amide.[10] That accepted, however, it is not surprising that *N,N*-dialkylformamides react more rapidly than higher acid amides. The procedure can be drastically simplified for formamides (entries 9–12 in Table 1) and yet gives better yields (69–74%). Although with two bulky isopropyl groups the reaction required heating under reflux for 3 days, the sterically congested cyclopropyldiisopropylamine **3m** was obtained from diisopropylformamide[11] in 76% yield, and even *N,N*-di-*tert*-butylformamide,[12] when treated with a threefold excess of the reagent at elevated temperatures for an extended time, gave cyclopropyldi-*tert*-butylamine (**3n**), the most highly congested tertiary amine known to date,[13] albeit in low yield. A competition experiment disclosed that the cyclopropanation of dibenzylformamide proceeds more rapidly than that of *tert*-butyl acetate. Dialkylformamides can also be cyclopropanated with reagents generated from β-substituted ethylmagnesium bromides and $Ti(OiPr)_4$, but the 2-alkyl-1-dialkylaminocyclopropanes **3o, p** are obtained with no or low diastereoselectivity only (entries 15, 16 in Table 1).

Experimental Procedure

General procedure for the cyclopropanation of acid *N,N*-dialkylamides: To a suspension of the alkylmagnesium bromide (50 mmol, 25% excess) in THF (200 mL, cooled to −78 °C) was added $Ti(OiPr)_4$ (20 mmol in 10 mL of THF) under nitrogen through a steel cannula. After the mixture had been stirred for 2 min, the dialkylamide (20 mmol in 10 mL of THF) was added, and the mixture allowed to warm to 20 °C. It was stirred for an additional 3 h before volatile amines (with boiling points close to that of THF and isopropyl alcohol together with THF were distilled from the reaction mixture, without adding water, under reduced pressure (100 Torr) into a cold trap (−78 °C). Addition of a solution of hydrogen chloride in ether precipitated the hydrochloride of the cyclopropylamine. The crystals were collected and recrystallized from $CHCl_3/Et_2O$.

Amines with higher boiling points (containing one or two benzyl, isopropyl, or cyclopropyl groups in addition to the newly formed cyclopropane ring) were isolated by first adding saturated ammonium chloride solution (150 mL) and water (50 mL), then filtering the solution to remove the any precipitate that may have formed, and extracting it with ether (3 × 50 mL) after the solution had been made basic (pH > 11) with 15% sodium hydroxide solution. The combined ethereal extracts were washed with saturated sodium chloride solution, dried over $MgSO_4$ or K_2CO_3, and concentrated under reduced pressure (amines with C_8–C_{11} were first converted into nonvolatile salts with hydrogen chloride solution). Large amounts were purified by distillation.

Simplified procedure for the transformation of dialkylformamides: To a solution of dialkylformamide (5 mmol) in THF (30 mL) was added $Ti(OiPr)_4$ (5.5 mmol) and then at ambient temperature within 20 s a 2.85 M ethylmagnesium bromide solution in ether (12.5 mmol, 4.4 mL). On warming to 45 °C the mixture turned black, and ethane was evolved. After the mixture had been stirred for an additional 10 h, it was treated with 15 mL of saturated ammonium chloride solution, filtered if necessary to remove precipitated TiO_2, and the filtrate extracted with ether (3 × 20 mL). The combined ethereal extracts were washed with 20 mL of sodium chloride solution, dried over K_2CO_3, and concentrated.

Received: June 30, 1995 [Z 8147 IE]
Publication delayed at authors' request
German version: *Angew. Chem.* **1996**, *108*, 491–492

Keywords: amides · amines · cyclopropanes · titanium compounds

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A Step-Growth Approach to Metal-Capped One-Dimensional Carbon Allotropes: Syntheses of C_{12}, C_{16}, and C_{20} μ-Polyynediyl Complexes[**]

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Roman Dembinski, and J. A. Gladysz*

The three-dimensional and two-dimensional carbon allotropes, diamond and graphite, have been known since antiquity. However, the one dimensional carbon allotrope, which would consist of sp hybridized carbons, remains by comparison only exigously described. Over the last thirty years several syntheses have been claimed.[1, 2] Recently mixtures of lower (C_{16}–C_{28}) and higher (C_{75}–C_{150}) oligomers have been prepared by novel synthetic techniques with various organic endgroups.[3–6] These reports foreshadow many fascinating properties, the precise delineation of which requires samples that are homogeneous in chain length.

