Synthesis and Structural Characterization of Hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene, Its Radical Cation Salt and Its Tricarbonylchromium Complex

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Abstract: The hexa-*tert*-butyl substituted hexa-*peri*-hexabenzocoronene was synthesized in an overall yield of 83% from 4-*tert*-butylphenylacetylene. The key step was the oxidative cyclodehydrogenation of hexa(4-*tert*-butylphenyl)benzene with anhydrous $FeCl_3$ in CH_2Cl_2. The high solubility of hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene in common organic solvents allowed a comprehensive spectroscopic characterization of this compound in solution. Electrochemical oxidation at −30 °C in the presence of tetrabutylammonium hexafluoroarsenate led to the formation of a stable radical cation salt. Reaction of hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene with an excess of tricarbonyl(naphthalene)chromium in THF/dioxane afforded a mixture of mono- and bis-tricarbonylchromium complexes which could be separated by chromatography. The molecular structures of the parent compound, its radical cation salt and its mono- tricarbonylchromium complex were determined by X-ray analysis and discussed in detail. Remarkably, the crystal structures of these compounds are mainly dominated by the formation of dimers of the aromatic cores.

Keywords: arene complexes • crystal structure • cyclodehydrogenation • electrocrystallization • PAH

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of interest because of their electronic and optoelectronic properties.[1] Furthermore, large PAHs serve as unique model compounds for graphite.[2]

Most of the smaller PAHs crystallize in a fashion in which there is little π interaction between the molecules.[3] A typical structure found in this class of compounds is the herringbone motif where the discs are oriented approximately perpendicular to each other. If the diameter of the discs increases, however, it is expected that at a certain point the herringbone packing is no longer stable and that columnar structures with strong π interactions are formed.[3, 4]

One of the difficulties dealing with larger PAHs is the fact that with increasing molecular weight the solubility of these compounds decreases dramatically. For instance, hexa-*peri*-hexabenzocoronene (**1a**) is so insoluble in common organic solvents that crystals for the structure determination had to be grown in pyrene melts.[4]

Sufficient solubility is, on the one hand, a prerequisite for the structural investigation and characterization of physical properties and, on the other hand, allows the derivatization of these compounds by chemical and electrochemical means.

Recently, we have described synthetic concepts toward alkyl-substituted derivatives of PAHs.[5–10] Owing to the good solubility of these compounds a spectroscopic characterization in solution became possible. Interestingly, the *n*-alkyl substituted compounds form discotic mesophases with a stack-like arrangement of the aromatic discs.[6] Furthermore, monomolecular adsorbate layers on graphite could be obtained which were characterized by scanning tunneling microscopy.[5, 8, 10]

Herein we describe a synthetic route toward hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene (**1b**). The good solubility of this compound allows the formation of the stable radical cation salt $[\mathbf{1b}]_2AsF_6$ upon electrochemical oxidation of **1b**, as well as the synthesis of the tricarbonylchromium complexes $[\mathbf{1b}]Cr(CO)_3$ (**6**) and $[\mathbf{1b}][Cr(CO)_3]_2$ (**7**). The crystal structure analyses of these compounds reveal a remarkable packing behavior of the aromatic discs in the solid state.

Results and Discussion

The synthesis of **1b**, outlined in Scheme 1, starts with 4-*tert*-butylphenylacetylene (**2**) which is coupled with 4-*tert*-butyliodobenzene (**3**) to yield di(4-*tert*-butylphenyl)acethylene (**4**) (92%).[11, 12] The $[Co_2(CO)_8]$ mediated cyclotrimerization of **4**

