Preparation, Properties, and Reactions of Metal-Containing Heterocycles, 99[≠]

Cage-Structured Triplatinacyclophanes

Ekkehard Lindner,*[a] Christian Hermann,[a] Gerhard Baum,[b][≠≠] and Dieter Fenske[b][≠≠]

Dedicated to Professor Jochen Ellermann on the occasion of his 65th birthday

Keywords: Cage compounds / Metallacyclophanes / P ligands / Platinum / Supramolecular chemistry

The synthesis of the tris(triflate) **4** (Scheme 1) has been achieved by means of a straightforward three-step reaction sequence. After initial lithiation of mesitylene, treatment of the obtained trilithium compound $C_6H_3(CH_2Li)_3$ (**2**) with oxirane results in the formation of 1,3,5-tris(3-hydroxypropyl)benzene (**3**), which is then transformed to **4** by reaction with $(CF_3SO_2)_2O$ in the presence of pyridine. Whereas **4** reacts with $Na_2[Os(CO)_4]$ in a somewhat complicated manner, similar reactions with $Na[Re(CO)_5]$ and $LiPPh_2$ give the hydrocarbon-bridged tris(rhenium) complex $C_6H_3[(CH_2)_3Re(CO)_5]_3$ (**5**) and the tris(phosphane) $C_6H_3[(CH_2)_3PPh_2]_3$ (**6**), respectively. Employing the high-dilution method, from **6** and $Cl_2Pt(NCPh)_2$ the nanoscaled tri- and hexaplatinacyclophanes **7** and **9** are available. Owing to the optimal geometry and flexibility of the cage in **7**, 1,2-dichloroethane can be reversibly encapsulated. The molecular structure of **7** · **7** 1,2-$Cl_2C_2H_4$ was determined by an X-ray structure analysis. The utility of the reactive metal centers in **7** has been demonstrated by replacing the chloro ligands by acetonitrile to give the cationic platinacyclophane **8**, in which, according to NMR studies, the cage-like structure is preserved.

Introduction

Cage-like molecules containing a macrobicyclic skeleton play an important role in host/guest chemistry[1] and as nanoscaled building blocks for the construction of supramolecular assemblies.[2] Attempts to construct such molecules through threefold carbon−carbon couplings necessitate multi-step procedures and high-dilution conditions, and ultimately give only low yields.[3] An attractive alternative, however, is the dimerization of trifunctional molecular precursors. Based on this method, several syntheses of three-dimensional cyclophanes have be realized.[1c,3a,4] Although these cage molecules also incorporated either transition or main-group metal centers, which could serve as anion receptors, they did not possess the classical threefold bridged cyclophane structure with aromatic units at the bottom and the top of the molecule, and where the metal atoms are located in the center of the aliphatic bridges.[5] Since the first typical metallaphanes appeared in the literature in 1994,[6] investigations have been mainly focused on two-dimensional systems.[7] The introduction of tetracarbonyliron and -osmium fragments into the cyclophane framework has a marked effect on the structures of these macrocycles. Moreover, these new reactive centers also permit the insertion of small molecules, such as carbon monoxide, into the metal−carbon σ bonds.

Unlike two-dimensional systems, *bona fide* three-fold bridged metallacyclophanes conforming to the classical cyclophane structure remain rather rare. Of the limited number of examples, most are not suited for host/guest chemistry owing to their rigid structures and/or the absence of an intramolecular cavity.[8] Recently, Fujita et al. introduced a remarkable template synthesis of a palladium-containing cyclophane with the ability to incorporate anions of aromatic carboxylic and sulfonic acids.[9] The same group,[10] as well as Steel[11] and Stang,[12] have also reported on six-fold bridged metallacyclophanes with tetrahedral symmetry. The rigidity of the employed triply functionalized ligands and palladium or platinum complex fragments is an essential prerequisite for this self-assembly. Some of these palladium-containing "nanometer-scale molecular container compounds" are also capable of encapsulating guest molecules.[10,11]

The present investigation relates to a synthetic route recently exploited by Balch et al.[8a] for the synthesis of novel three-fold bridged platinacyclophanes. The objective was to create a flexible ligand system based on an aromatic nucleus with three methylene groups as spacers, functionalized with tertiary phosphane end groups. It is envisaged that two of these ligands should be capable of assembly via three platinum atoms to furnish an elastic, three-dimensional molecular cage, in which the kinetics are sufficiently fast for host/guest complexation and decomplexation.[4c] To meet this re-

---

[≠] Part 98: E. Lindner, I. Krebs, R. Fawzi, M. Steimann, *Organometallics*, in press.

[≠≠] X-ray structure analysis.

[a] Institut für Anorganische Chemie der Universität,
Auf der Morgenstelle 18, D-72076 Tübingen, Germany
Fax: (internat.) + 49(0)7071/29-5306
E-mail: ekkehard.lindner@uni-tuebingen.de

[b] Institut für Anorganische Chemie der Universität (TH),
Engesserstraße, Geb.-Nr. 30.45, D-76128 Karlsruhe, Germany

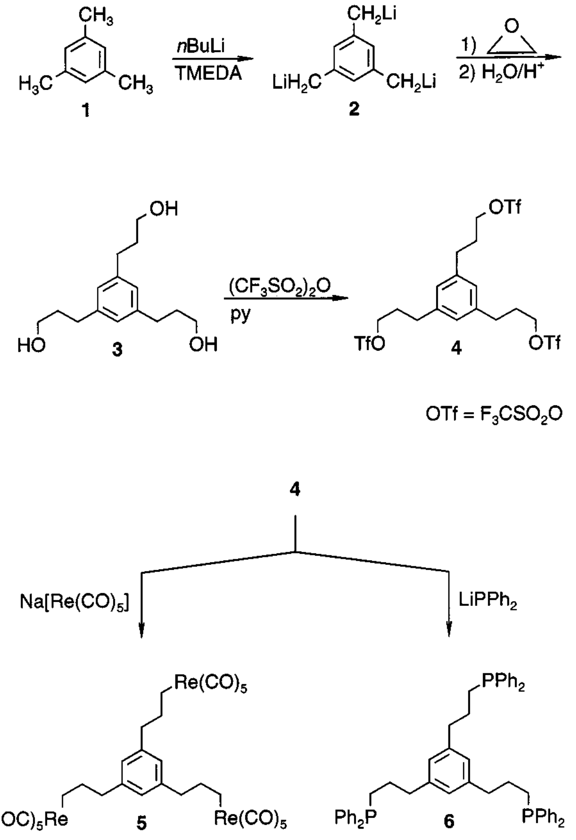
1434−1948/99/0404−0679 $ 17.50+.50/0

quirement, a symmetrically substituted tris(diphenylphosphanylpropyl)benzene has been synthesized from a suitable tris(triflate).

