En Route to 7,7,8,8-Tetraethynyl-*p*-quinodimethane (TEQ)[‡]

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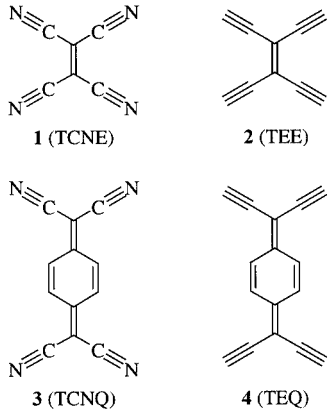
Dedicated to Professor Lutz F. Tietze on the occasion of his 60th birthday

Keywords: Alkynes / Dendralenes / Isomerization / Photochemistry / Polycycles / Sonogashira coupling

The cross-conjugated 1,1-diethynylethylene derivatives **8b**–**10b** were prepared from the corresponding bromides **16**, **19**, and **17** by Sonogashira coupling with trimethylsilylethyne and hydrolysis of the TMS-protected intermediates thus formed. Coupling of the tetrabromide **18** with (trimethylsilylethynyl)magnesium bromide in the presence of 1,3-[bis(diphenylphosphanyl)propane]nickel(II) chloride yielded the protected tetraalkyne **32**, from which the 7,7,8,8-tetraethynyl-tetrahydro-*p*-quinodimethane **33** was liberated by fluoride treatment. Although **33** is a highly unstable cross-conjugated hydrocarbon, it could be converted into its tetraphenyl derivative by Sonogashira coupling with phenyl iodide. Both **32** and the corresponding tetraphenyl derivative were oxidized to the 7,7,8,8-tetraethynyl-dihydro-*p*-quinodimethane derivatives **35** and **36**, respectively, on treatment with DDQ in dioxane. Further dehydrogenation of **35** to **34** failed, however. Alkylation of **9b** with trimethylaluminium in the presence of zirconocene dichloride as catalyst yielded the semicyclic dendralene **37**, which on irradiation isomerized to the tricyclic diene **42**, presumably via the bicyclobutane **39** and a vinylcyclopropane rearrangement. Hydration of **9b** furnished **43** and **44**, the primary hydration product **38** either undergoing ketene elimination (formation of **43**) or a 1,5-hydrogen shift reaction (to **44**) from its tautomer **41**. Analogously, the still more highly unsaturated derivative **31** was alkylated to give the [5]dendralene derivative **45** and hydrated to give a mixture of the β-diketones **46** and **49**, the latter being produced from **46** by 1,2-methyl migration. The thermal cyclization of **10b** to the homoacepentalene derivative **51** failed.

Introduction

Tetracyanoethylene (TCNE, **1**), prepared in 1957 by du Pont chemists,[2] was the first example of a percyanoolefin and quickly gained importance in preparative and mechanistic chemistry because of its high reactivity in addition and substitution reactions[3] and its ability to form charge-transfer complexes,[4] to name but a few of its numerous applications.[5] Only a few years later, another polycyano-substituted compound also destined to have a lasting influence on organic chemistry, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, **3**), was described.[6] This bis(vinylogous) derivative of **1** became prominent in particular for the preparation of highly conducting charge-transfer salts such as the tetrathiafulvalene−TCNQ complex,[7] thus contributing to the still intensely studied area of "organic metals".[8] The all-carbon parent systems of these strong electron acceptors are tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne, **2**) and 7,7,8,8-tetraethynyl-*p*-quinodimethane (TEQ, **4**, Scheme 1).



Scheme 1. A selection of important cross-conjugated systems

Whereas compound **2**, interest in which goes back to the late 1960s,[9] was finally synthesized by Diederich and coworkers in 1991,[10] the preparation of **4** has to the best of our knowledge[11] not so far been described. TEE and its

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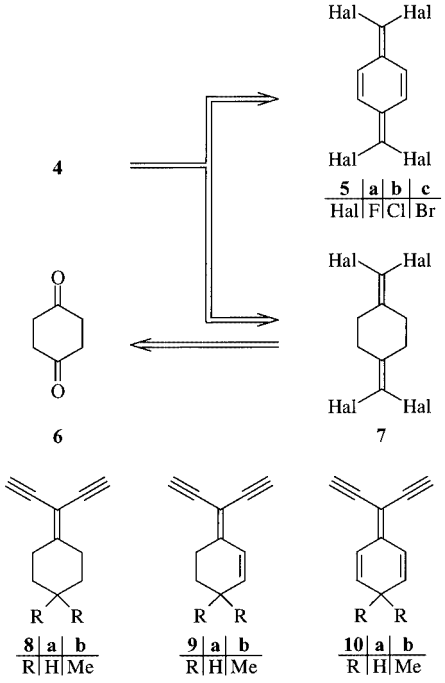
derivatives have proven to be most interesting π-systems for the construction of very large extended conjugated structures that show promise for applications in material science.[12] In this publication we describe our first efforts to prepare derivatives of and precursors for **4**. As will be shown, the most highly unsaturated derivatives of TEQ that we have so far been able to prepare are dihydro derivatives of the tetraphenyl- and tetrakis(trimethylsilyl)-protected compounds.

Results and Discussion

Preparation of Model Compounds and of Di- and Tetrahydro-TEQs

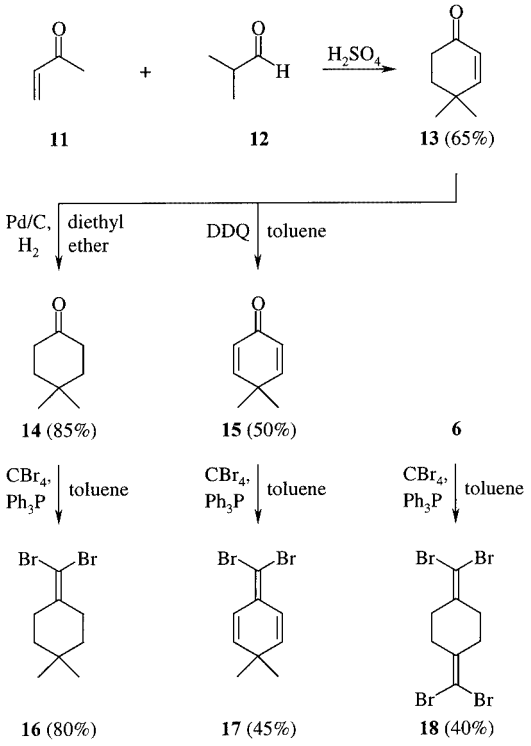
From the retrosynthetic viewpoint, promising starting materials for **4** offer themselves in the forms of the tetrahalo-*p*-xylylenes **5b**[13] and **5c**,[14] which – like their tetrafluoro analogue **5a**[15] – have been described several times in the literature. However, since we feared that their high reactivity, which results in dimerization (formation of [2.2]paracyclophane derivatives) and polymerization (production of halogenated "parylenes"), would interfere with the intended coupling reactions of these substrates with various (protected) acetylenes, we initially decided to aim for a lesser goal: the tetrahalides **7** (Scheme 2), obtainable from the commercial product 1,4-cyclohexanedione (**6**).



Scheme 2. Retrosynthesis of tetraethynyl-*p*-quinodimethane

In the semicyclic diene **7**, the two reactive parts are isolated from each other by ethano groups, which should readily allow independent acetylene coupling. In the resulting tetraalkynes, the two missing double bonds should finally be introducible by dehydrogenation. We also decided to prepare model compounds of types **8**–**10**, since we anticipated that these would be useful for spectral and chemical comparison. We were, in particular, interested in the *gem*-dimethyl-protected cross-conjugated[16] hydrocarbons **8b**–**10b**; the parent systems **8a**–**10a** would be expected to show an increasing tendency to aromatize: 3-methylene-1,4-cyclohexadiene ("isotoluene"), the parent hydrocarbon of **10a**, has long been known to isomerize rapidly to toluene under various conditions.[17]

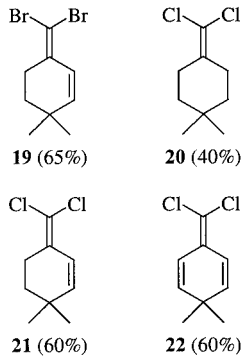
The monoketones **13**–**15**, the starting materials for most of the cross-conjugated derivatives described in this study, are easily available by known methods. Thus, Robinson annelation of methyl vinyl ketone (**11**) with 2-methylpropanal (**12**) furnished 4,4-dimethylcyclohex-2-enone (**13**).[18] This was hydrogenated to the saturated ketone **14** in the presence of palladium on carbon[19] and oxidized to **15** by DDQ treatment,[20] the yields being acceptable in all cases (Scheme 3).



Scheme 3. Preparation of starting materials for cross-conjugated enynes

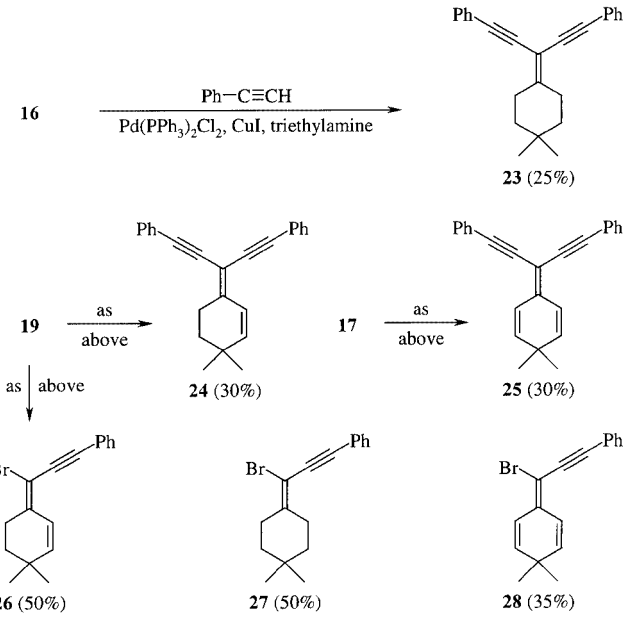
The next steps, affording the dihalides **16** and **17** and the tetrahalide **18**, were also routine. The reliable tetrabromomethane/triphenylphosphane method was employed for dibromoolefination of ketones,[21] and was also used to convert **13** into the dibromide **19**. Likewise, **13**–**15** were transformed into the dichlorides **20**–**22** by use of tetrachloromethane in place of its bromo analogue (Scheme 4).

The first coupling reactions were carried out with phenylacetylene, by use of the Sonogashira reaction. As expected, the ring-saturated dibromide **16** furnished the monoene **23** (25% yield), while **19** and **17** provided **24** and **25** (30% in each case). Whereas **24** was isolated as a yellow oil, the



Scheme 4. Additional dihalo olefins

more symmetrical products **23** and **25** were yellow, air- and light-stable solids. The structures of these hydrocarbons were determined by the usual spectroscopic methods (see Exp. Sect. for details), the UV/Vis spectra showing the expected bathochromic shifts on proceeding towards higher unsaturation; the absorption maxima were recorded (*n*-pentane) at 276 nm for **23** and at 332 and 356 nm for **24** and **25**, respectively (Scheme 5). On recrystallization from pentane the cross-conjugated derivative **25** provided single crystals suitable for X-ray structural analysis. As the results in Figure 1 show, the molecule displays no imposed symmetry. The central portion of the molecule (C3, C7−C11, C20) is planar to within 0.02 Å; the cyclohexadiene ring makes an angle of only 7° to this plane, and the phenyl ring C20−25 is inclined to it by only 18°; the ring C14−19, however, is almost perpendicular to it (79°). Most bond lengths and angles may be regarded as normal, but there are some perturbations in the region of the central C3=C7 double bond. This bond itself is rather long at 1.370(2) Å, which may be associated with some delocalization (cf.



