4,-11,-18), 2.54 (br. s, 8 H, H-14,-15), 6.60 (s, 4 H, H-6,-10), 6.98 (s, 2 H, H-8), 7.1−7.6 (m, 60 H, $P-C_6H_5$). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 22.0 (s, C3,12,17), 23.4 (s, $^2J_{PC}$ = 37 Hz, C13,16), 23.8 (d, $^2J_{PC}$ = 38 Hz, C2), 30.9 (t, $^1J_{PC}$ = 17 Hz, C14,15), 31.6 (t, $^1J_{PC}$ = 16 Hz, C1), 33.7 (s, C11,18), 34.2 (s, C4), 125.4 (s, C6,10), 126.1 (s, C8), 127.0 (t, $^3J_{PC}$ = 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, $^2J_{PC}$ = 6 Hz, *ortho*-$P-C_6H_5$), 140.4 (s, C7,9), 140.9 (s, C5). −

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

	9	**12**
Crystal data		
Empirical formula	$C_{51}H_{51}O_3P_3$	$C_{48}H_{45}P_3$
Molecular mass	804.83	714.75
Crystal system	cubic	monoclinic
Space group	$Pa\bar{3}$	$P2_1/n$
Z	8	4
$d_{calcd.}$ [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)
β [°]	90	99.118(14)
V *[A^3]*	11094(4)	3982(6)
μ [mm^{-1}]	0.140	0.182
F(000)	3408	1512
Data collection		
Radiation	Mo-K_α	Mo-K_α
Monochromator	graphite	graphite
Wave length [Å]	0.71073	0.71073
Crystal size [mm^3]	0.35 × 0.35 × 0.35	0.15 × 0.55 × 0.15
Temperature [K]	298(2)	293(2)
Scan mode	ω	ω
$\theta_{min/max}$ [°]	2.04/27.50	2.11/27.52
hkl range	$-1 \le h \le 28$ $-1 \le k \le 28$ $-28 \le l \le 1$	$-20 \le h \le 2$ $-13 \le k \le 13$ $-30 \le l \le 30$
Measured reflections	14521	20325
Independent reflections	4248 (R_{int} = 0.0680)	9147 (R_{int} = 0.1798)
Absorption correction	None	None
Refinement		
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	4248/0/173	9147/0/461
Hydrogen treatment	calculated	calculated
Final *R* values [$I > 2\sigma(I)$]		
*R*1$^{[a]}$	0.1358	0.0879
*wR*2$^{[b]}$	0.3171	0.1920
$\rho_{residual}$(max/min) [e Å^{-3}]	1.060/−0.291	0.907/−0.867

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

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 8.7 (sd, $^1J_{PtP}$ = 3648 Hz, 2 P, P^1), 14.7 (sd, $^1J_{PtP}$ = 2565 Hz, 4 P, P^2). − ^{195}Pt NMR ($CDCl_3$): δ = −3973 (t, $^1J_{PtP}$ = 2565 Hz, 2 Pt, Pt^2), − 4410 (t, $^1J_{PtP}$ = 3648 Hz, 1 Pt, Pt^1). − IR (KBr): $\tilde{\nu}$ = 3052 (aromatic CH), 2925, 2854 (CH_2), 1434 cm^{-1} (P−Ph). − MS (neg. FAB, NBA, 50 °C): *m*/*z* = 2395 [M^-]. − $C_{108}H_{114}Cl_6P_6Pt_3$ (2395.9): calcd. C 54.14, H 4.80; found C 54.28, H 4.76.

