Multiple Vinylation of Tribenzotriquinacenes and Fenestrindanes at Their Aromatic Peripheries by Use of Nájera's Catalyst

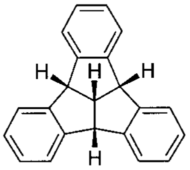
Xiao-Ping Cao,*[a] Dieter Barth,[b] and Dietmar Kuck*[b]

Keywords: Convex-concave molecules / Tribenzotriquinacenes / Fenestrindanes / Indane derivatives / Heck cross coupling reaction / Multiple vinylation

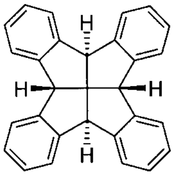
Highly efficient six- and eightfold Heck cross-coupling reactions were carried out with two related convex-concave and saddle-shaped hydrocarbons bearing several *ortho*-dibromo functionalities at the molecular periphery, viz. the hexabromotribenzotriquinacene **3a** and the octabromofenestrindane **4a**. In contrast to conventional palladium catalysts, use of Nájera's oxime-derived palladacycle catalyst **7** effected exhaustive vinylation with styrene or methyl acrylate in high yield and without concomitant formation of partial cross coupling or reduction products. The hexavinyltribenzotriquinacenes and octavinylfenestrindanes thus obtained are of interest as potential building blocks for novel organic networks.

Introduction

The tribenzotriquinacene **1** represents a derivative of triquinacene[1] in which the requirements of stability, reactivity and spatial geometry features are combined in a way which offers an access to a vast ground for novel molecular architecture.[2–4] A priori, the presence of three aromatic nuclei in tribenzotriquinacenes makes the rich methodology of arene chemistry applicable to these compounds, thus strongly increasing the potential for functionalization and substitution at the molecular periphery. The two different molecular surfaces of the tribenzotriquinacenes have revealed distinct reactivity towards complexation with tricarbonylmetal entities,[5,6] reflecting their recently calculated pronounced electrostatic potential of the concave surface.[7] The centrotetracyclic framework of fenestrindane **2** is closely related to **1** but the fourfold annelation of the indane units generates a saddle-like molecular shape being characteristic for the framework of *all-cis*-[5.5.5.5]fenestranes.[2,8–10] Both triquinacenes[1,2,11–16] and fenestranes[2,4,8–10,16–21] have inspired many chemists in view of their electronic, geometric and strain properties mostly at the central and peripheral bridgehead positions.



1



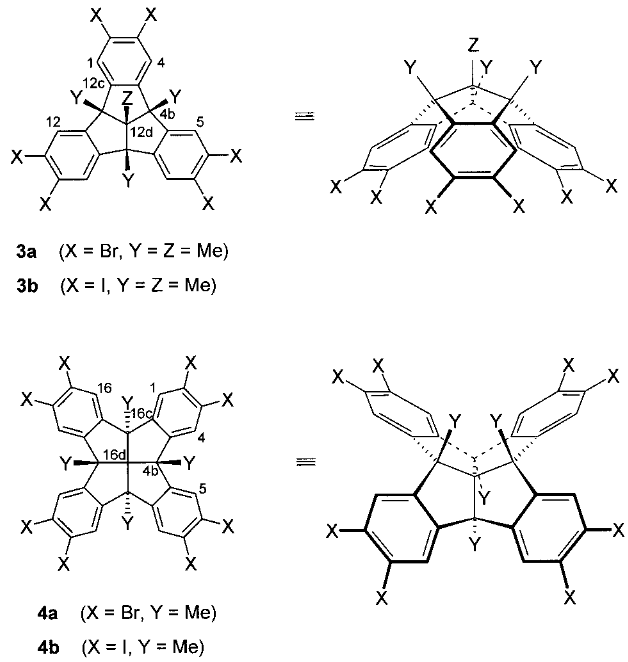
2

Beyond theoretical aspects, however, extension of the two complementary types of bent centropolyindane nuclei of **1** and **2** may lead to interesting novel, large carbon frameworks with unusual shapes and multiple functionalities, and such compounds can be of high interest for the future development of supramolecular compounds,[22] host-guest chemistry[23] and dendritic architectures.[24] Some examples involving multiple bromination and iodination of congeners of **1** and **2**, including compounds **3** and **4** (Scheme 1) and subsequent palladium-catalyzed phenylation and ethynylation reactions have been demonstrated recently.[3,9]

While the "exhaustive" Sonogashira and Suzuki coupling of tribenzotriquinacenes **3a** and **3b**, respectively, was found to occur in very good yields,[3] the corresponding reactions of the fenestrindanes **4a** and **4b** gave only moderate yields (29–35%), and a marked propensity for partial reduction of the halogene functionalities.[9,14,25–27] In fact, separation of minor amounts of the corresponding sevenfold C–C coupled fenestrindanes formed as a by-produces in both the Sonogashira and Suzuki coupling reactions proved to be difficult with fenestrindanes. Nevertheless, multiple vinylation by Pd^0-catalyzed C–C coupling at the aromatic peripheries of the bowl-shaped framework of tribenzotriquinac-

---

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, P. R. China
[b] Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 25, 33615 Bielefeld, Germany
Fax: +49-521-106-6417
E-mail: dietmar.kuck@uni-bielefeld.de



3a (X = Br, Y = Z = Me)
3b (X = I, Y = Z = Me)