Scheme 5. Preparation of phenyl-substituted cross-conjugated enynes

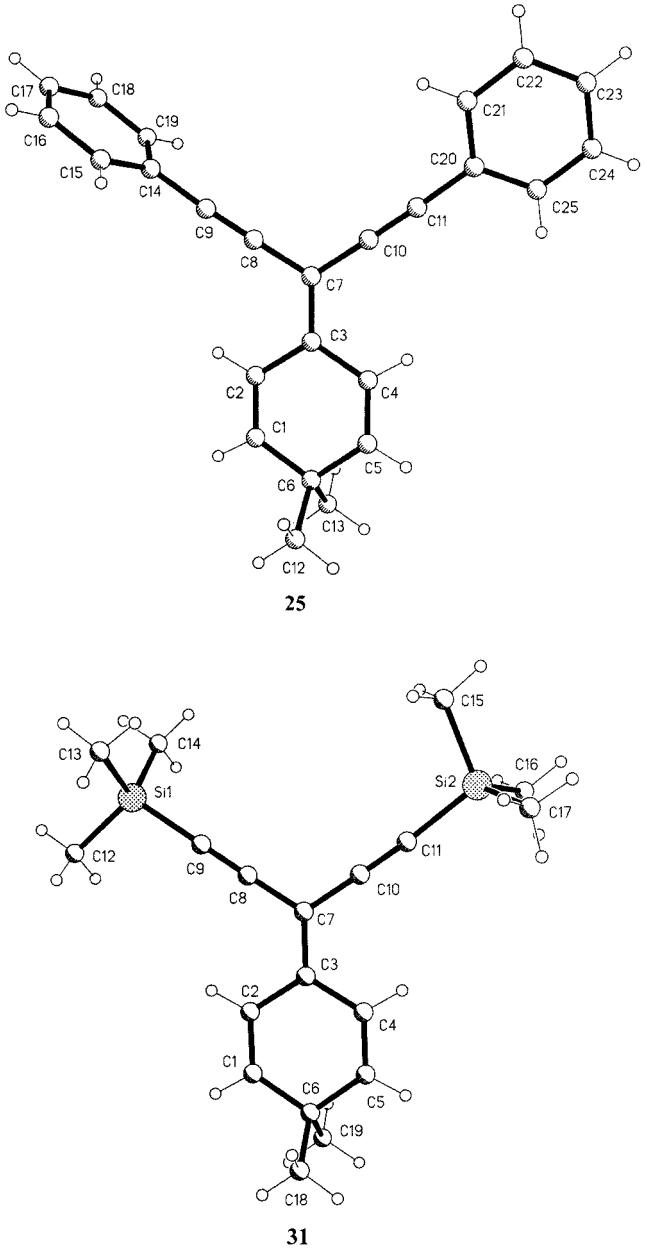


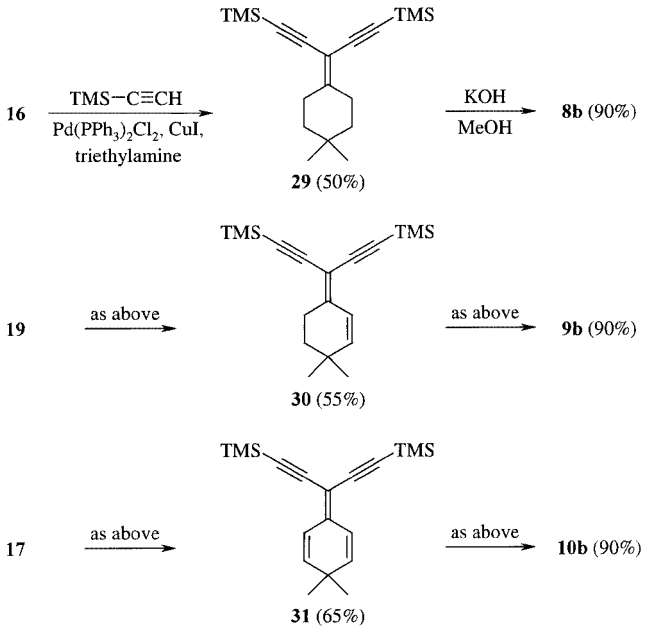
Figure 1. The structures of **25** and **31** in the crystal

C2−C3 and C3−C4 ca. 1.45 Å), and the angles C8−C7−C10 and C2−C3−C4 are narrow at 115.84(12) and 116.33(12)°. In the cyclohexadiene ring, the angles at C2 and C4 (ca. 122°) and C1 and C5 (ca. 124.5°) are widened to compensate for the narrow angle at the sp^3-hybridized C6.

These coupling processes take place stepwise via the corresponding monobromides; in fact, when the amount of phenylacetylene was reduced in the case of **19**, the monosubstitution product **26** was obtained in 50% yield. Interestingly, the process took place with high diastereoselectivity to afford only the (*E*) isomer of **26**, as was shown by NMR spectroscopy including NOE experiments (Scheme 5). The monobromides **27** (50%) and **28** (35%) were prepared analogously, from **16** and **17**, respectively. The oily vinyl brom-

ides **26**−**28** were stable in solution for several weeks and are of potential value as coupling partners for the preparation of other extended cross-conjugated enynes by, inter alia, dimerization.

In the next series of experiments, trimethylsilylacetylene was used as the coupling partner in order to provide a protective group that could be removed after successful Sonogashira coupling. The expected products **29**−**31** (Scheme 6) were all obtained in acceptable yields (50, 55, and 65%, respectively). Again, the less symmetrical diyne **30** was an oil, whereas the other two compounds crystallized as yellow needles. The molecular structure of **31** was determined by X-ray diffraction and the result is also reproduced in Figure 1. The atoms C1−11 are coplanar (mean deviation 0.02 Å), and the dimensions of the same moiety are very similar to those of the analogous portion of **25**.



Scheme 6. Preparation of the parent systems **8b**−**10b**

Varying amounts of the dimer of the acetylenic partner were produced in all coupling experiments, presumably by reductive elimination of an intermediately formed dialkynylpalladium(II) complex, a phenomenon often observed in these metal-mediated processes.[22]

For deprotection, the trimethylsilyl derivatives were stirred in methanolic KOH solution at room temperature; the hydrocarbons **8b**, **9b**, and **10b** were all formed in high yields (90%). Although all of them were unstable − showing strong tendencies to polymerize during workup and handling − their structures could be assigned unambiguously by spectroscopy (see Exp. Sect.). The absorption maxima in their electronic spectra (in *n*-pentane) shifted from 252 nm for **8b** through 292 nm for **9b** to 340 nm for **10b**, the last member of the series. Although **8b** was isolated as a low-melting solid (m.p. 54 °C), we were unable to obtain crystals suitable for X-ray diffraction. Compounds **9b** and **10b** were isolated as red oils, the latter possibly being noncrystalline because of impurities.

Having established the basic synthetic operations required in this area, the more demanding goal of preparing TEQ precursors or derivatives was addressed next. Surprisingly, Sonogashira coupling of the tetrabromide **18** either with phenylacetylene or with trimethylsilylacetylene failed under the above conditions, without even partially substituted derivatives being formed. Fortunately, however, Kumada coupling of (trimethylsilylethynyl)magnesium bromide in tetrahydrofuran in the presence of 1,3-[bis(diphenylphosphanyl)propane]nickel(II) chloride [(dppp)$NiCl_2$] was successful,[23] yielding **32** in 50% yield. This tetrahydro-TEQ derivative was an intensely yellow solid, displaying fluorescence in pentane solution. It was recrystallized from dichloromethane to provide single crystals of X-ray quality, and the result of the diffraction experiments is shown in Figure 2. The molecule displays crystallographic inversion symmetry. The atoms C1−8 are coplanar (mean deviation 0.03 Å). The central double bond C2=C4, at 1.348(4) Å, is of a normal length because the saturated ring precludes delocalization of the form seen in **25** and **31**. The angle C5−C4−C7 is still narrow at 117.1(2)°, which seems to be a general feature of the $C{=}C(C{\equiv}C)_2$ moiety.

Desilylation of **32** to 7,7,8,8-tetraethynyl-tetrahydro-*p*-quinodimethane (**33**) initially met with considerable difficulties. Deprotection under the above conditions (methanolic KOH solution) failed completely, with **32** being recovered quantitatively even after stirring for several hours at room temperature. On the other hand, when **32** was treated with tetrabutylammonium fluoride (TBAF) in moist tetrahydrofuran, the reaction mixture immediately turned black, and no products soluble either in pentane or in dichloromethane were obtained. However, when this homogenous reaction system was replaced by a vigorously stirred two-phase system, consisting of an aqueous TBAF solution covered by a pentane layer, **33** was generated from its trimethylsilyl-protected precursor in ca. 75% yield. The red solid polymerized within hours at room temperature, but was stable enough to be employed for further transformations (see below). On heating of a dioxane solution of **32** under reflux in the presence of a fourfold excess of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), dehydrogenation took place to furnish the dihydro-TEQ derivative **35** in 20% yield. Unfortunately, all attempts to oxidize this orange-colored solid further to **34** have so far failed. When the amount of oxidant or the reaction conditions were varied, only a black material that could not be characterized by physical or chemical methods was obtained in all cases (Scheme 7).

Since we expected that phenyl substituents in place of the TMS groups would exert a stabilizing influence on TEQ, we prepared the tetraphenyl derivative of **33** by subjecting the tetraacetylene (liberated in situ) to Sonogashira coupling with iodobenzene. The desired hydrocarbon, a stable, orange solid, was obtained in good yield (75%). However, its dehydrogenation with excess DDQ again stopped at the dihydro-TEQ stage, yielding the cross-conjugated derivative **36** in 20% yield. The orange hydrocarbon could be stored in the cold for several weeks before decomposition set in,