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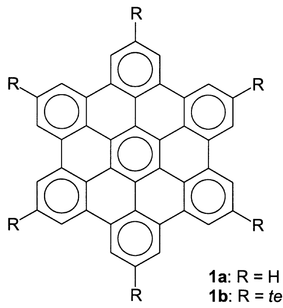
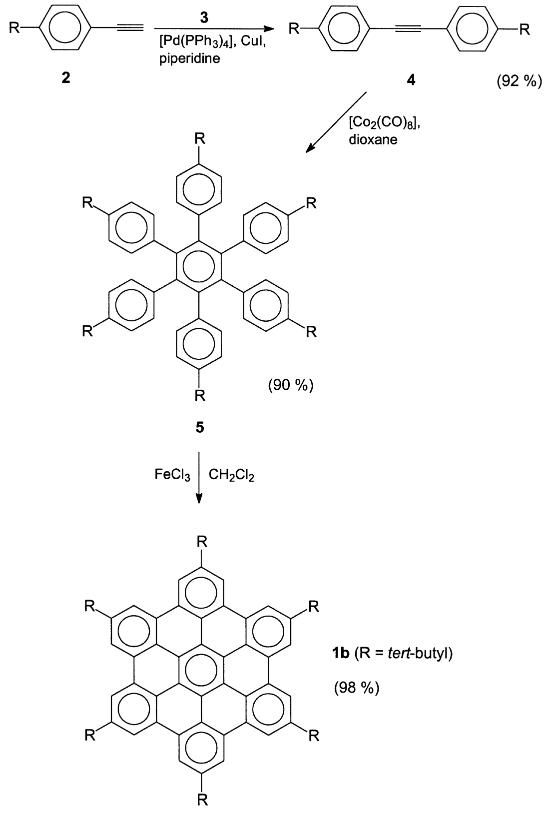


1a: R = H
1b: R = *tert*-butyl

generated hexa(4-*tert*-butylphenyl)benzene (**5**) in a yield of 90%.[13] The key step for the synthesis of **1b** is the oxidative cyclodehydrogenation of **5**. Using anhydrous $FeCl_3$ as oxidant, **1b** was obtained in nearly quantitative yield after reductive workup (Scheme 1).[14]



Scheme 1. Synthesis of hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene (**1b**).

The presence of the *tert*-butyl groups in **1b** improves the solubility significantly. In contrast to the parent compound **1a**, **1b** is soluble in several organic solvents (e.g. chlorinated aliphatic hydrocarbons and tetrahydrofuran) even at room temperature and therefore can be fully characterized by ^{1}H- and ^{13}C-NMR spectroscopy as well as UV/Vis spectroscopy. The cyclovoltammetric determination of the first reduction potentials shows the reversible formation of the mono- and dianion ($E_{1/2}{}^1 = -2.10$ V, $E_{1/2}{}^2 = -2.40$ V), the oxidation occurs at $E_{1/2}{}^1 = +0.99$ V and $E_{1/2}{}^2 = +1.42$ V and is reversible as well (Table 1).

Table 1. Cyclic voltammetric data of compound **1b**.[a]

	solvent	$E_{1/2}{}^1$[V]	$E_{1/2}{}^{12}$[V]
reduction	THF	-2.10	-2.40
oxidation	CH_2Cl_2	$+0.99$	$+1.42$

[a] Working and counter electrodes: Au; reference: SCE; supporting electrolyte: Bu_4PF_6 (0.1M); scan rate: 100 mV sec^{-1}.

Crystals suitable for X-ray structure analysis were obtained by slow evaporation of the solution of **1b** in THF/pentane at room temperature. The crystal structure shows the formation of dimers which are arranged in a herringbone-like motif which according to the classification of Desiraju and Gavezotti can be characterized as a sandwich herringbone packing (Figure 1a).[3]

It can be seen that the molecules are not strictly planar but slightly bent owing to the steric interaction of the *tert*-butyl groups. The largest deviation of the central atoms of the *tert*-butyl groups from the best plane calculated for the aromatic core is 0.56 Å (C55). Remarkably, the normal projection of the sandwich is comparable to the one of two graphite planes, that is each carbon atom in this projection is located in the center of a six-membered ring of the neighboring molecule (Figure 1b).

The interplanar distance of 3.44 Å is only slightly larger than in graphite (3.35 Å). This packing is quite different from **1a** which forms columns of flattened-out herringbones (according to Desiraju and Gavezotti called γ motif).[4] Apparently the bulky *tert*-butyl substituents hinder the formation of equidistant stacks so that strong π interaction is found only in a pair of molecules. At room temperature, two of the *tert*-butyl substituents are disordered, that is two orientations are observed which differ by approximately a 60° rotation. In Figure 1 only the majority positions are shown for clarity. It is interesting to note that these two substituents have no interdimer contacts and have apparently a sufficiently large cavity to perform a rotation. This motion is frozen in when the temperature is lowered. The occupancy factor for the majority methyl groups increases with decreasing temperature so that at 230 K the disorder for one of the *tert*-butyl groups is no longer observed. In the investigated temperature range the thermal motion of the aromatic core can be treated with good approximation as a rigid body motion and the vibrational amplitudes decrease in the expected fashion. Packing and the distortion out of planarity are not affected by temperature. Pertinent data on the temperature dependence are summarized in Table 2.