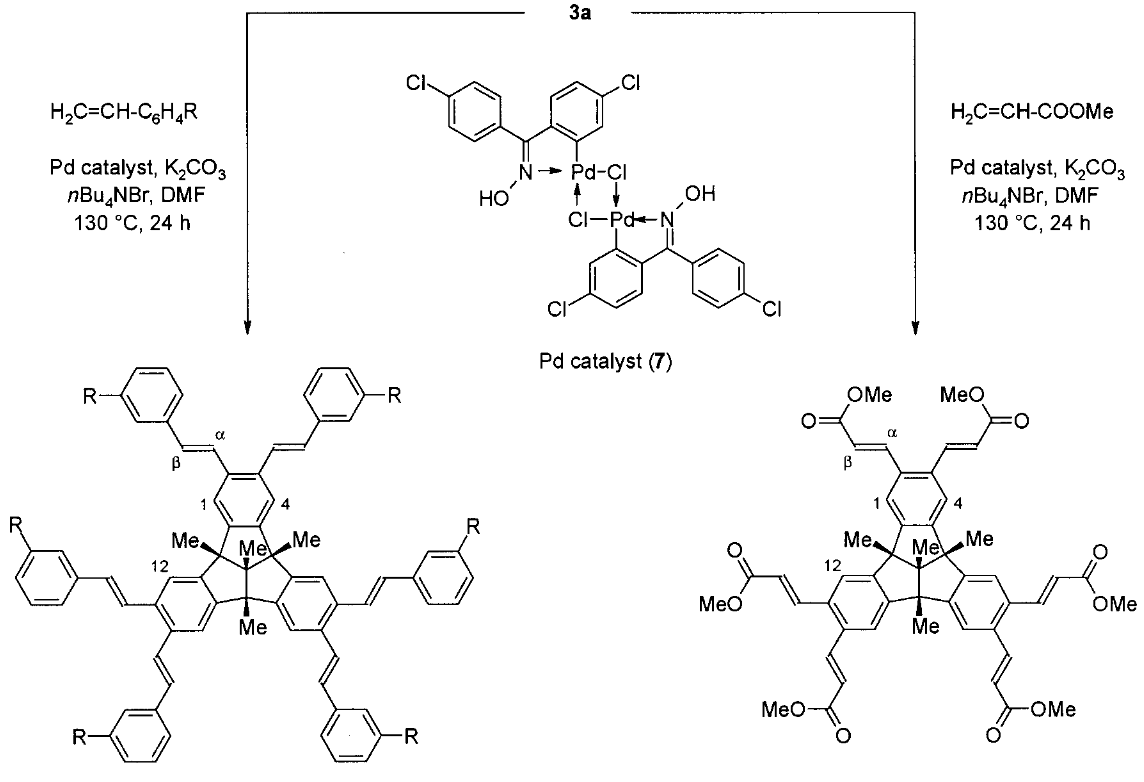
4a (X = Br, Y = Me)
4b (X = I, Y = Me)

Scheme 1. Tribenzotriquinacenes **3** and fenestrindanes (tetrabenzo[5.5.5.5]fenestranes) **4** bearing bridgehead methyl groups and fully halogene-functionalized peripheral arene positions.

enes **3** and saddle-like skeleton of fenestrindanes **4** represents a particular challenge since such compounds could prove useful for several further conversions, e.g., to novel cyclophanes consisting of two tribenzotriquinacene units. Moreover, the number of examples reported for the direct conversion of *ortho*-dihaloarenes into the corresponding *ortho*-diethenylarenes is rather limited.[26–28] Herein, we present the results of our study on the multiple vinylation of 2,3,6,7,10,11-hexabromo-4b,8b,12b,12d-tetramethyltribenzotriquinacene[3a] (**3a**) and 2,3,6,7,10,11,14,15-octabromo-4b,8b,12b,16b-tetramethylfenestrindane[9] (**4a**), which turned out to be highly efficient if one of the oxime-derived palladacycle catalysts introduced recently by Nájera and her associates[29–31] is used.

Results and Discussion

Sixfold vinylation of **3a** was studied by use of styrene, 3-nitrostyrene and methyl acrylate under conventional Heck coupling conditions.[26–28] Thus, **3a** was heated with styrene in a mixture of Pd^{II} acetate, potassium carbonate, tetrabu-



5a (R = H, 93%)
5b (R = NO_2, 88%)

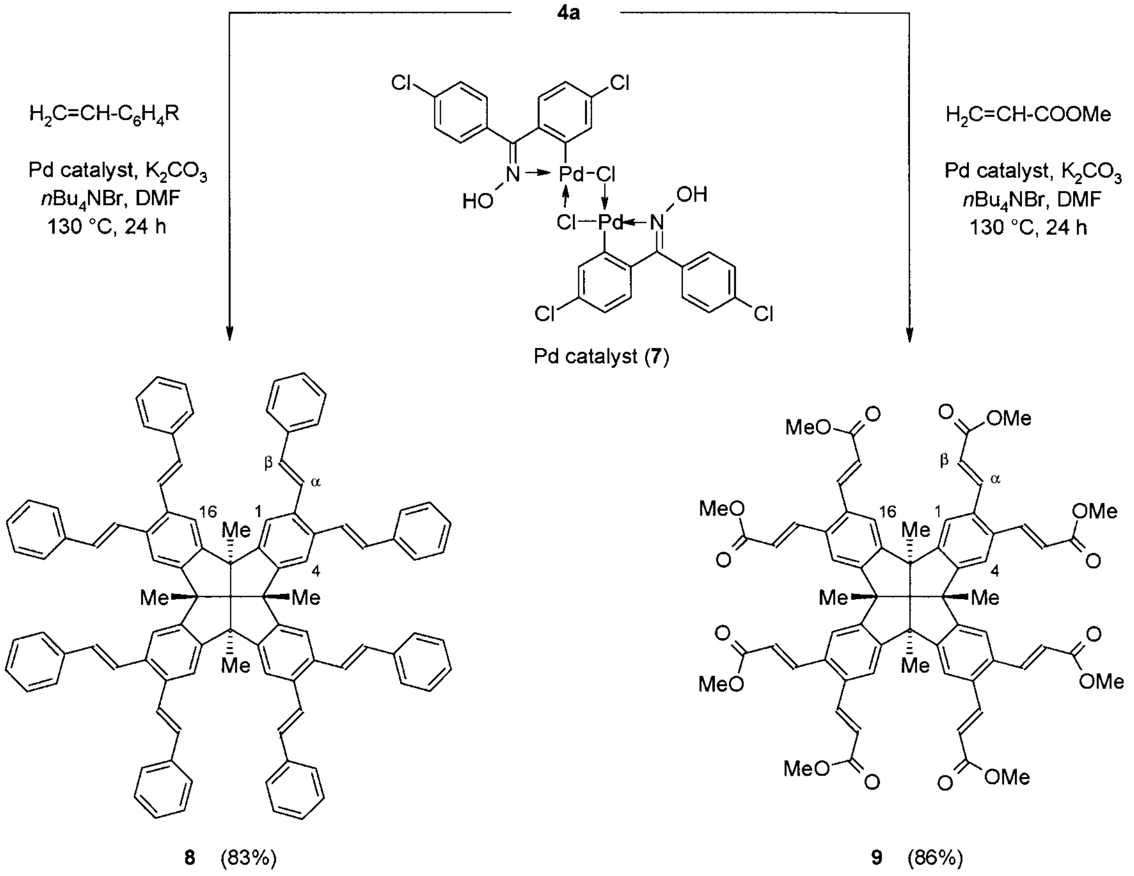
6 (90%)