We have sought to prepare compounds in which elemental carbon chains span two transition metals. We previously isolated dirhenium μ-polyynediyl complexes of the formula $[\{Re^*\}(C{\equiv}C)_n\{Re^*\}]$ (n = 2, **C4**; 3, **C6**; 4, **C8**; $\{Re^*\} = (\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)$) from coupling or cross-coupling reac-

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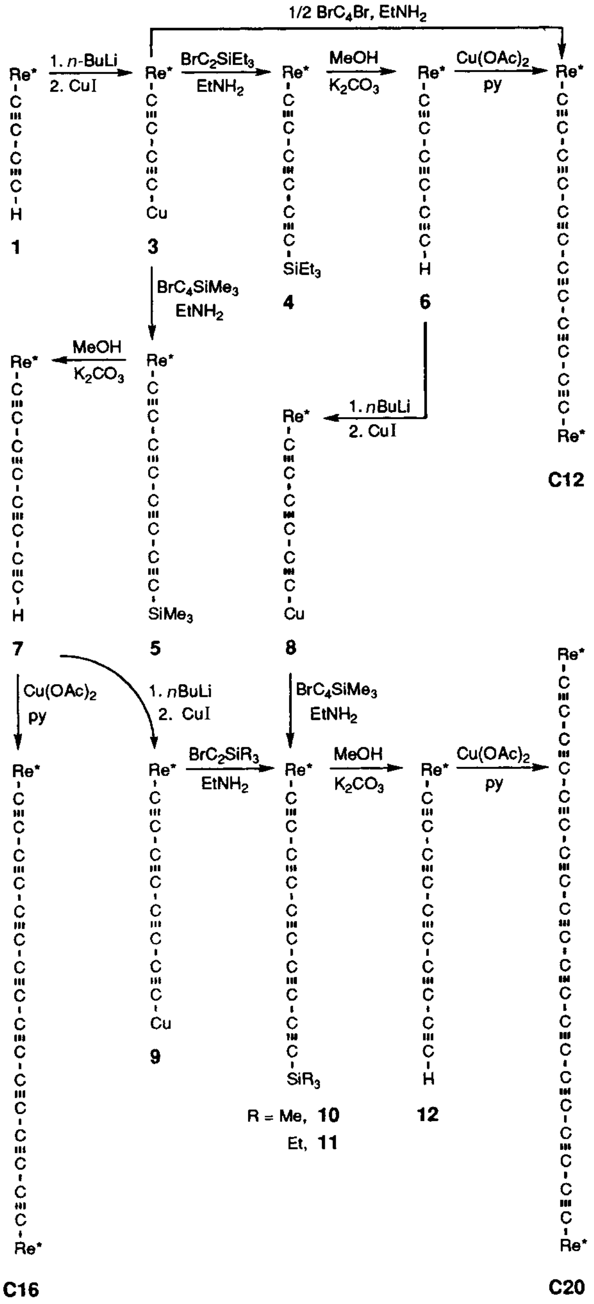
[**] We thank the National Science Foundation for support of this research.

tions of the corresponding [{Re*}(C≡C)$_n$H] species (n = 1, 2).[7] In this communication, we detail new step-growth chain extension methodology that leads to analogous complexes with up to twenty-carbon bridges. This strategy appears to carry no upper bound for chain length and should allow access to a complete family of well-defined oligomers.

The racemic butadiynyl complex [{Re*}(C≡CC≡CH)] (**1**; Scheme 1) was treated with nBuLi in THF (1.1 equiv, −45 °C) to generate the previously reported C_4Li complex [{Re*}(C≡C−C≡CLi)] (**2**).[8] Then CuI was added (−20 °C). The sample was warmed and kept at room temperature for a short time. IR and ^{31}P NMR spectra showed broad signals indicating complete conversion to a new complex or mixture of complexes. These were presumed to have the empirical formula [{Re*}(C≡CC≡CCu)] (**3**; Scheme 1).[9]



Scheme 1. Syntheses of [{Re*}(C≡C)$_n${Re*}] [n = 6 (**C12**), 8 (**C16**), 10 (**C20**)]; {Re*} = (η^5-C_5Me_5)Re(NO)(PPh_3); py = pyridine.