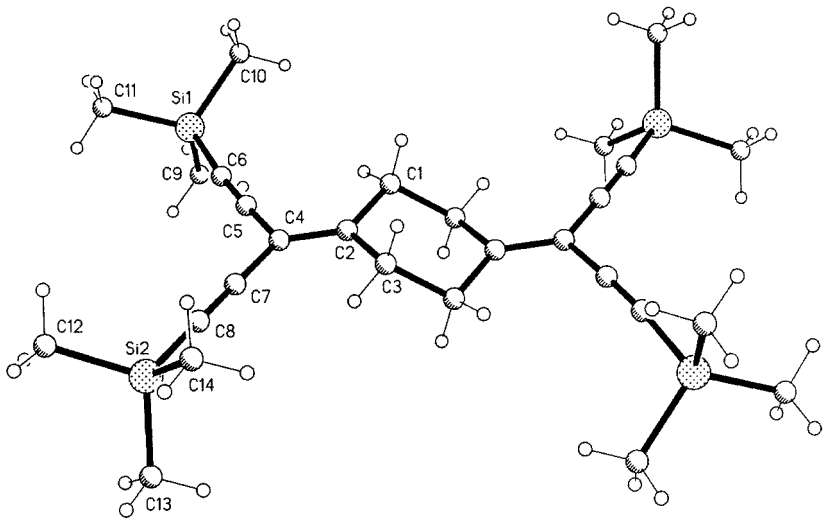


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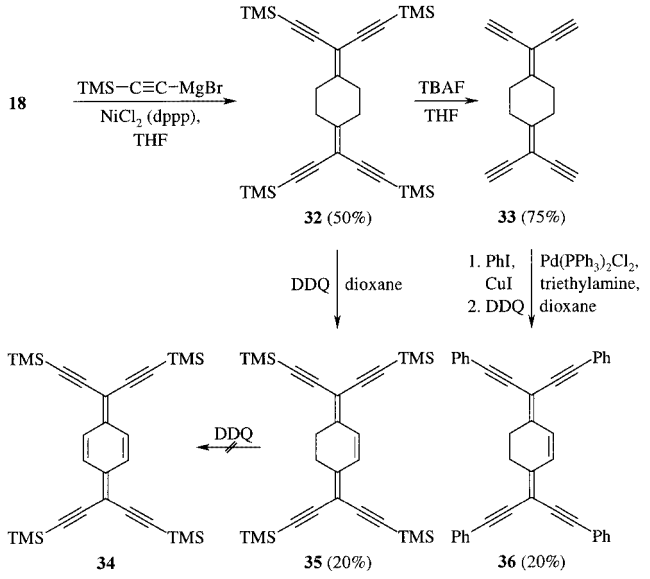
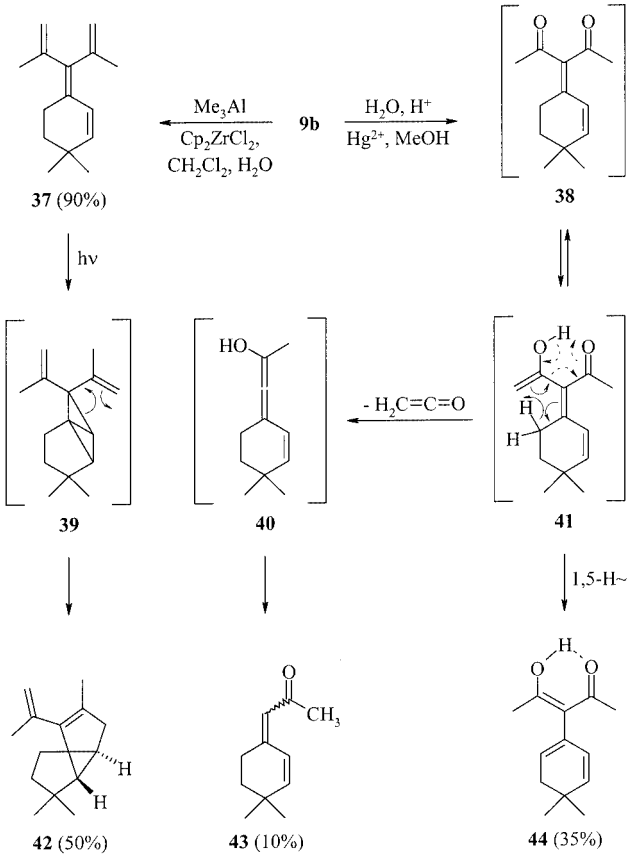
Figure 2. The structure of **32** in the crystal



Scheme 7. En route to tetraethynyl-*p*-quinodimethane derivatives

accompanied by a color change to black. Interestingly, (*E*)-7,8-diphenyl-*para*-quinodimethane has been obtained from its tetrahydro precursor by DDQ treatment in benzene.[24]

In order to gain an initial impression of the chemical behavior of some of the novel cross-conjugated systems prepared in this study, we selected the two derivatives **9b** and **31** as model compounds (Schemes 8, 9). When **9b** was hydrated in the presence of mercury(II) sulfate and sulfuric acid in methanol, the expected diketone **38** was not obtained, but rather a product mixture consisting of an isomer of **38**, the acetylacetone derivative **44** (35% yield) and the unsaturated monoketones **43** [yield 10%; (*Z*)-**43**: 67%, (*E*)-**43**: 33%]. We assume that the enol **41**, the immediate precursor of **38** during the hydration process, serves as a common intermediate for both **43** and **44**. To arrive at the former, **41** could lose ketene by the fragmentation process symbolized by the dotted arrows in Scheme 8; the resulting allenol **40** would subsequently tautomerize to (*E*)-/(*Z*)-**43**. To arrive at **44**, intermediate **41** would have to undergo a 1,5-

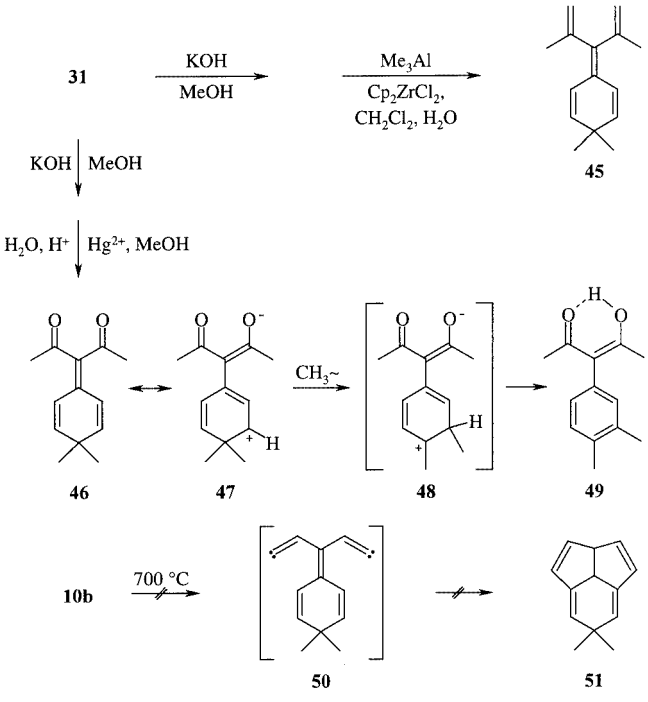


Scheme 8. The chemical behavior of **9b**

hydrogen shift, by which one of the hydrogen atoms of the (activated) ring methylene group would be transferred to the double bond of the enol (full arrows in **41**).

Carbalumination of **9b** with trimethylaluminium in the presence of Cp_2ZrCl_2 as catalyst in moist dichloromethane according to a procedure reported by Wipf and Lim[25] furnished the dendralene **37** in excellent yield (90%) as a yellow oil. When this hydrocarbon was irradiated with a low-pressure mercury lamp in pentane in a falling film apparatus at 256 nm, photoisomerization occurred, resulting in at least five photoproducts. The main product from the photolysate (50% by GC analysis) could be isolated by silica gel chromatography; according to its spectroscopic data (see Exp. Sect.) it had the bizarre structure **42**. Nevertheless, a relatively simple pathway for its formation suggests itself. In the first step, the sterically fixed butadiene subsystem of **37** ring-closes to the bicyclobutane derivative **39**, in analogy to the classical examples from the steroid field studied by Dauben and co-workers.[26] Intermediate **39**, being a strained vinylcyclopropane, can undergo the corresponding isomerization to yield the ultimately isolated rearrangement product **42**. This still contains a vinylcyclopropane subunit that could isomerize further to provide one of the other, unidentified photoproducts.

When the isotoluene derivative **31** was initially desilylated to **10b**, which was methylated in situ with trimethylaluminium as described above, the tetravinylethene derivative **45** was generated, the yield again being very good at ca. 90% over both steps. In contrast to **9b**, deprotection of **31** followed by $HgSO_4$-catalyzed hydration allowed the isolation of the diketone **46** in 40% yield. As a second major product (30%), the β-diketone **49** was produced, its formation obviously requiring a 1,2-methyl migration step. This could start



Scheme 9. The chemical behavior of **31**

with the resonance structure of **46** − structure **47** − whereby the intermediate **48** thus generated rearomatizes to **49** by proton transfer (Scheme 9). Since **46** does not possess activated methylene groups in its six-membered ring, no process similar to the **41**→**44** isomerization is possible.

The photochemical and thermal isomerization behavior of **10b** turned out to be disappointing. Under a variety of conditions (irradiation with a 15-W low-pressure mercury lamp in a falling film apparatus at different concentrations and reactions times), only polymeric material was obtained when the hydrocarbon was irradiated. Under flash vacuum conditions, no isomerization took place below 700 °C, and when the diacetylene was subjected to still harsher pyrolysis conditions only fragmentation to benzene, toluene, and the xylenes was detected. The intended thermal isomerization product, the homoacepentalene derivative **51**, which in principle could be generated via vinylidenecarbene precursors, as summarized in structure **50**, was not observed.

Experimental Section

General Remarks, Instrumentation: All solvents and starting materials employed were purified and dried according to standard procedures; experiments in anhydrous solvents were carried out under nitrogen. NMR: Bruker AC 200 F (200 MHz) and AM 400 (400 MHz) in $CDCl_3$ and [D_6]acetone, TMS as internal standard. ^{13}C NMR spectra are ^1H broad-band decoupled; multiplicities were determined by the DEPT technique. Signals marked with an asterisk are ambiguous and possibly interchangeable. IR: Nicolet DX 320 FT-IR spectrometer. UV/Vis: HP 8452 diode array spectrometer. GC/IR: Carlo Erba HRGC 5160 with a quartz capillary column (30 m DB 1, 100% dimethylpolysilicone) coupled to a Nicolet SX 740 FT-IR spectrometer. MS (EI): Finnigan MAT 8430, at 70 eV. GC/MS: Carlo Erba HRGC 5160 with a quartz capillary column (30 m DB 1, 100% dimethylpolysilicone) coupled to Finnigan 4515, EI at 40 eV.

4,4-Dimethylcyclohex-2-en-1-one (13): Freshly distilled methyl vinyl ketone (**11**, 70.1 g, 82.5 mL, 1.0 mol) was dissolved in 2-methylpropanal (**12**, 108.2 g, 137.0 mL, 1.5 mol) and concd. sulfuric acid (1 mL) was added to the mixture. The solution was carefully warmed to 45−50 °C, and when the exothermic reaction had started the internal temperature was kept at ca. 50 °C by external cooling. When the mixture had reached room temp. again, the water produced during the condensation was removed and the remaining oil was vacuum-distilled (b.p. 55 °C/8 Torr) to yield **13** (80.7 g, 65%) as a colorless oil. Although the ketone has been described in the literature,[18] its analytical data are incomplete. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.17 (s, 6 H, 7-H/8-H), 1.87 (ps-t, 2 H, $^3J_{5\text{-H},6\text{-H}}$ = 6.9 Hz, 5-H), 2.46 (ps-t, 2 H, $^3J_{5\text{-H},6\text{-H}}$ = 6.9 Hz, 6-H), 5.83 (d, $^3J_{2\text{-H},3\text{-H}}$ = 10.2 Hz, 1 H, 2-H), 6.66 (d, $^3J_{2\text{-H},3\text{-H}}$ = 10.2 Hz, 1 H, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7 (C-7/C-8), 32.8 (C-4), 34.4 (C-6), 36.1 (C-5), 126.8 (C-2), 159.5 (C-3), 199.5 (C-1). IR (film): $\tilde{\nu}$ = 3022 cm^{-1} (w), 2961 (s), 2930 (m), 2869 (m), 1683 (s), 1621 (w), 1471 (w), 1376 (m), 1236 (m), 1203 (w), 1122 (m), 1029 (w), 804 (m). UV (CH_3OH): λ_{max} (lg ε) = 226 nm (4.02). GC/MS (EI): *m*/*z* (%) = 124 (47) [M^+], 109 (8), 96 (80), 95 (13), 82 (100), 81 (75), 79 (17), 68 (33), 67 (54), 55 (13), 53 (28), 41 (29).