Scheme 2. Synthesis of sixfold vinylated tribenzotriquinacenes **5** and **6**.

tylammonium bromide and dimethylformamide at 130 °C for 24 h. A complex mixture consisting of at least six products (and only little starting material, if any) was found by TLC, showing similar but gradually decreasing elution behavior. Analysis of this mixture by EI mass spectrometry and direct electron ionization (DEI) mass spectrometry revealed the presence of the desired sixfold C–C coupling product together with the respective partial cross-coupling products containing all of the residual bromine functionalities. Noteworthily, products of partial reduction were not observed. The most polar vinylation product turned out to be the expected hexakis-(*E*)-(β-phenylvinyl)tribenzotriquinacene **5a** (see below), which was eluted as the last fraction. This compound was isolated in 13% yield as a colorless solid of m.p. 280 °C (see below). Remarkably, addition of further $Pd(OAc)_2$ and/or base did not allow us to drive the reaction to completion. Moreover, use of methyl acrylate in place of styrene under the same conditions led to virtually analogous results: again, a complex mixture of partially vinylated products retaining the residual bromine was obtained. Other commercially available palladium catalysts that are well-know to promote Heck coupling reactions, such as those based on $PdCl_2$ and $Pd(PPh_3)_4$,[26–28] did not give satisfactory results either.

Because of the low reactivity the hexabromo compound **3a** under standard cross coupling conditions, the suitability of oxime-based palladacycle catalysts recently developed by Nájera et al.[29–31] was tested for our purposes, that is, for multiple cross-coupling at the *ortho*-dibromobenzene units of **3a** and **4a**. It turned out that one of the most active of Nájera's catalysts (**7**), prepared from lithium tetrachloropalladate and benzophenone oxime according to the published procedure,[29] effected the sixfold vinylation in surprisingly high efficiency (Scheme 2).

When a solution of hexabromotribenzotriquinacene (**3a**) in DMF was treated with styrene in the presence of Nájera's catalyst **7**, potassium carbonate and tetrabutylammonium bromide at 130 °C for 24 h, only one single spot was observed upon TLC monitoring, in sharp contrast to the above-mentioned experiments. Hexakis-(*E*)-(β-phenylvinyl)-tribenzotriquinacene (**5a**) was isolated in 93% yield, again as a colorless solid of m.p. 280 °C. Mass spectrometry, including accurate mass measurements, and ^1H NMR and ^{13}C NMR spectroscopy clearly confirmed the identity and purity of **5a**. No hints to the formation of incompletely vinylated products were found. In line with expectations, the direct electron ionization (DEI) mass spectra of **5a** exhibit the molecular ion peak at *m*/*z* 948 and the $[M - Me]^+$ signal at *m*/*z* 933 as the base peak, with further fragmentation occurring only to very minor extent. The C_{3v} symmetry of **5a** was nicely confirmed by its ^1H NMR spectra showing three multiplets centered at δ = 7.24, 7.32 and 7.50 and a



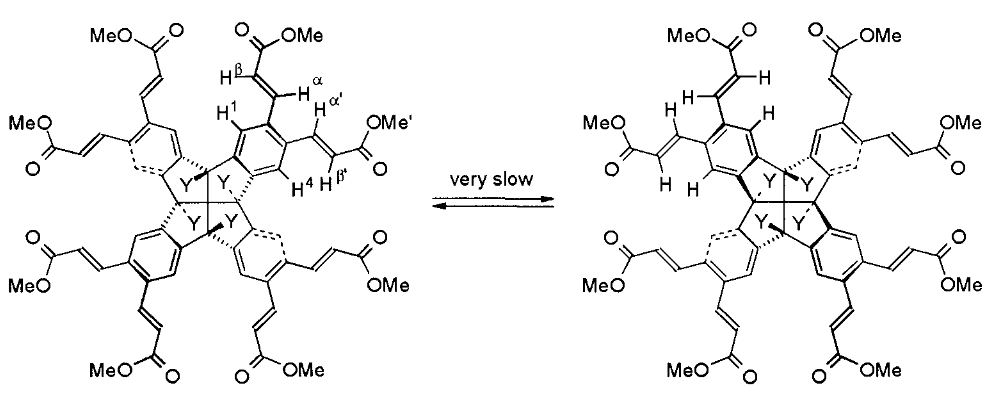
Scheme 3. Synthesis of eightfold vinylated fenestrindanes **8** and **9**.

well separated singlet at δ = 7.60 with integral ratios of 1:2:2:1, reflecting the four sets of protons at the *para*, *meta* and *ortho* positions of the phenyl rings and at the tribenzotriquinacene core, respectively. In addition, two doublets at δ = 6.94 and 7.40 ppm (^3J = 16.1 Hz) in a 1:1 ratio reflect the olefinic protons with mutual *trans* configuration. Finally, two singlets at δ = 1.44 and 1.81 ppm (1:3) were observed for the methyl protons. Accordingly, the ^{13}C NMR spectrum of **5a** also reflects its formal C_{3v} symmetry, exhibiting only nine resonances for the aromatic and olefinic carbons and four for the aliphatic ones. Attempts to achieve cyclodehydrogenation of **5a** to generate the corresponding hexaphenyl-substituted trinaphthotriquinacene proved to be unsuccessful. Thus, heating of **5a** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in xylene[32] under reflux for two days did not give any conversion to dehydrogenation products.

Similar to styrene, both 3-nitrostyrene and methyl acrylate were subjected to cross coupling with hexabromotribenzotriquinacene **3a** by use of catalyst **7** under the same conditions (Scheme 2). Remarkably, sixfold vinylation took place with similar efficiency and the corresponding products, **5b** and **6**, were also isolated in very good yields (88 and 90%, respectively). Again, incomplete vinylation was not observed and the products were found to be pure by mass spectrometry and NMR spectroscopy. Full assignment of the NMR resonances was achieved by means of HMBC and HMQC techniques (see Exp. Sect.).

