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Bromination of Unsaturated Dodecahedranes—En Route to C_{20} Fullerene

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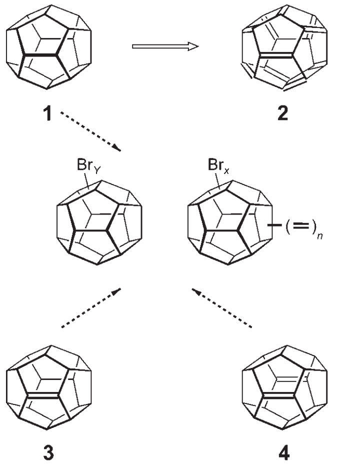
Abstract: As part of a study to achieve selective oligo(poly)bromination—ultimately perbromination—of the dodecahedral C_{20} skeleton, the extent and direction of the ionic bromination of dodecahedrene and 1,16-dodecahedradiene were explored. Along sequences of Br^+ additions/deprotonations and allylic rearrangements, up to ten hydrogen atoms were substituted (traces of $C_{20}H_xBr_{10}$). Tetrabromododecahedrenes obtained under defined conditions in up to 50 % total yield with three and four allylic bromine substituents protecting the extremely bent C=C bonds, proved highly unreactive even towards oxygen but reacted rapidly with CH_2N_2. Upon electron impact ionization (MS) of the newly secured oligo(poly)bromododecahedra(e)nes, sequential loss of the substituents ended generally in polyunsaturated dodecahedranes (in the extreme $C_{20}H_4$, "tetrahydro-C_{20} fullerenes"). Only subsequently did skeletal fragmentations occur. From X-ray crystal-structure analyses, more information was obtained on the structural response of the dodecahedral skeleton to the strain induced by the voluminous substituents. As Appendix, the forcing radical bromination of 1,6-dibromododecahedrane and exploratory *cis*-β-HBr/*cis*-β-Br_2 eliminations in bromododecahedranes with $[Fe_2(CO)_9]$, $P_2F/[FeCp_2]$ and [Fe(tmeda)Cp*Cl] (in situ protection) are presented.

Keywords: dodecahedranes · fullerenes · polycycles · strained molecules

Introduction



Ever since pentagonal dodecahedrane **1** became available in serviceable quantities,[1–3] the installation of an increasing number of C=C double bonds, ultimately leading to the synthesis of the hydrogen-free carbon cage **2**, the smallest possible fullerene, have been hotly pursued projects.[4,5] In this context oligo(poly)bromododecahedranes played a major role as the most promising precursor molecules. Perhalogenation of **1**, and generation and characterization of **2** will be detailed in the two subsequent papers.[6,7] As a prelude we present an updated report on attempts to achieve selective oligo(poly)bromination of the dodecahedral skeleton by starting with dodecahedrene **3** and 1,16-dodecahedradiene **4**. Both starting materials were available through practical syntheses, **3** through Paquette's highly efficient bromination protocol of **1**[3,8] and subsequent *cis*-β-HBr elimination with Schwesinger's P_2F base,[9] and **4** through flash-vacuum pyrolytic decomposition of a bis-β-lactone precursor.[4] These ball-shaped cycloalkenes feature strongly pyramidalized olefinic carbons and are extremely oxygen-sensitive yet can be handled at room temperature. Dimerization,[10] extremely rapid in similarly bent cycloalkenes, is efficiently inhibited by the four allylic hydrogen atoms. As Appendix a brief account is given of the radical bromination of 1,6-dibromododecahedrane and of experiments directed at (conjugated)

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dodecahedradienes to hexaenes ($C_{20}H_{16}$–$C_{20}H_8$) and their in situ protection as metal complexes.[11]

Results and Discussion

Electrophilic bromination of monoene 3 and diene 4: On a more theoretical background, the bromination experiments with **3** and **4** complement prior studies performed with the seco- and bisseco-dodecahedra(di)enes **5**(**6**)[12] and **7**(**8**)[13] and with derivatives of **3** and **4**, respectively (e.g. **19**, see Scheme 2) (Figure 1).[14] The dienes with through-space distances between the perfectly *syn*-planar C=C double bonds (d) increasing from about 2.8 to 3.5 (ca. 2.8 to 3.7 Å) and with the olefinic pyramidalization angle increasing from 17.1° to 39.3° (9.9° to 46.6°) became ideal objects for testing the geometrical boundaries of strictly in-plane π,π-interactions in the neutrals,[15] in the radical cations/dications ("σ-homoconjugation", "σ-homoaromaticity"),[16] and of primary relevance here, in the cations generated through electrophilic additions. The geometrical features now calculated for the protonated species H**4**$^+$, H**6**$^+$, and H**8**$^+$[17] at the B3LYP/6–31G* level (Figure 1)[17–19] substantiated the expectation that with increasing π,π-distance homoconjugate stabilization, hence homoconjugate addition, becomes less important. Addition reactions with Br_2 or HBr provided an experimental test: Diene **8** added Br_2 neatly via the homoconjugate "bromonium ion" Br**8**$^+$,[13,20] **6** least preferentially via the homoconjugate Br**6**$^+$,[12] derivatives of **4** neatly via the largely localized Br**4**$^+$ ions.[14] In the latter two cases, the interception by Br^- ions to give *cis*-vicinal dibromides had to compete with β-deprotonation leading to allylic bromides with migrated C=C double bonds, a phenomenon well studied for the addition of Br_2 to sterically encumbered olefins.[21] The monoenes **3**, **5**, and (functionalized) **7** fitted into this picture in that Br**7**$^+$ **neatly underwent *cis*-1,2-addition, whereas Br5$^+$ and derivatized Br3$^+$ showed dominant β-deprotonation.[14] There were good reasons to expect that in the case of the parents 3** and **4**, in the absence of sterically and electronically deactivating substituents, electrophilic addition of Br^+ would initiate repeating sequences of Br^+-addition/β-deprotonation steps.[12] As to the possible length and stereochemical direction of such sequences, hence the highest possibly achievable degree of bromination, it was understood, though, that with an increasing degree of skeletal bromination, addition of Br^+ would become increasingly slower and β-deprotonation would be more and more kinetically controlled.

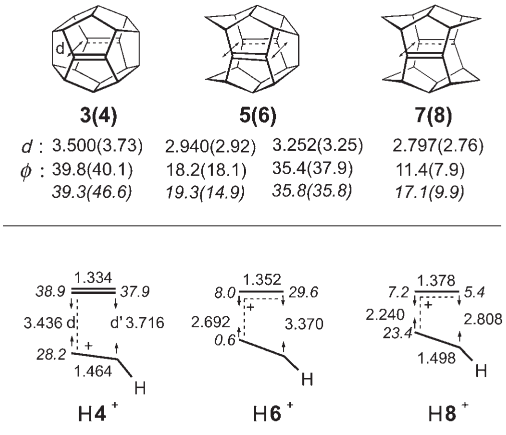
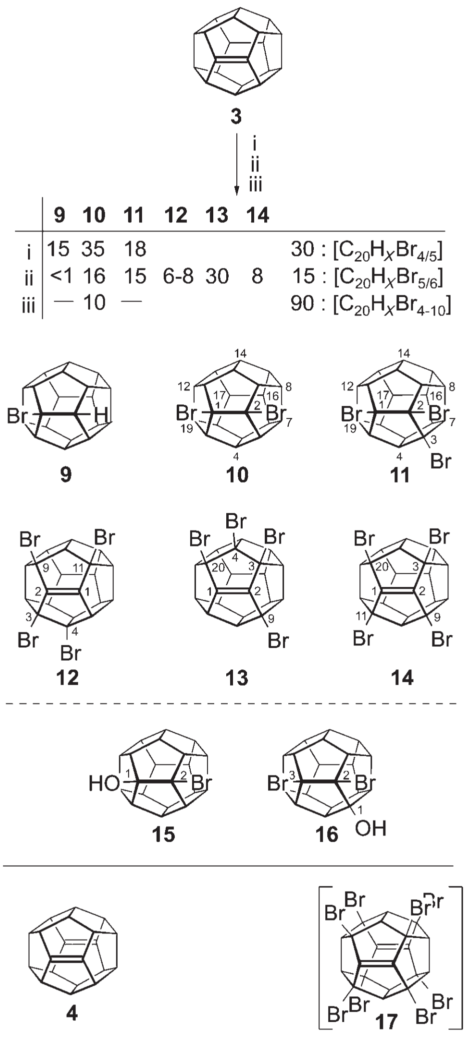


Figure 1. Calculated (B3LYP/6–31G*;[18a] in parentheses MM3[18b]) π,π-distances (*d*, [Å]), olefinic pyramidalization angles (*ϕ* [°]) of monoenes **3**, **5**, **7**, and (italics) of dienes **4**, **6**, **8**;[12] transcaveal distances (*d*/*d′* [Å]), selected bond lengths [Å] and olefinic pyramidalization angles (italics) of H**4**$^+$, H**6**$^+$, and H**8**$^+$.

The experimental results with **3** and the impact of broadly varied reaction conditions upon the extent and direction of the bromination can be illustrated with three sets of experimental conditions (Scheme 1). i) When a dilute solution of **3** in CH_2Cl_2 was titrated at room temperature with bromine, after consumption of one equivalent of Br_2 (ca. 2 min, con-

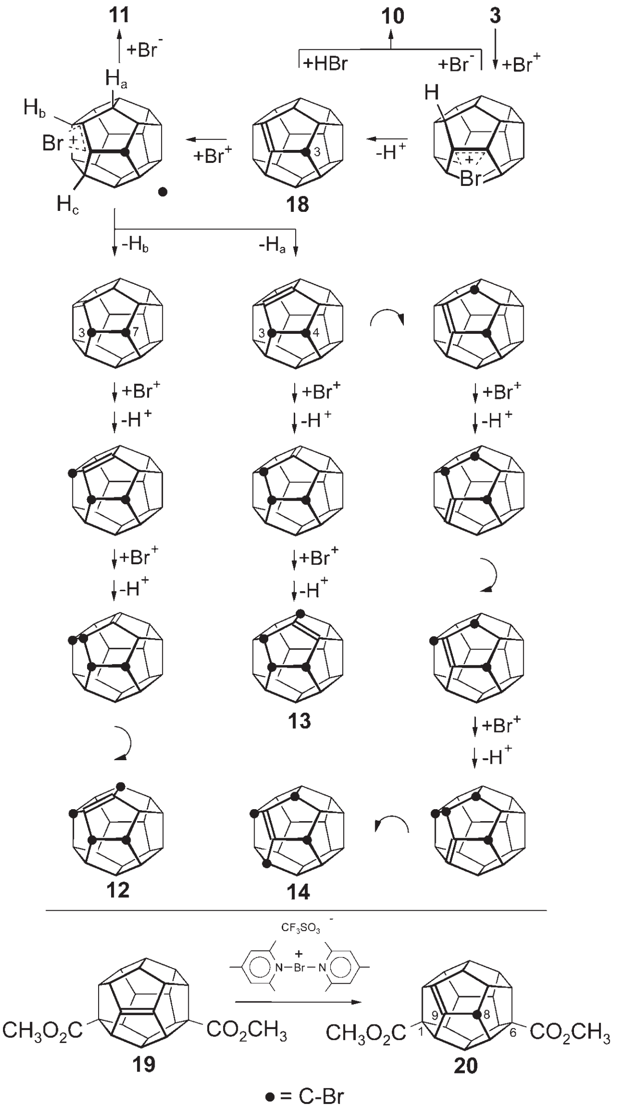


Scheme 1. i) **3** (0.20 mmol)/CH_2Cl_2 (5 mL)/RT/Br_2 (ca. 1 mmol); ii) **3** (0.30 mmol)/ethylene oxide (50 mmol)/Br_2 (3.0 mmol)/0 °C/2 min; iii) **3** (0.20 mmol)/Br_2 (200.0 mmol)/0 °C/4(7) days; yields (%).

comitant evolution of HBr), about 30 % of **3** remained. After consumption of five equivalents of bromine and total conversion of **3**, chromatographically 15 % of known monobromide **9**,[8] 35 % of 1,2-dibromide **10**, 18 % of 1,2,3-tribromide **11**, and about 30 % of a 5:1 mixture of at least six (unsaturated) tetra-/pentabromides were separated (TLC, MS, traces of hexabromides). ii) After treating a solution of **3** in CH_2Cl_2 with 10 equivalents of bromine in the presence of a vast excess of ethylene oxide as a scavenger of HBr, chromatographic workup after two minutes provided a trace of **9**, 16 % of **10**, 15 % of **11**, a fraction (ca. 50 %) of at least five tetrabromides (ca. 3:1:1, two traces) and a fraction (ca. 15 %) of penta-/hexabromides. Reverse-phase chromatography of the 50 % fraction allowed the separation of the 3,4,9,11-tetrabromoene **12** (5 %) from a 3:1 mixture of 3,4,9,20-/3,9,11,20-tetrabromoenes **13**/**14** (37 %). Through crystallization (THF/CH_3CN) of the latter mixture, the less soluble **13** was obtained in pure form and **14** was obtained as a highly enriched sample. iii) Upon stirring a solution of **3** in about 1000-fold excess of bromine at 0 °C for 4 days, the deeply red, high-melting material consisted of about 10 % of **9**, **10**, and **11** and a complex mixture of tetra- to hexabromides with traces of heptabromides. After seven days, higher bromides were present only in trace quantities with decabromides delineating the highest detected degree of bromination (TLC, MS, GCMS). In all these experiments, occasionally hydroxybromides **15** and **16** and others of composition $C_{20}H_{16}Br_2(OH)_2$/$C_{20}H_{16}Br_3OH$ (MS) were produced, which were attributed to the interception of H_2O under incompletely anhydrous reaction conditions, rather than due to hydrolysis during the separation procedures.