4,4-Dimethylcyclohexan-1-one (14): A solution of **13** (5.3 mL, 40 mmol) in anhydrous diethyl ether (70 mL) was hydrogenated in

the presence of Pd/C (0.5 g) at room temp. The catalyst was removed by filtration and the solvent was evaporated under vacuum. Chromatography on silica gel with pentane/diethyl ether (2:1) furnished **14** (4.3 g, 85%) as colorless needles, m.p. 41−42 °C. Although the ketone has been described in the literature,[19] its analytical data are incomplete. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (s, 6 H, 7-H/8-H), 1.67 (t, $^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}} = 7.0$ Hz, 4 H, 3-H/5-H), 2.32 (t, $^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}} = 7.0$ Hz, 4 H, 2-H/6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.9 (C-7/C-8), 29.2 (C-4), 37.3 (C-2/C-6), 38.5 (C-3/C-5), 210.9 (C-1). IR (KBr): $\tilde{\nu}$ = 2951 cm^{-1} (s), 2927 (m), 2911 (m), 2864 (m), 1706 (s), 1676 (w), 1474 (w), 1459 (w), 1234 (w), 1145 (m). UV (CH_3OH): end absorption. GC/MS (EI): *m/z* (%) = 126 (47) [M$^+$], 111 (16), 97 (8), 83 (13), 71 (100), 70 (52), 69 (29), 57 (35), 56 (43), 55 (86), 53 (10), 43 (89), 42 (14), 41 (57).

4,4-Dimethylcyclohexa-2,5-dien-1-one (15): Compound **13** (13.2 mL, 0.10 mol) was added to a solution of 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (DDQ, 45.4 g, 0.20 mol) in anhydrous toluene (350 mL), and the thoroughly stirred reaction mixture was heated under reflux for 24 h. The hydroquinone thus formed was removed by filtration and carefully washed with diethyl ether. The combined organic phases were washed with water and dried with $MgSO_4$. The solvent was removed in vacuo and the remaining oil was purified first by distillation [b.p. 55 °C/8 Torr) and then by silica gel chromatography with pentane/diethyl ether (2:1, v/v)], to yield analytically pure **15** (6.1 g, 50%). Although the ketone has been described in the literature,[20] its analytical data are incomplete. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 6 H, 7-H/8-H), 6.19 ($^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}} = 10.1$, $^4J_{2\text{-H},6\text{-H}} = 3.0$, $^5J_{2\text{-H},5\text{-H}} = {}^5J_{3\text{-H},6\text{-H}} = 0.1$ Hz, 2 H, 2-H/6-H), 6.85 (m, $^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}} = 10.1$, $^4J_{3\text{-H},5\text{-H}} = 1.9$, $^5J_{2\text{-H},5\text{-H}} = {}^5J_{3\text{-H},6\text{-H}} = 0.1$ Hz, 2 H, 3-H/5-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5 (C-7/C-8), 37.8 (C-4), 127.1 (C-2/C-6), 156.7 (C-3/C-5), 185.7(C-1). IR (film): $\tilde{\nu}$ = 3039 cm^{-1} (w), 2969 (m), 2931 (w), 2910 (w), 1689 (m), 1666 (s), 1633 (m), 1471 (w), 1403 (m), 1255 (w), 1105 (w) 861 (m). UV (CH_3OH): λ_{max} (lg ε) = 234 nm (4.12). GC/MS (EI): *m/z* (%) = 122 (22) [M$^+$], 107 (12), 94 (53), 93 (11), 91 (12), 79 (100), 78 (13), 77 (66), 67 (6), 65 (6), 53 (18), 51 (17), 41 (11).

1-(Dibromomethylidene)-4,4-dimethylcyclohexane (16): Compound **14** (3.2 g, 25 mmol) was added to a suspension of triphenylphosphane (26.2 g, 0.1 mol) and tetrabromomethane (16.6 g, 0.05 mol) in anhydrous toluene (125 mL).[21] The reaction mixture was heated under reflux for 18 h and the solid components were removed by filtration. After these had been washed carefully with pentane, the organic phases were combined and dried ($MgSO_4$), and the solvents were removed in vacuo. Column chromatography (silica gel, pentane) provided **16** (5.6 g, 80%) as a yellow, low-melting solid (m.p. 45−46 °C), which could be stored only for a limited time. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (s, 6 H, 8-H/9-H), 1.36 (t, $^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}} = 6.5$ Hz, 4 H, 3-H/5-H), 2.41 (t, $^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}} = 6.5$ Hz, 4 H, 2-H/6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7 (C-8/C-9), 29.8 (C-4), 30.6 (C-2/C-6), 39.0 (C-3/C-5), 81.6 (C-7), 114.7 (C-1). IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1} (s), 2920 (s), 2872 (m), 2844 (m), 1467 (m), 1452 (m), 1386 (w), 1367 (m), 1241 (m), 1224 (m), 1168 (m), 1017 (w), 966 (m), 886 (w), 792 (s), 772 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 208 nm (4.15), 216 (sh, 4.03). GC/MS (EI): *m/z* (%) = 284 (12) [M$^+$], 282 (24) [M$^+$], 280 (13) [M$^+$], 161 (11), 159 (13), 121 (50), 109 (58), 96 (100), 81 (61), 69 (57), 65 (38), 55 (44), 43 (22). $C_9H_{14}Br_2$ (282.0): calcd. C 38.33, H 5.00, Br 56.67; found C 38.22, H 5.01, Br 56.45.

3-(Dibromomethylidene)-6,6-dimethylcyclohexa-1,4-diene (17): Compound **15** (3.0 g, 25 mmol) was added to a suspension of triphenylphosphane (26.2 g, 0.1 mol) and tetrabromomethane (16.6 g, 0.05 mol) in anhydrous toluene (125 ml). The reaction mixture was heated at 85 °C for 18 h and the solid components were removed by filtration. After these had been washed carefully with pentane, the organic phases were combined and dried ($MgSO_4$), and the solvents were removed in vacuo. Column chromatography (silica gel, pentane) provided **17** (3.1 g, 45%) as a yellow oil, which quickly decomposed (even in solution). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (s, 6 H, 8-H/9-H), 5.86 (ps-d, $^3J_{1\text{-H},2\text{-H}} = {}^3J_{4\text{-H},5\text{-H}} = 10.2$ Hz, 2 H, 1-H/5-H), 6.48 (ps-d, $^3J_{1\text{-H},2\text{-H}} = {}^3J_{4\text{-H},5\text{-H}} = 10.2$ Hz, 2 H, 2-H/4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (C-8/C-9), 36.8 (C-6), 90.4 (C-7), 121.9 (C-2/C-4), 133.7 (C-3), 141.5 (C-1/C-5). IR (film): $\tilde{\nu}$ = 3039 cm^{-1} (w), 2961 (m), 2921 (m), 2866 (w), 1652 (w), 1533 (w), 1470 (m), 1267 (w), 925 (m), 844 (m), 812 (s), 795 (s), 661 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 268 nm (sh, 4.41), 274 (4.43). GC/MS (EI): *m/z* (%) = 280 (14) [M$^+$], 278 (22) [M$^+$], 276 (10) [M$^+$], 265 (53), 263 (100), 261 (50), 199 (46), 197 (40), 184 (24), 182 (18), 117 (29), 103 (85), 91 (26), 77 (47). $C_9H_{10}Br_2$ (278.0): calcd. C 38.89, H 3.63, Br 57.49; found C 38.79, H 3.67, Br 57.47.

1,4-Bis(dibromomethylidene)cyclohexane (18): Compound **6** (5.6 g, 0.05 mmol) was added to a suspension of triphenylphosphane (104.9 g, 0.40 mol) and tetrabromomethane (66.3 g, 0.20 mol) in anhydrous toluene (400 mL). The reaction mixture was heated under reflux for 18 h and the solid components were removed by filtration. After these had been washed carefully with pentane, the organic phases were combined and dried ($MgSO_4$), and the solvents were removed in vacuo. Column chromatography (silica gel, pentane) provided **18** (8.5 g, 40%) as colorless crystals, m.p. 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 2-H/3-H/5-H/6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.2 (C-2/C-3/C-5/C-6), 84.3 (C-7/C-8), 141.6 (C-1/C-4). IR (KBr): $\tilde{\nu}$ = 2985 cm^{-1} (w), 2906 (m), 2840 (w), 1436 (m), 1425 (m), 1253 (s), 1197 (m), 968 (s), 838 (m), 782 (s). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 208 nm (4.39), 216 (4.36). GC/MS (EI): *m/z* (%) = 428 (1) [M$^+$], 426 (5) [M$^+$], 424 (10) [M$^+$], 422 (6) [M$^+$], 420 (2) [M$^+$], 347 (2), 345 (7), 343 (7), 341 (2), 266 (47), 264 (100), 262 (53), 184 (13), 182 (13), 104 (32), 103 (33), 91 (16), 77 (20). $C_8H_8Br_4$ (423.8): calcd. C 22.87, H 1.92, Br 75.21; found C 22.73, H 1.77, Br 75.24.

3-(Dibromomethylidene)-6,6-dimethylcyclohex-1-ene (19): Compound **19** (4.5 g, 65%) was prepared from **13** (3.3 mL, 25 mmol) as described for **16**, as a yellow oil that was stable for months in dilute pentane solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 6 H, 8-H/9-H), 1.53 (ps-t, $^3J_{4\text{-H},5\text{-H}} = 6.5$ Hz, 2 H, 5-H), 2.49 (ps-t, $^3J_{4\text{-H},5\text{-H}} = 6.5$ Hz, 2 H, 4-H), 5.76 (d, $^3J_{1\text{-H},2\text{-H}} = 10.1$ Hz, 1 H, 1-H), 6.35 (d, $^3J_{1\text{-H},2\text{-H}} = 10.1$ Hz, 1 H, 2-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.2 (C-8/C-9), 28.3 (C-4), 32.1 (C-6), 36.0 (C-5), 87.7 (C-7), 123.4 (C-2), 138.3 (C-3), 143.8 (C-1). IR (film): $\tilde{\nu}$ = 3023 cm^{-1} (w), 2958 (s), 2935 (m), 2925 (s), 2866 (m), 1551 (w), 1469 (m), 1376 (w), 1249 (m), 827 (m), 809 (s), 775 (s). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 250 nm (4.12). GC/MS (EI): *m/z* (%) = 282 (23) [M$^+$], 280 (48) [M$^+$], 278 (25) [M$^+$], 267 (26), 265 (53), 263 (28), 251 (9), 237 (10), 201 (46), 199 (49), 186 (34), 184 (36), 171 (10), 120 (58), 119 (44), 107 (34), 105 (100), 91 (52), 77 (58). $C_9H_{12}Br_2$ (280.0): calcd. C 38.61, H 4.32, Br 57.07; found C 38.62, H 4.38, Br 57.02.