Compound 20: Yield 720 mg, 60%, pale yellow amorphous solid, m.p. 191−193 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.47, 1.85 (br. s, 24 H, H-2,-3,-12,-13,-16,-17), 2.13 (m, 8 H, H-14,-15), 2.37 (m, 4 H, H-1), 2.55 (br. s, 12 H, H-4,-11,-18), 6.82 (s, 4 H, H-6,-10), 6.92 (s, 2 H, H-8), 7.1−7.7 (m, 60 H, P−C_6H_5). − $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, 25 °C): δ = 24.4 (s, C3), 24.6 (s, C12,17), 25.9 (d, $^2J_{PC}$ = 45 Hz, C2), 27.5 (d, $^2J_{PC}$ = 48 Hz, C13,16), 32.9 (t, $^1J_{PC}$ = 16 Hz, C14,15), 33.6 (t, $^1J_{PC}$ = 13 Hz, C1), 35.5 (s, C11,18), 36.0 (s, C4), 126.1 (s, C8), 126.6 (s, C6,10), 128.1 (t, $^3J_{PC}$ = 5 Hz, *meta*-$P^2-C_6H_5$), 128.3 (s, $^3J_{PC}$ = 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, $^2J_{PC}$ = 5 Hz, *ortho*-$P^2-C_6H_5$), 133.5 (t, $^2J_{PC}$= 5 Hz, *ortho*-$P^1-C_6H_5$), 141.8 (s, C7,9), 142.3 (s, C5). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 6.7 (sd, $^1J_{PtP}$ = 3610 Hz, 4 P, P^2), 8.7 (sd, $^1J_{PtP}$ = 3635 Hz, 2 P, P^1). − ^{195}Pt NMR ($CDCl_3$): δ = − 4431 (t, $^1J_{PtP}$ = 3610 Hz, 2 Pt, Pt^2), − 4413 (t, $^1J_{PtP}$ = 3635 Hz, 1 Pt, Pt^1). − IR (KBr): $\tilde{\nu}$ = 3051 (aromatic CH), 2925, 2853 (CH_2), 1435 (P−Ph) cm^{-1}. − MS (neg. FAB, NBA, 50 °C): *m*/*z* = 2395 [M^-]. − $C_{108}H_{114}Cl_6P_6Pt_3$ (2395.9): calcd. C 54.14, H 4.80; found C 54.50, H 4.91.

X-ray Structure 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 a random search. Intensities were collected by the ω-scan technique. No absorption correction was made. While **12** crystallized in the monoclinic space group $P2_1/n$ (Z = 4), **9** crystallized in the cubic space group *Pa*3bar (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)[31] 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 (**9**) and -158456 (**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: deposit@ccdc.cam.ac.uk].

Acknowledgments

Support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. Degussa AG is thanked for supplying starting materials.

[1] G. F. Swiegers, T. A. Malefetse, *Chem. Rev.* **2000**, *100*, 3483.

[2] [2a] B. Olenyuk, A. Fechtenkötter, P. J. Stang, *J. Chem. Soc., Dalton Trans.* **1998**, 1707. − [2b] L. R. MacGillivray, J. L. Atwood, *Angew. Chem.* **1999**, *111*, 1080; *Angew. Chem. Int. Ed.* **1999**, *38*, 1018. − [2c] M. Albrecht, *Angew. Chem.* **1999**, *111*, 3671; *Angew. Chem. Int. Ed.* **1999**, *38*, 3463.

[3] C. J. Jones, *Chem. Soc. Rev.* **1998**, *27*, 289.

[4] F. N. Diederich, *Cyclophanes*, *Royal Society of Chemistry Monographs in Supramolecular Chemistry* (Ed. J. F. Stoddart), Royal Society of Chemistry, Cambridge, **1991**.

[5] [5a] S. Hiraoka, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 10239. − [5b] F. Ibukuro, T. Kusukawa, M. Fujita, *J. Am. Chem. Soc.* **1998**, *120*, 8561. − [5c] T. Kusukawa, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 1397. − [5d] T. Kusukawa, M. Fujita, *Angew. Chem.* **1998**, *110*, 3327; *Angew. Chem. Int. Ed.* **1998**, *37*, 3142. − [5e] M. Fujita, S.-Y. Yu, T. Kusukawa, H. Funaki, K. Ogura, K. Yamaguchi, *Angew. Chem.* **1998**, *110*, 2192; *Angew. Chem. Int. Ed.* **1998**, *37*, 2082. − [5f] E. Leize, A. van Dorsselaer, R. Krämer, J.-M. Lehn, *J. Chem. Soc., Chem. Commun.* **1993**, 990. − [5g] C.-K. Chan, K.-K. Cheung, C.-M. Che, *Chem. Commun.* **1996**, 227. − [5h] P. J. Stang, B. Olenyuk, D. C. Muddinan, R. D. Smith, *Organometallics* **1997**, *16*, 3094. − [5i] M. Fujita, D. Ogura, M. Miyazama, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469. − [5j] C. M. Harshorn, P. J. Steel, *Chem. Commun.* **1997**, 541. − [5k] S. Aoki, M. Shiro, E. Kimura, *J. Am. Chem. Soc.* **2000**, *122*, 570. − [5l] R. L. Paul, S. M. Couchman, J. C. Jefferey, J. A. McCleverty, Z. R. Reeves, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **2000**, 845. − [5m] F. A. Cotton, L. M. Daniels, C. A. Murillo, *Chem. Commun.* **1999**, 841. − [5n] J. A. R. Navarro, E. Freisinger, B. Lippert, *Inorg. Chem.* **2000**, *39*, 2301.