Under suitable conditions copper-substituted and bromine-substituted alkynes couple to 1,3-diynes.[10] However, to our knowledge such "Cadiot-Chodkiewicz" protocols have not been applied in metal coordination spheres. Thus, solutions of **3** were treated with excess $EtNH_2$ (−20 °C). Then BrC≡CSiEt$_3$[11] or BrC≡CC≡CSiMe$_3$[12] (1.0–1.1 equiv) were added. Workup gave the analytically pure C_6Si and C_8Si complexes [{Re*}(C≡CC≡CC≡CSiEt$_3$)] (**4**) and [{Re*}(C≡CC≡CC≡CC≡CSiMe$_3$)] (**5**) in 51–77% yield after crystallization. Complexes **4** and **5** exhibited spectroscopic properties similar to those of lower homologs reported earlier.[7] However, IR spectra showed additional $\nu_{C\equiv C}$ bands.[9b]

Reactions of **4** and **5** with K_2CO_3/CH_3OH gave the corresponding C_6H and C_8H complexes [{Re*}(C≡CC≡CC≡CH)] (**6**) and [{Re*}(C≡CC≡CC≡CC≡CH)] (**7**) in 91–98% yield after workup. These were moderately air-sensitive as solids, and more air-sensitive in solution (**7** > **6**). Subsequent reactions with $Cu(OAc)_2$ (1.0 equiv, 50 °C) in pyridine gave the μ-dodecahexaynediyl and μ-hexadecaoctaynediyl complexes [{Re*}(C≡C)$_6${Re*}] (**C12**) and [{Re*}(C≡C)$_8${Re*}] (**C16**) in 71–67% yield. Key properties are summarized below.

"Second generation" chain extensions of **6** and **7** were investigated. Reactions with nBuLi and CuI similar to those above were presumed to generate the C_6Cu and C_8Cu species [{Re*}(C≡CC≡CC≡CCu)] (**8**) and [{Re*}(C≡CC≡CC≡CC≡CCu)] (**9**). Treatment of **8** with excess $EtNH_2$ and then with BrC≡CC≡CSiMe$_3$, as described for **3** above, gave the analytically pure $C_{10}Si$ complex [{Re*}(C≡CC≡CC≡CC≡CC≡CSiMe$_3$)] (**10**) in 51% yield. Similar reactions of **8** and BrC≡CC≡CSiEt$_3$[13] or **9** and BrC≡CSiEt$_3$ gave the triethylsilyl analog **11** in 24–26% yields.

Reaction of **11** and K_2CO_3/MeOH gave a $C_{10}H$ complex, [{Re*}(C≡CC≡CC≡CC≡CC≡CH)] (**12**), which was partially characterized. The crude sample was treated with $Cu(OAc)_2$ in pyridine as described above. Workup gave the μ-icosadecaynediyl complex [{Re*}(C≡C)$_{10}${Re*}] (**C20**) in 41% yield. Finally, a more convergent chain extension route was probed. The C_4Cu species **3** was treated with excess $EtNH_2$ and then the *di*bromide BrC≡CC≡CBr.[14] Workup gave **C12** in 45% yield.

The sp carbon chains in **C12**, **C16**, and **C20** are by far the longest tether between two metals to date.[7, 8, 15, 16] All three compounds are microcrystalline or amorphous powders and show only slight decomposition after one week in air at room temperature. When heated they decompose (above 100 °C) without melting or explosion. Mass spectra exhibit strong molecular ions. Correct microanalyses have been obtained for **C12** and **C16**, but not yet for **C20**. Solubilities are high in CH_2Cl_2 and THF but low in hexane. In solution **C20** is noticeably more labile than **C12** or **C16**.[16]

Some physical properties of **C12**–**C20** should asymptotically approach those of a one-dimensional sp carbon allotrope. For example, ^{13}C NMR spectra show Re$C\equiv C$ signals at δ = 127–114. Interestingly, the remaining signals cluster in the narrow range of δ = 68–63 (Fig. 1). Similar trends occur in mixtures of oligomers with organic endgroups, reported by Lagow.[3] Also, the colors of solutions deepen from red (**C12**) to black cherry (**C16**) to brown-black (**C20**). Accordingly, UV/Vis spectra exhibit progressively red-shifted bands of markedly increasing intensities, as illustrated in Figure 2. Some have molar extinction coefficients of well over 100000 $M^{-1}cm^{-1}$. Importantly, PES and MO studies of metal ethynyl and butadiynyl complexes[17] suggest that the HOMOs of **C12**–**C20** likely have appreciable metal d *and* (C≡C)$_n$ π character.