1-(Dichloromethylidene)-4,4-dimethylcyclohexane (20): Tetrachloromethane (0.48 mL, 5.0 mmol), triphenylphosphane (2.62 g, 10.0 mmol), and zinc powder (0.65 g, 10.0 mol) were added to a solution of **14** (0.32 g, 2.5 mmol) in anhydrous dichloromethane (30 mL). The reaction mixture was heated under reflux for 18 h, and the solid residue was removed by filtration and carefully washed with pentane. The solvents were removed in vacuo, and the

remaining oil was purified by silica gel chromatography with pentane to yield **20** (0.19 g, 40%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 6 H, 8-H/9-H), 1.36 (t, $^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}}$ = 6.5 Hz, 4 H, 3-H/5-H), 2.39 (t, $^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}}$ = 6.5 Hz, 4 H, 2-H/6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.6 (C-2/C-6), 27.7 (C-8/C-9), 29.8 (C-4), 38.9 (C-3/C-5), 110.9 (C-7), 137.6 (C-1). IR (film): $\tilde{\nu}$ = 2955 cm^{-1} (s), 2922 (s), 2868 (m), 2850 (m), 1619 (w), 1460 (m), 1444 (m), 966 (w), 905 (s), 865 (s). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 206 nm (4.08), 210 (sh, 4.03). GC/MS (EI): *m*/*z* (%) = 194 (31) [M$^+$], 192 (48) [M$^+$], 179 (8), 177 (13), 141 (17), 121 (24), 109 (100), 96 (86), 91 (21), 81 (82), 77 (28), 69 (87). $C_9H_{14}Cl_2$ (193.1): calcd. C 55.98, H 7.31, Cl 36.72; found C 55.98, H 7.33, Cl 36.67.

3-(Dichloromethylidene)-6,6-dimethylcyclohex-1-ene (21): Compound **21** (0.29 g, 60%) was prepared from **13** (0.33 mL, 2.5 mmol) as described for **20**, as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 6 H, 8-H/9-H), 1.53 (ps-t, 5-H, $^3J_{4\text{-H},5\text{-H}}$ = 6.6 Hz, 2 H, 5-H), 2.51 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.6 Hz, 2 H, 4-H), 5.74 (d, $^3J_{1\text{-H},2\text{-H}}$ = 10.1 Hz, 1 H, 1-H), 6.31 (d, $^3J_{1\text{-H},2\text{-H}}$ = 10.1 Hz, 1 H, 2-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4 (C-4), 28.3 (C-8/C-9), 31.9 (C-6), 35.7 (C-5), 115.2 (C-7), 121.2(C-2), 132.1 (C-3), 143.1 (C-1). IR (film): $\tilde{\nu}$ = 3026 cm^{-1} (w), 2959 (s), 2926 (s), 2867 (m), 1572 (m), 1470 (m), 917 (s), 886 (s), 850 (m), 776 (s). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 246 nm (sh, 4.32), 252 (4.36), 258 (sh, 4.23). GC/MS (EI): *m*/*z* (%) = 192 (33) [M$^+$], 190 (52) [M$^+$], 177 (64), 175(100), 161 (17), 157 (25), 155 (78), 147 (17), 139 (38), 125 (14), 119 (21), 107 (23), 103 (34), 91 (30), 77 (43), 63 (17), 51 (19), 41 (29). $C_9H_{12}Cl_2$ (191.1): calcd. C 56.57, H 6.33, Cl 37.10; found C 56.71, H 6.48, Cl 36.95.

3-(Dichloromethylidene)-6,6-dimethylcyclohexa-1,4-diene (22): Compound **22** (0.28 g, 60%) of was prepared from **15** (0.31 mL, 2.5 mmol) as described for **20**, as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = (s, 6 H, 8-H/9-H), 5.86 (ps-d, $^3J_{1\text{-H},2\text{-H}} = {}^3J_{4\text{-H},5\text{-H}}$ = 10.1 Hz, 2 H, 1-H/ 5-H), 6.47 (ps-d, $^3J_{1\text{-H},2\text{-H}} = {}^3J_{4\text{-H},5\text{-H}}$ = 10.1 Hz, 2 H, 2-H/4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.9 (C-8/C-9), 36.4 (C-6), 117.0 (C-7), 119.6 (C-2/C-4), 128.3 (C-3), 140.9 (C-1/C-5). IR (film): $\tilde{\nu}$ = 3045 cm^{-1} (w), 2964 (m), 1555 (m), 1468 (m), 925 (s), 894 (s), 857 (s), 795 (s), 662 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 268 nm (4.45), 276 (sh, 4.39). GC/MS (EI): *m*/*z* (%) = 190 (13) [M$^+$], 188 (20) [M$^+$], 177 (10), 175 (64), 173 (100), 153 (20), 138 (17), 103 (14), 102 (16), 77 (11), 51 (10). $C_9H_{10}Cl_2$ (189.1): calcd. C 57.17, H 5.33, Cl 37.50; found C 57.31, H 5.49, Cl 37.41.

1-(1,5-Diphenylpenta-1,4-diyn-3-ylidene)-4,4-dimethylcyclohexane (23): Dichloro-bis(triphenylphosphane)palladium(II) (0.140 g, 0.20 mmol) and copper(I) iodide (19 mg, 0.10 mmol) were added to a mixture of **16** (1.41 g, 5.0 mmol) and phenylacetylene (1.32 mL, 12.0 mmol) in anhydrous triethylamine (60 mL). After the mixture had been stirred for several days at room temp., the reaction was complete (TLC monitoring), and the solid precipitate was removed by filtration and washed thoroughly with pentane. The solvents were removed in vacuo and the remaining crude coupling products were purified by column chromatography on silica gel with pentane; besides small amounts of 1,4-diphenylbuta-1,3-diyne and 1-(1-bromo-3-phenylpropynylidene)-4,4-dimethylcyclohexane (**27**, see below), compound **23** (0.41 g, 25%) was obtained as a yellow solid, m.p. 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (s, 6 H, 2 × CH_3), 1.46 (t, $^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}}$ = 6.5 Hz, 4 H, 3-H, 5-H), 2.66 (t, $^3J_{2\text{-H},3\text{-H}} = {}^3J_{5\text{-H},6\text{-H}}$ = 6.5 Hz, 4 H, 2-H/6-H), 7.29−7.34 (m, 6 H, arom. H), 7.51−7.53 (m, 4 H, arom. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8 (2 × CH_3), 28.9 (C-2/C-6), 30.2 (C-4), 39.9 (C-3/C-5), 86.1 (acetylenic C), 90.9 (acetylenic C), 98.0 (C-7), 123.4 (arom. C), 128.0 (arom. C), 128.2 (arom. C), 131.5 (arom. C) 161.1 (C-1). IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (w), 2952 (s), 2912 (s), 2863 (m), 2846 (m), 1590 (m), 1490 (s), 1443 (m), 1385 (m), 756 (s), 691 (s). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 194 nm (4.75), 224 (4.35), 268 (sh, 4.48), 276 (4.58), 302 (sh, 4.42). GC/MS (EI): *m*/*z* (%) = 324 (100) [M$^+$], 309 (11), 267 (30), 252 (33), 239 (15), 228 (41), 215 (20), 115 (14). $C_{25}H_{24}$ (324.5): calcd. C 92.54, H 7.46; found C 92.49, H 7.63.

3-(1,5-Diphenylpenta-1,4-diyn-3-ylidene)-6,6-dimethylcyclohex-1-ene (24): Compound **24** (0.48 g, 30%) was prepared from **19** (1.40 g, 5.0 mmol) as described above for **23**, as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (s, 6 H, 2 × CH_3), 1.61 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.5 Hz, 2 H, 5-H,), 2.80 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.5 Hz, 2 H, 4-H), 5.87 (d, $^3J_{1\text{-H},2\text{-H}}$ = 9.9 Hz, 1 H, 1-H), 6.80 (d, $^3J_{1\text{-H},2\text{-H}}$ = 9.9 Hz, 1 H, 2-H), 7.29−7.34 (m, 6 H, arom. H), 7.48−7.51 (m, 4 H, arom. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6 (C-4), 28.4 (2 × CH_3), 32.6 (C-6), 36.1 (C-5), 85.9 and 86.7 (acetylenic C), 93.0 and 94.5 (acetylenic C), 99.2 (C-7), 123.4 (arom. C), 124.3 (C-2), 128.1 and 128.2 (arom. C), 128.3 (arom. C), 131.5 (arom. C), 145.5 (C-1), 151.0 (C-3). IR (film): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2957 (s), 2924 (m), 2864 (m), 2208 (w), 1596 (m), 1490 (s), 1469 (m), 1361 (m), 1070 (w), 784 (m), 754 (s), 690 (s). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 196 nm (4.74), 230 (4.29), 276 (sh, 4.39), 280 (4.40), 292 (4.56), 332 (4.51). MS (EI): *m*/*z* (%) = 322 (100) [M$^+$], 308 (10), 307 (40), 291 (12), 279 (9), 229 (10), 215 (17). HRMS ($C_{25}H_{22}$): calcd. 322.172; found 322.172 ± 2 ppm.

3-(1,5-Diphenylpenta-1,4-diyn-3-ylidene)-6,6-dimethylcyclohexa-1,4-diene (25): Compound **25** (0.48 g, 30%) was prepared from **17** (1.39 g, 5.0 mmol) as described above for **23**, as a yellow needles (pentane), m.p. 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (s, 6 H, 2 × CH_3), 6.03 (ps-d, $^3J_{1\text{-H},2\text{-H}} = {}^3J_{4\text{-H},5\text{-H}}$ = 10.1 Hz, 2 H, 1-H/5-H), 6.93 (ps-d, $J_{1\text{-H},2\text{-H}} = {}^3J_{4\text{-H},5\text{-H}}$ = 10.1 Hz, 2 H, ^{3}2-H/4-H), 7.31−7.35 (m, 6 H, arom. H), 7.51−7.53 (m, 4 H, arom. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.7 (2 × CH_3), 37.7 (C-6), 86.7 (acetylenic C), 94.7 (acetylenic C), 97.8 (C-7), 122.4 (C-2/C-4), 123.3 (arom. C), 128.2 (arom. C), 128.3 (arom. C), 131.5 (arom. C), 143.1 (C-3), 143.3 (C-1/C-5). IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1} (w), 1646 (m), 1488 (m), 923 (m), 813 (m), 752 (s), 688 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 196 nm (4.80), 232 (4.32), 282 (4.40), 300 (4.58), 356 (4.58), 368 (sh, 4.55). GC/MS (EI): *m*/*z* (%) = 320 (15) [M$^+$], 306 (25), 305 (100), 302 (10), 289 (9), 214 (24). $C_{25}H_{20}$ (320.5): calcd. C 93.71, H 6.29; found C 93.67, H 6.38.