Encouraged by these highly efficient multiple vinylation reactions, the octabromofenestrindane **4a** was also used as the starting material, in particular in view of its reduced reactivity towards C–C cross coupling in Sonogashira and Suzuki reactions as compared to the respective tribenzotriquinacenes.[9a] And, in fact, vinylation of fenestrane **4a** with both styrene and methyl acrylate in the presence of catalyst **7** was found to occur with surprisingly high efficiency as well (Scheme 3). Thus, octa-(*E*)-(β-phenylvinyl)-fenestrindane **8** was isolated in good yield (83%) as a yellowish, amorphous solid. Likewise, eightfold vinylation of **4a** with methyl acrylate took place with similar efficiency and fenestrindane octaester **9** was isolated in excellent yield (86%). In both cases, products formed by partial cross coupling or reduction were not observed. Therefore, Nájera's catalyst **7** proved to be very useful to effect multiple cross coupling even with bromine-substituted fenestrindanes. In contrast to styrene and methyl acrylate, however, 3-nitrostyrene did not give satisfactory results upon our attempts to perform eightfold cross coupling with fenestrindane **4a** under similar conditions.

DEI mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy unequivocally documented the identity and purity of the fenestranes **8** and **9**. However, a particularly noteworthy feature of the fenestrindanes bearing sterically interacting bridgehead substitutents (Y = Me in the present case) was encountered in the NMR spectra of **8** and **9**. For example, the eight *ortho* protons of the fenestrindane core of the octastyrylfenestrindane **8** give rise to two clearly separated singlets at δ = 7.47 (4 H) and δ = 7.78 (4 H). Likewise, the olefinic protons are reflected in two sets of four equivalent AB spin systems centered at δ = 7.02 and 7.46 ppm and, likewise, at δ = 7.14 and 7.54 ppm (^3J = 16.1 Hz for 4 H in both cases). This clearly reflects our previous finding that the molecular framework of the fenestrindanes adopt two equivalent and apparently static S_4-symmetric conformations, rather than a single D_{2d}-symmetrical one.[8,19] Accordingly, the ^{13}C NMR spectrum of **8** exhibits nine pairs of resonances for the formally equivalent carbons at the indane junctions, for the eight *ortho* positions and eight peripheral positions of the fenestrindane core and even for those at the pendant styryl groups. Assignment of the resonances was again achieved by applying two-dimensional NMR techniques (see Exp. Sect.). Similar splitting of ^{1}H- and ^{13}C NMR resonances into two sets was found for the fenestrindane octaester **9**, reflecting its two equivalent S_4-symmetrical ground state conformers, **9A** and **9A′** (Scheme 4 and Figure 1).



rotamer **9A** (Y = Me) rotamer **9A'**

Scheme 4. Conformational equilibrium of the S_4-symmetrical conformers of fenestrindane **9**.

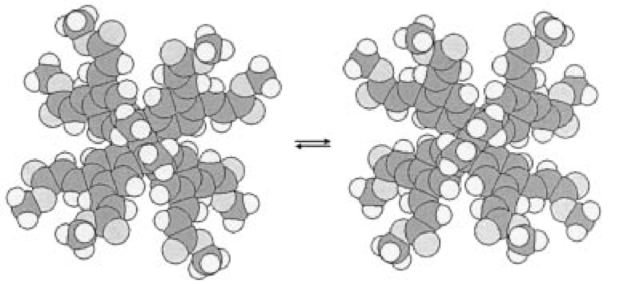


Figure 1. The two (equivalent) conformers of fenestrindane octaester **9**, as calculated by molecular mechanics (HYPERCHEM™ 6.01); grey (C), light grey (O), white (H).

Conclusions

The results presented here demonstrate that multiple Heck-type cross C–C coupling reactions can be performed with great efficiency by use of Nájera's 4,4′-dichlorobenzophenone oxime derived palladium catalyst **7**. It is particularly noteworthy that *ortho*-divinylation of three and even four 1,2-dibromobenzene units is very efficient. In this way, several sixfold vinylated tribenzotriquinacenes and eightfold vinylated fenestrindanes have become accessible and extension of the convex-concave or saddle-shaped carbon framework promises a facile access to a great variety of novel organic architectures bearing these centropolyindane cores.

Experimental Section

General: Melting points (uncorrected): Electrothermal Melting point apparatus. IR spectroscopy: Nicolet AVATAR 360 FT-IR. NMR spectroscopy: Bruker DRX 500 (^{1}H at 500 MHz, ^{13}C at 125.7 MHz) and Bruker Avance 600 (^{1}H at 600 MHz, ^{13}C at 150.9 MHz) using the DEPT technique. Mass spectrometry: Fisons VG Autospec; accurate mass measurements were performed by use of the peak-matching method at a resolution of $m/\Delta m$ = 8000 (10% valley). HPLC purification of compound **8** was performed by use of a Merck–Hitachi instrument equipped with an L-6250 Intelligent Pump, an L-7420 UV/Vis detector and a Hibar column packed with LiChrosorb Si 60 (Ø, 7 µm). The isocratic runs (cyclohexane/CHCl$_3$, 2:1, v/v) were monitored at λ = 280 nm.