Results and Discussion

Synthesis of Ligands and Reactions with Metal Lewis Bases

In analogy to previous studies on the generation of osma- and ferracyclophanes,[6,7c,7d] our strategy was to treat the tris(triflate) **4** (Scheme 1) with a suspension of the organometallic Lewis base, $[Os(CO)_4]^{2-}$ or $[Fe(CO)_4]^{2-}$, in dimethyl ether at −25°C, so as to obtain the corresponding triosma- and triferracyclophane species. The tris(triflate) **4** could be obtained by treatment of the triol **3** with $(CF_3SO_2)_2O$[13] in the presence of pyridine at −30°C.[14] In turn, the triol **3**[15] was conveniently prepared by a two-step reaction starting from mesitylene (**1**). Lithiation of **1** with *n*BuLi/TMEDA afforded the trilithium derivative **2**,[16] and subsequent treatment of a suspension of **2** in diisopropyl ether with an equivalent amount of oxirane led directly to the triol **3** (Scheme 1). After purification by column chromatography, the tris(triflate) **4** was obtained as a colorless, viscous, moisture-sensitive, thermally labile oil, which could be stored without any decomposition below −35°C. It was found to be freely soluble in common organic solvents. The molecular composition of **4** was determined from its FD mass spectrum, which showed the molecular ion peak at $m/z = 647.6$.



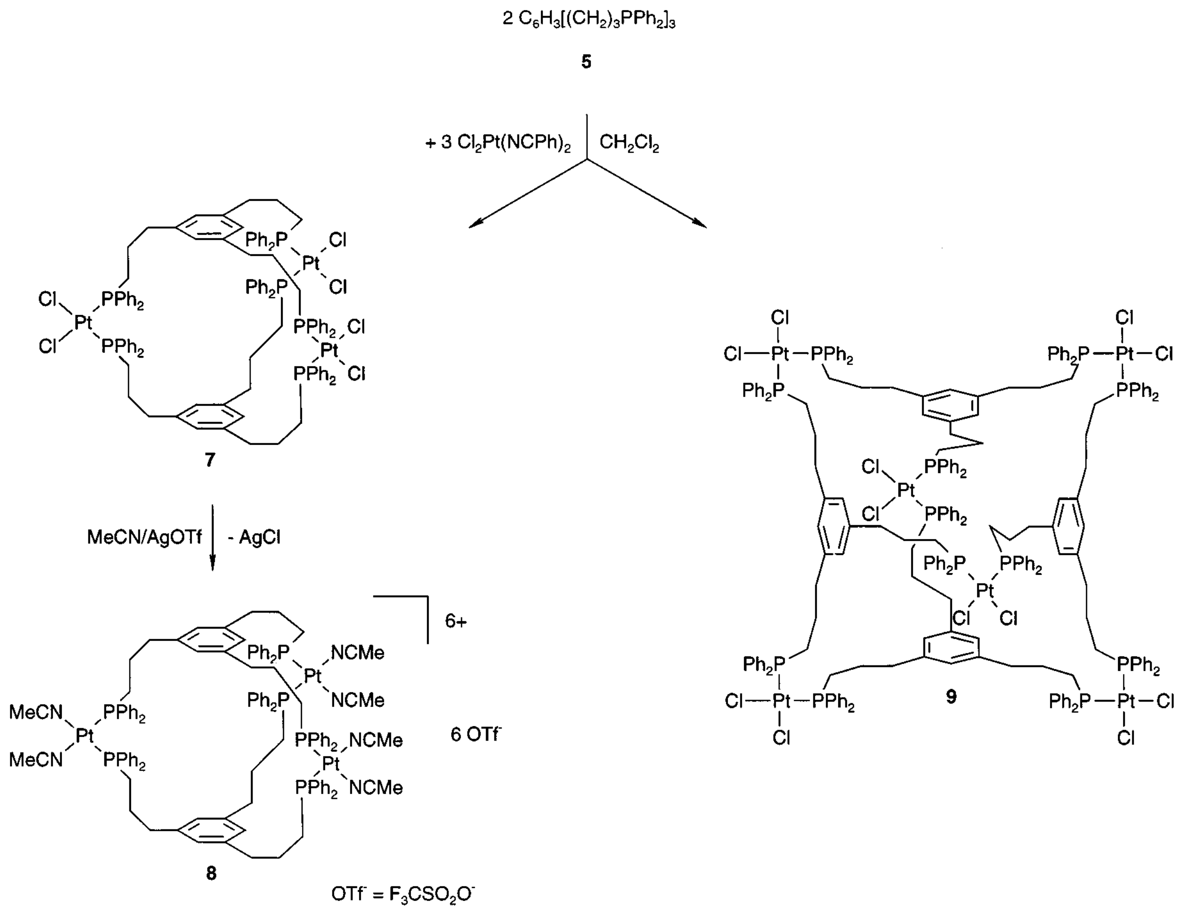
Scheme 1. Synthesis of the rhenium complex **5** and the tris(phosphane) **6**

Reaction of the tris(triflate) **4** with $Na_2[Os(CO)_4]$ in boiling dimethyl ether[6,7c,7d,14] did not lead to the expected triosmacyclophane with D_3 symmetry. Only oligo- or polymeric species precipitated from the reaction mixture. The yellow solid collected exhibited four terminal carbonyl absorptions in its IR spectrum (in KBr: $\tilde{\nu} = 2124$ cm^{-1}, 2040, 2038, 2009), which are characteristic of *cis*-$Os(CO)_4$ units. The failure of this attempt to gain access to a triosmacyclophane cannot be attributed to any lack of reactivity of the tris(triflate) **4**. When a THF solution of $Na[Re(CO)_5]$ was treated with **4** at −20°C, the colorless, rather stable tris(pentacarbonylrhenium) complex **5** was formed in satisfactory yields. A similar trinuclear rhenium complex with an aromatic unit in the center of the molecule was reported by Beck et al. several years ago.[17] The ^{1}H-NMR spectrum of complex **5** exhibits three complex multiplets at $\delta = 0.9$, 2.0, and 2.5, corresponding to AA′XX′, AA′MM′XX′, and AA′MM′ spin systems for the α-, β-, and γ-methylene protons. This suggests a hindered rotation about the $C_\alpha-C_\beta$ bonds due to the bulky $Re(CO)_5$ fragments at the α-methylene groups.[18]

In our quest to find an alternative approach for the construction of three-dimensional, triply bridged metallaphanes, we considered a cage structure incorporating metal−phosphorus bonds instead of metal−carbon σ linkages. In order to assess this possibility, a prerequisite was the synthesis of the tris(phosphane) **6**, which was achieved by reaction of **4** with $LiPPh_2$ in diethyl ether at −30°C (Scheme 1). After column-chromatographic work-up of the reaction mixture, the phosphane **6** was isolated as a rather air-sensitive, viscous oily liquid, which was found to be freely soluble in common organic solvents. In the FD mass spectrum, the molecular ion peak was observed at $m/z = 756.9$. Such phosphanes represent suitable starting materials for the reaction with substitution-labile platinum complexes to give access to cage-like molecules.[8a]