For diene **4**, with homoconjugate addition excluded, originally a chance, admittedly remote, was seen that the bromination patterns of **12**–**14** could be installed on both sides to provide inter alia the highly desired I_h symmetrical octabromodiene **17**. Extensive experimentation did not, however, fulfill expectations. In fact, the results were not significantly different from those with the corresponding 1,6-diester.[14a] Under the conditions applied for experiment ii, extremely complex reaction mixtures were generated, not amenable to GC/MS analysis and chromatographic separation, consisting mainly of a multitude of penta-/hexabromides, traces of hepta- to decabromides and of hydroxylated species (e.g. $C_{20}H_{16}Br_2(OH)_2$). Only the known 1,6- (**28**, see Figure 4)[14c] and 1,16-dibromide[22] resulting from the addition of two equivalents of HBr to **4** could be identified in minute quantities.

Pathways to 12–14: In Scheme 2, the formation of the tetrabromoenes **12**–**14**, which at first sight exhibit surprising substitution patterns of three or all four bromine substituents in allylic positions, can be rationalized in analogy to prior argumentation.[12,14] The point is stressed, though, that at every stage allylic bromination is an alternative. With this proviso, only the 3,4,9,20-tetrabromo pattern of **13** can be traced back exclusively to a sequence of addition/deprotonation steps. In this case the C=C double bond migrated four times.



Scheme 2.

The route to 3,4,9,11-tetrabromide **12** branches off at the stage of the second bromonium ion through loss of H_b.[23] Two subsequent addition/deprotonation steps produce a contiguous tetrabromide, the high strain of which is reduced by an allylic rearrangement (the fifth C=C migration, calculated $\Delta E_{str} \approx 15\,kcal\,mol^{-1}$). From the 3,4-dibromoene, the route to **14** starts with an allylic shift and encompasses, based on **3**, three such shifts and four Br^+-addition/deprotonation events (seven C=C migrations). Furthermore, not only the two unidentified $C_{20}H_{12}Br_4$ trace isomers leave room for additional pathways. Attempts to independently prepare the 3-bromoene **18**, which is rapidly consumed under the described conditions, through controlled Br^+ transfer to **3** with the use of bis(sym-collidine)bromonium triflate[24] failed. Even with equimolar amounts of reagent up to three bromine substituents were introduced. The two ester groups of **19** made the difference. The highly oxygen-sensitive yet thermally rather stable monobromide **20** proved sufficiently resistant to further Br^+ addition to allow its selective preparation.[25]

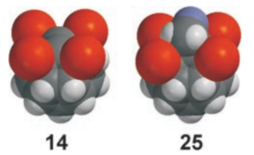
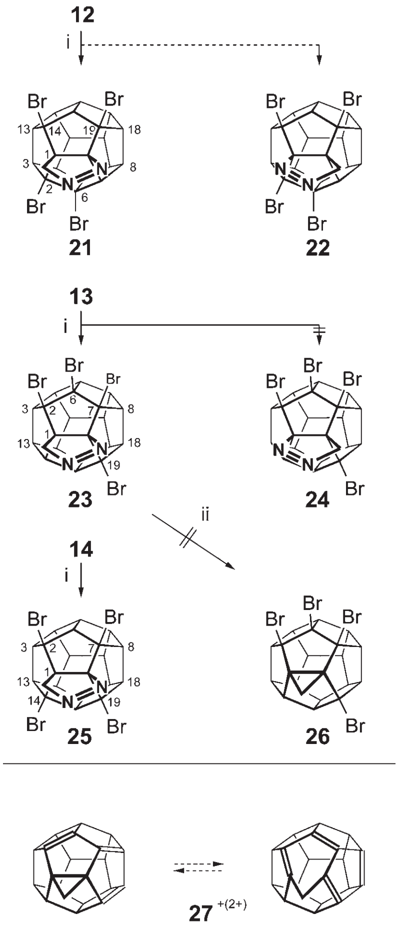


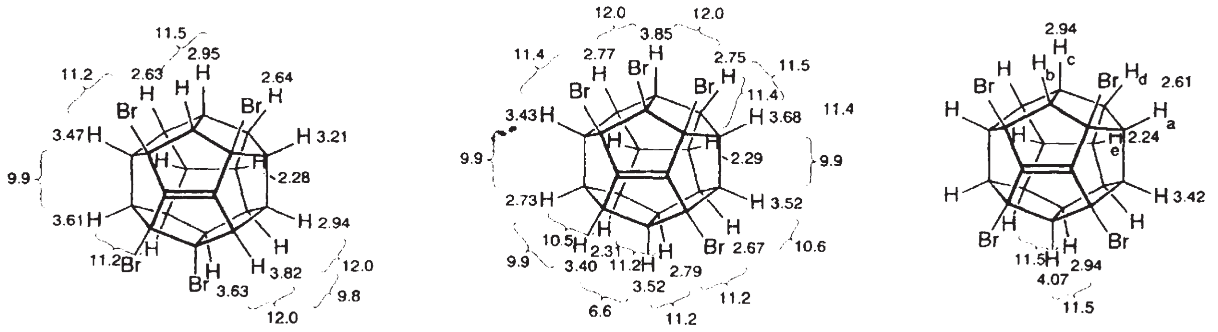
Figure 2. Space-filling models of **14** and **25** (MMFF[32]).

Reactivity of 12–14: Highly bent C=C double bonds surrounded by voluminous bromine substituents (cf. **14**, Figure 2) as structural elements in practically insoluble precursor molecules of fullerene **2** ("per(poly)brominated dodecahedrenes") are the subject of the follwing paper.[6] In this context, the soluble tetrabromoenes **12**–**14** served as most welcome model compounds. The inductive deactivation and steric protection of the highly bent C=C double bonds had, compared with the extreme reactivity of parent **3**, indeed impressive consequences. With bromine only slowly reacting, these tetrabromoenes resisted day-long exposure to oxygen. The lowered HOMOs presumably did not allow an initiating electron transfer.[26] *N*-Methyltriazolinedione, a powerful electrophile towards unsaturated dodecahedranes[27] as well as dimethyl dioxirane, a proven epoxidation reagent of electronically deactivated, sterically congested alkenes,[28] had no effect. Diels–Alder cycloadditions with furan, or inverse Diels–Alder reactions with 3,6-bistrifluoromethyl-1,2,4,5-tetrazine, rapid with **3** and **4**,[4a,27] could not be enforced. It was only the 1,3-dipolar diazomethane which was smoothly added to give the respective Δ1-pyrazolines (Scheme 3). Out of a mixture of **12**–**14** from **12**, adduct **21** together with very small amounts of (presumably) **22**, from **13** adduct **23** (no **24**) and from **14** adduct **25** were secured. The ease of the additions and the regioselectivity observed with **21** (**12**: $\delta_{C1}=161.8$ ppm, $\delta_{C2}=163.1$ ppm) and **23** (**13**: $\delta_{C1}=158.2$ ppm, $\delta_{C2}=162.8$ ppm) are in line with the expectation for HOMO(dipole)–LUMO(dipolarophile) control.[29] As tested with **23** ($\lambda_{max}=312$ nm, CH_3CN), neither photolysis (150-W high-pressure Hg lamp, benzene solution, $n\rightarrow\pi^*$ excitation) nor very forcing thermolysis delivered the cyclopropano derivative **26**. Interception of intermediate (diazenyl, methylene) radicals by the nearby bromine substituents (cf. **25**, Figure 2) is the explanation previously forwarded for similar situations. Direct photoexcitation of the mono-(bis)pyrazolines derived from **3** and **4** neatly ended in the respective cyclopropanododecahedranes.[30] On the other hand, in the MS spectra of **21** and **23** loss of N_2 and (H)Br along differing sequences produced $C_{21}H_{16-11}$ ions (*m/z* 268–263; *m/z* 133), possibly indicative of potentially valence-isomeric "homododecahedrenes" such as from **23** (-Br_2-2 HBr) the $C_{21}H_{14}$ ions $\mathbf{27}^{+(2+)}$.[31]



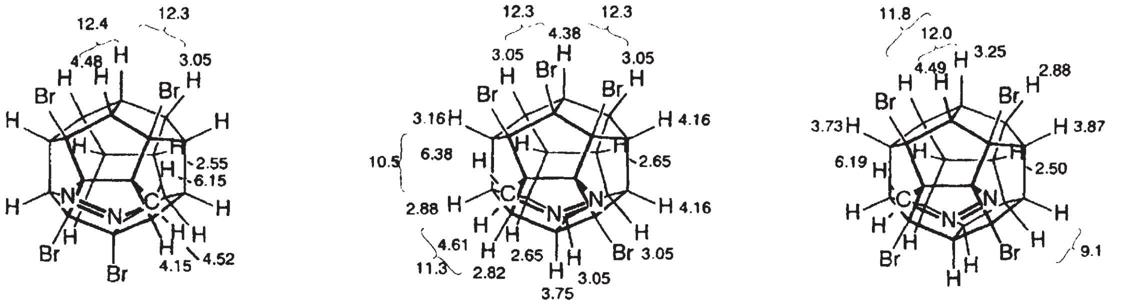
Scheme 3. i) **12**–**14** (0.10 mmol)/CH_2Cl_2 (10 mL)/CH_2N_2 (diethyl ether, vast excess/0 C/RT/10 h; ii) **23** (0.10 mmol)/benzene (5 mL)/RT/*hν* (150-W high-pressure Hg lamp).

NMR/MS spectral analyses: The substitution patterns of the bromides **10**–**16** and **20**, and the pyrazolines **21**, **23**, and **25** were derived from extensive ^1H and ^{13}C NMR analyses (Figure 3). The individual assignments were based on decoupling and 2D FT COSY or C/H heterocorrelation spectra with the chemical shifts reflecting the established additive increments for protons/carbons α/β- or γ-positioned to C–Br[8] and C=C double bonds, the smaller $^3J_{H,H}$ coupling constants on the flattened olefinic sides, and the pronounced solvent effects ($CDCl_3$ vs. C_6D_6).[4,6,8,12,14] The fragmentation patterns manifested in the MS spectra of individual bromides as well as of complex mixtures were in line with the known trends. The composition of essential ions was confirmed by high-resolution measurements.[4,6,12,14] Upon exclusive α-cleavage, sequential loss of (H)Br from the parent and daughter ions ended in unsaturated dodecahedranes ranging from (protonated) $C_{20}H_{14}$ trienes to $C_{20}H_4$ octaenes (*m/z* 255/254–245/244). It is only after loss of the Br substituents that skeletal fragmentation commenced. Weaker signals at least in part belong to doubly charged ions. High intensity particularly of *m/2z* 125/126 signals, and a signal with *m/z* 83.33 for a triply charged pentaene, are indicative of C=C/C=C (cross)conjugation in the $C_{20}H_{10(12)}$ polyenes. There were generally no indications for any skeletal disrupture en route to the ultimate polyenes of the type noted for **4** (→ C_9 + C_{11}) and 1,7,17-dodecahedratriene (→ C_5 + C_{15}).[14b] The congested situation around the CH_2N_2 units in **21**, **23**, and **25** (Figure 2) with calculated shortest nonbond-



12 **13** **14**

2 C=C	:	163.1 – 161.6	2 C=C	:	162.8 – 156.2
4 C-Br	:	93.3 – 91.4	4 C-Br	:	98.1 – 90.1
6 $\underline{C}$H-CBr	:	78.9 – 74.2	5 $\underline{C}$H-CBr	:	78.9 – 75.9
8 C	:	63.4 – 59.1	9 C	:	64.9 – 59.4

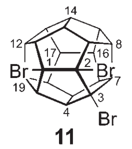


21 **23** **25**

4 C-Br	:	95.9 – 92.2	4 C-Br	:	103.7 – 92.6	4 C-Br	:	102.5, 94.0
6 $\underline{C}$H-CBr	:	85.5 – 78.3	7 $\underline{C}$H-CBr/C	:	82.8 – 71.5	6 $\underline{C}$H-CBr	:	78.8, 78.1
0 CH/C	:	65.1 – 61.4	9 CH	:	64.8 – 61.1	10 CH/C	:	65.1 – 63.3
CH_2	:	29.7	CH_2	:	30.1	CH_2	:	29.8

Figure 3. ^{1}H and ^{13}C NMR assignments for tetrabromides **12**–**14** and cycloadducts **21**, **23**, and **25** (C_6D_6, δ, J [Hz]).

ing Br···HCH distances of about 2.6, 1.9, and 2.6 Å, respectively, was convincingly manifested in $\Delta\delta_{CH_2}$ (C_6D_6) $=1.63$ and 1.77 for **21** ($\delta=6.15/4.52$) and **23** ($\delta=6.38/4.61$), respectively (cf. $\delta_{CH_2}=6.31$ for **25**, which is *C*s symmetrical, and thus different from the MMFF structure in Figure 2).