Cyclic voltammograms of **C4**–**C8** show two chemically reversible one-electron oxidations under suitable conditions.[7b]

These generate monocations and dications, which have been isolated in the C_4 series. Data acquired under identical conditions with **C12**–**C20** are summarized in Table 1. Some striking trends are evident. For example, as the carbon chain lengthens, the first oxidation potential becomes thermodynamically less favorable (**C4** vs. **C16**, $\Delta E^\circ = 0.56$ V). The second potential varies by a smaller amount (**C4**/**C6** vs. **C16**, $\Delta E^\circ = 0.12/0.18$ V). Consequently, the E° values approach each other, and with **C20** they merge to give a single—presumably two-electron—oxidation. This signifies the chain length at which the two rhenium atoms start to behave independently, at least in a redox sense.

The final step in each synthesis of **C12**–**C20** can be viewed as "convergent". However, especially for **C20**, a number of iterative steps are required. Importantly, many ways can be envisioned to optimize or combine the individual steps, or to employ longer building blocks. In summary, we have shown that it is possible to rationally synthesize metal-capped oligomers of sp carbon atoms that are homogeneous in chain length. Additional properties of the title compounds, and syntheses of analogs, will be reported in the near future.

Received: October 6, 1995 [Z 8453 IE]
German version: *Angew. Chem.* **1996**, *108*, 467–469

Keywords: alkynyl complexes · carbon allotropes · polyynes · rhenium compounds

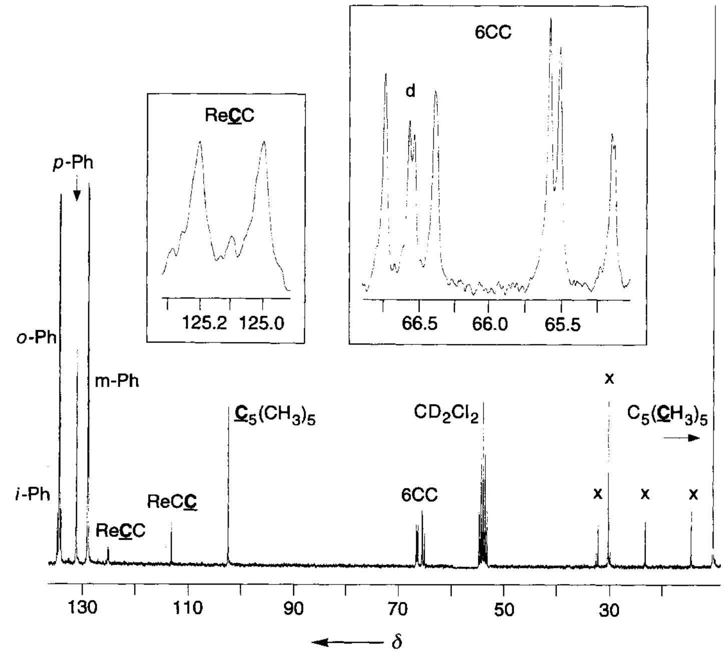


Fig. 1. ^{13}C NMR spectrum of **C16** (75 MHz, CD_2Cl_2, 20 °C) and expanded sp carbon region (insets); x = solvent impurities; d = doublet.

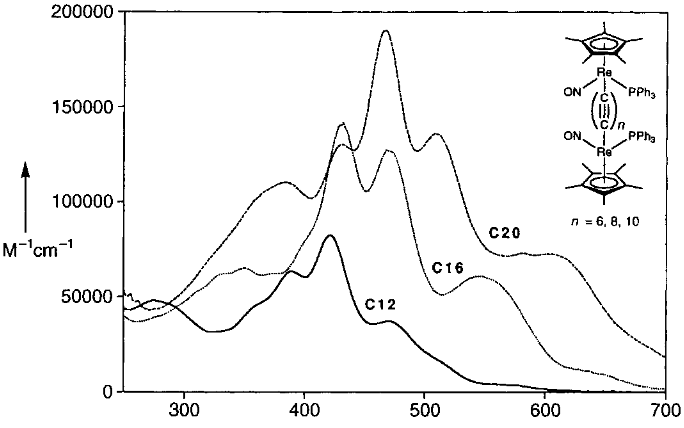


Fig. 2. UV/Vis spectra of **C12**, **C16**, and **C20** (CH_2Cl_2, ambient temperature).