Platinacyclophanes

Since the discovery of crown ethers by Pedersen[19] in 1967, the chemistry of synthetic hosts for specific complexation of organic and inorganic guest molecules has developed rapidly. In particular, investigations on the use of cyclophanes as hosts have contributed to an understanding of the complexation of neutral organic guest molecules such as arenes or chlorinated hydrocarbons in aqueous and organic media.[20] The introduction of transition metal units into the framework of a cyclophane has an effect on the geometric properties of the cavity formed by the resulting metallacyclophane. In order to achieve the generation of a three-fold bridged metallaphane, the platinum complex $Cl_2Pt(NCPh)_2$ was treated with the tris(phosphane) **6** according to the high-dilution method.[21] Indeed, the hexachlorotriplatinacyclophane **7** was obtained in rather good yields (Scheme 2). Because of entropic factors, the formation of oligomeric and polymeric species was suppressed. The energy cost associated with the loss of several



Scheme 2. Synthesis of the platinacyclophanes **7**−**9**

degrees of freedom for the components of the assembly is not so large for a system with a smaller number of units.[12,22]

The $^{31}P\{^1H\}$-NMR spectrum of **7** reveals a singlet for the six chemical equivalent phosphorus atoms at $\delta = 8.8$ and a doublet for the ^{195}Pt satellites, which is typical for *cis*-$PtCl_2$ fragments. This assignment is confirmed by the ^{195}Pt-NMR spectrum, which displays a triplet at $\delta = -4414$ with a coupling constant of $^1J_{PtP} = 3660$ Hz. Most characteristic for the $^{13}C\{^1H\}$-NMR spectrum of **7** are three complex multiplets with AXX′ spin systems at $\delta = 127.9$, 38.0, and 30.6 which are assigned to the *o*-carbon atoms of the $(C_6H_5)_2P$ units and to the carbon atoms of the α- and β-methylene groups of the hydrocarbon chains, respectively.[5a] To the best of our knowledge, **7** is the first metallacyclophane which is able to encapsulate a lipophilic guest molecule like dichloroethane. In contrast to the cage-like palladium-containing system of Fujita,[9] **7** is also obtainable without a guest (template). The complexation/decomplexation process is reversible, which was proved by microelemental analyses and ^1H- as well as $^{13}C\{^1H\}$-NMR spectra of the complex **7** · 7 $C_2H_4Cl_2$, which in addition to the signals of **7** exhibit the ^{13}C peaks for $C_2H_4Cl_2$. The integration of the ^1H signals in the ^1H-NMR spectrum and the crystal structure analysis corroborate the stoichiometry of **7** · 7 $C_2H_4Cl_2$.[23] One of the dichloroethane molecules is located in the cavity, the others are positioned at the exterior of the cage in interstices of the crystal. In the case of the complexation of exolipophilic guests no specific linkages between guests and hosts are present, but the guests have to fit geometrically into the cavity.[4c] Owing to its alkylene units, the cage **7** is sufficiently flexible to exhibit satisfactorily fast kinetics for complexation and decomplexation reactions. The hexachlorotriplatinacyclophane **7** exhibits an L_2M_3 composition (L = ligand, M = transition metal fragment) with C_3 symmetry of the ring skeleton. In view of the bulky phenyl substituents at the *cis*-platinum-coordinated phosphorus atoms, the trigonal-prismatic cavity of the cage containing the encapsulated 1,2-dichloroethane molecule is well-shielded from the exterior (Figure 1). The length of the edges of this cavity is approximately 8 Å and its height is about 4.8 Å.

Owing to the C_3 axis passing through the phenylene rings of the cyclophane, the embedded dichloroethane had to be refined at three split positions. The centers of both phenylene groups, which are arranged almost parallel, are located approximately one upon the other. All three distorted square-planar coordinated platinum atoms of **7** lie within a circular area, midway between the aromatic rings of the two ligands. The Pt−Cl and Pt−P connections are arranged

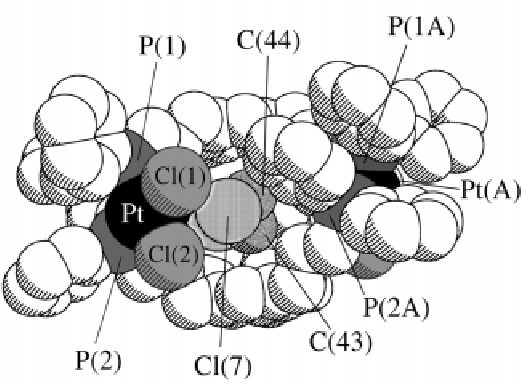


Figure 1. Molecular structure of **7**·7 1,2-$Cl_2C_2H_4$ (space-filling representation); the complete envelopment of 1,2-dichloroethane [gray spheres in center: C(43), C(44), Cl(7)], which is located in one of three possible split positions, is evident

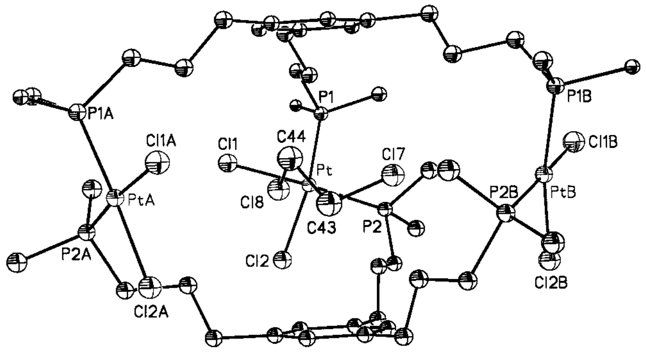


Figure 2. Molecular structure of **7**·7 1,2-$Cl_2C_2H_4$ in the crystal; ORTEP plot with thermal ellipsoids at 20% probability; hydrogen atoms and phenyl groups at the phosphorus atoms are omitted for clarity; selected distances [Å]: Pt−PtA = Pt−PtB = PtA−PtB 9.91(3), P1−P1A = P1−P1B = P1A−P1B 10.94(3), P2−P2A = P2−P2B = P2A−P2B 10.15(2), P1−P2 = P1A−P2A = P1B−P2B 3.44(3), Cl7−Pt 5.98(5), Cl7−PtB 4.30(4), Cl8−Pt 4.03(6), Cl8−PtA 6.12(4), distance between the centers of the phenylene groups of the ligands 8.01(2); torsion angle between the phenylene groups of the ligands 20.0(2)°

above and below this area. The distance between each platinum atom and the center of the circular area is 5.721(3) Å (Figure 2).