(*E*)-3-(1-Bromo-3-phenylpropyn-1-ylidene)-6,6-dimethylcyclohex-1-ene (26): Dichloro-bis(triphenylphosphane)palladium(II) (0.035 g, 0.05 mmol) and copper(I) iodide (0.005 g, 0.03 mmol) were added to a solution of **19** (0.70 g, 2.5 mmol) and phenylacetylene (0.33 mL, 3.0 mmol) in anhydrous triethylamine (30 mL). The mixture was stirred for several days at room temp. and when the coupling process was complete (TLC monitoring), the solid precipitates were removed by filtration and washed carefully with pentane. The organic layers were combined, the solvent was removed in vacuo, and the remaining oily crude product was purified by thick layer chromatography (silica gel, pentane) to yield **26** (0.38 g, 50%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 6 H, 2 × CH_3), 1.55 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.6 Hz, 2 H, 5-H), 2.56 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.6 Hz, 2 H, 4-H), 5.79 (d, $^3J_{1\text{-H},2\text{-H}}$ = 10.0 Hz, 1 H, 1-H), 6.58 (d, $^3J_{1\text{-H},2\text{-H}}$ = 10.0 Hz, 1 H, 2-H), 7.27−7.31 (m, 3 H, arom. H), 7.42−7.47 (m, 2 H, arom. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.5 (C-4), 28.3 (2 × CH_3), 32.4 (C-6), 36.0 (C-5), 86.7 (acetylenic C), 95.4 (acetylenic C), 98.6 (C-7), 122.5 (arom. C), 123.6 (C-2), 128.4 (arom. C), 128.7 (arom. C), 131.5 (arom. C), 143.6 (C-1), 143.8 (C-3). IR (film): $\tilde{\nu}$ = 3022 cm^{-1} (w), 2957 (s), 2924 (m), 2865 (m), 2195 (w), 1598 (w), 1489 (m), 1443 (m), 1296 (m), 835 (m), 781 (m), 755 (s), 732 (s), 689 (m). UV/Vis (*n*-C_5H_{12}):

λ_{max} (lg ε) = 194 nm (4.51), 230 (sh, 4.17), 240 (4.20), 298 (4.29), 310 (4.30), 330 (4.17). GC/MS (EI): *m/z* (%) = 302 (96) [M^+], 300 (100) [M^+], 287 (27), 285 (28), 221 (69), 206 (35), 205 (40), 191 (77), 189 (56), 178 (74), 165 (51), 152 (22), 139 (26), 128 (27), 115 (56), 95 (23), 91 (43), 89 (45). $C_{17}H_{17}Br$ (301.2): calcd. C 67.79, H 5.69, Br 26.53; found C 67.83, H 5.59, Br 26.61.

1-(1-Bromo-3-phenylpropyn-1-ylidene)-4,4-dimethylcyclohexane (27): Compound **27** (0.38 g, 50%) was prepared from **16** (0.71 g, 2.5 mmol) as described for **26**, as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 6 H, 2 × CH_3), 1.40 (t, $^3J_{5\text{-H},6\text{-H}}$ = 6.5 Hz, 2 H, 5-H*), 1.42 (t, $^3J_{2\text{-H},3}$ = 6.5 Hz, 2 H, 3-H*), 2.49 (t, $^3J_{5\text{-H},6\text{-H}}$ = 6.5 Hz, 2 H, H-6*), 2.58 (t, $^3J_{2\text{-H},3\text{-H}}$ = 6.5 Hz, 2 H, 2-H*), 7.30−7.35 (m, 3 H, arom. H), 7.43−7.46 (m, 2 H, arom. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7 (2 × CH_3), 29.9 (C-2*), 30.04 (C-6*), 30.05 (C-4), 39.3 (C-5*), 39.6 (C-3*), 86.6 (acetylenic C), 92.8 (acetylenic C), 93.5 (C-7), 122.6 (arom. C), 128.3 (arom. C), 128.5 (arom. C), 131.5 (arom. C), 150.7 (C-1). IR (Film): $\tilde{\nu}$ = 3081 cm^{-1} (w), 3060 (w), 2953 (s), 2919 (s), 2848 (w), 2200 (w), 1490 (m), 1442 (m), 1386 (m), 1232 (m), 1169 (w), 755 (s), 689 (s). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 192 nm (4.47), 224 (4.20), 260 (4.16), 272 (4.21), 282 (4.24), 300 (4.17). GC/MS (EI): *m/z* (%) = 304 (54) [M^+], 302 (56) [M^+], 289 (2), 287 (2), 233 (44), 208 (46), 206 (40), 193 (18), 181 (54), 167 (96), 165 (100), 152 (65), 139 (55), 127 (76), 115 (56), 105 (20), 91 (53), 81 (30). $C_{17}H_{19}Br$ (303.3): calcd. C 67.33, H 6.32, Br 26.35; found C 67.38, H 6.32, Br 26.37.

3-(1-Bromo-3-phenylpropyn-1-ylidene)-6,6-dimethylcyclohexa-1,4-diene (28): Compound **28** (0.26 g, 35%) was prepared from **17** (0.69 g, 2.5 mmol) as described for **26**, as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 6 H, 2 × CH_3), 5.91 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 10.0, $^4J_{1\text{-H},5\text{-H}}$ = 2.1 Hz, 1 H, 1-H), 5.99 (dd, $^3J_{4\text{-H},5\text{-H}}$ = 10.0, $^4J_{1\text{-H},5\text{-H}}$ = 2.1 Hz, 1 H, 5-H), 6.67 (dd, $^3J_{4\text{-H},5\text{-H}}$ = 10.0, $^4J_{2\text{-H},4\text{-H}}$ = 2.1 Hz, 1 H, 4-H), 6.74 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 10.0, $^4J_{1\text{-H},5\text{-H}}$ = 2.1 Hz, 1 H, 2-H), 7.32−7.35 (m, 3 H, arom. H), 7.46−7.49 (m, 2 H, arom. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (2 × CH_3), 37.4 (C-6), 87.5 (acetylenic C), 97.6 (acetylenic C), 97.7 (C-7), 121.9 (C-2), 122.5 (arom. C), 122.6 (C-4), 128.3 (arom. C), 128.7 (arom. C), 131.4 arom C), 136.8 (C-3), 141.3 (C-1), 143.8 (C-5). IR (film): $\tilde{\nu}$ = 3036 cm^{-1} (w), 2963 (m), 1650 (m), 1486 (m), 1468 (m), 1442 (m), 925 (m), 845 (s), 803 (s), 754 (s), 688 (s), 669 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 194 nm (4.50), 232 (4.11), 240 (4.11), 318 (4.14), 330 (4.17), 356 (4.13). GC/MS (EI): *m/z* (%) = 300 (24) [M^+], 298 (24) [M^+], 285 (27), 283 (100), 219 (65), 204 (77), 203 (44), 202 (84), 189 (54), 176 (9), 150 (7), 101 (16). $C_{17}H_{15}Br$ (299.2): calcd. C 68.24, H 5.05, Br 26.70; found C 68.25, H 5.15, Br 26.68.

1-[1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-ylidene]-4,4-dimethylcyclohexane (29): Dichlorobis(triphenylphosphane)palladium(II) (0.280 g, 0.40 mmol) and copper(I) iodide (0.038 g, 0.20 mmol) were added to a solution of **16** (2.82 g, 10.0 mmol) and trimethylsilylacetylene (3.32 mL, 24.0 mmol) in anhydrous triethylamine (120 mL). After the mixture had been stirred for several days at room temp., with the progress of the reaction monitored by TLC, the precipitates were removed by filtration and washed thoroughly with pentane. The solvents were removed in vacuo and the product mixture was purified by column chromatography on silica gel with pentane. Besides traces of 1,4-bis(trimethylsilyl)buta-1,3-diyne and 1-[1-bromo-3-(trimethylsilyl)propyn-1-ylidene]-4,4-dimethylcyclohexane, compound **29** (1.58 g, 50%) was obtained as a yellow solid, m.p. 73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 [s, 18 H, 2 × $(CH_3)_3Si$], 0.96 (s, 6 H, 2 × CH_3), 1.40 (t, $^3J_{2\text{-H},3\text{-H}}$ = $^3J_{5\text{-H},6\text{-H}}$ = 6.5 Hz, 4 H, 3-H/5-H), 2.52 (t, $^3J_{2\text{-H},3\text{-H}}$ = $^3J_{5\text{-H},6\text{-H}}$ = 6.5 Hz, 4 H, 2-H/6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0 [2 × $(CH_3)_3Si$], 27.8 (2 × CH_3), 28.7 (C-2/C-6), 30.1 (C-4), 39.7 (C-3/C-5), 96.1 (acetylenic C), 98.4 (C-7), 101.2 (acetylenic C), 163.5 (C-1). IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (m), 2920 (m), 2850 (m), 2150 (m), 1249 (m), 844 (s), 761 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 210 nm (3.88), 218 (3.94), 266 (4.28). GC/MS (EI): *m/z* (%) = 318 (2) [M^+], 317 (3) [M^+], 316 (18) [M^+], 301 (12), 172 (10), 109 (17), 95 (10), 73 (100). $C_{19}H_{32}Si_2$ (316.7): calcd. C 72.07, H 10.19, Si 17.74; found C 72.14, H 10.12, Si 17.79.

4,4-Dimethyl-1-(penta-1,4-diyn-3-ylidene)cyclohexane (8b): Compound **29** (0.32 g, 1.0 mmol) was added to methanolic potassium hydroxide solution (1 M, 4 mL), and the mixture was stirred for 1 h at room temp. A few mL of pentane were added, the organic phase was separated, and the product mixture was purified by column chromatography on silica gel with pentane to yield **8b** (0.16 g, 90%); the solid (m.p. ca. 54 °C) quickly turned red and polymerized. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 6 H, 2 × CH_3), 1.41 (t, $^3J_{1\text{-H},2\text{-H}}$ = 6.5 Hz, 4 H, 3-H/5-H), 2.55 (t, $^3J_{1\text{-H},2\text{-H}}$ = 6.5 Hz, 4 H, 2-H/6-H), 3.08 (s, 2 H, acetylenic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7 (2 × CH_3), 28.7 (C-2/C-6), 30.1 (C-4), 39.6 (C-3/C-5), 79.2 (terminal acetylenic C), 79.9 (acetylenic C), 95.9 (C-7), 164.4 (C-1). GC/IR: $\tilde{\nu}$ = 3303 cm^{-1} (s), 2955 (s), 2921 (s), 2865 (m), 2849 (m), 2101 (w), 1592 (m), 1462 (m), 1441 (m), 1388 (m), 1170 (m), 977 (w). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 198 nm (3.72), 252 (4.18). GC/MS (EI): *m/z* (%) = 172 (82) [M^+], 157 (55), 143 (19), 142 (39), 129 (65), 128 (42), 116 (31), 115 (100), 102 (36), 96 (37), 91 (15), 81 (39), 77 (18). HRMS ($C_{13}H_{16}$): calcd. 172.125; found 172.125 ± 2 ppm.

3-[1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-ylidene]-6,6-dimethylcyclohex-1-ene (30): Compound **30** (1.73 g, 55%) was prepared from **19** (2.80 g, 10.0 mmol) as described for **29**, as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.208 and 0.214 [2 × s, 18 H, 2 × $(CH_3)_3Si$], 1.03 (s, 6 H, 2 × CH_3), 1.54 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.6 Hz, 2 H, 5-H), 2.63 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.6 Hz, 2 H, 4-H), 5.83 (d, $^3J_{1\text{-H},2\text{-H}}$ = 9.9 Hz, 1 H, 1-H), 6.63 (d, $^3J_{1\text{-H},2\text{-H}}$ = 9.9 Hz, 1 H, 2-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0 and 0.1 [2 × $(CH_3)_3Si$], 25.5 (C-4), 28.4 (2 × CH_3), 32.6 (C-6), 36.0 (C-5), 98.2 and 99.9 (acetylenic C), 99.3 (C-7), 100.8 and 102.0 (acetylenic C), 124.2 (C-2), 146.0 (C-1), 153.2 (C-3). IR (film): $\tilde{\nu}$ = 2959 cm^{-1} (m), 2925 (m), 2148 (m), 2132 (w), 1250 (s), 1205 (w), 843 (s), 759 (m), 668 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 216 nm (3.99), 224 (4.05), 308 (4.39). GC/MS (EI): *m/z* (%) = 316 (16) [M^+], 315 (17) [M^+], 314 (63) [M^+], 302 (7), 301 (3), 299 (27), 211 (8), 142 (31), 107 (17), 97 (12), 83 (9), 73 (100), 59 (18). $C_{19}H_{30}Si_2$ (314.7): calcd. C 72.54, H 9.61, Si 17.85; found C 72.64, H 9.59, Si 17.71.