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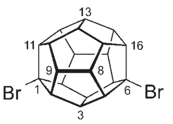

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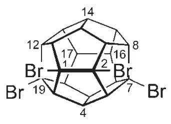


29

X-ray crystal structures:[33] From X-ray crystal-structural analyses of dodecahedral bromides more information was expected as to the way the rigid dodecahedral skeleton adjusts to the strain introduced by voluminous substituents.[7,34] Unfortunately, of the newly prepared oligobromides only crystals of 1,2,3-tribromide **11** proved suitable for an analysis.[35] As complementation, in

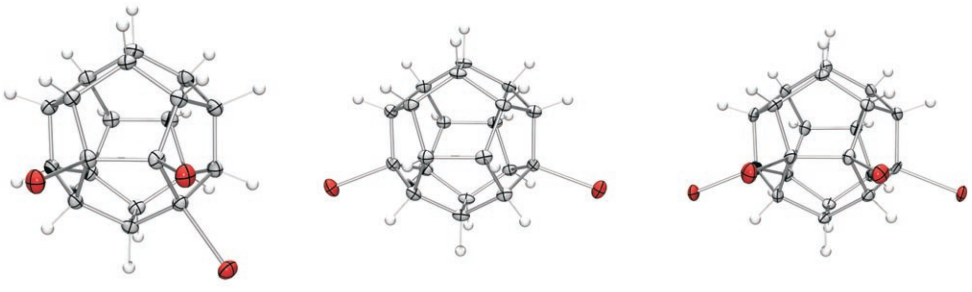

11 **28a** **29**

Figure 4. ORTEP plots of **11, 28**, and **29**.

Figure 4 the structures secured for the 1,6-dibromide **28** (see Scheme 4) and 1,2,7,19-tetrabromide **29** are presented. The latter had been obtained through brominative decarboxylation of the 8,9-dibromo-1,6-dicarboxylic acid.[14c] To reduce rigid-body motions, the measurements were made at 100 K.

The two reported X-ray diffraction structures of parent $C_{20}H_{20}$ dodecahedrane show perfectly eclipsed hydrogen atoms around the periphery, average pentagon angles of 107.6° (108.0°) and C−C bond lengths of 1.545 (1.538) Å[1a,36] (1.545 Å calculated, MM3).[37] Recent IR, Raman, and inelastic neutron scattering spectra make it likely that the experimental C−C bond lengths are shortened by disorder in the crystals and should be revised to 1.558 Å (periodic DFT calculation).[38] It was understood that the crystal structures of the bromides **11**, **28**, and **29** could be even more influenced by intermolecular forces (repulsion, electrostatic, and dispersion terms).[39]

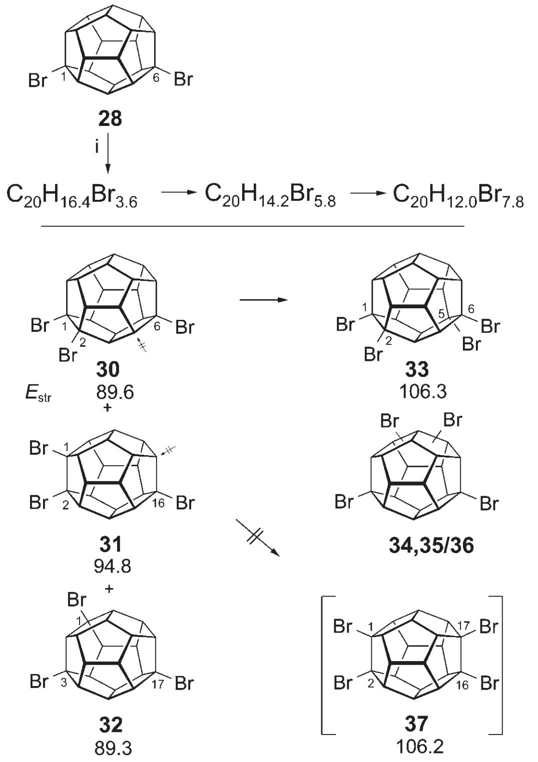
For C_{2v}-symmetrical **28** with its two bromine atoms far apart from each other, the unit cell comprises two different nonsymmetrical molecules (a, b) for which the two halves of the molecule lie on a plane of symmetry. The C−C bond lengths vary between 1.540–1.559 (1.539–1.558) Å, the C−CBr bonds between 1.543–1.556 (1.536–1.555) Å, the C-C-C angles between 107.0–109.5 (107.1–109.3)°, and the C-C-Br angles between 109.6–111.1 (109.6–110.6)°. In both isomers, one of the two C−Br bonds is somewhat shorter (1.966/1.954 Å; 1.992/2.002 Å), undoubtedly due to the packing in the unit cell. In the crystal structure of tetrabromide **29** with its additional pair of vicinal bromine atoms, symmetry is again lost. The variation of the C−C (1.531–1.560 Å) and C−CBr (1.532–1.568 Å) bond lengths is somewhat broader than in **28**(a,b). At a Br1···Br2 nonbonding distance of 3.29 Å—considerably smaller than the sum of the van-der-Waals radii (3.8–4.0 Å) and even smaller than the shortest intermolecular Br···Br distance in crystalline bromine (3.31 Å)[40]—the BrC−CBr bond (1.567 Å) is not extraordinarily elongated. The C-C-C angles (107.0–109.1°) vary as in **28**(a,b). Of the C-C-Br angles, the vicinal ones are considerably larger (108.0–116.8° vs. 108.3–110.1°). The two vicinal C−Br bonds (1.964, 1.968 Å) are at first sight surprisingly, not only significantly shorter than the non-vicinal ones (1.983, 1.985 Å) but also nearly ecliptical (Br-C1-C2-Br 0.3(4)°). Significant torsional Br-C-C-H/H-C-C-H angles exist (with considerable uncertainty) such as Br-C1-C11-H 8(4)°, Br-C3-C7-H 12(3)°, Br-C**7**-C8-H 7(4)°, Br-C19-C20-H 5(4)°, H-C3-C4-H 4(6)°, H-C4-C5-H 8(6)°, H-C9-C10-H 10(6)°, and H-C12-C13-H 9(6)°. In the again unsymmetrical structure of tribromide **11** with its three contiguous C−Br bonds, the length of the C−C (1.536–1.555 Å) and C−CBr bonds (1.543–1.555 Å), the angles C-C-C (106.4–108.8°) and C-C-Br (113.9–115.9°) are close to those in **29.** The two BrC−CBr bonds (1.578, 1.578 Å) are as opposed to those in **29** substantially elongated, the three C−Br bonds (1.965, 1.971, 1.975 Å), at Br···Br distances of 3.22 and 3.26 Å, are of equal length and similar to the vicinal C−Br bonds in **29**. Remarkable torsional angles are found, again with high uncertainty, for Br-C1-C2-Br 5.4(2)°, Br-C2-C3-Br 4.2(3)°, H-C4-C20-H, H-C12-C19-H 3(4)°, and H-C19-C20-H 4(4)°.

Conclusion

Electrophilic bromination of monoene **3** and diene **4** did not allow selective oligobromination. Under forcing conditions traces of $C_{20}H_xBr_{10}$ decabromides marked the highest observable degree of substitution. Nevertheless, the di-/tribromides **10/11** and tetrabromoenes **12–14** were obtained in manageable quantities. Particularly the latter ones gave insight into the reactivity of such highly bent yet inductively and sterically highly deactivated C=C double bonds and thus became much appreciated model compounds for the hardly workable products met en route to the C_{20} fullerene.[6,7,14] The X-ray analyses for bromides **11, 28**, and **29** not only confirmed the NMR spectral assignments but illustrated once more[35] how, irrespective of packing effects, the rigid dodecahedral skeleton copes with steric overcrowding by voluminous substituents, particularly bromine atoms, in fact by a sum of measures of different weighting such as changes in bond lengths, bond angles, and out-of-plane distortions. The experiments summarized in the Appendix again exclude any preparatively exploitable steric control by bromine substituents and, with the view on C_{20} fullerene as the ultimate target,[6,7] add to our understanding, i) that installation of more than eight to ten bromine atoms onto **1** would require extreme reaction conditions, ii) that in dodecahedral bromides with $[Fe_2(CO)_9]$ *cis*-1,2-HBr/*cis*-Br_2 eliminations can be effected with in situ complexation of the highly bent olefins, and iii) that even η^5-complexation might be a helpful protecting measure. All novel functionalized dodecahedranes survived the electron-impact induced loss of their functionalities without damage to the dodecahedral skeletons, additional support for the prior interpretation that the observed $C_{20}H_X{}^+$ ions do indeed represent (hydro)fullerenes.

Appendix

Radical bromination of 1,6-dibromododecahedrane (28): Very early in our explorative search for defined oligobromododecahedranes as precursor molecules of unsaturated dodecahedranes it was clear that due to the rapidly increasing number of isomers selective oligobromination of parent dodecahedrane **1** would be problematic (see Table 1 in ref. [6]). It was—admittedly naively—speculated that a calculated (MM2) increase in strain energy of about 3.5 kcal mol^{-1} for 1,2- verus 1,3-dibromination (see Table 2 in ref. [6]) might exert a preparatively exploitable steric effect in the ultimate selective formation of the T_h-symmetrical 1,3,5,8,10,13,16,19-octabromide (tetrahydro-**17**), the highest non-vicinally brominated derivative of **1**.[5] As a supplement to the bromination study with **1**,[5,6] bromination of the 1,6-dibromide **28** in boiling $BrCCl_3$, with the relatively voluminous CCl_3 radical as chain carrier, was investigated (Scheme 4). The dibromide **28** had been obtained in very high yield from the respective dicarboxylic acid via a Barton brominative decarboxylation protocol with $BrCCl_3$ as bromine source.[1a] With the here reported study, the side products (up to 10 %) could be identified as tribromides **12**–**14**. Under the given conditions, the intermediate "Platonic radicals"[41] were obviously structurally inert, in contrast to the cationic intermediates of Scheme 2.

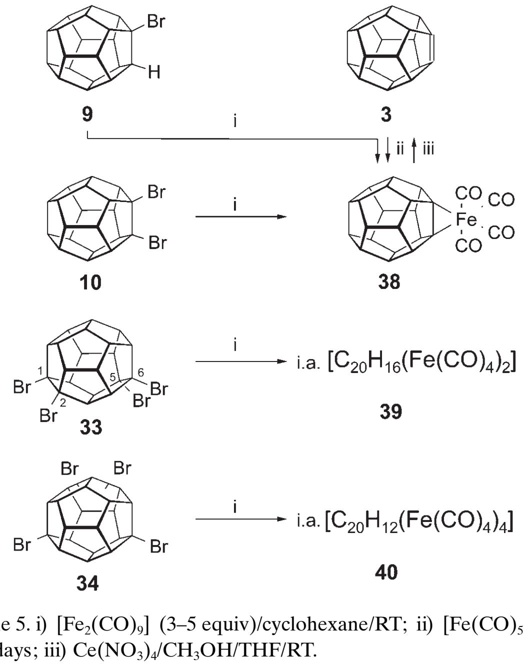


Scheme 4. **28** (0.2 mmol)/$BrCCl_3$ (0.2 mol)/reflux/24 h (i); 4 days (ii); 8 days (iii). Calculated strain energies (kcal mol^{-1}, B3LYP/6–31G*[18]).