According to the considerations of Stang et al.,[12] supramolecular systems containing palladium or platinum complex fragments as that described above are able to form even higher units with the compositions L_4M_6, L_8M_{12}, and $L_{20}M_{30}$ with *T*, *O*, and *I* symmetry, respectively. In fact, in addition to the expected triplatinacyclophane (L_2M_3) **7**, traces of the hexaplatinacyclophane **9** (Scheme 2) with the composition L_4M_6 were also formed in the reaction of **6** with $Cl_2Pt(NCPh)_2$. This system, with a cavity formed by six platinum atoms, was detected in the FAB mass spectrum, which featured the $[M^+ - Cl]$ peak at *m*/*z* = 4589. Ideally, such molecules adopt an adamantanoid structure with *T* symmetry.[11,12] Whereas the aromatic rings are placed at the vertices of a tetrahedron, the metal atoms are located at the vertices of an octahedron.

In a subsequent experiment, the triplatinacyclophane **7** was employed as a starting compound in order to obtain a modified cyclophane in which the cage-like structure was preserved, but which exhibited different properties. Thus, by treatment of **7** with silver trifluoromethanesulfonate in a mixture of acetonitrile/dichloromethane (1:1), all the chloro ligands were replaced by acetonitrile and the six-fold positively charged triplatinacyclophane **8** was isolated as a thermally stable white solid (Scheme 2). The composition of this three-fold bridged, cationic macrocycle was confirmed by elemental analysis and by its FAB mass spectrum. In agreement with symmetry requirements, the $^{31}P\{^1H\}$-NMR spectrum of **8** displays a singlet, with appropriate ^{195}Pt satellites, for the six equivalent phosphorus atoms. From the size of the $^1J(Pt,P)$ couplings, it can be concluded that the phosphorus donors still occupy *cis* positions. The presence of the triflate anions is confirmed by a singlet at $\delta = -78.8$ in the ^{19}F-NMR spectrum of **8**. Although complex, the ^1H- and $^{13}C\{^1H\}$-NMR spectra are not only diagnostic of the proposed structure of **8**, but they are also consistent with the corresponding NMR data of the chloro derivative **7**, the structure of which was elucidated by an X-ray structural determination.[23]

A brief discussion of the $^{13}C\{^1H\}$-NMR spectrum is restricted to the ring skeleton. Two singlets at $\delta = 141.1$ and 126.8 can be assigned to the quaternary (DEPT-135 experiment) and tertiary carbon atoms bonded to the phosphorus atoms of the cage. At higher field ($\delta = 36.4$), an AXX′ pattern can be ascribed to the carbon atoms of the methylene groups adjacent to the phenyl rings. Complex multiplets at $\delta = 26$ are attributable to the remaining methylene functions. Two further singlets at $\delta = 117.9$ and 2.0 are attributable to the nitrile and methyl carbon atoms of the acetonitrile ligands attached to the platinum centers.

Conclusion

Cyclophane chemistry has made a valuable contribution in the field of molecular recognition, since it has led to the development of a multitude of architecturally impressive molecules, with various structural features and functionalities, in which guest molecules can be embedded.[1e,20] The incorporation of transition metals into the aliphatic framework of cyclophanes offers an ingenious means of controlling the inclusion of potential host systems[9−11] and of creating new reactive centers.[7c,7d] Trimetalla- (L_2M_3, L = tripodal ligand, M = transition metal fragment) and even hexametallacyclophanes (L_4M_6), with cavities suitable for the encapsulation of neutral molecules or anions of aromatic carboxylic and sulfonic acids, have hitherto only been prepared by self-assembly, employing nitrogen-containing ligands.[9−12] However, Balch recently succeeded in synthesizing a cage-like molecule composed of aromatic tris(phosphane) ligands,[8a] although due to its rigid structure and limited solubility in nearly all common solvents, this system was not suited for host-guest chemistry. By constructing such a tridentate phosphane around an additional flexible alkane backbone, we have prepared the three-dimensional platinacyclophane **7**, which, by virtue of its size, is able to reversibly encapsulate 1,2-dichloroethane.[23] Remarkably, in the same reaction, the dodecachlorohexaplatinacyclophane (L_4M_6) **9** was also formed in trace amounts. The ligands attached to the platinum atoms in **7** can easily be exchanged with preservation of the cage-like structure, enabling adaptation of the cyclophane molecules to specific conditions. In this context, the new cationic hexakis(acetonitrile)triplatinacyclophane **8** was prepared, which exhibited quite different properties.

Experimental Section

General: All reactions and manipulations were carried out under dry argon using standard Schlenk techniques. Solvents were dried with appropriate reagents and stored under argon. − Column chromatography: Activated silica gel, 0.063−0.200 mm (Merck); column dimensions are reported in the specific sections describing the synthesis of the compounds. − Elemental analyses: Carlo Erba 1106. − F and S analyses were carried out according to Schöniger[24] and determined as described by Brunisholz and Michod[25], and by Wagner[26], respectively. − Rhenium and platinum were determined with a Varian AA20 spectrometer. − FD and FAB MS: Finnigan 711A (8 kV), modified by AMD. − IR: Bruker IFS 48 FT-IR. − ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, ^{19}F, and ^{195}Pt NMR: Bruker DRX 250 spectrometer operating at 250.13, 62.90, 101.26, 235.33, and 53.55 MHz, respectively. ^1H chemical shifts were referenced to the residual proton peaks of the solvents and are quoted in ppm downfield from TMS. ^{13}C chemical shifts were calibrated against the deuterated solvent multiplet and referenced to TMS. ^{31}P chemical shifts were measured relative to external 85% H_3PO_4 with downfield values being taken as positive. ^{19}F chemical shifts were measured relative to external 0.05% 1,3,5-trifluorotoluene. ^{195}Pt chemical shifts were measured relative to external 37.5% $Na_2[PtCl_6] \cdot 6\,H_2O$. Oxirane was of commercial grade and was used without further purification; 1,3,5-tris(lithiomethyl)benzene,[16] $(CF_3SO_2)_2O$,[13] $LiPPh_2$,[27] and $Cl_2Pt(NCPh)_2$[28] were synthesized according to literature methods.