Many other smaller aromatic compounds form crystals of radical cation salts which precipitate on the anode when a solution is oxidized in the presence of a suitable supporting electrolyte (e.g. tetrabutylammonium hexafluoroarsenate).[15–17] With **1b**, however, an oxidation in methylene chloride yielded a stable red solution from which upon cooling at −30 °C shiny black crystals precipitated. The X-ray structural analysis of these crystals (Figure 2a) shows the formation of a radical cation salt with the stoichiometry [**1b**]$_2$AsF$_6$.

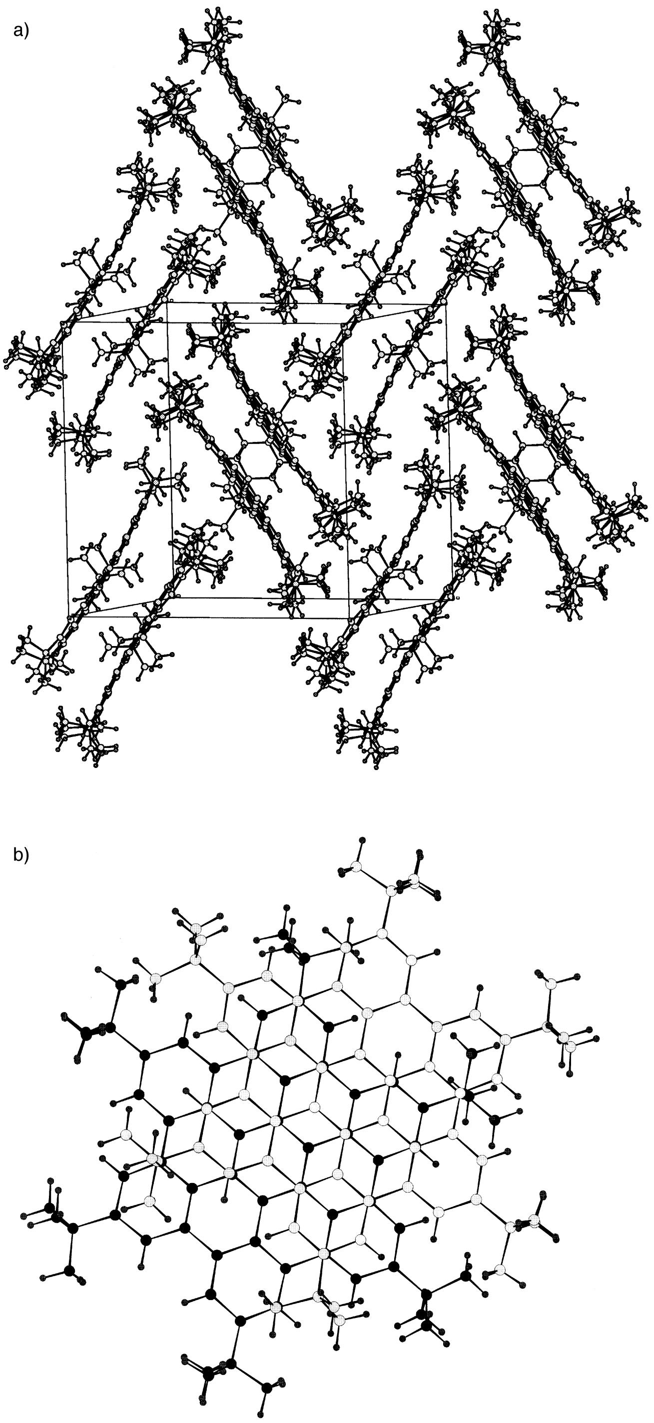


Figure 1. a) Crystal structure of **1b**. b) Normal projection of a dimer of **1b**.