After refluxing **28** in a vast excess of $BrCCl_3$ for 24 h, the product mixture of more than ten components (TLC, MS, 110 mg) and an elemental composition of $C_{20}H_{16.4}Br_{3.6}$ consisted mainly of tri- and tetrabromides. After four days, the elemental composition had changed to $C_{20}H_{14.2}Br_{5.8}$ and contained mainly hexabromides, and after eight days it had changed further to $C_{20}H_{12.0}Br_{7.8}$ and contained mainly hepta-/octabromides with traces of nonabromides. Even longer reaction times raised the bromine content somewhat yet not significantly above the highest degree of bromination. The fraction obtained through exhaustive extraction of the $C_{20}H_{16.4}Br_{3.6}$ product mixture with CCl_4 could be separated by high-pressure liquid chromatography (HPLC, reverse phase) and crystallization into three tribromides (**30** (1,2,6), **31** (1,2,16), **32** (C_s, 1,3,17)) and four tetrabromides (**33** (C_2, 1,2,5,6), **34** (unknown substitution pattern), **35**/**36** (not separated, unknown patterns)). The C_{2v}-symmetrical 1,2,16,17-tetrabromide **37**,[14d] which is comparably strained to **33** and of particular interest as an alternative precursor of diene **4**,[4b] could be confidently excluded. The substitution patterns of **30**–**33** are based on the NMR/MS spectral criteria. Clearly, the bromine substituents in **28** do not exert the originally aspired steric control. Of the four characterized tri-/tetrabromides three, like **10**, **11**, **12**, and **13** of Scheme 1, feature vicinal disubstitution and the radical bromination even under these rather forcing reaction conditions ended with traces of $C_{20}H_{11(9)}Br_9$ nonabromides, far from the desired $C_{20}Br_{20}$.[6]

Explorative elimination/in situ complexation experiments: From prior experimentation it had been learnt that besides $C_{20}H_{16}$ dienes such as **4**, more strained $C_{20}H_{14}$ trienes, and even $C_{20}H_{12}$ tetraenes have a limited lifetime in degassed solution even at room temperature as long as the highly bent C=C double bonds are nonconjugated and protected against dimerization by four allylic hydrogens.[4,14] With the C_{20} fullerene as the ultimate synthetic goal, the question was posed up to what degree of unsaturation, dodecahedranes with C=C double bonds increasingly less protected, as neutrals or anions, could—like fully unsaturated oligoquinanes[42]—be stabilized as metal complexes. With the π-electron density shifted to the outer faces, such highly bent cycloalkenes seemed predisposed for complexation.

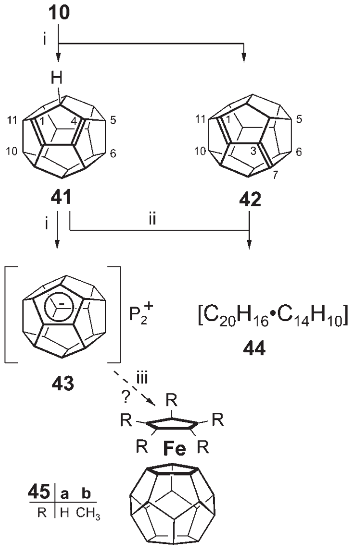
As announced in a preliminary communication and detailed in the Experimental Section $[Fe_2(CO)_9]$ effects in the sterically compressed periphery of monobromide **9** *cis*-β-HBr eliminations and in 1,2-dibromide **10** *cis*-β-Br_2 elimination providing in situ protection by rather strongly coordinated $Fe(CO)_4$ ligands.[11d,43] The $[C_{20}H_{18}Fe(CO)_4]$ complex **38**, isolated in good yield (75–80 %) and spectroscopically fully characterized (IR, ^1H, ^{13}C NMR, MS), also arose from the reaction of dodecahedrene **3** with $Fe(CO)_5$ (Scheme 5).[43,44] It proved persistent for days in solution



Scheme 5. i) $[Fe_2(CO)_9]$ (3–5 equiv)/cyclohexane/RT; ii) $[Fe(CO)_5$ /THF/RT/3 days; iii) $Ce(NO_3)_4/CH_3OH/THF/RT$.

($CHCl_3$, benzene) and as a solid in air. Mild oxidation conditions ($Ce(NO_3)_4/CH_3OH$/THF/RT) deprotected **38** to **3** (E_p ≈1.4 eV[15b]). Explorative experiments with the tetrabromides **33** and **34** furnished pertinent information. Analogous treatment of **33** and **34** with $[Fe_2(CO)_9]$ caused primarily elimination of two equivalents of Br_2 and four equivalents of HBr, respectively. According to the MS and TLC analyses the beige crystalline solids secured after repeated crystallization of the bromine-free reaction products from ethanol consisted largely of a bis complex (presumably **39**, ca. 85 %) and at least partially a mixture of tetrakis complexes (**40**). As noted before, the MS (EI) spectra were somewhat puzzling in that the sequential loss of the $[Fe(CO)_4]$ ligands was accompanied by a significant uptake of hydrogen.

With 1,2-dibromide **10** a possibility arose to directly identify a first dodecahedrane with conjugated C=C double bonds. Conjugation in the s-*cis*/s-*trans* dienes **41**/**42** (Scheme 6) would create, compared with diene **4** (Figure 1), even higher olefinic pyramidalization (ϕ up to 52°, MM3), reduced steric protection, and particularly enhanced tendency for thermal dimerization or polymerization. As repeatedly pointed out, *cis*-β-eliminations on the very encumbered dodecahedral periphery are (only) possible with the very small, very strong but weakly nucleophilic "naked" F^- Schwesinger-base (P_2F, pH° in benzene ca. 35[9c]). Though *cis*-isomer **41**, which is somewhat more stable than **42**,[45] was calculated to be a much weaker acid than cyclopentadiene (pK_s ca. 24 versus ca. 18 (CH_3CN), B3LYP/6–32G*)[11c,27b]—the p orbitals of the cyclopentadienyl anion **43** deviate significantly from parallel orientation—it should still be amenable to deprotonation by the F^- base. Upon mixing about 10^{-2} M C_6D_6 solutions of **10** and six equivalents of perdeuterated, possibly not perfectly dry base ($[D_{36}]P_2F$ was kindly provided by the Schwesinger group) P_2Br was momentarily deposited. After total consumption (NMR control), the MS spectrum displayed intense *m/z* 256 ions for **41**/**42** (and *m/z* 274 for $[C_{20}H_{17}OH]^+$, hydroxylated monoene(s), cf. **15**, **16**).[46] With numerous ^1H multiplets between $\delta = 3.6$–2.4 ppm, and 27 ^{13}C signals between $\delta = 168.8$–163.4 (C=C) and 80.4–60.0 ppm (114.5–103.5 for C–OH), the evidence for the formation of **41** and **42** was rather convincing (cf. for diene **4**: ^1H: 3.60–2.94 ppm; ^{13}C: 170.5, 73–57 ppm)[4b]). The spectra recorded for various runs were, however, too complex, to establish the presence of anion **43**. Whilst dimerization of **41**/**42** was apparently still rather slow, cycloaddition of anthracene (persistent towards P_2F) was rapid. After addition of the reagent (3 equiv) to a freshly prepared reaction solution, MS control confirmed the formation of unsaturated $C_{20}H_{16}$·anthracene monoadducts (**44**, *m/z* 435 (44) $[M+H]^+$, 434 (30) $[M]^+$, 257 (100), 256 (45) $[\mathbf{41/42}]^+$). The oxygen-sensitivity of the cycloadducts prohibited their separation, and their steric hindrance the catalytic hydrogenation to give the common, fully characterized saturated $C_{20}H_{18}$·anthracene adduct obtained from **3**.[4c] Since anion **43** could not be spectroscopically identified, its possible interception with $[FeCp_2]$ (ferrocene) or [Fe(tmeda)/Cp*Cl] (Cp* = C_5Me_5) was tested, efficient, against P_2F sufficiently inert [FeCp(Cp*)] transfer reagents.[47] Indeed, exposure of **10** to P_2F in the presence of $[FeCp_2]$ or [Fe(tmeda)/Cp*Cl] provided after standard workup very complex (TLC) dark lime-colored solids, for which MS analyses indicated the presence of **45a**,**b**.[48]



Scheme 6. i) $[D_{36}]P_2F$ (6 equiv)/C_6D_6/RT; ii) anthracene (3 equiv)/RT; iii) $[FeCp_2]$ (ferrocene), [Fe(tmeda)/Cp*Cl]/RT.

Experimental Section

General: Melting points (m. p.) were determined on a Monoskop IV (Fa. Bock) instrument and are uncorrected. Elemental analyses were performed by the Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. Analytical TLC: Merck silica gel plates with F254 indicator with detection by UV, $KMnO_4$ or phosphomolybdic acid solution (PMS). IR spectra were recorded with a Perkin Elmer 457 spectrometer, UV spectra with Perkin Elmer Lamda 15 spectrometer, MS spectra with Finnigan MAT 44S and MAT 8200 instruments (EI, 70 eV, if not specified otherwise), ^1H NMR spectra with Bruker WM 250, AM 400, and DRX 500 spectrometers (if not specified otherwise the 400 MHz spectra in $CDCl_3$ are given), ^{13}C NMR spectra with Bruker AM 400 (100.6 MHz), DRX 500 (125.7 MHz) spectrometers (if not specified otherwise, the 100.6 MHz spectra in $CDCl_3$ are given); chemical shifts (ppm) were recorded relative to TMS ($\delta = 0$), and coupling constants are in Hertz. Assignments marked with an asterisk are interchangeable. Assignments have been confirmed by homo- and heteronuclear decoupling and H′H, H′X correlation experiments. The silica gel used for column chromatography was Merck (0.040–0.063 mm) or ICN Biomedicals GmbH (0.032–0.063 mm). All reactions have been performed in anhydrous, degassed solutions with carefully dried reagents, the reactions with P_2F bases and metal complexes in a glovebox (M. Braun Labmaster 130, the O_2 and H_2O values were below 1 ppm, solvents removed from the atmosphere by a special charcoal filter).

Bromination of 3:

i): A suspension of **3** (52 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) was titrated with a solution of Br_2/CH_2Cl_2 (ca. 2×10^{-1} M; instantaneous evolution of HBr). After consumption of about one equivalent of Br_2 (ca. 1 mL), the homogeneous solution contained about 17 mg of residual **3**. After consumption of about five equivalents of bromine (ca. 5 mL of reagent solution), **3** was totally consumed. On concentration in vacuo the solid brownish residue (ca. 120 mg) consisting of a multitude of components (TLC, GC/MS) was chromatographed on silica gel (CCl_4/cyclohexane 1:1) providing **9** (10 mg, 15 %), **10** (29 mg, 35 %), **11** (18 mg, 18 %), and an approximate 5:1 mixture (42 mg) of mainly unsaturated tetra-/pentabromides (at least six, TLC, MS).

ii): To a suspension of **3** (78 mg, 0.30 mmol) in a mixture of CH_2Cl_2 (5 mL)/ethylene oxide (2.0 g, 50 mmol) at 0 °C, Br_2 (480 mg, 3.0 mmol) was added (no evolution of HBr). After stirring for 2 min the homogeneous solution was concentrated in vacuo, the red solid residue chromatographically (silica gel, CCl_4/*n*-hexane 1:4) separated into **9** (trace), **10** ($R_f = 0.36$, 20 mg, 16 %), **11** ($R_f = 0.21$, 21 mg, 14 %), unsaturated tetrabromides ($C_{20}H_{14}Br_4$, $R_f = 0.06–0.08$, up to 85 mg, ca. 50 %), and (unsaturated) penta-/hexabromides ($R_f = 0.5–0.4$, ca. 15 %). The 50 % fraction consisting of three major and two trace components (TLC) was separated by reverse-phase chromatography (LiChrospher RP-18 column/CH_3CN (68 %)/THF(2 %)/H_2O(30 %)/flow rate of 1 mL min^{-1}, detection at 246 nm) into **12** (8–10 mg, retention time 9.8 min), and a ca. 3:1 mixture of **13**/**14** (60 mg, retention time 11.2 min). Through crystallization (THF/CH_3CN 1:1), the mixture of **13**/**14** was separated into pure **13** (30 mg, $R_f = 0.64$, CCl_4/CH_2Cl_2 5:1) and highly enriched **14** (10 mg, $R_f = 0.52$, CCl_4/CH_2Cl_2 5:1). When such a run was worked up after 15 min, trace quantities of **9**, **10** (and **11**?), and about 15 % each of **12** and **13** were isolated in addition to (unsaturated) penta-/hexabromides and traces of heptabromides ($C_{20}H_{15(13)/14(12)/13(11)}Br_{5/6/7}$).

iii): A solution of **3** (52 mg, 0.2 mmol) in bromine (36.0 g, 200.0 mmol) was stirred at 0 °C for four days. After evaporation in vacuo, TLC/GC/MS analysis of the dark red solid residue attested to the presence of altogether 10 % of **9**, **10**, and **11**, and of several (unsaturated) tetra-/penta-/hexabromides ($C_{20}H_{16(14)/15(13)/14(12)}Br_{4/5/6}$) and traces of heptabromides ($C_{20}H_{13(11)}Br_7$). After a reaction time of seven days, hepta- to decabromides were still present in only trace quantities (MS).