4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexakis[(*E*)-2-phenylvinyl]-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (5a): A mixture of the hexabromotribenzotriquinacene **3a** (162 mg, 0.20 mmol), phenylethylene (208 mg, 2.0 mmol), potassium carbonate (303 mg, 2.2 mmol), (n-C$_4$H$_9$)$_4$NBr (103 mg, 0.32 mmol), catalyst **7** (3.26 mg, 4 µmol, 0.4 mol-% Pd), and dimethylformamide (4 mL) was heated at 130 °C under argon for 24 h. The reaction mixture was allowed to cool and then poured into ice-cold water. This mixture was extracted several times with ethyl acetate, the combined extracts were dried with magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (hexane/CHCl$_3$, 10:1, gradient to 3:1) to give compound **5a** (176 mg, 93%) as a slightly yellow, amorphous solid, m.p. 280 °C (decomp.), R_f 0.5 (hexane/CHCl$_3$, 3:1). IR (KBr): $\tilde{\nu}$ = 3023 cm^{-1}, 2962, 1598, 1493, 957, 907, 748, 731, 692. UV/Vis (CHCl$_3$, c = 1.11 × 10^{-6} mol·L^{-1}): $\lambda_{\max}$ (lg ε) = 301 nm (1.07). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.44 (s, 3 H, 12d-CH$_3$), 1.80 (s, 9 H, 4b-CH$_3$ etc.), 6.94 (d, ^3J = 16.1 Hz, 6 H, β-H), 7.24 (t, ^3J = 7.6 Hz, 6 H, H$^{\mathrm{Ph}(para)}$), 7.32 (t, ^3J = 7.6 Hz, 12 H, H$^{\mathrm{Ph}(meta)}$), 7.40 (d, ^3J = 16.1 Hz, 6 H, α-H), 7.50 (d, ^3J = 7.6 Hz, 12 H, H$^{\mathrm{Ph}(ortho)}$), 7.60 (s, 6 H, 1-H etc.). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ = 16.2 (p, 12d-CH$_3$), 25.9 (p, 4b-CH$_3$ etc.), 62.6 (q, 4b-C etc.), 70.8 (q, 12d-C), 121.2 (t, 1-C etc.), 126.6 (t, C$^{\mathrm{Ph}(ortho)}$), 127.3 (t, C-β), 127.7 (t, C-α), 128.7 (t, C$^{\mathrm{Ph}(meta)}$), 131.2 (t, C$^{\mathrm{Ph}(para)}$), 136.4 (q, C$^{\mathrm{Ph}(ipso)}$), 137.5 (q, C-2 etc.), 148.7 (q, C-4a etc.). MS (DEI, 70 eV): m/z (rel. int.,%) = 948 (M$^{\cdot+}$, 41), 933 (100, [M – CH$_3$]$^+$), 842 (21), 647 (15). Accurate mass determined by DEI-MS (C$_{74}$H$_{60}$): calcd. 948.4695; found 948.4644.

4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexakis[(*E*)-2-(3-nitrophenyl)vinyl]-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (5b). A mixture of the hexabromotribenzotriquinacene **3a** (81 mg, 0.1 mmol), (3-nitrophenyl)ethylene (150 mg, 1.0 mmol), K$_2$CO$_3$ (151 mg, 1.1 mmol), (n-C$_4$H$_9$)$_4$NBr (51 mg, 0.16 mmol), catalyst **7** (1.63 mg, 2.0 µmol, 0.2 mol-% Pd), and dimethylformamide (4 mL) was heated at 130 °C under argon for 24 h. The reaction mixture was then worked up following the same procedure as that described in compound **5a**. The residue was purified by flash chromatography (hexane/CHCl$_3$, 1:1) to give compound **5b** (107 mg, 88%) as a yellow, amorphous solid with m.p. > 300 °C, R_f 0.4 (hexane/CHCl$_3$, 2:1). IR (KBr): $\tilde{\nu}$ = 2921 cm^{-1}, 1608, 1070, 1024, 758. UV/Vis (CHCl$_3$, c = 1.80 × 10^{-6} mol·L^{-1}): $\lambda_{\max}$ (lg ε) = 279 nm (0.90). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.48 (s, 3 H, 12d-CH$_3$), 1.83 (s, 9 H, 4b-CH$_3$ etc.), 6.99 (d, ^3J = 16.1 Hz, 6 H, β-H), 7.49 (d, ^3J = 16.1 Hz, 6 H, α-H), 7.52 (t, ^3J = 8.0, 6 H, H$^{\mathrm{Ph}(5)}$), 7.63 (s, 6 H, 1-H etc.), 7.79 (d, ^3J = 8.1 Hz, 6 H, H$^{\mathrm{Ph}(4)}$), 8.10 (d, ^3J = 8.1 Hz, 6 H, H$^{\mathrm{Ph}(6)}$), 8.30 (s, 6 H, H$^{\mathrm{Ph}(2)}$). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.46 (s, 3 H, 12d-CH$_3$), 1.85 (s, 9 H, 4b-CH$_3$ etc.), 7.53 (d, ^3J = 16.1 Hz, 6 H, β-H), 7.64 (t, ^3J = 8.0, 6 H, H$^{\mathrm{Ph}(5)}$), 7.95 (d, ^3J = 16.1 Hz, 6 H, α-H), 8.10 (dd, ^3J = 8.2, ^4J = 2.0 Hz, 6 H, H$^{\mathrm{Ph}(4)}$), 8.21 (s, 6 H, 1-H etc.), 8.27 (d, ^3J = 7.9 Hz, 6 H, H$^{\mathrm{Ph}(6)}$), 8.44 (s, 6 H, H$^{\mathrm{Ph}(2)}$). ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 15.7 (p, 12d-CH$_3$), 25.1 (p, 4b-CH$_3$ etc.), 62.6 (q, C-4b etc.), 69.8 (q, C-12d), 120.9 (t, C-1 etc.), 121.7 (t, C$^{\mathrm{Ph}(5)}$), 122.1 (t, C$^{\mathrm{Ph}(4)}$), 128.3 (t, C-β), 128.7 (t, C-α), 130.1 (t, C$^{\mathrm{Ph}(6)}$), 132.4 (t, C$^{\mathrm{Ph}(2)}$), 135.3 (q, C-2 etc.), 139.3 (q, C$^{\mathrm{Ph}(1)}$), 148.3 (q, C$^{\mathrm{Ph}(3)}$), 149.5 (q, C-4a etc.). Various attempts to characterize **5b** by mass spectrometry, including DEI, APCI and MALDI as ionization techniques, were unsuccessful.