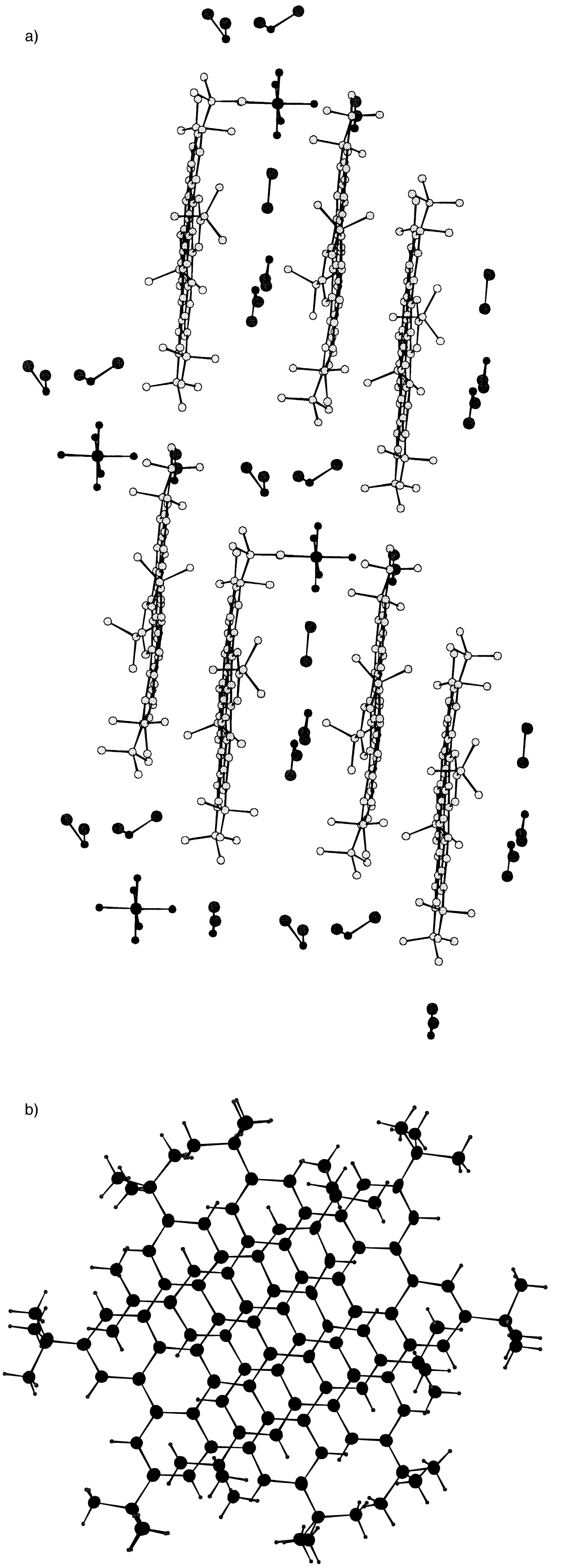


Figure 2. a) Crystal structure of **[1b]$_2$AsF$_6$**. b) Normal projection of a dimer of **[1b]$_2$AsF$_6$**.

The radical cation salts of smaller aromatic compounds form columnar structures in which stacks of the disc-like molecules are placed in a fashion leaving channels in which the counterions are found.[15–17] Here no continuous stacks are formed, but a layer of solvent molecules is intercalated in the stacks, separating pairs of **1b**. The molecular overlap in such a pair which is shown in Figure 2b differs from the graphite-like arrangement of the parent compound. With respect to this packing the rings are shifted by half a C–C bond length so that the centers of the bond intersect in the normal projection. This

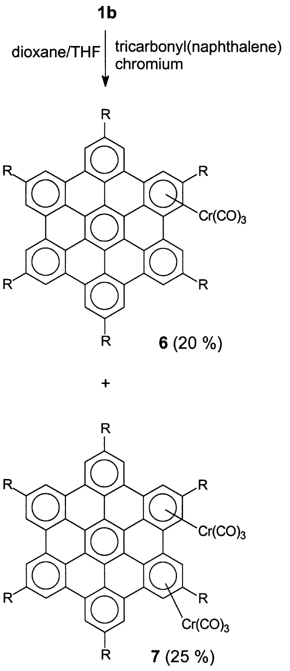
Table 2. Temperature dependence of the occupancy factors of the disordered atoms and the eigenvalues of the mean square librational amplitudes L_i as determined by the TLS analysis.