1,3,5-Tris(3-hydroxypropyl)benzene (3): Pyrophoric 1,3,5-tris(lithiomethyl)benzene (**2**), prepared from 500 mL of a solution of *n*-butyllithium (1.6 M in *n*-hexane), 92.97 g (800.0 mmol) of TMEDA, and 16.03 g (133.4 mmol) of mesitylene, was filtered off from the reaction mixture (P3) and washed with *n*-pentane until the washings were almost colorless. After drying in vacuo, **2** was suspended in 500 mL of diisopropyl ether and the suspension was cooled to −30°C. Then, 17.62 g (400.0 mmol) of oxirane was condensed into the reaction vessel over a period of 2 h. The resulting mixture was stirred at −30°C for 1 h and then allowed to warm to room temperature. The orange suspension obtained was then rapidly poured into 150 mL of iced water, and 2 N H_2SO_4 was added until pH = 2 was attained. The organic layer was separated and the aqueous phase was washed with diethyl ether (3 × 150 mL). The combined organic phases were dried with Na_2SO_4 and the solvent was evaporated. The product was purified by column chromatography (CH_2Cl_2/MeOH/*n*-hexane, 15:2:1, diameter/length of column 7/50 cm). Yield 7.82 g (24.6%), colorless oil. − ^1H NMR ([D$_6$]acetone): $\delta = 6.87$ (s, 3 H, aromatic H), 3.56 (t, $^3J_{HH} = 6.4$ Hz, 6 H, CH_2OH), 2.61 (t, $^3J_{HH} = 7.7$ Hz, 6 H, $CH_2CH_2CH_2OH$), 1.79 (m, 6 H, CH_2CH_2OH). − $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): $\delta = 142.7$ (s, aromatic C), 126.4 (s, aromatic CH), 61.5 (s, CH_2OH), 35.2 (s, $CH_2CH_2CH_2OH$), 32.4 (s, CH_2CH_2OH). − MS (FD, 35°C); *m*/*z*: 252.5 [M$^+$]. − $C_{15}H_{24}O_3$ (252.4): calcd. C 71.39, H 9.59; found C 70.95, H 9.56.

1,3,5-Tris[3-(trifluoromethylsulfonyloxy)propyl]benzene (4): To a suspension of 3.43 g (13.58 mmol) of **3** in 100 mL of dichloromethane, 3.38 g (42.78 mmol) of pyridine was added dropwise. The resulting clear solution was cooled to −30°C and $(CF_3SO_2)_2O$ (12.64 g, 44.81 mmol) was added over a period of 1 h. The reaction mixture was stirred for a further 1 h at −30°C, then filtered (P 3), and washed with water (3 × 50 mL). The organic layer was dried with Na_2SO_4 and then concentrated to a volume of 20 mL under reduced pressure. The product was purified by column chromatography (CH_2Cl_2, diameter/length of column 2/10 cm). Yield 5.92 g (67.2%), colorless oil. − IR (film): $\tilde{\nu} = 1412$ cm^{-1}, 1246, 1211, 1146, 931 (CH_2, CF_3, SO_2, SOC). − ^1H NMR ($CDCl_3$): $\delta = 6.86$ (s, 3 H, aromatic H), 4.49 (t, $^3J_{HH} = 6.1$ Hz, 6 H, CH_2O), 2.70 (t, $^3J_{HH} = 7.5$ Hz, 6 H, $CH_2CH_2CH_2O$), 2.10 (m, 6 H, CH_2CH_2O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 141.0$ (s, aromatic C), 127.3 (s, aromatic CH), 119.2 (q, $^1J_{FC} = 317.7$ Hz, CF_3), 77.2 (s, CH_2O), 31.4 (s, $CH_2CH_2CH_2O$), 31.0 (s, CH_2CH_2O). − MS (FD, 35°C); *m*/*z*: 647.6 [M$^+$]. − $C_{18}H_{21}F_9O_9S_3$ (647.5): calcd. C 33.34, H 3.26, F 26.36, S 14.83; found C 33.49, H 3.62, F 25.94, S 14.59.

1,3,5-Tris[3-(pentacarbonylrhenio)propyl]benzene (5): A solution of $Na[Re(CO)_5]$ in 20 mL of THF, prepared from 502.3 mg (0.77 mmol) of Re_2CO_{10} and sodium amalgam, was added to a solution of 316.8 mg (0.49 mmol) of the tris(triflate) **4** in 50 mL of THF at −20°C. After stirring for 4 h at −20°C, the reaction mixture was allowed to warm to room temperature and the solvent was removed in vacuo. The residue was suspended in 10 mL of a mixture of CH_2Cl_2/*n*-pentane (2:1) and the solid material was filtered off (P4). The filtrate was then purified by column chromatography (CH_2Cl_2/*n*-pentane, diameter/length of column 2/10 cm). The collected product was finally washed with *n*-pentane (5 × 3 mL). Yield 272 mg (47.3%), white solid, m.p. 97°C. − IR (CH_2Cl_2): $\tilde{\nu} = 2125$ cm^{-1}, 2008, 1981 (CO). − ^1H NMR ($CDCl_3$): $\delta = 6.77$ (s, 3 H, aromatic H), 2.49 (m,[29] $N = 7.7$ Hz, 6 H, $CH_2CH_2CH_2Re$), 2.00 (m,[30] 6 H, CH_2CH_2Re), 0.95 (m,[31] $N = 17$ Hz, 6 H, CH_2Re). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 186.2$ (s, equatorial CO), 181.7 (s, axial CO), 142.7 (s, aromatic C), 126.3 (s, aromatic CH), 44.4 (s, $CH_2CH_2CH_2Re$), 41.7 (s, CH_2CH_2Re), −9.0 (s, CH_2Re). − MS (FD, 30°C); *m*/*z*: 1180.0 [M$^+$]. − $C_{30}H_{21}O_{15}Re_3$ (1180.1): calcd. C 30.53, H 1.79, Re 47.34; found C 30.70, H 1.98, Re 47.46.

1,3,5-Tris[3-(diphenylphosphanyl)propyl]benzene (6): To a suspension of $LiPPh_2$ in 50 mL of *n*-pentane, prepared from 2.071 g (11.12 mmol) of $HPPh_2$ and 6.95 mL of a solution of *n*-butyllithium (1.6 M in *n*-hexane), a solution of 2.004 g (3.09 mmol) of **4** in 30 mL of diethyl ether was added at −35°C. The reaction mixture was stirred for 12 h at −35°C and then the LiOTf formed was filtered off by passage through a short silica-gel column (1 cm). After evaporation of the solvent, the product **6** was redissolved in 15 mL of a mixture of *n*-pentane/diisopropyl ether (2:1) and purified by column chromatography (*n*-pentane/diisopropyl ether, 2:1, diameter/length of column 2/20 cm). Yield 1.028 g (44.0%), colorless oil. − ^1H NMR ($CDCl_3$): $\delta = 7.6-7.4$ (m, 30 H, C_6H_5), 6.95 (s, 3 H, C_6H_3), 2.85 (t, $^3J_{HH} = 7.2$ Hz, 6 H, $CH_2CH_2CH_2P$), 2.26, 1.97 (m, 12 H, CH_2CH_2P). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 142.5$ (s, *quat*-C_6H_3), 139.6 (d, $^1J_{PC} = 12.6$ Hz, *ipso*-C_6H_5), 133.5 (d, $^2J_{PC} = 18.9$ Hz, *o*-C_6H_5), 129.3 (s, *m*-C_6H_5), 129.1 (s, *p*-C_6H_5), 127.0 (s, *tert*-C_6H_3), 37.8 (d, $^3J_{PC} = 12.6$ Hz, $CH_2CH_2CH_2P$), 28.6−28.3 (m, CH_2CH_2P). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -15.0$ (s). − MS (FD, 30°C); *m*/*z*: 756.9 [M$^+$]. − $C_{51}H_{51}P_3$ (756.9): calcd. C 80.93, H 6.79; found C 80.77, H 7.11.