2,3,6,7,10,11-Hexakis[(*E*)-2-(methoxycarbonyl)vinyl]-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (6): A mixture of the hexabromotribenzotriquinacene **3a** (81 mg, 0.10 mmol), methyl acrylate (86 mg, 1.0 mmol), potassium carbonate (151 mg, 1.1 mmol), (n-C$_4$H$_9$)$_4$NBr (51 mg, 0.16 mmol), catalyst **7** (1.63 mg, 2.0 µmol, 0.2 mol-% Pd), and dimethylformamide (4 mL) was heated at 130 °C under argon for 24 h. The reaction mixture was then worked up following the same procedure as that described above. The residue was purified by flash chromatography (hexane/CHCl$_3$, 1:1) to give compound **6** (76 mg, 90%) as a yellow, amorphous solid with m.p. 284 °C (decomp.), R_f 0.5 (CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2951 cm^{-1}, 1718, 1634, 1279, 1173, 976, 864, 731. UV/Vis (CHCl$_3$, c = 1.15 × 10^{-6} mol·L^{-1}): $\lambda_{\max}$ (lg ε) = 283 nm (1.48). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.35 (s, 3 H, 12d-CH$_3$), 1.67 (s, 9 H, 4b-CH$_3$ etc.), 3.81 (s, 18 H, OCH$_3$), 6.28 (d, ^3J = 15.8 Hz, 6 H, β-H), 7.46 (s, 6 H, 1-H etc.), 7.91 (d, ^3J = 15.8 Hz, 6 H, α-H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ = 16.0 (p, 12d-CH$_3$), 25.7 (p, 4b-CH$_3$ etc.), 51.9 (p, OCH$_3$), 62.7 (q, C-4b etc.), 71.0 (q, C-12d), 121.7 (t, C-β), 122.3 (t, C-1 etc.), 134.8 (q, C-2 etc.), 141.8 (t, C-α), 150.3 (q, C-4a etc.), 166.7 (q, CO). MS (DEI, 70 eV): m/z (rel. int.,%) = 840 (M$^{\cdot+}$, 28), 825 (60, [M – CH$_3$]$^+$), 809 (31, [M – OCH$_3$]$^+$), 749 (100), 717 (56), 689 (47). MS [ESI(+), CHCl$_3$/MeOH, (1:1), NaBF$_4$]: m/z (rel. int.,%) = 863.5 (100) [M + Na]$^+$, 443 (5, [M + 2 Na]$^{2+}$). Accurate mass determined by ESI-FTMS of [M + Na]$^+$ ($C_{50}H_{48}NaO_{12}$): calcd. 863.3038; found 863.3019.

4b,8b,12b,16b-Tetramethyl-2,3,6,7,10,11,14,15-octakis[(*E*)-2-phenylvinyl]-4b,8b,12b,16b-tetrahydrodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene, [4b,8b,12b,16b-Tetramethyl-2,3,6,7,10,11,14,15-octa-(*E*)-(β-phenylvinyl)fenestrindane] (8): A mixture of the octabromo-tetramethylfenestrindane **4a** (106 mg, 0.10 mmol), phenylethylene (124 mg, 1.2 mmol), potassium carbonate (186 mg, 1.34 mmol), (n-$C_4H_9)_4NBr$ (62 mg, 0.20 mmol), catalyst **7** (1.63 mg, 2.0 µmol, 0.2 mol-% Pd), and dimethylformamide (4 mL) was heated at 130 °C under argon for 24 h. The reaction mixture was then worked up following the same procedure as that described above for the tribenzotriquinacenes **5** and **6**. The residue was purified by flash chromatography (hexane/$CHCl_3$, 1:1) followed by HPLC (silica gel, cyclohexane/$CHCl_3$, 2:1, v/v) to give compound **8** (103 mg, 83%) as a yellow, amorphous solid, m.p. 240 °C (decomp.), R_f 0.5 (hexane/$CHCl_3$, 4:1). IR (KBr): $\tilde{\nu}$ = 3022 cm^{-1}, 2961, 1597, 1492, 1474, 1446, 957, 900, 747, 691. UV/Vis ($CHCl_3$, $c = 1.25\times10^{-6}$ mol·L^{-1}): λ_{max} (lg ε) = 298 nm (1.29). ^{1}H NMR ($CDCl_3$): δ = 1.41 (s, 12 H, CH_3), 7.02 (d, ^3J = 16.1 Hz, 4 H, β-H), 7.14 (d, ^3J = 16.1 Hz, 4 H, β′-H), 7.25 (t, ^3J = 7.6 Hz, 4 H, $H^{Ph(para)}$), 7.27 (t, ^3J = 7.6 Hz, 4 H, $H^{Ph'(para)}$), 7.33 (t, ^3J = 8.0 Hz, 8 H, $H^{Ph(meta)}$), 7.37 (t, ^3J = 7.7 Hz, 8 H, $H^{Ph'(meta)}$), 7.46 (d, ^3J = 16.1 Hz, 4 H, α-H), 7.47 (s, 4 H, 1-H, 5-H, 9-H, 13-H), 7.52 (d, ^3J = 7.3 Hz, 8 H, $H^{Ph(ortho)}$), 7.54 (d, ^3J = 16.1 Hz, 4 H, α′-H), 7.57 (d, ^3J = 7.6 Hz, 8 H, $H^{Ph'(ortho)}$), 7.78 (s, 4 H, 4-H, 8-H, 12-H, 16-H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 28.3 (p, CH_3), 58.9 (q, 4b-C etc.), 89.2 (q, 16d-C), 119.9 (t, 1-C, 5-C, 9-C, 13-C), 122.0 (t, 4-C, 8-C, 12-C, 16-C), 126.5 (t), 126.63 (t), 127.0 (t), 127.2 (t), 127.7 (t), 128.5 (t), 128.71 (t), 128.75 (t), 130.9 (t), 131.3 (t), 135.7 (q), 136.2 (q), 137.57 (q, 2-C, 6-C, 10-C, 14-C), 137.58 (q, 3-C, 7-C, 11-C, 15-C), 146.6 (q), 151.7 (q). MS (DEI, 70 eV): m/z (rel. int.,%) = 1240.6 (28, $M^{\cdot+}$), 1241.7 (28, [$^{13}C_1$][$M^{\cdot+}$]), 1225.6 (100, [M – CH_3]$^+$), 1226.6 (97, [$^{13}C_1$][M – CH_3]$^+$), 1124 (34), 1123 (34), 620 (6, M^{2+}), 613 (7, [M – CH_3]$^{2+}$), 567 (10), 262 (42), 181 (72). MS [APCI(+)]: m/z (rel. int.,%) = 1241.6 (100) [M + H]$^+$, 1242.6 (98, [$^{13}C_1$][M + H]$^+$). Accurate mass determined by ESI-FTMS of [M + H]$^+$ ($C_{97}H_{77}$): calcd. 1241.6020; found 1241.6030.