Table 1. Cyclic voltammetry data [a].

Compound	$E_{p,a}$ [V]	$E_{p,c}$ [V]	E^0 [V]	ΔE [mV]	i_a/i_c [b]
C4	0.15	0.06	0.11	90	1
	0.68	0.59	0.64	90	1
C6	0.24	0.17	0.20	70	1
	0.62	0.55	0.58	70	1
C8	0.37	0.30	0.34	70	>1
	0.66	0.59	0.62	70	>1
C12	0.60	0.52	0.56	80	≫1
	0.79	0.69	0.75	100	≫1
C16	0.70	0.64	0.67	60	≫1
	0.79	0.73	0.76	60	≫1
C20	0.80	0.67	0.74	130	⋙1

[a] The first line shows the potential of the first oxidation, and the second line that of the second oxidation. **C20** undergoes only one oxidation (see text). $7-9 \times 10^{-5}$ M in 0.1 M $Bu_4N^+BF_4^-/CH_2Cl_2$ at ambient temperature, Pt working and counter electrodes, ferrocene standard, potential vs. Ag wire pseudoreference; scan rate 100 mVs^{-1}. p = potential. a = anode. c = cathode. [b] Improved reversibility is generally seen at lower temperatures.

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[16] Presumably **C12**–**C20** are 50:50 mixtures of diastereomers, as established for lower homologs **C4**–**C8**. However, in each case only a single set of NMR signals is observed. Other spectroscopic properties, and redox behavior, are also presumed to be identical. We have not yet been able to obtain single crystals, perhaps in part due to the presence of two diastereomers.

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Photochemically Induced Metathesis Reactions of Tetradehydrodianthracene: Synthesis and Structure of Bianthraquinodimethanes[**]

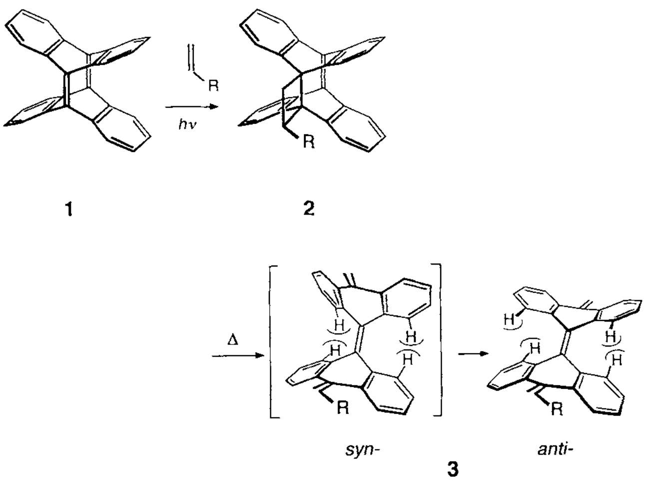
Stefan Kammermeier and Rainer Herges*

Dedicated to Professor Ivar Ugi
on the occasion of his 65th birthday

Photochemical [2+2] cycloadditions[1] with subsequent [2+2] cycloreversion in the sense of an overall metathesis reaction often lead to interesting products that are otherwise difficult to prepare.[2] With the example of 5,12:6,11-di[1,2]benzenodibenzo[*a,e*]cyclooctene[3] (9,9′,10,10′-tetradehydrodianthracene, ethylenosuperphane;[4] **1**), we demonstrate that this concept of two-step (photochemical and thermal) metathesis can be used to synthesize spherically deformed, polycyclic, aromatic hydrocarbons.