[6] [6a] S. M. Woessner, J. B. Helms, Y. Shen, B. P. Sullivan, *Inorg. Chem.* **1998**, *37*, 5406. − [6b] K. D. Benkstein, J. T. Hupp, C. L. Stern, *Inorg. Chem.* **1998**, *37*, 5404. − [6c] M. Fujita, M. Aoyagi, K. Ogura, *Inorg. Chim. Acta* **1995**, *246*, 53. − [6d] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853. − [6e] D. L. Caulder, K. N. Raymond, *J. Chem. Soc., Dalton Trans.* **1999**, 1185. − [6f] K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975. − [6g] E. Lindner, M. Mohr, C. Nachtigal, R. Fawzi, G. Henkel, *J. Organomet. Chem.* **2000**, *595*, 166. − [6h] E. Lindner, R. Veigel, K. Ortner, C. Nachtigal, M. Steimann, *Eur. J. Inorg. Chem.* **2000**, 959. − [6i] E. Lindner, I. Krebs, R. Fawzi, M. Steimann, B. Speiser, *Organometallics* **1999**, *18*, 480. − [6j] E. Lindner, M. F. Günther, H. A. Mayer, R. Fawzi, M. Steimann, *Chem. Ber./Recueil* **1997**, *130*, 1815. − [6k] E. Lindner, M. Pitsch, R. Fawzi, M. Steimann, *Chem. Ber.* **1996**, *129*, 639. − [6l] E. Lindner, R. Wassing, R. Fawzi, M. Steimann, *Angew. Chem.* **1994**, *106*, 363; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 321. − [6m] E. Lindner, R. Wassing, R. Fawzi, M. Steimann, *Inorg. Chim. Acta* **1994**, *220*, 107.

[7] [7a] A. Marquis−Rigault, A. Dupont−Gervais, P. N. W. Baxter, A. van Dorsseler, J.-M. Lehn, *Inorg. Chem.* **1996**, *35*, 2307. − [7b] P. Baxter, J.-M. Lehn, A. Decian, J. Fischer, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69. − [7c] J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 102. − [7d] P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 113. − [7e] J.-M. Lehn, *Supramolecular Chemistry*, VCH Publishers, Weinheim, Germany, **1995**. − [7f] A. M. Carcia, D. M. Bassani, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 1234.

[8] [8a] F. Barrigelletti, L. Flamingni, J.-P. Collin, J.-P. Sauvage, *Chem. Commun.* **1997**, 333. − [8b] J.-P. Collin, P. Gavina, V. Heitz, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **1998**, 1. − [8c] J.-P. Sauvage, J. P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. Decola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993.

[9] [9a] J.-C. Chambron, C. O. Dietrich−Buchecker, J.-P. Sauvage, *Comprehensive Supramolecular Chemistry*, Elsevier, London, **1996**, vol. 9. − [9b] M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53. − [9c] C. P. McArdle, M. J. Irwin, M. C. Jennings, R. J. Puddephat,

Angew. Chem. **1999**, *111*, 3571; *Angew. Chem. Int. Ed.* **1999**, *38*, 3376.

[10] [10a] M. Hong, Y. Zhao, W. Su, R. Cao, M. Fujita, Z. Zhou, A. S. C. Chan, *J. Am. Chem. Soc.* **2000**, *122*, 4819. – [10b] P. M. Van Calcar, M. M. Olmstead, A. L. Balch, *Chem. Commun.* **1996**, 2597. – [10c] M. Fujita, S. Nagao, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 1649.

[11] [11a] P. G. Edwards, J. S. Fleming, S. J. Coles, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1997**, 3201. – [11b] P. G. Edwards, F. Ingold, S. J. Coles, M. B. Hursthouse, *Chem. Commun.* **1998**, 45.