2,3,6,7,10,11,14,15-Octakis[(*E*)-2-(methoxycarbonyl)vinyl]-4b,8b,12b,16b-tetramethyl-4b,8b,12b,16b-tetrahydrodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene, {4b,8b,12b,16b-tetramethyl-2,3,6,7,10,11,14,15-octakis[(*E*)-2-(methoxycarbonyl)vinyl]fenestrindane} (9): A mixture of the octabromo-tetramethylfenestrindane **4a** (106 mg, 0.10 mmol), methyl acrylate (103 mg, 1.2 mmol), potassium carbonate (186 mg, 1.34 mmol), (n-$C_4H_9)_4NBr$ (62 mg, 0.20 mmol), catalyst **7** (1.63 mg, 2.0 µmol, 0.2 mol-% Pd), and dimethylformamide (4 mL) was heated at 130 °C under argon for 24 h. The reaction mixture was then worked up following the same procedure as described above. The residue was purified by flash chromatography (hexane/$CHCl_3$, 1:1) to give compound **9** (94 mg, 86%) as a yellow, amorphous solid, m.p. 280 °C (decomp.), R_f 0.5 ($CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 1720, 1633, 1173, 976, 864, 730. UV/Vis ($CHCl_3$, $c = 1.60\times10^{-6}$ mol·L^{-1}): λ_{max} (lg ε) = 275 nm (1.24). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (s, 12 H, CH_3), 3.84 (s, 12 H, OCH_3), 3.81 (s, 12 H, OCH_3), 6.32 (d, ^3J = 15.8 Hz, 4 H, β-H), 6.47 (d, ^3J = 15.8 Hz, 4 H, β′-H), 7.36 (s, 4 H, 1-H, 5-H, 9-H, 13-H), 7.66 (s, 4 H, 4-H, 8-H, 12-H, 16-H), 8.00 (d, ^3J = 15.8 Hz, 4 H, α-H), 8.04 (d, ^3J = 15.8 Hz, 4 H, α′-H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 28.0 (p, CH_3), 51.93 (p, OCH_3), 51.94 (p, OCH_3), 58.8 (q, 4b-C etc.), 88.9 (q, 16d-C), 120.7 (t, 1-C, 5-C, 9-C, 13-C), 121.6 (t, β-C), 121.8 (t, β′-C), 123.1 (t, 4-C, 8-C, 12-C, 16-C), 134.4 (q, 2-C, 6-C, 10-C, 14-C), 134.9 (q, 3-C, 7-C, 11-C, 15-C), 141.2 (t, α-C), 141.3 (t, α′-C), 147.9 (q), 153.0 (q), 166.68 (q, CO), 166.76 (q, CO’). MS (DEI, 70 eV): m/z (rel. int.,%) = 1096 (< 1, $M^{\cdot+}$), 1081 (52, [M – CH_3]$^+$), 1005 (30), 945 (12), 933 (5). MS [ESI(+), $CHCl_3$/MeOH, 1:1, $NaBF_4$]: m/z (rel. int.,%) = 1119.4 (75, [M + Na]$^+$), besides 685.4 (85, unknown) and 413.3 (100, unknown). Accurate mass determined by ESI-FTMS of [M + Na]$^+$ ($C_{65}H_{60}NaO_{16}$): calcd. 1119.3774; found 1119.3774.

Acknowledgments

We would like to thank Mr Olaf Barton for providing the catalyst and for valuable discussions, and Dr Andreas Mix and Dr Matthias Letzel, respectively, for their careful NMR spectroscopic and mass spectrometric measurements, respectively. We are also grateful to the German Science Foundation (DFG, 446 CHV 112/40/03), the Ministry of Education (MoE) and the National Natural Science Foundation of China (20472025, QT 20021001), for financial support.

---

[1] R. B. Woodward, T. Fukunaga, R. C. Kelly, *J. Am. Chem. Soc.* **1964**, *86*, 3162–3164.

[2] D. Kuck, *Top. Curr. Chem.* **1998**, *196*, 167–220.

[3] a) D. Kuck, A. Schuster, R. A. Krause, J. Tellenbröker, C. P. Exner, M. Penk, H. Bögge, A. Müller, *Tetrahedron* **2001**, *57*, 3587–3613; b) J. Tellenbröker, D. Kuck, *Angew. Chem.* **1999**, *111*, 1000–1004; *Angew. Chem. Int. Ed.* **1999**, *38*, 919–922.

[4] H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**.

[5] A. Ceccon, A. Gambaro, F. Manoli, A. Venzo, D. Kuck, T. E. Bitterwolf, P. Ganis, G. Valle, *J. Chem. Soc. Perkin Trans. 2* **1991**, 233–241.

[6] C. A. Dullaghan, G. B. Carpenter, D. A. Sweigart, D. Kuck, C. Fusco, R. Curci, *Organometallics* **2000**, *19*, 2233–2236.

[7] a) M. Kamieth, F. G. Klärner, F. Diederich, *Angew. Chem.* **1998**, *110*, 3497–3500; *Angew. Chem. Int. Ed.* **1998**, *37*, 3303–3306; b) F. G. Klärner, J. Panitzky, D. Preda, L. T. Scott, *J. Mol. Mod.* **2000**, *6*, 318–327.

[8] D. Kuck, in: *Advances in Theoretically Interesting Molecules* (Ed.: R. P. Thummel), JAI Press, Greenwich, London, **1998**, vol. 4, pp. 81–155.

[9] J. Tellenbröker, D. Kuck, *Eur. J. Org. Chem.* **2001**, 1483–1489.

[10] a) B. Bredenkötter, U. Flörke, D. Kuck, *Chem. Eur. J.* **2001**, *7*, 3387–3400; b) B. Bredenkötter, D. Barth, D. Kuck, *J. Chem. Soc. Chem. Commun.* **1999**, 847–848.