	room temperature	230 K	155 K
OCC (C441-C461)	0.71	1.0	1.0
OCC (C561-C581)	0.59	0.67	0.87
L_1 (deg^2)	0.91	0.84	0.72
L_2 (deg^2)	2.35	2.04	1.11
L_3 (deg^2)	3.45	3.03	2.09

overlap pattern has been frequently observed in the radical cation salts of other arenes, e. g. pyrene and perylene.[15, 17]

The reason for the formation of segragated dimers in the radical cation salt is not clear. As in **1b** steric hindrance of the bulky substituents is a possible explanation for this behavior. On the other hand, it seems possible to form a columnar structure by rotating adjacent molecules by 60° with respect to each other thus avoiding this hindrance and allowing a close stacking. Thus, another explanation is that the π-system in **1b** is already sufficiently extended in order to effectively stabilize the charge in a dimer, whereas in the salts of smaller arenes the infinite stack of molecules is needed to obtain a stable salt.

Many tricarbonyl(arene)chromium complexes can be synthesized by treatment of the corresponding arene with tricarbonyl(naphthalene)chromium.[18] When **1b** was reacted with an excess of tricarbonyl(naphthalene)chromium in a mixture of dioxane/tetrahydrofuran, complexes **6** and **7** were formed, which could be separated by column chromatography (Scheme 2).



Scheme 2. Synthesis of compounds **6** and **7**.

Both the ^{1}H- and ^{13}C-NMR spectra of **6** establish unequivocally the position of the $Cr(CO)_3$ group, which is ligated to an electron-rich, *tert*-butyl substituted benzene ring. In the case of **7**, inspection of the NMR spectra reveals that the two $Cr(CO)_3$ groups are placed at adjacent *tert*-butyl substituted benzene rings. Due to the symmetry of this molecule, a discrimination between the two possible sterioisomers, namely the *cis* and the *trans* isomer, by spectroscopic methods is prevented. However, due to repulsive interactions between the $Cr(CO)_3$ ligands the formation of the *trans* isomer is more likely.

In order to obtain information about the influence of the tricarbonylchromium group on the packing behavior of the aromatic core in the crystal, a X-ray structural analysis of **6** was performed. Suitable crystals were grown by slow diffusion of ethanol into a solution of **6** in methylene chloride. Remarkably, the crystal structure is again dominated by the formation of dimers. The crystal structure of **6** is shown in two projections in Figure 3.

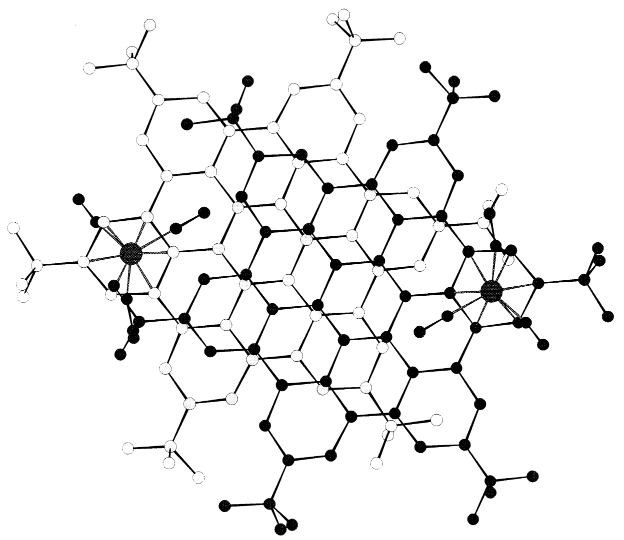


Figure 3. Crystal structure of **6**.

The structure contains two molecules CH_2Cl_2 in the asymmetric unit. A dimer is formed in which the $Cr(CO)_3$ ligands point in opposite directions and are located with maximal distance at the periphery of the dimer. In some respects the structure of the $Cr(CO)_3$ complex resembles the parent compound. The molecules are not strictly planar (maximal deviation from the best plane 0.31 Å). The interplanar spacing of 3.59 Å is well within the distance expected for aromatic rings in the absence of any π–π interaction. As in **1b** the packing can be described as a double herringbone structure with almost graphite-like overlap within a dimer pair.