5,5,20,20,35,35-Hexachloro-4,4,6,6,19,19,21,21,34,34,36,36-dodecaphenyl-4,6,19,21,34,36-hexaphospha-5,20,35-triplatina[9$_3$](1,3,5)-cyclophane (7): Solutions of $Cl_2Pt(NCPh)_2$ (1.040 g, 2.202 mmol;

−30°C) and of **6** (1.111 g, 1.468 mmol) in 200 mL each of dichloromethane were *simultaneously* added dropwise during 12 h into 500 mL of stirred dichloromethane. Then the solvent was evaporated in vacuo and the residue was extracted with 150 mL of dichloromethane. After concentration of the solvent under reduced pressure to a volume of 20 mL and addition of 100 mL of CCl_4, oligomeric and polymeric fractions were precipitated. The product **7** was precipitated from the remaining solution by addition of diethyl ether. After filtration (P3) the residue was washed three times with 10 mL of diethyl ether to give the pure product. Yield 645.3 mg (38%), white solid, m.p. > 230°C (dec.). − IR (CsCl): $\tilde{\nu}$ = 316 cm^{-1}, 291 (*cis*-$PtCl_2$). − ^1H NMR (CD_2Cl_2): δ = 7.4−7.1 (m, 60 H, C_6H_5), 6.77 (s, 6 H, C_6H_3), 2.49 (t, $^3J_{HH}$ = 7.7 Hz 12 H, $CH_2CH_2CH_2P$), overlapping with 2.38 (br. s, 12 H, CH_2P), 2.11 (br. s, 12 H, CH_2CH_2P). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 141.4 (s, *ipso*-C_6H_5), 132.7 (s, *m*-C_6H_5), 130.7 (s, *p*-C_6H_5), 129.8 (s, *quat*-C_6H_3), 127.9 (m[32], *N* = 13 Hz, *o*-C_6H_5), 126.1 (s, *tert*-C_6H_3), 38.0 (m[32], *N* = 17 Hz, CH_2P), 30.6 (m[32], *N* = 44 Hz, CH_2CH_2P), 28.8 (s, $CH_2CH_2CH_2P$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 8.8 (s, d, $^1J_{PtP}$ = 3660 Hz). − ^{195}Pt NMR (CD_2Cl_2): δ = −4414 (t, $^1J_{PtP}$ = 3660 Hz). − MS (FAB, 30°C, positive ions); *m*/*z*: 2331.4 [M^+ + Na], 2274.5 [M^+ − Cl], 2238.6 [M^+ − 2 Cl], 2203.2 [M^+ − 3 Cl]. − MS (FAB, 30°C, negative ions); *m*/*z*: 2344.1 [M^- + Cl], 2311.0 [M^-], 2272.9 [M^- − Cl]. − $C_{102}H_{102}Cl_6P_6Pt_3$ (2311.8): calcd. C 52.99, H 4.45, Cl 9.20, Pt 25.32; found C 52.80, H 4.39, Cl 9.43, Pt 25.06.

5,5,20,20,35,35-Hexachloro-4,4,6,6,19,19,21,21,34,34,36,36-dodecaphenyl-4,6,19,21,34,36-hexaphospha-5,20,35-triplatina[9_3](1,3,5)-cyclophane (7) · 7 1,2-$Cl_2C_2H_4$: Complex **7** (60.1 mg, 26.0 mmol) was dissolved in 20 mL of 1,2-dichloroethane. By removal of the excess solvent in vacuo, **7** · 7 1,2-$Cl_2C_2H_4$ was obtained. Yield quantitative, white solid. − ^1H NMR (CD_2Cl_2), additional to the signals of **7**: δ = 3.60 (s, 28 H, 1,2-$Cl_2C_2H_4$). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2), additional to the signals of **7**: δ = 43.7 (s, 1,2-$Cl_2C_2H_4$). − $C_{116}H_{130}Cl_{20}P_6Pt_3$ (3004.5): calcd. C 46.37, H 4.36, Cl 23.60, Pt 19.48; found C 46.11, H 4.08, Cl 23.34, Pt 19.71. − Upon warming **7** · 7 1,2-$Cl_2C_2H_4$ for 12 h to 70°C in vacuo 1,2-$Cl_2C_2H_4$ was removed quantitatively and **7** was obtained without any solvent.

Hexaplatinacyclophane 9: In the course of the reaction of the tris(phosphane) **6** with $Cl_2Pt(NCPh)_2$ in CH_2Cl_2 according to high-dilution techniques, not only the hexachlorotriplatinacyclophane **7** was formed, but also the hexaplatinacyclophane **9**. After evaporation of the solvent and extraction of the product **7** with CCl_4, the remaining residue was subjected to mass-spectrometric analysis, which revealed the presence of the hexaplatinacyclophane **9**. − MS (FAB, 30°C); *m*/*z*: 4653.4 [M^+ + Cl], 4588.5 [M^+ − Cl], 4554.5 [M^+ − 2 Cl].

5,5,20,20,35,35-Hexakis(acetonitrile)-4,4,6,6,19,19,21,21,34,34,36,36-dodecaphenyl-4,6,19,21,34,36-hexaphospha-5,20,35-triplatina-[9_3](1,3,5)cyclophane Hexakis(trifluoromethanesulfonate) (8): To a solution of 115.6 mg (0.05 mmol) of the hexachlorotriplatinacyclophane **7** in 60 mL of a mixture of CH_2Cl_2/acetonitrile (1:1), 115.6 mg (0.45 mmol) of silver trifluoromethanesulfonate was added and the reaction mixture was stirred at room temperature for 72 h under exclusion of light. After the addition of 60 mL of CH_2Cl_2, the suspended solid components were centrifuged off, and the supernatant solution was decanted and concentrated under reduced pressure to a volume of 10 mL. Upon addition of *n*-pentane, cage compound **8** was precipitated, which was filtered off and dried in vacuo. Yield: 118.3 mg (73%), white solid, m.p. > 125°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1251 cm^{-1}, 1230, 1178, 1032 (SO_3, CF_3). − ^1H NMR (CD_2Cl_2): δ = 7.5−7.2 (m, 60 H, C_6H_5), 6.99 (s, 6 H, C_6H_3), 2.8−2.3 (br. m, 36 H, $CH_2CH_2CH_2P$), 2.03 (s, CH_3). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 141.1 (s, *quat*-C_6H_3), 139.1−129.6 (m, *o*-, *m*-, and *p*-C_6H_5), 126.8 (s, *tert*-C_6H_3), 125.5 (m, *ipso*-C_6H_5), 121.2 (q, $^1J_{FC}$ = 320.8 Hz, CF_3), 117.9 (s, CN), 36.4, 26.4, 24.9 (br. s, $CH_2CH_2CH_2P$), 2.0 (s, CH_3). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −2.7 (s, d, $^1J_{PtP}$ = 3617 Hz). − ^{19}F NMR (CD_2Cl_2): δ = −78.8 (s). − MS (FAB, 30°C); *m*/*z*: 3099.7 [M^+ − OTf], 2844.4 [M^+ − OTf − 6 CH_3CN], 2695.2 [M^+ − 2 OTf − 6 CH_3CN], 2542.7 [M^+ − 3 OTf − 6 CH_3CN], 2393.6 [M^+ − 4 OTf − 6 CH_3CN], 2246.4 [M^+ − 5 OTf − 6 CH_3CN]. − $C_{120}H_{120}F_{18}N_6P_6Pt_3O_{18}S_6$ (3239.7): calcd. C 44.49, H 3.73, F 10.56, N 2.59, Pt 18.06, S 5.94; found C 44.06, H 3.52, F 10.97, N 2.41, Pt 17.82, S 6.28.