If in these bromination experiments moisture was not perfectly excluded hydroxylated bromides **15** (R_f (CCl_4/CH_2Cl_2 5:1) = 0.64), **16** (R_f (CCl_4/CH_2Cl_2 5:1) = 0.52), and of composition $C_{20}H_{16}Br_{2(3)}OH_{2(1)}$ were formed in varying quantities.

1,2-Dibromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]-icosane (10): Colorless crystals, m. p. 257 °C; IR: $\tilde{\nu} = 2944, 871, 745, 690$ (C-Br) cm^{-1}; ^{1}H NMR: $\delta = 4.10$ (m, 3-,9-,11-,20-H), 3.68 (m, 7-,8-,12-,19-H), 3.54 (m, 4-,10-H), 3.41 ppm (m, 5-,6-,13-,14-,15-,16-,17-,18-H); $J_{3,4(4,20;9,10;10,11)} = 12.0$ Hz; ^{1}H NMR (C_6D_6): $\delta = 4.08$ (m, 3-,9-,11-,20-H), 3.25 (m, 7-,8-,12-,19-H), 3.11 (m, 4-,10-H), 2.86 ppm (m, 5-,6-,13-,14-,15-,16-,17-,18-H); ^{13}C NMR (C_6D_6): $\delta = 98.4$ (C-1,-2), 80.5 (C-3,-9,-11,-20), 66.0 (C-5,-14)*, 65.9 (C-16,-17)*, 65.8 (C-7,-8,-12,-19)*, 65.8 (C-6,-13,-15,-18)*, 62.0 ppm (C-4,-10); MS: *m/z* (%): (339 (97), 337 (100)) $[M-(H)Br]^+$, (258 (20), 257 (39), 256 (10)) $[M-2(H)Br]^+$, 215 (5), 207 (10), 152 (6), (129 (14), 128 (13)) $[M-2(H)Br]^{2+}$, 127 (6), 44 (17); elemental analysis calcd (%) for $C_{20}H_{18}Br_2$ (418.2): C 57.45, H 4.34; found: C 57.21, H 4.22.

1,2,3-Tribromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]-icosane (11): Colorless crystals, m. p. 256 °C (CH_2Cl_2, decomp); IR: $\tilde{\nu} = 2948, 858, 760, 680$ (C-Br) cm^{-1}; ^{1}H NMR: $\delta = 4.31$ (t, 9-H), 4.14 (m, 4-,7-,11-,20-H), 3.68 (m, 5-,14-,15-,19-H), 3.57 (m, 8-,10-H), 3.42 ppm (m, 6-,12-,13-,16-,17-,18-H); $J_{8,9} = 12.2$ Hz; ^{1}H NMR (C_6D_6): $\delta = 4.19$ (t, 9-H), 4.02 (m, 4-,7-,11-,20-H), 3.18 (m, 5-,14-,15-,19-H), 3.06 (m, 8-,10-H), 2.78 (m, 6-,12-,13-,16-H), 2.72 ppm (17-,18-H); $J_{8,9} = 12.2$ Hz; ^{13}C NMR: $\delta = 101.8$ (C-2), 97.5 (C-1,-3), 80.7 (C-4,-9,-20)*, 80.4 (C-7,-11)*, 67.7 (C-14,-15), 65.9, 65.7, 65.4, 65.3, 61.8 ppm (C-8,-10); MS: *m/z* (%): 497 (1) $[M]^+$, (418(28), 417 (12), 416 (53), 415 (28)) $[M-(H)Br]^+$, (339 (97), 337) $[M-2(H)Br]^+$, 258 (32), (257 (35), 256 (15)) $[M-3(H)Br]^+$, 215 (5), 207 (11), 165 (10), 129 (19), 128 (18) $[M-2Br-HBr]^{2+}$, 115 (12), 44 (21); elemental analysis calcd (%) for $C_{20}H_{17}Br_3$ (497.1): C 48.33, H 3.45; found: C 48.49, H 3.18.

Crystals suitable for the X-ray analysis were obtained through diffusion of diethyl ether into a saturated solution of **11** in CH_2Cl_2.

3,4,9,11-Tetrabromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}-.0^{13,17}]icos-1-ene (12): Colorless crystals, m.p. 183 °C (THF/CH_3CN 1:1); IR (PTFE): $\tilde{\nu} = 2950, 2920, 1729, 1555, 1472, 1005, 940, 634, 504$ cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 4.08$ (d, 10-H), 3.82 (d, 20-H), 3.63 (t, 5-H), 3.61 (dd, 7-H), 3.47 (m, 8-H), 3.21 (dd, 12-H), 2.95 (q, 14-H), 2.94 (dd, 19-H), 2.78 (dd,, 18-H), 2.68 (dd, 6-H), 2.64 (q, 13-H), 2.63 (q, 15-H), 2.28 ppm (m, 16-,17-H); $J_{5,6} = J_{5,18} = 12.0$, $J_{6,7} = 11.2$, $J_{7,8} = 9.9$, $J_{8,15} = 11.2$, $J_{10,14} = 11.5$, $J_{17,18} = 11.2$, $J_{18,19} = 12.0$, $J_{19,20} = 9.8$ Hz; ^{1}H NMR (500 MHz): $\delta = 4.16$ (d, 10-H), 4.06 (d, 20-H), 4.02 (t, 5-H), 3.90 (m, 7-H)*, 3.75 (m, 8-H)*, 3.72 (m, 12-H), 3.65 (m, 14-,18-,19-H)*, 3.55 (m, 6-,13-,15-H)*, 3.25 ppm (m, 16-,17-H); $J_{10,14} = 11.5$, $J_{19,20} = 9.6$ Hz; ^{13}C NMR (C_6D_6): $\delta = 163.1$ (C-2), 161.8 (C-1), 93.3 (C-3)*, 92.7 (C-4)*, 91.5 (C-9)**, 91.4 (C-11)**, 78.9 (C-10), 75.9 (C-20)**, 74.9 (C-5)**, 74.6 (C-7)***, 74.5 (C-8)***, 74.2 (C-12)***, 63. 4, 63.2, 62.5, 61.9, 61.9, 61.7, 61.4, 59.1 ppm; MS: *m/z* (%): (496 (35), 495 (21), 494 (100), 493 (98.7), 490 (33)) $[M-(H)Br]^+$, (415 (5), 414 (3), 413 (6), 412 (1)) $[M-2(H)Br]^+$, (336 (2), 335 (12), 334 (3), 333 (11)) $[M-3(H)Br]^+$, (255 (3), 254 (13), 253 (19), 252 (16), 250 (10)) $[M-4(H)Br]^+$, 227 (2), (127 (13), 126.5 (16), 126 (35), 125 (11)) $[M-4(H)Br]^{2+}$, 113 (19), 80 (4); $C_{20}H_{14}Br_4$ (574.0); $C_{20}H_{14}{}^{79}Br^{81}Br_2$; HRMS: *m/z* calcd: 492.8625, found: 492.8622; $C_{20}H_{13}{}^{79}Br^{81}Br$; calcd: 412.9363, found: 412.9363. $C_{20}H_{14}{}^{79}Br$; calcd: 333.0280, found: 333.0278; $C_{20}H_{13}$; calcd: 253.1018, found: 253.1017; $C_{10}H_6$; calcd: 126.0469, found: 126.0469.

3,4,9,20-Tetrabromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}-.0^{13,17}]icos-1-ene (13): Colorless crystals, m. p. 192 °C (THF/CH_3CN 1:1); IR: $\tilde{\nu} = 2959, 2929, 1724, 1452, 645, 628, 559, 516$ cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): $\delta = 3.85$ (t, 5-H), 3.68 (dd, 7-H), 3.52 (m, 8-H), 3.50 (10-H), 3.43 (m, 19-H), 3.40 (m, 11-H), 2.79 (m, 14-H), 2.77 (m, 18-H), 2.75 (m, 6-H), 2.73 (m, 12-H), 2.67 (m, 15-H), 2.31 (m, 13-H), 2.29 ppm (m, 16-,17-H); $J_{5,6} = J_{5,18} = 12.0$, $J_{7,8} = 9.9$, $J_{8,15} = 10.6$, $J_{10,11} = 11.2$, $J_{11,12} = 10.5$, $J_{12,13} = 9.9$, $J_{13,14} = J_{14,15} = 11.2$ Hz; ^{1}H NMR (500 MHz): $\delta = 4.15$ (t, 5-H), 4.00 (dd, 7-H), 3.93 (m, 8-,10-H), 3.83 (t, 11-H), 3.78 (dd, 19-H), 3.65 (q, 14-H), 3.52 (m, 6-,12-,15-,18-H), 3.38 (m, 13-H), 3.68 ppm (m, 16-,17-H); $J_{5,6} = J_{5,18} = 12.3$, $J_{6,7} = 10.2$, $J_{7,8} = 10.2$, $J_{10,11} = 11.3$. $J_{11,12} = 10.7$, $J_{13,14} = 11.0$ Hz; ^{13}C NMR: $\delta = 162.8$ (C-2), 158.2 (C-1), 98.1 (C-4), 93.3 (C-3)*, 91.9 (C-9)*, 90.1 (C-20)*, 78.9, 78.8, 78.3, 78.1, 77.3, 75.9, 64.9, 63.1, 62.8, 62.4, 62.0, 61.5, 60.1, 59.4 ppm; MS: *m/z* (%): 576 (1), (575 (2), 574 (1), 573 (3), 572 (1), 571 (2)) $[M]^+$, (498 (6), 497 (31), 496 (15), 495 (100), 494 (12), 493 (99), 492 (6), 491 (32)) $[M-(H)Br)]^+$, (416 (3), 415 (18), 414 (4), 413 (20), 412 (6)) $[M-2(H)Br]^+$, (337 (7), 336 (5), 335 (26), 334 (6), 333 (22), 332 (2), 331 (3)) $[M-3(H)Br]^+$, 257 (3), 256 (2), 255 (8), (254 (21), 253 (35) 252 (35), 251 (9), 250 (15)) $[M-4(H)Br]^+$, 248 (3), 247 (2), 246 (2), 240 (3), 226 (11), 207 (5), 127 (4), 126 (17), 125 (5) $[M-4HBr]^{2+}$, 120 (4), 113 (9), 112 (2), 57 (2); $C_{20}H_{13}$ (253.3); HRMS: *m/z* calcd: 253.1018, found: 253.1017; elemental analysis calcd (%) for $C_{20}H_{14}Br_4$ (574.0): C 41.85, H 2.46; found: C 41.69, H 2.30.

3,9,11,20-Tetrabromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}-.0^{13,17}]icos-1-ene (14): Colorless crystals (ca. 85 % pure). ^{1}H NMR (500 MHz, C_6D_6): $\delta = 4.07$ (d, 4-,10-H), 3.42 (m, 7-,8-,12-,19-H), 2.94 (q, 5-,14-H), 2.61 (m, 6-,13-,15-,18-H), 2.24 ppm (m, 16-,17-H); $J_{4,5} = J_{10,14} = 11.5$, $J_{5,6} = J_{5,18} = J_{13,\ 14} = J_{14,15} = 11.5$ Hz; ^{13}C NMR (C_6D_6): $\delta = 164.4$ ppm (C-1,-2).

2-Bromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosanol (15): Colorless crystals, m. p. 232 °C. ^{1}H NMR (C_6D_6): $\delta = 4.02$ (t, 3-,9-H), 3.65 (t, 11-,20-H), 3.40 (m, 7-,8-H), 3.3–3.35 (m, 4-,10-,12-,19-H), 3.15 (br. m., 5-,14-H), 3.0–2.9 ppm (m, 6-,13-,15-,16-,17-,18-H); ^{1}H NMR (500 MHz): $\delta = 4.01$ (m, 11-,20-H), 3.82 (t, 3-,9-H), 3.62 (m, 7-,8-H), 3.52 (m, 12-,19-H), 3.49 (br. m.,4-,5-,10-,14-H), 3.4–3.3 ppm (m, 6-,13-,15-,16-,17-,18-H); $J_{10,11} = 11.6$ Hz; ^{13}C NMR (C_6D_6): $\delta = 118.2$ (C-OH), 96.6 (C-Br), 80.0 (C-3,-9), 68.2 (C-11,-20), 66.5, 66.2, 66.1, 66.0, 65.7, 65.5, 65.2, 61.7 ppm; MS: *m/z* (%): (340 (6), 339 (25)) $[M-OH]^+$, 338 (10), 337 (26), 259 (100), 258 (51) $[M-OH-Br]^+$, 257 (37), 256 (6) $[M-HOH-HBr]^+$**;** elemental analysis calcd (%) for $C_{20}H_{19}BrO$ (355.3): C 67.62, H 5.29; found: C 67.43 H 5.01.