[11] a) L. A. Paquette, S. V. Ley, S. Maiorana, D. F. Schneider, M. J. Broadhurst, R. A. Boggs, *J. Am. Chem. Soc.* **1975**, *97*, 4658–4667, cf. footnote 25 therein; b) L. A. Paquette, *Top. Curr. Chem.* **1979**, *79*, 41–165; c) L. A. Paquette, *Top. Curr. Chem.* **1984**, *119*, 1–160; d) L. A. Paquette, A. M. Doherty, *Polyquinane Chemistry, Synthesis and Reactions*, Springer-Verlag, Berlin, **1987**.

[12] a) J. F. Liebman, L. A. Paquette, J. R. Peterson, D. W. Rogers, *J. Am. Chem. Soc.* **1986**, *108*, 8267–8268; b) M. J. Dewar, A. J. Holder, *J. Am. Chem. Soc.* **1989**, *111*, 5384–5397; c) J. W. Storer, K. N. Houk, *J. Am. Chem. Soc.* **1992**, *114*, 1165–1168; d) A. Holder, *J. Comput. Chem.* **1993**, *14*, 251; e) S. P. Verevkin, H. D. Beckhaus, C. Rüchardt, R. Haag, S. I. Kozhushkov, T. Zywietz, A. de Meijere, H. Jiao, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1998**, *120*, 11130–11135; f) D. W. Rogers, F. J. McLafferty, *J. Phys. Chem. A* **2000**, *104*, 9356–9361.

[13] a) R. Haag, A. de Meijere, *Top. Curr. Chem.* **1998**, *196*, 135–163; b) A. de Meijere, R. Haag, F. M. Schüngel, S. I. Kozhushkov, I. Emme, *Pure Appl. Chem.* **1999**, *71*, 253–264.

[14] a) D. Kuck, A. Schuster, B. Ohlhorst, V. Sinnwell, A. de Meijere, *Angew. Chem.* **1989**, *101*, 626–628; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 595–597; b) R. Haag, B. Ohlhorst, M. Noltemeyer, R. Fleischer, D. Stahlke, A. Schuster, D. Kuck, A. de Meijere, *J. Am. Chem. Soc.* **1995**, *117*, 10474–10485.

[15] A. Schuster, D. Kuck, *Angew. Chem.* **1991**, *103*, 1717–1720; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1699–1702.

[16] D. Kuck, A. Schuster, C. Fusco, M. Fiorentino, R. Curci, *J. Am. Chem. Soc.* **1994**, *116*, 2375–2381.

[17] a) M. Thommen, R. Keese, *Synlett* **1997**, 231–240; b) W. Luef, R. Keese, in: (Ed.:B. Halton), *Advances in Strain in Organic Chemistry*, *Vol. 3*, JAI Press, Greenwich, CT, **1993**, pp. 229–267.

[18] a) R. Hoffmann, R. Alder, C. F. Wilcox, *J. Am. Chem. Soc.* **1970**, *92*, 4992–4993; b) R. Hoffmann, *Pure Appl. Chem.* **1971**, *28*, 181–194.

[19] D. Kuck, A. Schuster, R. A. Krause, *J. Org. Chem.* **1991**, *56*, 3472–3475.

[20] A. K. Gupta, X. Fu, J. P. Snyder, J. M. Cook, *Tetrahedron* **1991**, *47*, 3665–3710.

[21] a) D. Kuck, A. Schuster, D. Gestmann, F. Posteher, H. Pritzkow, *Chem. Eur. J.* **1996**, *2*, 58–67; b) D. Kuck, A. Schuster, D. Gestmann, *J. Chem. Soc. Chem. Commun.* **1994**, 609–610.

[22] a) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; b) H. Dodziuk, *Introduction to Supramolecular Chemistry*, Kluwer Academic Publishers, Dordrecht, **2002**; c) C. A. Schalley, *Mass Spectrom. Rev.* **2001**, *20*, 253–309.

[23] a) D. J. Cram, J. M. Cram, *Container Molecules and Their Guests*, The Royal Society of Chemistry, Cambridge, **1994**; b) M. Vincenti, *J. Mass Spectrom.* **1995**, *30*, 925–939; c) M. W. P. L. Baars, E. W. Meijer, *Top. Curr. Chem.* **2000**, *210*, 131–182.

[24] a) J. Issberger, R. Moors, F. Vögtle, *Angew. Chem.* **1994**, *106*, 2507–2514; *Angew. Chem. Int. Ed. Engl.; Angew. Chem. Int. Ed.* **1994**, *33*, 2413–2420; b) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules. Concepts, Syntheses, Perspectives*, Wiley-VCH, Weinheim, **1996**; c) S. C. Zimmerman, L. J. Lawless, *Top. Curr. Chem.* **2001**, *217*, 95–120.

[25] J. Nierle, D. Barth, D. Kuck, *Eur. J. Org. Chem.* **2004**, 867–872.

[26] A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473–2506; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379–2411.

[27] W. Tao, S. Nesbitt, R. F. Heck, *J. Org. Chem.* **1990**, *55*, 63–69.

[28] a) J. E. Plevyak, R. F. Heck, *J. Org. Chem.* **1978**, *43*, 2454–2456; b) J. E. Plevyak, J. E. Dickerson, R. F. Heck, *J. Org. Chem.* **1979**, *44*, 4078–4080.

[29] a) D. A. Alonso, C. Nájera, M. C. Pacheco, *J. Org. Chem.* **2002**, *67*, 5588–5594; b) D. A. Alonso, C. Nájera, M. C. Pacheco, *Org. Lett.* **2000**, *2*, 1823–1826**.**

[30] D. A. Alonso, L. Botella, C. Nájera, C. Pacheco, *Tetrahedron Lett.* **2002**, *43*, 9365–9368.

[31] a) D. A. Alonso, L. Botella, C. Nájera, C. Pacheco, *Synthesis* **2004**, 1713–1718; b) L. Botella, C. Nájera, *Tetrahedron Lett.* **2004**, *45*, 1833–1836; c) L. Botella, C. Nájera, *J. Organomet. Chem.* **2002**, *663*, 46–57.

[32] O. Reiser, B. König, K. Meerholz, J. Heinze, T. Wellauer, F. Gerson, R. Frim, M. Rabinovitz, A. de Meijere, *J. Am. Chem. Soc.* **1993**, *115*, 3511–3518.

Received: March 4, 2005