X-ray Structure Determination of 5,5,20,20,35,35-Hexachloro-4,4,6,6,19,19,21,21,34,34,36,36-dodecaphenyl-4,6,19,21,34,36-hexaphospha-5,20,35-triplatina[9_3](1,3,5)cyclophane (7) · 7 1,2-$Cl_2C_2H_4$:[23] Single crystals of **7** · 7 $C_2H_4Cl_2$ were obtained from a 1,2-dichloroethane/*n*-octane solution. Diffractometer STOE IPDS, Mo-K_α radiation, λ = 0.71069 Å. No absorption correction was applied. The structure was solved by direct methods (SHELXS) and refined by last-square methods with the full matrix, based on F_o^2 (SHELXL). Hydrogen atoms bound to carbon atoms are located at calculated positions. − Crystallographic data: $C_{102}H_{102}Cl_6P_6Pt_3 \cdot 7\ C_2H_4Cl_2 \cdot 1.5\ Et_2O$, M_r = 3115.5, $d_{calcd.}$ = 1.242 gcm^{-3}, crystal dimension 0.2 × 0.2 × 0.1 mm^3, trigonal, space group $P31c$, $a = b$ = 22.596(3), c = 18.842(4) Å, V = 8331(2) $Å^3$, Z = 2, T = 200 K, μ(Mo-K_α) = 2.928 mm^{-1}, $F(000)$ = 3106. − Data collection: 2Θ = 4.68−51.88° in $-26 \le h \le 27$, $-20 \le k \le 27$, $-20 \le l \le 22$. 16498 measured reflections, of which 7922 were symmetry-independent and 7441 were observed with $I > 2\ \sigma(I)$. − Solution of the structure: An LP correction was applied with $R_{int.}$ = 0.0470. The applied absolute structural parameter was −0.012(9).[33] Parts of the host lattice are refined isotropically with a disorder (first order). The diethyl ether molecules are refined without hydrogen atoms at half-occupied positions. Maximum and minimum peaks in the final synthesis were 1.435 and −0.704 $eÅ^{-3}$. 13 geometrical restraints, 335 parameters, $R1$ = 0.0487, $wR2$ = 0.1437 (all data, $w = 1/[s^2(F_o^2) + [0.1019[(F_o^2 + 2\ F_c^2)/3]^2 + 8.6742[(F_o^2 + 2\ F_c^2)/3]])$, GOF = S = 1.093; residual electron density min./max. = −0.704/1.435 e $Å^{-3}$.[23]

Acknowledgments

Support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. Degussa AG are thanked for supplying starting materials. We are also indebted to Priv.-Doz. Dr. H. A. Mayer and M. Steimann, Institut für Anorganische Chemie II, University of Tübingen, for helpful discussions regarding the interpretation of the NMR spectra and X-ray structural analyses, respectively. Dipl.-Chem A. Hagenbach, Institut für Anorganische Chemie I, University of Tübingen, is gratefully thanked for the determination of the cell constants.

---

[1] [1a] D. J. Cram, J. M. Cram, in *Container Molecules and Their Guests: Monographs in Supramolecular Chemistry* (Ed.: J. F. Stoddart), The Royal Society of Chemistry, Cambridge, **1994**. − [1b] B. J. Whitlock, H. W. Whitlock, *J. Am. Chem. Soc.* **1994**, *116*, 2301−2311. − [1c] B. Dietrich, P. Viout, J.-M. Lehn, *Macrocyclic Chemistry: Aspects of Organic and Inorganic Supramolecular Chemistry*, VCH, Weinheim, **1993**. − [1d] R. J. Pieters, F. Diederich, *J. Chem. Soc., Chem. Commun.* **1996**, 2255−2256. − [1e] C. Seel, F. Vögtle, *Angew. Chem.* **1992**, *104*, 542−563; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 528−549.

[2] [2a] J. S. Moore, J. Zhang, *Angew. Chem.* **1992**, *104*, 873−874;

Angew. Chem. Int. Ed. Engl. **1992**, *31*, 922−923. − [2b] Z. Wu, S. Lee, J. S. Moore, *J. Am. Chem. Soc.* **1992**, *114*, 8730−8732. − [2c] F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123−1146; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101−1124. − [2d] F. Diederich, *Nature* **1994**, *369*, 199−207. − [2e] R. W. Saalfrank, *Nature* **1996**, *383*, 124−125.

[3] [3a] F. Vögtle, *Cyclophane Chemistry*, Wiley, Chichester, **1993**. − [3b] J. Breitenbach, F. Ott, F. Vögtle, *Angew. Chem.* **1992**, *104*, 360−362; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 307−309. − [3c] M. Nakazaki, K. Yamamoto, T. Toya, *J. Org. Chem.* **1980**, *45*, 2553−2554. − [3d] D. O'Krongly, S. R. Denmeade, M. Y. Chiang, R. Breslow, *J. Am. Chem. Soc.* **1985**, *107*, 5544−5545. − [3e] A. J. Hubert, M. Hubert, *Tetrahedron Lett.* **1966**, 5779−5782. − [3f] T. J. Seiders, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1996**, *118*, 2754−2755. − [3g] Y. Rubin, T. C. Parker, S. I. Khan, C. L. Holliman, S. W. KcElvany, *J. Am. Chem. Soc.* **1996**, *118*, 5308−5309.