2,3-Dibromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]-icosanol (16): Colorless crystals, m. p. 242 °C. ^{1}H NMR (C_6D_6): $\delta = 4.14$ (t, 7-H), 4.07 (m, 9-H), 3.95 (t, 4-H), 3.68 (m, 20-H), 3.61 (m, 11-H), 3.38 (m, 10-H), 3.32 (m, 8-H), 3.22 (m, 6-,12-H), 3.05 (m, 3 H), 2.85 (br.m., 3 H), 2.72 ppm (m, 2 H); $J_{8,9} = 11.8$, $J_{10,11} = 12.2$, $J_{15,20} = 10.9$ Hz; ^{1}H NMR (500 MHz): $\delta = 4.21$ (t, 7-H), 4.08 (m, 4-,9-H), 3.82 (m, 11-,20-H), 3.65 (m, 8-,10-H), 3.56 (m, 4 H), 3.43–3.31 ppm (br.m., 6 H); ^{13}C NMR (C_6D_6): $\delta = 117.8$ (C-1), 100.5 (C-2), 97.6 (C-3), 80.9 (C-4)*, 80.9 (C-7)*, 77.1 (C-

9)*, 70.4, 66.3, 66.2, 65.7, 65.5, 65.5, 65.0, 64.9, 64.8, 64.7, 64.3, 64.0, 62.0, 61.2 ppm; MS: *m/z* (%): (420 (4), 419 (20), 418 (10), 417 (40)) $[M-\mathrm{OH}]^+$, 416 (6), 415 (21), (339 (45), 338 (13), 337 (53)) $[M-\mathrm{OH}-(\mathrm{H})\mathrm{Br}]^+$, 336 (3), 335 (8), 301 (6), 300 (1), 299 (8), 298 (1), 297 (3), 259 (22), 258 (27), 257 (100) $[M-\mathrm{OH}-2\mathrm{Br}]^+$, 256 (10), 255 (15), 254 (8) $[M-\mathrm{HOH}-2\mathrm{HBr}]^+$; elemental analysis calcd (%) for $C_{20}H_{18}Br_2O$ (434.2): C 55.33, H 4.18; found: C 55.10, H 4.01.

Bromination of 4: To a suspension of **4** (38 mg, 0.15 mmol) in a mixture of CH_2Cl_2 (5 mL) and ethylene oxide (2.0 g, 50 mmol) stirred at 0 °C, bromine (480 mg, 3.0 mmol) was added (no evolution of HBr). After 2 min it was concentrated in vacuo. Chromatographically (silica gel, CCl_4/*n*-hexane 1:4), only traces of the 1,6-/1,16-dibromides[14c,22] could be identified. MS analysis revealed the formation of mainly (unsaturated) penta-/hexabromides, traces of hepta- to decabromides and occasionally some hydroxylated species (e.g. $C_{20}H_{16}Br_2(OH)_2$). After a reaction time of 1 h, no higher bromides were detected.

Dimethyl 8-bromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icos-9-ene-1,6-dicarboxylate (20): To a solution of **19** (20 mg, 0.05 mmol) in benzene (2 mL) at room temperature, a suspension of bis(sym-collidine)bromonium triflate (28 mg, 0.05 mmol) in benzene (2 mL) was added. The rapidly formed homogeneous, yellow solution was stirred until complete conversion (TLC, ca. 20 min), filtered through silica gel, and concentrated in vacuo. The solid residue (one main, two trace components, TLC) was rapidly chromatographed on silica gel (cyclohexane/ethyl acetate 4:1); colorless, air-sensitive crystals of **20** were isolated (18 mg; 79 %), m. p. 157 °C. IR: $\tilde{\nu}=2948$, 2903, 1735, 1435, 1395, 1269, 1203, 1143, 1016, 798, 533 cm^{-1}; ^{1}H NMR (C_6D_6): $\delta=4.58$ (dd, 2-H), 4.52 (d, 7-H), 4.17 (dd, 15-H), 4.02 (dd, 12-H), 3.97 (dd, 14-H), 3.92 (dd, 11-H), 3.60 (ddd, 3-H), 3.58 (m, 20-H), 3.45 (s, OCH_3), 3.41 (m, 5-H), 3.39 (s, OCH_3), 3.30 (ddd, 4-H), 3.20 (dd, 16-H), 3.15 (m, 13-H), 2.78 ppm (m, 17-H); ^{13}C NMR (C_6D_6): $\delta=176.0$ (C=O), 175.9 (C=O), 158.3 (C-9)*, 152.2 (C-10)*, 90.6 (C-Br), 83.9 (C-1)*, 83.1 (C-6)*, 82.1, 78.7, 74.6, 72.4, 70.6, 70.2, 69.9, 68.1, 66.1, 66.0, 65.8, 65.7, 65.6, 62.4, 61,6 ppm; MS: *m/z* (%): (455 (7), 454 (26), 453 (8), 452 (28), 451 (30)) $[M]^+$, (396 (3), 395 (9), 394 (4), 393 (13)) $[M-\mathrm{HCO_2CH_3}]^+$, (375 (5), 374 (26), 373 (83), 372 (21), 371 (15)) $[M-(\mathrm{H})\mathrm{Br}]^+$, (335 (15), 334 (3), 333 (12)) $[M-2\mathrm{HCO_2CH_3}]^+$, 315 (20), 258 (4), 257 (14), 256 (21), 255 (64), 254 (17), 253 (30), 252 (22) $[M-2\mathrm{HCO_2CH_3}-\mathrm{HBr}]^+$, 251 (6), 128 (4), 127.5 (2), 127 (8), 126 (8) $[M-2\mathrm{HCO_2CH_3}-\mathrm{HBr}]^{2+}$, 125.5 (2); elemental analysis calcd (%) for $C_{24}H_{21}BrO_4$ (453.3): C 63.59, H 4.67; found: C 63.39, H 4.45.

2,6,14,19-, 2,6,7,19- and 2,7,14,19-Tetrabromo-21,22-diazadodecacyclo[12.9.0.0^{1,20}.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{15,19}]tricos-21-enes (21), (23), and **(25):** To a solution of the crude mixture of **12–14** ($C_{20}H_{14}Br_4$ fraction, 60 mg, ca. 0.10 mmol) in CH_2Cl_2 (10 mL), a vast excess of CH_2N_2 in diethyl ether was added at 0 °C (solution remained at room temperature yellowish for ten hours). After evaporation in vacuo, the residue was chromatographed (silica gel, CH_2Cl_2) to give colorless crystals of **23** ($R_f=0.31$, 20 mg, 32 %), **21** ($R_f=0.36$. 15 mg, 24 %, trace of **22** ?), and **25** ($R_f=0.5$, 7 mg, 11 %). **21**: M. p. 212 °C; UV: λ_{max} (CH_3CN) = 312 nm; ^{1}H NMR (500 MHz): 6.27 (d, CH_2), 4.92 (d, CH_2), 4.45 (d, 7-,15-H), 4.28 (t, 5-H), 4.08 (m, 3-,13-H), 3.99 (m, 18-H), 3.92 (q, 16-H), 3.82 (m, 8-H), 3.71–3.52 (m,4-,9-,12-,17-H), 3.45 ppm (m, 10-,11-H); $J_{CH2}=19.7$, $J_{4,5}=11.3$, $J_{5,9=}12.4$ Hz; ^{1}H NMR (C_6D_6): $\delta=6.15$ (d, CH_2), 4.52 (d, CH_2), 4.48 (d, 15-H), 4.15 (d, 7-H), 3.95 (t, 5-H), 3.7–3.6(m, 4 H), 3.21 (m, 1 H), 3.03 (t, 1 H), 2.92 (m, 3 H), 2.86 (m, 1 H), 2.55 ppm (m, 10-,11-H); $J_{CH2}=19.7$ $J_{15,16}=12.4$, $J_{8,7}=11.6$ Hz; ^{13}C NMR (C_6D_6): $\delta=95.9$ (C-2), 93.9 (C-6), 92.9 (C-14)*, 92.2 (C-19)*, 85.5, 81.1, 79.8, 78.9, 78.7, 78.3, 65.1, 64.8, 64.8, 64.7, 64.7, 64.9, 64.6, 63.9, 61.4, 61.4, 29.7 ppm; MS: *m/z* (%): [618 (66), 617 (25), 616 (100), 614 (69)] $[M]^+$, 587 (3) $[M-\mathrm{N_2}]^+$, (537 (51), 535 (53)) $[M-(\mathrm{H})\mathrm{Br}]^+$, 509 (40) 507 (39) $[M-\mathrm{N}_{2-}(\mathrm{H})\mathrm{Br}]^+$, (496 (14), 495 (18)) $[M-(\mathrm{H})\mathrm{Br}-\mathrm{CH_2N_2}]^+$, (458 (38), 457 (29), 456 (73), 455 (29), 454 (38)) $[M-2(\mathrm{H})\mathrm{Br}]^+$, (427 (60), 425 (33)) $[M-\mathrm{N_2}\text{–}2(\mathrm{H})\mathrm{Br}]^+$, (415 (21), 414 (10)), $[M-2(\mathrm{H})\mathrm{Br}-\mathrm{CH_2N_2}]^+$, (378 (22), 376 (28), 375 (91)) $[M-3(\mathrm{H})\mathrm{Br}]^+$, 349 (22), 347 (26), 344 (24), 296 (42), 295 (44) $[M-4(\mathrm{H})\mathrm{Br}]^+$, 268 (43), 267 (59), 266 (33) $[M-\mathrm{N_2}\text{–}2\mathrm{HBr}-2\mathrm{Br}]^+$/$[C_{21}H_{14}]^+$, 265 (36), 263 (20) $[C_{21}H_{11}]^+$, 253 (30), 252 (47) $[M-\mathrm{CH_2N_2}-2\mathrm{HBr}-2\mathrm{Br}]^+$/$[C_{20}H_{12}]^+$, 239 (40), 227 (23), 226 (26), 202 (20), 189 (29), 147 (26), 146 (20), 140 (24), 133 (34) $[C_{21}H_{14}]^{2+}$, 132 (29), 127 (21), 126 (27) $[C_{20}H_{12}]^{2+}$, 119 (26); $C_{21}H_{16}{}^{79}Br_2{}^{81}Br_2N_2$; HRMS: *m/z* calcd: 615.8002; found: 615.8004; **23**: M. p. >300 °C. UV: λ_{max} (CH_3CN) = 312 nm; ^{1}H NMR (500 MHz, C_6D_6): $\delta=6.38$ (d, CH_2), 4.61 (d, CH_2), 4.38 (t, 5-H), 4.16 (m, 3-, 8-, 18-H), 3.75 (t, 15-H), 3.05 (m, 4-, 9-, 16-, 17-H), 2.88 (q, 13-H), 2.82 (t, 14-H), 2.65 ppm (m, 10-, 11-, 12-H); $J_{CH2}=19.7$, $J_{3,13}=10.5$, $J_{4,5}=J_{5,9}=12.3$, $J_{14,13}=J_{14,15}=11.3$ Hz; ^{1}H NMR: $\delta=6.33$ (d, CH_2), 4.93 (d, CH_2), 4.55 (t, 3-H), 4.42 (t, 5-H), 4.38 (m, 8-, 18-H), 4.03 (t, 15-H), 3.67 (m, 4-,9-,16-,17-,13-H), 3.43 ppm (m, 10-,11-, 12-,14-H); $J_{CH2}=19.8$, $J_{5,4}=12.0$, $J_{5,9}=12.0$, $J_{8,9}=12.3$, $J_{8,18}=12.0$, $J_{15,14}=11.5$, $J_{15,16}=11.2$ Hz; ^{13}C NMR (C_6D_6): $\delta=103.7$ (C-6), 101.9 (C-7), 94.6-(C-2), 92.6 (C-19), 82.8, 80.9, 79.6, 79.6, 77.7, 77.6, 71.5 (7 C-Br/$C_{substit}$), 64.8, 64.6, 64.5, 64.5, 64.1, 63.9, 61.5, 61.2, 61.1, 30.1(CH_2) ppm; $C_{21}H_{16}Br_4N_2$ (615.9); $C_{21}H_{16}{}^{79}Br_2{}^{81}Br_2N_2$, HRMS: m/z calcd: 615.8002; found: 615.8001. **25:** M. p. > 300 °C. ^{1}H NMR (500 MHz): $\delta=6.19$ (s, CH_2), 4.49 (d, 6-,15-H), 4.21 (dd, 8-,18-H)*, 4.11 (dd, 3-,13-H)*, 3.92 (q, 5-,16-H), 3.75 (m, 4-,9-,12-,17-H), 3.45 ppm (br.m, 10-,11-H); $J_{6,15}=J_{15,16}=12.0$ Hz; ^{1}H NMR (500 MHz, C_6D_6): $\delta=6.31$ (s, CH_2), 4.48 (d, 6-,15-H), 3.87 (dd, 8-,18-H)*, 3.73 (dd, 3-,13-H)*, 3.25 (q, 5-,16-H), 2.88 (m, 4-,9-, 12-,17-H), 2.50 ppm (br.m., 10-,11-H); $J_{6,15}=J_{15,16}=12.0$ Hz; ^{13}C NMR (C_6D_6): $\delta=102.5$ (C-7, −19), 94.0 (C-2, −14), 78.8 (C-6, −15),78.1 (C-3, −8, −13, −18), 65.1 (C-4, −9, −12, −17), 64.8 (C-5, −16), 64.7 (C-1), 64.6 (C-10, −11), 63.3 (C-20), 29.8 (CH_2) ppm; MS: *m/z* (%): (618 (4), 617 (6), 616 (12), 614 (66)), 612 (4) $[M]^+$, 588 (2) $[M-\mathrm{N_2}]^+$, (537 (3), 535 (3)) $[M-(\mathrm{H})\mathrm{Br}]^+$, (511 (33), 510 (22), 509 (96), 508 (23), 507 (100), 505 (35)) $[M-\mathrm{N}_{2-}(\mathrm{H})\mathrm{Br}]^+$, (429 (36), 428 (19), 427 (65), 425 (32)) $[M-\mathrm{N}_{2-}2(\mathrm{H})\mathrm{Br}]^+$, (349 (25), 347 (11), 346 (26)) $[M-\mathrm{N_2}-3(\mathrm{H})\mathrm{Br}]^+$, (268 (27), 267 (98), 266 (19)) $[M-2\mathrm{HBr}-2\mathrm{Br}-\mathrm{N_2}]^+$/$[C_{21}H_{14}]^+$, 265 (26), 263 (15) $[C_{21}H_{11}]^+$, 253 (23), 252 (36) $[M-\mathrm{CH_2N_2}-2\mathrm{HBr}-2\mathrm{Br}]^+$, 125 (14), 120 (24), 82 (16); $C_{21}H_{16}{}^{79}Br_2{}^{81}Br_2N_2$; HRMS: *m/z* calcd: 615.8002; found: 615.8005.