The highly strained, but stable diene **1** contains two bridgehead double bonds 2.42 Å apart,[3] which are *syn*-pyramidalized.[5] The unusual configuration (pyramidalization, through-space interaction) gives rise to a decrease in the $\pi-\pi^*$ gap, which is mainly due to a lowering of the LUMO.[6] Consequently, the reactivity of the double bonds towards electrophilic[7] and (even more pronounced) towards nucleophilic[8] reagents should be enhanced. Therefore **1** should be particularly reactive towards electron-rich alkenes in cycloadditions. As part of our investigations into the reactivity of **1** we performed photochemical [2+2] cycloadditions with a number of alkenes and cycloalkenes. Compound **1** gives three absorption bands in the UV range above 200 nm: 282 ($\varepsilon = 1270$), 270 ($\varepsilon = 2500$), and 233 nm ($\varepsilon = 10700$). The longest wavelength band can probably be attributed to the symmetry-forbidden $\pi-\pi^*$ transition and therefore to the excited state that correlates with the [2+2] cycloadducts.

Ethene adds photochemically (benzene, 150 W Hg high-pressure lamp, quartz, room temperature, 90 min) to **1** forming a very strained but isolable cyclobutane derivative **2a** in 32% yield (Scheme 1). Upon heating (toluene, 90 °C, 30 min) a cycloreversion[9] takes place to give the previously unknown, unsubstituted bianthraquinodimethane **3a** (yield 57%).[10, 11] Because of the repulsion between the *peri*-hydrogen atoms the bianthraquinoid systems cannot adopt a planar conformation. In contrast to bianthrone, which avoids this steric hindrance by distorting to a (more stable) *anti*-pyramidalized or a (less stable) twist conformation,[12] bianthraquinodimethane **3a** has, according to our calculations[13] at different levels of theory, an *anti*- and a *syn*-pyramidalized form as conformational minima. The twist conformation in this case is not a minimum. As expected, the *anti*-pyramidalized form (C_{2h} symmetry) is more stable than the *syn* isomer (C_{2v} symmetry).[6] At the highest level of theory applied the energy difference is 9.35 $\mathrm{kcal\,mol^{-1}}$ (Table 1). Presumably the *syn*-pyramidalized bianthraquinodimethane **3a**, which is formed upon thermochemical ring opening of **2a**, immediately changes pyramidalization to give the more stable *anti*-conformation (Scheme 1).



Scheme 1. Metathesis of tetradehydrodianthracene **1** with acyclic alkenes; **a**, R = H; **b**, R = Me. Important data of compounds **2a**, **3a**, and **3b** are given in Table 2.

Table 1. Absolute electronic energies E_{tot} of both isomeric forms of the unsubstituted bianthraquinodimethane **3a** calculated at different levels of theory.

Level of theory	E_{tot} [Hartree] *anti*-Isomer	E_{tot} [Hartree] *syn*-Isomer	ΔE [$\mathrm{kcal\,mol^{-1}}$]
HF/3-21G	−1141.27370	−1141.25725	10.32
HF/6-31G*	−1147.68297	−1147.66766	9.60
Becke3LYP/6-31G*//HF/6-31G*	−1155.21041	−1155.19551	9.35

The product of the photochemical [2+2] cycloaddition with propene (**2b**) is not stable under our reaction conditions (see above). The thermochemical [2+2] cycloreversion giving **3b** (yield 53%) proceeds so fast that the cyclobutane intermediate could not be detected. This agrees with observations that the [2+2] cycloreversion of cyclobutanes is accelerated by alkyl substituents.[9] A rough estimation of the Gibbs activation energies[14] predicts that in our case the methyl group lowers the barrier of activation for the [2+2]cycloreversion by at least 5.5 $\mathrm{kcal\,mol^{-1}}$. This is substantially more than in the cyclobutane parent system (1.3 $\mathrm{kcal\,mol^{-1}}$).[9]

With cycloalkenes as reaction partner (toluene:cycloalkene = 5:1, 150 W Hg high-pressure lamp, quartz, room temperature, 120 min) cyclophane-like bridged bianthraquinodimethanes **5a** and **5c**–**e** (Scheme 2) were formed. In this case as well, the cyclobutane intermediates **4** could not be isolated. A by-product in all reactions is bianthryl (probably formed by hydrogen transfer from the cycloalkene to one of the double bonds of **1** and subsequent electrocyclic ring opening[15]). The cyclophane-like bridged bianthraquinodimethanes **5a** and **5c**–**e** are fixed by the alkane chain in the usually less stable *syn*-pyramidalized form. Moreover, the X-ray analysis of **5d** (Fig. 1)[16]

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (Scholarship to S.K.).