[4] [4a] F. Diederich in *Cyclophanes: Monographs in Supramolecular Chemistry* (Ed.: J. F. Stoddart), The Royal Society of Chemistry, Cambridge, **1994**. − [4b] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**. − [4c] F. Vögtle in *Cyclophan-Chemie* (Eds.: C. Elschenbroich, F. Hensel, H. Hopf), Teubner, Stuttgart, **1990**. − [4d] F. Vögtle in *Supramolekulare Chemie* (Eds.: C. Elschenbroich, F. Hensel, H. Hopf), Teubner, Stuttgart, **1992**.

[5] [5a] H. A. Mayer, W. C. Kaska, *Chem. Ber.* **1995**, *128*, 95−98. − [5b] E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1998**, *110*, 977−981; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 932−935. − [5c] K. Worm, F. P. Schmidtchen, *Angew. Chem.* **1995**, *107*, 71−73; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 65−66. − [5d] P. Jacopozzi, E. Dalcanale, *Angew. Chem.* **1997**, *109*, 665−667; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 613−615. − [5e] J. S. Fleming, K. L. V. Mann, C.-A. Carraz, J. C. Jeffery, E. Psillakis, J. A. McCleverty, M. D. Ward, *Angew. Chem.* **1998**, *110*, 1315−1318; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1279−1281. − [5f] R. Vilar, D. M. P. Mingos, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1323−1326; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1258−1261. − [5g] S. Roche, C. Haslam, H. Adams, S. L. Heath, J. A. Thomas, *J. Chem. Soc., Chem. Commun.* **1998**, 1681−1682. − [5h] C. Brückner, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1937−1940; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1837−1839. − [5i] D. L. Caulder, R. E. Powers, T. N. Parac, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1940−1943; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1840−1843.

[6] E. Lindner, W. Wassing, R. Fawzi, M. Steimann, *Angew. Chem.* **1994**, *106*, 363−365; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 321−323.

[7] [7a] P. J. Stang, *Chem. Eur. J.* **1998**, *4*, 19−27. − [7b] M. Fujita, K. Ogura, *Coord. Chem. Rev.* **1996**, *148*, 249−264. − [7c] E. Lindner, M. W. Pitsch, R. Fawzi, M. Steimann, *Chem. Ber.* **1996**, *129*, 639−645. − [7d] E. Lindner, W. Wassing, M. W. Pitsch, R. Fawzi, M. Steimann, *Inorg. Chim. Acta* **1994**, *220*, 107−113. − [7e] E. E. Nifantyev, E. N. Rasadkina, L. K. Vasyanina, V. K. Belsky, A. I. Stash, *J. Organomet. Chem.* **1997**, *529*, 171−176. − [7f] J. R. Farrell, C. A. Mirkin, I. A. Guzei, L. M. Liable-Sands, A. L. Rheingold, *Angew. Chem.* **1998**, *110*, 484−487; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 465−467.

[8] [8a] P. M. Van Calcar, M. M. Olmstead, A. L. Balch, *J. Chem. Soc., Chem. Commun.* **1996**, 2597−2598. − [8b] F.-Q. Liu, G. Harder, T. D. Tilley, *J. Am. Chem. Soc.* **1998**, *120*, 3271−3272.

[9] M. Fujita, S. Nagao, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 1649−1650.

[10] [10a] M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469−471. − [10b] M. Fujita, S.-Y. Yu, T. Kusukawa, H. Funaki, K. Ogura, K. Yamaguchi, *Angew. Chem.* **1998**, *110*, 2192−2196; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2082−2085.

[11] C. M. Hartshorn, P. J. Steel, *J. Chem. Soc., Chem. Commun.* **1997**, 541−542.

[12] P. J. Stang, B. Olenyuk, D. C. Muddiman, R. D. Smith, *Organometallics* **1997**, *16*, 3094−3096.

[13] C. D. Beard, K. Baum, A. Grakauskas, *J. Org. Chem.* **1973**, *38*, 3673−3677.

[14] [14a] E. Lindner, E. Schauss, W. Hiller, R. Fawzi, *Angew. Chem.* **1984**, *96*, 727−728; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 711−712. − [14b] E. Lindner, R.-M. Jansen, H. A. Mayer, *Angew. Chem.* **1986**, *98*, 1000−1001; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1008−1009. − [14c] E. Lindner, R.-M. Jansen, W. Hiller, R. Fawzi, *Chem. Ber.* **1989**, *122*, 1403−1409.

[15] F. Effenberger, W. Kurtz, *Chem. Ber.* **1973**, *106*, 511−524.

[16] J. Klein, A. Medlik, A. Y. Meyer, *Tetrahedron* **1976**, *32*, 51−56.

[17] M. J. Schweiger, U. Nagel, W. Beck, *J. Organomet. Chem.* **1988**, *355*, 289−296.

[18] E. Lindner, M. Pabel, K. Eichele, *J. Organomet. Chem.* **1990**, *386*, 187−194.

[19] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017−7036.

[20] F. Diederich, *Angew. Chem.* **1988**, *100*, 372−396; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 362, and references therein.

[21] [21a] L. Rossa, F. Vögtle in *Synthesis of Medio- and Macrocyclic Compounds by High Dilution Principle Techniques: Topics in Current Chemistry* (Ed.: F. Vögtle), Springer, Heidelberg, **1983**, vol. 113, *Cyclophanes I*, p. 1. − [21b] P. Knops, N. Sendhoff, H.-B. Mekelburger, F. Vögtle in *High Dilution Reactions − New Synthetic Applications: Topics in Current Chemistry* (Eds.: E. Weber, F. Vögtle), Springer, Heidelberg, **1992**, vol. 161, *Macrocycles*, p. 1.

[22] [22a] B. L. Shaw, *J. Organomet. Chem.* **1980**, *200*, 307−318. − [22b] X. Chi, A. J. Guerin, R. A. Haycock, C. A. Hunter, L. D. Sarson, *J. Chem. Soc., Chem. Commun.* **1995**, 2563−2565.

[23] Crystallographic data (excluding structural factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102873. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road. GB-Cambridge CB2 1EZ, UK [Fax: (internat.) code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[24] [24a] W. Schöniger, *Microchim. Acta* **1955**, 123−129. − [24b] W. Schöniger, *Microchim. Acta* **1956**, 869−876.

[25] G. Brunisholz, J. Michod, *Helv. Chim. Acta* **1954**, *37*, 598−602.

[26] H. Wagner, *Microchim. Acta* **1957**, 19.

[27] S. Meyer, Ph. D. Thesis, University of Tübingen, **1987**.

[28] T. Uchiyama, Y. Toshiyasu, Y. Nakamura, T. Miwa, S. Kawaguchi, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 181−185.

[29] m: AA′MM′ pattern.

[30] m: AA′MM′XX′ pattern.

[31] m: AA′XX′ pattern.

[32] m: AXX′ pattern.

[33] H. D. Flack, *Acta Crystallogr. Sect A* **1983**, *39*, 876−881.

Received October 8, 1998
[I98342]