6,6-Dimethyl-3-(penta-1,4-diyn-3-ylidene)cyclohex-1-ene (9b): Compound **30** (0.31 g, 1.0 mmol) was hydrolyzed with methanolic potassium hydroxide as described for **8b** to yield **9b** (0.15 g, 90%), which quickly turned red and polymerized (even in solution). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 6 H, 2 × CH_3), 1.56 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.6 Hz, 2 H, 5-H), 2.67 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.6 Hz, 2 H, 4-H), 3.20 (s, 1 H, 9-H), 3.27 (s, 1 H, 11-H), 5.87 (d, $^3J_{1\text{-H},2\text{-H}}$ = 9.9 Hz, 1 H, 1-H), 6.64 (d, $^3J_{1\text{-H},2\text{-H}}$ = 9.9 Hz, 1 H, 2-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4 (C-4), 28.3 (C-12/C-13), 32.5 (C-6), 35.8 (C-5), 79.7 (C-8), 80.7 (C-10), 81.1 (C-9), 82.5 (C-11), 96.9 (C-7), 123.7 (C-2), 146.6 (C-1), 154.0 (C-3). IR (film): $\tilde{\nu}$ = 3307 cm^{-1} (s), 3298 (s), 2958 (s), 2926 (s), 2866 (m), 2098 (w), 1604 (w), 1470 (m), 1460 (w), 1361 (w), 914 (w), 790 (m), 653 (s). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 200 nm (3.80), 292 (4.24). GC/MS (EI): *m/z* (%) = 170 (100) [M^+], 155 (72), 154 (17), 153 (40), 152 (26), 141 (26), 139 (28), 129 (18), 128 (56), 127 (55), 115 (39), 107 (19), 91 (18), 77 (21). HRMS ($C_{13}H_{14}$): calcd. 170.110; found 170.110 ± 2 ppm.

3-[1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-ylidene]-6,6-dimethylcyclohexa-1,4-diene (31): Compound **31** (2.03 g, 65%) was prepared from **17** (2.78 g, 10.0 mmol) as described for **29**, as a yellow solid, m.p. 77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.22 [s, 18 H, 2 × $(CH_3)_3Si$], 1.12 (s, 6 H, 2 × CH_3), 5.99 (ps-d, $J_{1\text{-H},2\text{-H}}$ = $^3J_{4\text{-H},5\text{-H}}$ = 10.1 Hz, 2 H, 1-H, 5-H), 6.77 (ps-d, $^3J_{1\text{-H},2\text{-H}}$ = $^3J_{4\text{-H},5\text{-H}}$ = 10.1 Hz, 2 H, 2-H, 4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0 [2 × $(CH_3)_3Si$], 28.6 (C-12/C-13), 37.7 (C-6), 97.8 (C-7), 100.3 (acetylenic C), 101.5 (acetylenic C), 122.3 (C-2/C-4), 143.7 (C-1/C-5), 145.0 (C-3). IR (KBr): $\tilde{\nu}$ = 3037 cm^{-1} (m), 3010 (m), 2960 (s), 2933 (m), 2918 (m), 2899 (m), 2145 (s), 2135 (m), 2124 (m), 1647 (m), 1324 (m), 1251 (s), 1208 (m), 1119 (m), 1008 (m), 923 (m), 854 (s), 841 (s), 813 (s), 757 (s), 700 (m), 685 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 226 nm (4.03), 242 (3.99), 250 (3.96), 340 (4.52), 354 (sh, 4.37). GC/MS (EI): *m*/*z* (%) = 314 (2) [M$^+$], 313 (5) [M$^+$], 312 (12) [M$^+$], 299 (4), 298 (11), 297 (24), 282 (5), 255 (9), 224 (39), 206 (13), 191, 179 (26), 173 (11), 141, 97 (17), 73 (100). $C_{19}H_{28}Si_2$ (312.65): calcd. C 73.00, H 9.03, Si 17.97; found C 73.06, H 9.17, Si 17.98.

6,6-Dimethyl-3-(penta-1,4-diyn-3-ylidene)cyclohexa-1,4-diene (10b): Compound **31** (0.31 g, 1.0 mmol) was hydrolyzed with methanolic potassium hydroxide as described for **8b** to yield **10b** (0.15 g, 90%) as a red oil that quickly polymerized (even in solution). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (s, 6 H, 12-H/13-H), 3.32 (s, acetylenic H), 6.03 (ps-d, $^3J_{1\text{-H},2\text{-H}}$ = $^3J_{4\text{-H},5\text{-H}}$ = 10.1 Hz, 2 H, 1-H/5-H), 6.79 (ps-d, $^3J_{1\text{-H},2\text{-H}}$ = $^3J_{4\text{-H},5\text{-H}}$ = 10.1 Hz, 2 H, H-2/H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (C-12/C-13), 37.7 (C-6), 80.5 (C-8/C-10), 82.8 (C-9/C-11), 95.4 (C-7), 122.0 (C-2/C-4), 144.4 (C-1/C-5), 145.9 (C-3). GC/IR: $\tilde{\nu}$ = 3325 cm^{-1} (s), 2973 (m), 2877 (w), 2097 (w), 1650 (w), 1195 (m), 921 (m), 810 (m). HPLC/UV (*n*-C_5H_{12}): λ_{max} = 240 nm, 340. GC/MS (EI): *m*/*z* (%) = 168 (26) [M$^+$], 154 (30), 153 (100), 152 (42), 151 (16), 127 (6), 77 (9). HRMS ($C_{13}H_{12}$): calcd. 168.094; found 168.094 ± 2 ppm.

1,4-Bis[1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ylidene]cyclohexane (32): A solution of methylmagnesium bromide in diethyl ether (3 M, 9.50 mL, 28.5 mmol) was slowly added at −78 °C to a solution of trimethylsilylacetylene (4.15 mL, 30.0 mmol) in anhydrous THF (40 mL). The resulting suspension was allowed to warm to room temp. and heated to reflux for 2 h. The reaction mixture was again cooled to −78 °C, and **18** (2.12 g, 5.0 mmol) in anhydrous THF (50 mL) and [1,3-bis(diphenylphosphanyl)propane]nickel(II) chloride (0.54 g, 1.0 mmol) were swiftly added. The reaction mixture was again slowly allowed to warm to room temp. and 150 mL of saturated ammonium chloride solution was added for hydrolysis. After the addition of 20 mL of diethyl ether and 20 mL of pentane, the organic phase was separated, washed with water, and dried with Na_2SO_4. The solid remaining after solvent removal in vacuo was recrystallized from diethyl ether to yield **32** (1.23 g, 50%) as an intensely yellow solid, m.p. 236 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.21 [s, 36 H, 4 × $(CH_3)_3Si$], 2.63 (s, 8 H, 2-H/3-H/5-H/6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0 [4 × $(CH_3)_3Si$], 31.3 (C-2/C-3/C-5/C-6), 97.3 (acetylenic C), 100.3 (C-7/C-12), 100.6 (acetylenic C), 159.8 (C-1/C-4). IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1} (m), 2899 (w), 2152 (m), 2125 (w), 1310 (w), 1249 (s), 1210 (w), 1005 (m), 856 (s), 841 (s), 759 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 208 nm (4.19), 218 (4.23), 284 (4.54), 292 (sh, 4.39). MS (EI): *m*/*z* (%) = 496 (2) [M$^+$], 495 (5) [M$^+$], 494 (14) [M$^+$], 493 (25) [M$^+$], 492 (48) [M$^+$], 477 (13), 420 (12), 419 (17), 404 (12), 389 (21), 332 (12), 331 (26), 316 (15), 315 (16), 301 (12), 285 (12), 257 (9), 155 (7), 73 (100). ($C_{28}H_{44}Si_4$, 493.1): calcd. C 68.26, H 9.01, Si 22.73; found C 68.11, H 8.91, Si 22.65.

1,4-Bis(penta-1,4-diyn-3-ylidene)cyclohexane (33): A solution of tetra-*n*-butylammonium fluoride in water (1 M, 1 mL) was added to a solution of **32** (0.10 g, 0.20 mmol) in pentane (6 mL). The two-phase reaction mixture was vigorously stirred for 18 h, and after the organic layer had been separated the solvent was removed in vacuo. The remainder was taken up in dichloromethane and chromatographed on silica gel to yield **33** (0.030 g, 75%) as a red solid, m.p. 155 °C, which (even in dilute solution) rapidly polymerized. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.68 (s, 8 H, 2-H/3-H/5-H/6-H), 3.14 (s, 4 H, acetylenic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4 (C-2/C-3/C-5/C-6), 79.4 (acetylenic C), 80.4 (terminal acetylenic C), 98.2 (C-7/C-12), 160.5 (C-1/C-4). UV/Vis (acetonitrile): λ_{max} (lg ε) = 198 nm, 266. MS (EI): *m*/*z* (%) = 204 (42) [M$^+$], 202 (100), 189 (29), 176 (22), 165 (10), 152 (9), 115 (14), 89 (8). HRMS ($C_{16}H_{12}$): calcd. 204.094; found 204.094 ± 2 ppm.

1,4-Bis[1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ylidene]cyclohex-2-ene (35): 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.090 g, 0.40 mmol) was added to a solution of **32** (0.049 g, 0.10 mmol) in anhydrous dioxane (3 mL) and the reaction mixture was heated to reflux for 4 h. Without further workup, the product mixture was subjected to thick-layer chromatography on silica gel (pentane) to yield **35** (0.010 g, 20%) as an orange solid, m.p. 222 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.22 and 0.23 [2 × s, 2 × 18 H, 4 × $(CH_3)_3Si$], 2.71 (s, 4 H, 5-H/6-H), 6.94 (s, 2 H, 2-H/3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0 [4 × $(CH_3)_3Si$], 26.9 (C-5/C-6), 100.1, 100.5, 101.9, 102.2 and 102.6 (C-7/C-12 and acetylenic C), 130.5 (C-2/C-3), 151.3 (C-1/C-4). IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1} (m), 2924 (m), 2854 (w), 2144 (m), 2129 (w), 1323 (w), 1247 (m), 1220 (w), 1014 (m), 853 (s), 843 (s), 757 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 226 nm (4.03), 242 (3.99), 250 (3.96), 340 (4.52), 354 (sh, 4.37). MS (EI): *m*/*z* (%) = 494 (2) [M$^+$], 493 (9) [M$^+$], 492 (26) [M$^+$], 491 (51) [M$^+$], 490 [M$^+$] (100), 73 (26). HRMS ($C_{28}H_{42}Si_4$): calcd. 490.236; found 490.236 ± 2 ppm.