Conclusion

Compound **1b** was obtained by a convenient three-step synthesis in high yield. The presence of the *tert*-butyl substituents in **1b** led to a good solubility which allowed the transformation of **1b** into the radical cation salt $[\mathbf{1b}]_2AsF_6$ as well as into the tricarbonylchromium complexes **6** and **7**. X-ray crystallographic analyses elucidated the molecular structures of **1b**, $[\mathbf{1b}]_2AsF_6$, and **6**. In contrast to the parent compound **1**, the crystal structure of **1b** is characterized by a sandwich-herringbone packing. $[\mathbf{1b}]_2AsF_6$ forms dimers in the crystal which are separated by solvent molecules. This result is in sharp contrast to the crystal structures of the radical cation salts of smaller aromatic compounds which are characterized by the formation of continuous stacks. Finally, the tendency of **1b** to form dimers in the solid state is established by the crystal structure of **6**. We are currently investigating the chemical and physical properties of even larger, solubilized PAHs. It will be of utmost interest to see whether the results presented in this paper are a general feature of large, alkyl substituted PAHs.

Experimental Section

General: Commercially available reagents were used without further purification unless otherwise stated. All reactions were carried out under an atmosphere of argon with freshly distilled solvents under anhydrous conditions. Melting points were determined on a Büchi melting point apparatus and are uncorrected. UV/Vis spectra were recorded at room temperature on Perkin–Elmer Lambda9 or Perkin–Elmer Lambda15 spectrophotometers. NMR spectra were recorded at ambient or specified temperatures on Varian Gemini 2000, Bruker AM300 or Bruker AMX500 instruments and calibrated with the solvent as the internal reference. Mass spectra were recorded on VG TRIO 2000 EI or ZAB2-SE-FPD equipment. Elemental analyses were performed by the Institut für Organische Chemie, Johannes Gutenberg-Universität in Mainz (Germany).

Di(4-*tert*-butylphenyl)acethylene (4):[12] At room temperature **3** (4.4 g, 16.94 mmol) was added to a solution of $[Pd(PPh_3)_4]$ (0.48 g, 0.42 mmol) and CuI (0.16 g, 0.85 mmol) in piperidine (250 mL). After stirring for 30 min, **2** (2.67 g, 16.94 mmol) was added and stirring was continued for a further 6 h. The mixture was diluted with CH_2Cl_2 (200 mL), washed with saturated NH_4Cl solution (2 × 200 mL) and H_2O (2 × 200 mL) and dried ($MgSO_4$). The solvent was removed in vacuo and the residue recrystallized from MeOH/EtOH to furnish **4** as colorless crystals (4.52 g, 92 %). M.p.: 177 °C (lit.: 177–178 °C[12]); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.36$ (s, 18 H), 7.39 (m, 4 H), 7.50 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 31.71$, 35.26, 89.43, 121.08, 125.81, 131.84, 151.81; MS (EI): *m*/*z* (%): 290.0 (48) $[M]^+$; anal. calcd for $C_{22}H_{26}$ (290.03): C 90.98, H 9.02; found C 90.93, H 9.03.

Hexa(4-*tert*-butylphenyl)benzene (5): $[Co_2(CO)_8]$ (150 mg, 0.43 mmol) was added to a solution of **4** (4.11 g, 14.17 mmol) in dioxane (200 mL). The mixture was stirred and heated under reflux for 20 h. After the reaction mixture had been allowed to cool down to room temperature, the crystalline precipitate was filtered off and dissolved in CS_2. Filtration of this solution and removal of the solvent under reduced pressure afforded pure compound **5** as a white microcrystalline powder (3.7 g, 90 %). M.p.: > 300 °C; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): $\delta = 1.06$ (s, 54 H), 6.65 (m, 12 H), 6.74 (m, 12 H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 100°C): $\delta = 31.44$, 34.13, 123.00, 131.53, 138.45, 140.42, 147.60; MS (FD): *m*/*z* (%): 870.1 (100) $[M]^+$; anal. calcd for $C_{66}H_{78}$ (870.1): C 90.98, H 9.02; found C 90.89, H 9.06.

Hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene (1b): Anhydrous $FeCl_3$ (1.78 g, 11.02 mmol) was added to a solution of **5** (0.2 g, 0.229 mmol) in CH_2Cl_2 (100 mL). The resulting green rection mixture was stirred for 18 h at room temperature and then quenched with MeOH (10 mL), whereupon the color turned yellow. The solution was washed with 5 N hydrochloric acid (5 × 200 mL), H_2O (2 × 200 mL) and dried over $MgSO_4$. Filtration over silica gel (CH_2Cl_2) afforded the pure compound **1b** as a yellow solid (0.196 g, 98 %). M.p.: > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.81$ (s, 54 H), 9.30 (s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 32.02$, 35.73, 118.91, 120.51, 124.04, 130.55, 149.04; UV/Vis (cyclohexane): S_{max} (lg*M*) = 340 (4.76), 355 (5.11), 387 nm (4.72); MS (FD): *m*/*z* (%): 858.52 (100) $[M]^+$; anal. calcd for $C_{66}H_{66}$ (859.25): C 92.26, H 7.74; found C 91.90, H 7.70.

Radical cation salt $[\mathbf{1b}]_2AsF_6$: A solution of **1b** (400 mg, 0.46 mmol) and tetrabutylammonium hexafluoroarsenate (8.62 g, 20 mmol) in CH_2Cl_2 (200 mL) was cooled to −30 °C and electrolyzed between platinum-wire electrodes at a constant low current (2 mA) under an atmosphere of argon. After two days, shiny black crystals of compound $[\mathbf{1b}]_2AsF_6$ were collected and subjected to X-ray analysis.

Tricarbonylchromium complexes 6 and 7: Tricarbonyl(naphthalene)chromium-tricarbonyl (317 mg, 1.2 mmol) was added to a solution of **1b** (100 mg, 0.12 mmol) in a mixture of dioxane/THF 3:1 (200 mL). The solution was heated under reflux for 3 h with exclusion of light. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel (pentane/CH_2Cl_2 5:1). The first fraction gave unreacted **1b**, the second fraction complex **6** [orange solid (23 mg, 20 %); m.p.: 172 °C (decomp.); ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 1.77$ (s, 9 H), 1.81 (s, 18 H), 1.83 (s, 18 H), 1.84 (s, 9 H), 7.36 (s, 2 H), 8.84 (s, 2 H), 9.33 (m, 4 H), 9.37 (s, 2 H), 9.38 (s, 2 H); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 31.63$, 31.96, 32.10, 32.14, 35.22, 36.10, 36.16, 36.17, 86.77, 98.51, 100.35, 119.10, 119.59, 119.80, 119.87, 120.00, 121.26, 121.48, 122.05, 122.81, 123.64, 123.80, 123.95, 129.95, 130.38, 130.89, 131.14, 131.23. 150.38, 150.58, 150.86; UV/Vis (cyclohexane): S_{max} (lg*M*) = 354 (5.01), 379 (4.58), 388 (4.55), 418 nm (4.08); MS (FD): *m*/*z* (%): 995.8 (100) $[M]^+$; anal. calcd for $C_{69}H_{66}O_3Cr$ (995.28): C 83.27, H 6.68; found C 83.01, H 6.65], and the third fraction complex **7** [orange solid (32 mg, 25 %); m.p.: 170 °C (decomp.); ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 1.74$ (s, 18 H), 1.80 (s, 18 H), 1.82 (s, 18 H), 6.75 (s, 2 H), 7.31 (s, 2 H), 8.82 (s, 2 H), 9.34 (m, 4 H), 9.39 (s, 2 H); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 31.46$, 31.87, 32.02, 35.19, 36.11, 36.18, 85.40, 86.33, 96.76, 98.71, 98.90, 119.37, 120.07, 120.20, 120.43, 121.25, 121.95, 122.62, 123.03, 123.22, 123.40, 129.34, 130.58, 131.07, 131.24, 151.03, 151.30, 233.62; UV/Vis (cyclohexane): S_{max} (lg*M*) = 346 (4.85), 381 (4.54), 420 nm (4.26); MS (FD): *m*/*z* (%): 1130.8 (100) $[M]^+$; anal. calcd for $C_{72}H_{66}O_6Cr_2$ (1131.30): C 76.44, H 5.88; found C 76.22, H 5.75].