Bromination of 28: A solution of **28** (84 mg, 0.20 mmol) in $BrCCl_3$ (40 g, 0.20 mol) was refluxed for 24 h. A sample analyzed after concentration in vacuo ($C_{20}H_{16.4}Br_{3.6}$ elemental composition), consisted of at least eight components (TLC) and showed tetrabromides as highest masses (MS, *m/z* [577 (4), 576 (3), 575 (6), 574 (2), 573 (4)]). After four days reflux, the elemental composition had changed to $C_{20}H_{14.2}Br_{5.8}$ (a multitude of non-separable components, mainly hexabromides), after eight days to $C_{20}H_{12.0}Br_{7.8}$ (multitude of non-separable components, mainly saturated octabromides, occasionally a trace of nonabromides). Whilst various attempts for column chromatographic separation proved fruitless, HPLC ($CH_3CN/THF/H_2O$ 78:2:20, LiChrospher RP-18, flow 1 mL min^{-1}, detection at 246 nm) of the $C_{20}H_{16.4}Br_{3.6}$ sample provided **35/36** as a mixture (retention time (rt) = 9.0 min, 11 mg), **34** (rt = 9.6 min, 27 mg), **32** (rt = 10.0 min, 11 mg), **30/31** as mixture (rt = 10.1 min, 32 mg) and **33** (rt = 10.8 min, 8 mg). Crystallization of the mixture **30/31** from diethyl ether delivered pure **31** and nearly pure **30**.

1,2,6-Tribromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (30): Colorless crystals. ^{1}H NMR: $\delta=4.42$ (m, 3-H), 4.10 (m, 5-,7-, 20-H), 3.91 (m, 8-,9-,11-,16-H), 3.80 (m, 4-,10-,12-,15-H), 3.57 (m, 14-,17-, 18-,19-H), 3.41 ppm (m, 13-H); ^{1}H NMR (C_6D_6): $\delta=4.58$ (m, 3-H), 3.88 (m, 5-,7-,20-H), 3.65 (m, 8-,9-,11-,16-H), 3.30–3.20 (m, 10-,12-,15-H), 2.95 (m, 14-,17-,18-,19-H), 2.75 ppm (m, 13-H); ^{13}C NMR (C_6D_6): $\delta=$[92.1, 92.0, 91.7] (C-Br), [79.5, 79.2, 78.8, 78.7, 78.3] (β-C-Br), 65.4, 65.1, 65.1, 65.0, 64.7, 64.4, 64.4, 64.3, 64.0, 63.9, 63.6, 63.4; MS: *m/z*: (499 (2), 498 (3), 497 (7), 496 (4), 495 (6)) $[M]^+$, (420 (28), 418 (36), 417 (21)) $[M-(\mathrm{H})\mathrm{Br}]^+$, 258 (23), [257 (38), 256 (23), 255 (27), 254 (22) $[M-3(\mathrm{H})\mathrm{Br}]^+$, (128 (45), 127 (26), 126 (22)) $[M-3(\mathrm{H})\mathrm{Br}]^{2+}$. $C_{20}H_{17}Br_3$ (497.1); $C_{20}H_{17}{}^{79}Br{}^{81}Br_2$; HRMS *m/z* calcd: 497.8844; found: 497.8830.

1,2,16-Tribromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (31): Colorless crystals, m. p. 276 °C (decomp). ^{1}H NMR (C_6D_6): $\delta=3.98$ (m, 3-,9-,11-,20-H), 3.75 (m, 6-,15-,17-H), 3.53 (m, 7-,8-H), 3.25 (m, 4-,5-,10-,13-,14-,18-H), 2.96 ppm (m, 12-,19-H); ^{13}C NMR (C_6D_6): $\delta=$ 95.6 (C-16), 95.5 (C-1, C-2), 80.3, 80.1 (β-C-Br), 70.6, 66.7, 66.5, 66.1, 65.9, 65.7, 65.6 ppm; MS: *m/z*: 497 (0.1), (420 (10), 418 (18), 417 (16), 416 (18), 415 (10), 414 (9), 412 (11)) $[M-(\mathrm{H})\mathrm{Br}]^+$, (339 (1), 337 (7)) $[M-2(\mathrm{H})\mathrm{Br}]^+$, 259 (20), 258 (25), (257 (100), 256 (4), 254 (1)) $[M-3(\mathrm{H})\mathrm{Br}]^+$, 128 (10), 127 (4), 124 (2), 123 (9), 115 (10), 112 (4), 109

(6), 97 (14), 85 (11), 81 (11), 70 (100); elemental analysis calcd (%) for. $C_{20}H_{17}Br_3$ (497.1): C 48.33, H 3.45; found: C 48.60, H 3.20.

1,3,17-Tribromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (32): Colorless crystals, m. p. 283 °C; ^{1}H NMR (C_6D_6): $\delta = 4.59$ (d, 2-H), 3.87 (m, 4-,20-H), 3.64 (m, 7-,11-, 13-,16-,18-H), 3.25 (m, 5-,9-,14-, 15-,19-H), 2.95 ppm (m, 6-,8-,12-,10-H); $J_{2,9} = 12.4$ Hz; ^{1}H NMR (500 MHz): $\delta = 4.42$ (d, 2-H), 4.10 (m, 4-,20-H), 3.90 (br. m, 7-,11-,13-,16-, 18-H), 3.80 (br. m, 5-,9-,14-,15-,19-H), 3.60 ppm (m, 6-,8-,10-,12-H); $J_{2,9} = 12.6$ Hz; ^{13}C NMR (C_6D_6): $\delta = 92.8$ (C-17), 92.5 (C-2), 89.9 (C-1), 89.8 (C-3), [79.6, 79.6, 78.5] (C-4,-7,-8,-10,-13,-18), [65.0, 64.4, 64.2, 63.7 ppm] (C-5,-6,-11,-12,-14,-15,-19,-20); MS (EI): *m/z* (%): (498 (2), 497 (3), 496 (2), 495 (1)) $[M]^+$, (420 (10), 419 (48), 418 (21), 417 (100)) $[M-(H)Br]^+$, (256 (12), 255 (30), 254 (24)) $[M-3(H)Br]^+$, 253 (11), 252 (10), 241 (15), 240 (17), 239 (29), 229 (7), 228 (10), 227 (12), 226 (13), 215 (15), 202 (12), 191 (12), 178 (22), 165 (18), 153 (20), 152 (25), 129 (12), (128 (57), 127 (37) 126 (23)) $[M-3(H)Br]^{2+}$, 119 (35), 102 (13), 77 (11). $C_{20}H_{17}Br_3$ (497.1); $C_{20}H_{17}{}^{79}Br^{81}Br_2$; HRMS *m/z* calcd: 497.8844; found: 497.8843.

1,2,5,6-Tetrabromoundecacylo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (33): Colorless crystals, m. p. 293 °C; ^{1}H NMR (C_6D_6): $\delta =$ 3.88 (m, 3-,4-,7-,20-H), 3.62 (m, 9-,11-,16-,18-H), 3.25 (m, 8-,10-,15-,17-, 19-H), 2.92 ppm (m, 12-,13-,14-H); ^{1}H NMR (500 MHz): $\delta = 4.07$ (m, 3-, 4-,7-,20-H), 3.92 (m, 9-,11-,16-,18-H), 3.80 (m, 8-,10-,15-,17-,19-H), 3.60 ppm (m, 12-,13-,14-H); ^{13}C NMR (C_6D_6): $\delta = 92.5$ (C-1,-6), 92.3 (C-2,-5), [79.36, 79.34, 78.8, 77.9] (C-3,-7,-4,-9,-11,-20), [64.8, 64.4, 64.1, 63.8, 63.7 ppm] (C-8,-10,-12,-13,-14,-15,-16,-17,-19]; MS: *m/z* (%): (580 (4), 578 (10), 576 (14), 574 (10), 572 (4)) $[M]^+$, (500 (4), 499 (17), 498 (4), 497 (18), 496 (5), 495 (18), 493 (6)) $[M-(H)Br]^+$, (420 (10), 419 (53), 418 (22), 417 (100), 416 (12), 415 (54), 414 (5), 413 (9)) $[M-2(H)Br]^+$, 371 (3), (338 (4), 337 (19), 336 (5), 335 (18)) $[M-3(H)Br]^+$, 257 (13), (256 (3), 255 (9), 254 (2), 253 (2)) 252 (1) $[M-4(H)Br]^+$, 251 (8), 240 (19), 239 (4), 227 (12), (128 (9), 127 (9), 126 (5)) $[M-4(H)Br]^{2+}$, 120 (3); $C_{20}H_{16}Br_4$ (576.0); $C_{20}H_{16}{}^{79}Br_2{}^{81}Br_2$; HRMS *m/z* calcd: 575.7943; found: 575.7942.

1,*x*,*x*,6-Tetrabromoundecacylo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (34): Colorless crystals, m. p. 273 °C; ^{1}H NMR (C_6D_6): $\delta =$ 4.65 (t, 1 H), 4.42 (m, 2 H), 4.02 (t, 1 H), 3.92–3.85 (m, 1 H), 3.7–3.6 (m, 3 H), 3.47 (m, 1 H), 3.30 (m, 1 H), 3.10 (m, 3 H), 2.8–2.7 ppm (m, 3 H); ^{1}H NMR (500 MHz): $\delta = 4.56$ (t, 1 H), 4.38 (dd, 2 H), 4.27 (t, 2 H), 4.0–4.1 (m, 3 H), 3.92 (m, 1 H), 3.82 (m, 2 H), 3.82 (m, 3 H), 3.7–3.6 ppm (m, 3 H); ^{13}C NMR (C_6D_6): $\delta = 92.3$, 91.8, 91.1, 91.0, 79.4, 79.1, 78.8, 78.6, 78.3, 77.5, 77.0, 76.8, 64.8, 64.6, 64.5, 64.0, 63.5, 62.9, 62.8, 62.5 ppm; MS: *m/z* (%): (578 (2), 576 (4), 574 (6), 572 (2)) $[M]^+$, (499 (32), 498 (21), 497 (96), 496 (24), 495 (100), 494 (10), 493 (35)) $[M-(H)Br]^+$, (420 (3), 419 (13), 418 (8), 417 (25), 416 (6), 415 (20), 414 (5), 413 (9)) $[M-2(H)Br]^+$, 375 (2), (338 (5), 337 (17), 336 (3), 335 (10)) $[M-3(H)Br]^+$, 257 (4), (255 (4), 254 (4), 253 (3), 252 (1)) $[M-4(H)Br]^+$, 251 (8), 240 (19), 239 (4), (128 (3), 127 (5), 126 (3)) $[M-4(H)Br]^{2+}$, 120 (3); $C_{20}H_{16}Br_4$ (576.0); $C_{20}H_{16}{}^{79}Br_2{}^{81}Br_2$; HRMS *m/z* 575.7943; found: 575.7942.