[12] P. Steenwinkel, S. Kolmschot, R. A. Gossage, P. Dani, N. Veldman, A. L. Spek, G. van Koten, *Eur. J. Inorg. Chem.* **1998**, 477.

[13] T.-L. Ho, *Symmetry, A Basis for Synthesis Design*, Wiley, New York, **1995**.

[14] [14a] T. Beissel, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1996**, *108*, 1166; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1084. – [14b] A. Müller, C. Beugholt, *Nature* **1996**, *383*, 296.

[15] I. Hargittai, M. Hargittai, *Symmetry Through the Eyes of a Chemist*, Plenum, New York, **1995**.

[16] E. Lindner, C. Hermann, G. Baum, D. Fenske, *Eur. J. Inorg. Chem.* **1999**, 679.

[17] Y. Yamagiwa, Y. Koreishi, S. Kiyozumi, M. Kobayashi, T. Kamikawa, M. Tsukino, H. Goi, M. Yamamoto, M. Munakata, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3317.

[18] [18a] I. P. Beletskaya, A. V. Chuchurjukin, H. P. Dijkstra, G. P. N. van Klink, G. van Koten, *Tetrahedron Lett.* **2000**, *41*, 1075. – [18b] I. P. Beletskaya, A. V. Chuchurjukin, H. P. Dijkstra, G. P. N. van Klink, G. van Koten, *Tetrahedron Lett.* **2000**, *41*, 1081.

[19] P. Knops, N. Sendhoff, H.-B. Mekelburger, F. Vögtle, *High Dilution Reactions – New Synthetic Applications: Topics in Current Chemistry* (Eds. E. Weber, F. Vögtle), Springer, Heidelberg, **1992**.

[20] X. Chi, A. J. Gurrin, R. A. Haycock, C. A. Hunter, L. D. Sarson, *J. Chem. Soc., Chem. Commun.* **1995**, 2563, and references therein.

[21] [21a] W. E. Hill, J. G. Taylor, C. P. Falshaw, T. J. King, B. Beagley, D. M. Tonge, R. G. Pritchard, C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.* **1986**, 2289.[21b] W. Hill, D. M. A. Minahan, J. G. Taylor, C. A. McAufliffe, *J. Am. Chem. Soc.* **1982**, *104*, 6011. – [21c] S. O. Grim, R. L. Keiter, W. McFarlane, *Inorg. Chem.* **1967**, *6*, 1133. – [21d] W. McFarlane, *J. Chem. Soc. A* **1967**, 1922.

[22] [22a] E. Diez-Barra, J. C. Garcia-Martinez, J. Rodriguez-Lopez, *Tetrahedron Lett.* **1999**, *40*, 8181. – [22b] M. Lehmann, B. Schartel, M. Hennecke, H. Meier, *Tetrahedron* **1999**, *55*, 13377.

[23] K. M. Petrusevich, V. E. Kataev, I. I. Patsanovskii, L. V. Ermolaeva, E. A. Ishmaeva, A. V. Kataev, W. Wieczorek, K. Zygo, *Russ. J. Gen. Chem.* **1998**, *68*, 1510.

[24] R. F. Beeston, W. S. Aldridge, J. A. Treadyway, M. C. Fitzgerald, B. A. DeGraff, S. E. Stitzel, *Inorg. Chem.* **1998**, *37*, 4368.

[25] W. P. Cochrane, P. L. Pauson, T. S. Stevens, *J. Chem. Soc. C* **1968**, 630.

[26] J. Klein, A. Medlik, A. Y. Meyer, *Tetrahedron* **1976**, *32*, 51.

[27] R. Rabinowitz, J. Pellon, *J. Org. Chem.* **1961**, *26*, 4623.

[28] T. Uchiyama, Y. Toshiyasu, Y. Nakamura, T. Miwa, S. Kawaguchi, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 181.

[29] E. Lindner, M. Khanfar, *Phosphorus Sulfur Silicon Relat. Elem.*, in press.

[30] G. V. Bodrin, M. I. Kabachnick, N. E. Kochetkova, T. Ya. Medved, B. F. Myasoedov, Yu. M. Polikarpov, M. K. Chmutova, *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1979**, 2572; *Engl. Trans.* **1980**, 2388.

[31] G. M. Sheldrick, *SHELXTL V5.03, Program for crystal structure refinement*, University of Göttingen, Germany **1995.**

Received February 23, 2001
[I01066]