X-ray crystallography: All data with the exception of the low-temperature structures of **1b** were collected on a Nonius CAD4 diffractometer using graphite monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å).[18] The latter were collected on a Nonius KCCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). Data on the CAD4 diffractometer were collected in the θ-2θ scan mode. Data collections at low temperature were carried out with a cooled nitrogen stream. Unit cell parameters were determined from a least-squares fit of 25 reflections with $\theta > 20°$. An empirical absorption correction was applied to the data. The structures were solved with direct methods (Shelxs) and refined by full matrix least-squares analyses on *F* with anisotropic temperature factors for all non-hydrogen atoms. The latter were placed at the calculated positions and included in the refinement with fixed isotropic temperature factors in the riding mode. For the disordered *tert*-butyl groups occupancy factors (x, $1 - x$) were refined.

Compound **1b** (room temperature): monoclinic, $P2_1/c$, $a = 15.0568(9)$, $b = 18.094(1)$, $c = 18.136(1)$ Å, $\beta = 94.976(5)°$, $V = 4922.4$ Å^3, $Z = 4$, $D_x = 1.159$ g cm^{-3}, $\mu = 4.547$ cm^{-1}, 8449 reflections measured ($\theta_{max} = 64°$) 3234 observed ($I > 3\sigma(I)$), $R = 0.064$, $R_w = 0.067$ (unit weights).

Compound **1b** (230 K): monoclinic, $P2_1/c$, $a = 15.0800(2)$, $b = 18.0961(5)$, $c = 18.1310(5)$ Å, $\beta = 95.059(1)°$, $V = 4928.5$ Å^3, $Z = 4$, $D_x = 1.158$ gcm^{-3}, $\mu = 0.61$ cm^{-1}, 12511 reflections measured ($\theta_{max} = 29°$) 4617 observed ($I > 3\sigma(I)$), $R = 0.055$, $R_w = 0.055$ (unit weights).

Compound **1b** (155 K): monoclinic, $P2_1/c$, $a = 15.0703(6)$, $b = 18.0203(7)$, $c = 18.0498(6)$ Å, $\beta = 94.917(2)°$, $V = 4883.8$ Å^3, $Z = 4$, $D_x = 1.169$ gcm^{-3}, $\mu = 0.61$ cm^{-1}, 12410 reflections measured ($\theta_{max} = 29°$) 4745 observed ($I > 3\sigma(I)$), $R = 0.053$, $R_w = 0.054$ (unit weights).

Compound $[\mathbf{1b}]_2AsF_6(CH_2Cl_2)_{12}$: triclinic, $P-1$, 165 K, $a = 18.869(5)$, $b = 11.354(5)$, $c = 28.771(5)$ Å, $\alpha = 87.979(8)$, $\beta = 90.058(9)$, $\gamma = 88.237(8)°$, $V = 6157$ Å^3, $Z = 2$, $D_x = 1.302$ g cm^{-3}, $\mu = 32.857$ cm^{-1}, 15113 reflections measured ($\theta_{max} = 60°$) 8909 observed ($I > 3\sigma(I)$), $R = 0.074$, $R_w = 0.077$ (unit weights).

Compound **6** $(CH_2Cl_2)_2$: monoclinic, $P2_1/n$, 165 K, $a = 17.162(1)$, $b = 12.187(1)$, $c = 29.315(2)$ Å, $\beta = 91.140(4)°$, $V = 6130$ Å^3, $Z = 4$, $D_x = 1.262$ g cm^{-3}, $\mu = 35.493$ cm^{-1}, 11490 reflections measured ($\theta_{max} = 60°$) 5890 observed ($I > 3\sigma(I)$), $R = 0.071$, $R_w = 0.077$ (unit weights).

Acknowledgement

Financial support by the Volkswagen-Stiftung and the TMR European Research Programme through the Sisitomas project is gratefully acknowledged.

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[19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142006 for **1b** (room temp.), CCDC-142007 for **1b** (230 K), CCDC-142008 for **1b** (155 K), CCDC-142009 for [**1b**]$_2$ AsF$_6$(CH$_2$Cl$_2$)$_{12}$ and CCDC-142010 for **6** $\cdot$ (CH$_2$Cl$_2$)$_2$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: July 13, 1999 [F1909]