1,*x*,*x*,6-Tetrabromoundecacylo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosanes (35/36): Colorless crystals; ^{1}H NMR (500 MHz, C_6D_6): $\delta =$ 4.61 (m, 1 H), 4.40 (m, 1 H), 3.88 (m, 2 H), 3.7–3.6 (m, 4 H), 3.42 (m, 1 H), 3.31 (m, 2 H), 3.10 (m, 2 H), 2.92 (m, 2 H), 2.80 ppm (m, 1 H); ^{13}C NMR (C_6D_6): $\delta = 92.5$, 92.3, 91.9, 91.6, 91.1, 90.7, 90.2, 89.8, 79.9, 79.6, 79.3, 79.2, 79.1, 78.7, 78.45, 78.4 78.3, 78.2, 78.1, 79.9, 77.6, 77.5, 77.4, 77.2, 77.0, 76.7, 65.0, 64.6, 64.4, 64.2, 64.1, 64.0, 63.9, 63.7, 63.4, 63.3, 63.1, 62.9, 62.5 ppm; MS: *m/z* (%): (578 (1), 576 (41), 574 (4), 572 (1)) $[M]$, (499 (32), 498 (22), 496 (100), 495 (21), 494 (90), 493 (36)) $[M-(H)Br]^+$, (417 (17), 416 (8), 415 (33), 414 (5), 413 (18)) $[M-2(H)Br]^+$, (337 (23), 336 (9), 335 (36), 333 (11)) $[M-3(H)Br]^+$, (256 (12), 255 (33), 254 (15), 253 (25), 252 (20)) $[M-4(H)Br]^+$, 250 (6), 240 (16), 239 (33), 226 (12), (128 (18), 126 (33)) $[M-4(H)Br]^{2+}$, 125 (18), 113 (39); $C_{20}H_{16}Br_4$ (576.0); $C_{20}H_{16}{}^{79}Br_2{}^{81}Br_2$; HRMS *m/z* calcd: 575.7943; found: 575.7942.

$C_{20}H_{18}Fe(CO)_4$ complex 38: From 9: A solution of **9** (68 mg, 0.02 mmol) and Fe_2CO_9 (240 mg, 0.06 mmol) in cyclohexane (5 mL) was stirred at room temperature for 12 h (complete conversion, MS). After filtration of the yellow solution through silica gel and concentration in vacuo, the green residue was repeatedly crystallized from ethanol: 65 mg (75 %) of a beige, homogeneous solid were isolated, m. p. 125–126 °C; IR: 2076 (CO), 2042 (CO), 1994 (CO), 1972 (CO) cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 3.36$ (m, 3-,4-,9-,10-,11-,20-H), 3.21 (m, 5-,14-,16-,17-H), 3.12 ppm (m, 6-,7-,8-, 12-,13-,15-,18-,19-H); ^{13}C NMR (C_6D_6): 212.0 (CO), 70.8 (C-4,-10), 70.4 (C-5,-14), 67.1 (C-1,-2), 66.7 (C-16,-17), 65.3 (C-6,-13,-15,-18), 65.3 (C-7, -8,-12,-19), 64.6 ppm (C-3,-9-,-11,-20); MS: *m/z*: 426(1), 425 (3) $[M]^+$, 399 (4) (398 (3), 397 (3)) $[M-CO]^+$, 371 (6), (370 (6), 369 (2)) $[M-2CO]^+$, 344 (2), 343 (14), (342 (52), 341 (5)) $[M-3CO]^+$, 340 (4), 316 (3), 315 (25), 314 (100) $[(C_{20}H_{18}\cdot Fe)^+]$, 313 (14), 312 (21), 311 (7), 310 (3), 260 (27), 265 (48), 259 (48), 258 (19) $[C_{20}H_{18}]^+$, 239 (9), 215 (7), 202. (7); $C_{24}H_{18}O_4Fe$; HRMS *m/z* calcd: 426.0555; found: 426.0546.

From 10: After for 4 h at room temperature (complete conversion, MS) a solution of **10** (42 mg, 0.01 mmol) and $[Fe_2CO_9]$ (200 mg, 0.05 mmol) in cyclohexane (5 mL) was filtered through silica gel. Concentration of the yellow solution in vacuo afforded a greenish residue which was repeatedly crystallized from ethanol to give **39** (35 mg; 80 %).

From 3: A solution of **3** (25 mg, 0.01 mmol) and $[Fe(CO)_5]$ (200 mg, 1.0 mmol) in THF (2 mL) was stirred at room temperature for 3 h (complete conversion, MS). After concentration of the blue-green solution in vacuo and crystallization (ethanol), **39** was isolated (32 mg; 75 %).

$[C_{20}H_{16}\{Fe(CO)_4\}_2]$ complex 39: Analogous to the preparation of **38.** Compound **33** (28 mg, 0.05 mmol)/$[Fe_2CO_9]$ (90 mg, 0.30 mmol)/cyclohexane (10 mL)/room temperature/4 h (complete conversion, MS). After filtration through silica gel, extraction with THF, concentration in vacuo and repeated crystallization (ethanol): 25 mg of a beige solid were isolated. ^{1}H NMR (C_6D_6): $\delta = 3.90$ (br.m), 3.3–3.0 ppm (br. m); MS: *m/z* (%): 592 (0.5) $[M]^+$, 564 (0.5), 536 (0.4), 508 (0.9), 480 (0.6) $[M-CO]^+$, [424-422 (2)] $[M-Fe(CO)_4]^+$, 420 (2) 396 (1), 394 (2), 368 (3), 364 (1). 342 (4), 340 (6), 315 (2), 314 (8), 312 (12) $[C_{20}H_{16}Fe]$, 311 (3) 287 (5), 285 (6), 259 (16), 258 (27), 257 (27), 256 (16) $[C_{20}H_{16}]^+$, 215 (5), 202 (4), 189 (5), 184 (60), 178 (6); $C_{28}H_{16}O_8Fe_2$ (592.1).

Mixture of $[C_{20}H_{12}\{Fe(CO)_4\}_4]$ complexes (40): Analogous to the preparation of **38.** Compound **34** (14 mg, 0.025 mmol)/Fe_2CO_9 (62 mg, 0.2 mmol)/ cyclohexane (5 mL)/room temperature/60 h (complete conversion, MS). After filtration, extraction with THF, concentration and repeated crystallization (ethanol), 9 mg of a beige, not homogeneous solid were isolated. MS: *m/z* (%): 756 (0.03), 754 (0.02) $[M-Fe(CO)_4]^+$, 730 (0.02), 728 (0.03) $[M-Fe(CO)_4-CO]^+$, 702 (0.1), 700 (0.2), 674 (0.7), 672 (0.2), 646 (0.2), 618 (0.2), 590 (0.9), 588 (0.9) $[M-2Fe(CO)_4]^+$, 562 (0.7), 536 (1), 508 (3), 480 (3), 452 (3), 424 (3), 422 (4), 420 (6) $[M-3Fe(CO)_4]^+$, 396 (4). 394 (3), 392 (2), 370 (3), 366 (2), 342 (4), 340 (4), 338 (2), 314 (3), 312 (8), 311 (2), 310 (3), 259 (5), 257 (7), 256 (3), 253 (3), 252 (3) $[C_{20}H_{12}]^+$, 239 (3), 157 (2), 103 (3), 71 (100); MS (CI, isobutane): *m/z* (%): 924 (<0.1) $[M]^+$, 896 (< 0.1) $[(M-CO)]^+$; $C_{36}H_{12}O_{16}Fe_4$ (924.3).

Undecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosa-1,3-/1,3(7)-dienes (41/42): A solution of **10** (22 mg, 0.05 mmol) and $[D_{36}]P_2F$ (80 mg, 0.2 mmol) in C_6D_6 (5 mL) was stirred at room temperature until complete conversion (ca. 1 min). The precipitated P_2Br was rapidly filtered off (silica gel), and the solution was immediately analyzed by ^{1}H and MS spectroscopy (30 min later, no change was noted). ^{1}H NMR (500 MHz, C_6D_6): A series of multiplets between $\delta = 3.6$ and 2.45 ppm; ^{13}C NMR (C_6D_6): $\delta = 168.8$, 165.7, 163.4, 114.2, 108.6, 103.5, 73.9, 73.6, 72.3, 72.3 (2), 69.2 (2), 68.9, 66.5, 65.9, 65.1, 65.0, 64.4, 64.3, 64.2, 63.9, 63.7 (6), 63.7(3), 63.6, 63.5, 63.4, 63.4, 63.3, 62.8, 62.5, 62.5, 62.4, 61.3, 61.2, 60.5 ppm; MS: *m/z*: 292 (51) $[M+2\ H_2O]^+$, 276 (12), 258 (3), 257 (1), 256 (8) $[M]^+$, 128 (4) $[M]^2$; $C_{20}H_{16}$ (256.4); HRMS *m/z* calcd: 256.1252; found: 256.1234.

$C_{20}H_{16}\cdot$anthracene adduct 44: To a freshly prepared solution of **41/42** (0.05 mmol **10**; possibly containing **43**), anthracene (25 mg, 0.15 mmol) was added. After the mixture had been stirred until complete consumption of **41/42** (1 h), methanol (2 mL) was added, the filtered solution concentrated in vacuo, and residual anthracene sublimed off. The solid residue consisting of at least three components (TLC) rapidly decomposed on contact with air. MS (CI, isobutane): *m/z*: 452 (12) $[M+H_2O]^+$, 435 (44), 434 (10) $[C_{20}H_{16}C_{14}H_{10}]^+$, 17 (16), 292 [**35/36**$\cdot 2\,H_2O]^+$, 276 (4), 259 (55), 258 (51), 257 (100) $[C_{20}H_{17}]^+$, 178 (71) $[C_{14}H_{10}]^+$; $C_{34}H_{26}$ (434.6) HRMS: *m/z* calcd: 434.2035; found: 434.2020.

$[C_{20}H_{15}FeCp]$ complex 45a: A solution of **10** (11 mg, 0.025 mmol), ferrocene ($[FeCp_2]$, 10 mg, 0.05 mmol) and P_2F (36 mg, 0.10 mmol) in THF

(5 mL) was stirred at room temperature for 3 h. The brownish solution was filtered through silica gel, concentrated in vacuo, and the brownish residue crystallized from ethanol. Not totally uniform, dark yellow crystals (11 mg) were isolated. ^{1}H NMR (C_6D_6): $\delta = 3.58$ (br., 6H), 3.48 (br., 4H), 3.05 ppm (br., 5H); MS: *m/z* (%): 377 (15), 376 (100) $[M]^+$, 276 (45), 260 (11), 228 (7); $C_{25}H_{20}Fe$ (376.3); HRMS: *m/z* calcd: 376.0914; found: 376.0911.

$[C_{20}H_{15}FeCp^*]$ complex 45b: A solution of **10** (11 mg, 0.025 mmol), [Fe(tmeda)Cp*Cl] (65 mg, 0.19 mmol) and P_2F (36 mg, 0.10 mmol) in THF (5 mL) was stirred at room temperature for 3 h. The green solution was filtered through a short pad of silica gel and concentrated in vacuo. The green, extremely air-sensitive residue was analyzed as such. ^{1}H NMR ([D_8]THF): $\delta = 3.35$ (br., 5H), 2.85 (br., 6H), 2.50 (br., 4H), 1.65 ppm (br., 15H); ^{1}H NMR (C_6D_6): $\delta = 3.61$ (br., 5H), 3.30 (br., 6H), 3.10 (br., 4H), 1.65 ppm (br., 15H); MS: *m/z* (CI, NH_3): (448 (8), 447 (2), 445 (5), 443 (2)) $[M]^+$, 433 (7), 432 (24), 431 (100) $[M-CH_3]^+$, 430, (20), 400 (10), 356 (6), 340 (2), 300 (3), 255 (5), 166 (44), 148 (37), 81 (55); $C_{30}H_{30}Fe$ (446.4); HRMS: *m/z* calcd: 446.1697; found: 446.1679.

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