1,4-Bis(1,5-diphenylpenta-1,4-diyn-3-ylidene)cyclohex-2-ene (36)

a) For the preparation of this dihydro-TEQ derivative, compound **32** (0.49 g, 1.0 mmol) in anhydrous THF (5 mL) was first treated with a solution of tetra-*n*-butylammonium fluoride in THF (1 M, 5 mL, 5.0 mmol). After 5 min, the desilylated hydrocarbon **33** was added to a suspension of phenyl iodide (0.54 mL, 4.8 mmol), dichlorobis(triphenylphosphano)palladium(II) (0.281 g, 0.4 mmol), and copper(I) iodide (0.038 g, 0.2 mmol) in anhydrous triethylamine (15 mL). After the reaction mixture had been stirred for 3 h at room temp., the solid residue was removed by filtration and carefully washed with pentane. The solvents were removed in vacuo, and excess phenyl iodide was removed by silica gel chromatography (pentane). Additional thick-layer chromatography (silica gel, pentane/dichloromethane, 1:1, v/v) furnished orange-colored 1,4-bis(1,5-diphenylpenta-1,4-diyn-3-ylidene)cyclohexane (0.050 g, 10%), m.p. 270 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (s, 8 H, 2-H/3-H/5-H/6-H), 7.31−7.35 (m, 12 H, arom. H), 7.50−7.52 (m, 8 H, arom. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.9 (C-2/C-3/C-5/C-6), 85.6 (acetylenic C), 91.9 (acetylenic C), 100.0 (C-7/C-12), 123.1 (arom. C), 128.3 (arom. C), 128.3 (arom. C), 131.5 (arom. C), 157.5 (C-1/C-4). IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} (w), 2960 (w), 2201 (w), 1950 (w), 1490 (s), 1442 (m), 755 (s), 689 (s). UV/Vis (acetonitrile): λ_{max} (lg ε) = 194 nm (5.00), 224 (4.57), 266 (4.65), 278 (4.73), 308 (4.63). MS (EI): *m*/*z* (%) = 508 (100) [M$^+$], 493 (9), 431 (26), 415 (29), 353 (14), 339 (14), 252 (10), 213 (13), 115 (14). HRMS ($C_{40}H_{28}$): calcd. 508.219; found 508.219 ± 2 ppm.

b) 1,4-Bis(1,5-diphenylpenta-1,4-diyn-3-ylidene)cyclohex-2-ene (36): 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.045 g, 0.20 mmol)

was added to a solution of the hydrocarbon prepared under a) (0.025 g, 0.05 mmol) in anhydrous dioxane (2 mL), and the mixture was heated under reflux for 4 h. Without further workup, the mixture was subjected to thick-layer chromatography (silica gel, pentane) to yield orange-colored **36** (0.005 g, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.96 (s, 4 H, 5-H/6-H), 7.17 (s, 2 H, 2-H/3-H), 7.34−7.37 (m, 12 H, arom. H), 7.51−7.54 (m, 8 H, arom. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.2 (C-5/C-6), 85.9 and 87.4 (acetylenic C), 94.5 and 96.4 (acetylenic C), 102.5 (C-7/C-12), 123.0 and 123.1 (arom. C), 128.3 and 128.4 (arom. C), 128.5 and 128.6 (arom. C), 130.2 (C-2/C-3), 131.6 (arom. C), 149.4 (C-1/C-4). IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} (w), 2925 (m), 2854 (w), 2188 (w), 1490 (m), 753 (s), 688 (s). UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (5.00), 238 (4.54), 292 (4.50), 308 (4.53), 434 (4.65). MS (EI): *m*/*z* (%) = 506 (100) [M$^+$], 427 (5), 352 (2), 291 (6), 253 (11). HRMS ($C_{40}H_{26}$): calcd. 506.203; found 506.203 ± 2 ppm.

3-(2,4-Dimethylpenta-1,4-dien-3-ylidene)-6,6-dimethylcyclohex-1-ene (37): Water (0.22 mL) was slowly added at −23 °C, with vigorous stirring, to a solution of trimethylaluminium (2 M in hexane, 12 mL, 24.0 mmol) and dicyclopentadienezirconium dichloride (0.47 g, 1.6 mmol) in anhydrous dichloromethane (30 mL). After 10 min, compound **9b** (0.68 g, 4.0 mmol) in dichloromethane (6.5 mL) was added, and the mixture was stirred for an additional 10 min at −23 °C. The reaction mixture was allowed to warm to room temp., and satd. aqueous potassium carbonate solution (3 mL) was added. After completion of the hydrolysis, magnesium sulfate (5 g) was added for drying, the solid material was removed by filtration, and the mother liquor was extracted with pentane. The solvents were removed in vacuo, and the remaining oil was purified by column chromatography on silica gel with pentane to yield **37** (0.73 g, 90%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (s, 6 H, *gem*-dimethyl), 1.49 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.4 Hz, 2 H, 5-H), 1.75 (s, 3 H, CH_3), 1.77 (s, 3 H, CH_3), 2.38 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.4 Hz, 2 H, 4-H), 4.75 (m, 2 H, =CH_2), 5.05−5.07 (m, 2 H, =CH_2), 5.47 (d, $^3J_{1\text{-H},2\text{-H}}$ = 10.1 Hz, 1 H, 1-H), 6.27 (d, $^3J_{1\text{-H},2\text{-H}}$ = 10.1 Hz, 1 H, H-2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6 (2 × CH_3), 24.8 (C-4), 29.1 (*gem*-dimethyl), 32.0 (C-6), 37.4 (C-5), 114.8 (=CH_2), 115.8 (=CH_2), 124.9 (C-2), 128.9 (C-3), 139.2 (C-1), 141.0 (C-7), 143.6 (C=), 143.9 (C=). IR (film): $\tilde{\nu}$ = 3078 cm^{-1} (m), 3020 (m), 2956 (s), 2940 (s), 2918 (s), 2865 (m), 1629 (m), 1469 (m), 1450 (m), 1370 (m), 1359 (w), 898 (s), 785 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 192 nm (4.11), 256 (4.15). GC/MS (EI): *m*/*z* (%) = 202 (44) [M$^+$], 187 (59), 160 (18), 159 (23), 146 (41), 145 (64), 143 (10), 132 (13), 131 (100), 129 (19), 128 (17), 119 (21), 117 (18), 115 (19), 107 (14), 105 (38), 93 (14), 91 (50), 81 (23). $C_{15}H_{22}$ (202.4): calcd. C 89.04, H 10.96; found C 89.00, H 10.98.

5,5-Dimethyl-2-[1-(1-oxoethyl)-2-oxopropyl]cyclohexa-1,3-diene (44): A solution of **9b** (0.68 g, 4.0 mmol) in methanol (2 mL) was added to a mixture of concd. sulfuric acid (0.6 mL), water (1.2 mL), and mercury(II) sulfate (0.025 g). After having been heated at 60 °C for 4 h, the reaction mixture was allowed to cool to room temp., and diethyl ether (50 mL) was added. The mixture was washed several times with water, the organic phase was dried, and after solvent removal in vacuo, the remainder was purified by column chromatography followed by thick-layer chromatography on silica gel with pentane/diethyl ether (9:1, v/v) to yield **44** (0.24 g, 35%) as a yellow oil and 6,6-dimethyl-3-(2-oxopropylidene)cyclohex-1-ene (**43**, 0.070 g, 10%) as a mixture of isomers [(*E*): 67%, (*Z*): 33%; GC analysis].

a) Compound 44: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 6 H, *gem*-dimethyl), 2.04 (s, 6 H, 2 × CH_3), 2.21 (d, $^3J_{1\text{-H},6\text{-H}}$ = 4.5 Hz, 2 H, 6-H), 5.57 (ddt, $^3J_{1\text{-H},6\text{-H}}$ = 4.5, $^4J_{1\text{-H},3\text{-H}}$ = 1.5, $^5J_{1\text{-H},4\text{-H}}$ = 1.1 Hz, 1 H, 1-H), 5.61 (dd, $^3J_{3\text{-H},4\text{-H}}$ = 9.6, $^4J_{1\text{-H},3\text{-H}}$ = 1.5 Hz, 1 H, 3-H), 5.64 (dd, $^3J_{3\text{-H},4\text{-H}}$ = 9.6, $^5J_{1\text{-H},4\text{-H}}$ = 1.1 Hz, 1 H, 4-H), 16.41 (s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5 (2 × CH_3), 27.7 (*gem*-dimethyl), 30.4 (C-5), 38.1 (C-6), 114.2 (C-7), 125.4 (C-3), 126.9 (C-1), 130.7 (C-2), 138.9 (C-4), 190.8 (C−O). IR (film): $\tilde{\nu}$ = 3024 cm^{-1} (w), 2958 (s), 2923 (m), 2869 (m), 2809 (w), 1606 (s), 1579 (s), 1468 (m), 1420 (s), 1405 (s), 1359 (m), 1334 (m), 1301 (m), 990 (m), 920 (m), 763 (m), 651 (m). UV/Vis (methanol): λ_{max} (lg ε) = 204 nm (3.62), 282 (3.96). GC/MS (EI): *m*/*z* (%) = 206 (21) [M$^+$], 191 (13), 163 (10), 150 (15), 131 (9), 43 (100). $C_{13}H_{18}O_2$ (206.3): calcd. C 75.69, H 8.80, O 15.51; found C 75.59, H 8.70, O 15.50.

b) Compound 43: ^{1}H NMR (400 MHz, $CDCl_3$): (*E*) isomer: δ = 1.04 (s, 6 H, *gem*-dimethyl), 1.53 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.6 Hz, 2 H, 5-H), 2.21 (s, 3 H, CH_3-CO), 2.97 (ps-dt, $^3J_{4\text{-H},5\text{-H}}$ = 6.6, $^4J_{4\text{-H},7\text{-H}}$ = 1.9 Hz, 2 H, 4-H), 5.92 (d, $^3J_{1\text{-H},2\text{-H}}$ = 9.8 Hz, 1 H, 1-H), 5.98 (s, 1 H, 7-H), 6.01 (d, $^3J_{1\text{-H},2\text{-H}}$ = 9.8 Hz, 1 H, 2-H); (*Z*) isomer: δ = 1.05 (s, 6 H, *gem*-dimethyl), 1.62 (ps-t, $^3J_{4\text{-H},5\text{-H}}$ = 6.5 Hz, 2 H, 5-H), 2.19 (s, 3 H, CH_3-CO), 2.39 (ps-dt, $^3J_{4\text{-H},5\text{-H}}$ = 6.5, $^4J_{4\text{-H},7\text{-H}}$ = 1.3 Hz, 2 H, 4-H), 5.88 (s, 1 H, 7-H), 5.97 (d, $^3J_{1\text{-H},2\text{-H}}$ = 10.2 Hz, 1 H, 1-H), 7.31 (d, $^3J_{1\text{-H},2\text{-H}}$ =10.2 Hz, 1 H, 2-H). ^{13}C NMR (100 MHz, $CDCl_3$): (*E*) isomer: δ = 23.8 (C-4), 28.1 (*gem*-dimethyl), 28.3 (CH_3-CO), 32.2 (C-6), 35.7 (C-5), 122.4 (C-7), 127.8 (C-2), 149.4 (C-1), 152.0 (C-3), 199.1 (C=O); (*Z*) isomer: δ = 28.1 (*gem*-dimethyl), 29.2 (C-4), 31.7 (CH_3-CO), 32.7 (C-6), 36.5 (C-5), 120.8 (C-7), 122.7 (C-2), 149.4 (C-1), 150.4 (C-3), 198.7 (C=O). IR (film), mixture of isomers: $\tilde{\nu}$ = 3017 cm^{-1} (w), 2957 (s), 2937 (m), 2925 (s), 2866 (m), 1678 (s), 1610 (s), 1585 (s), 1470 (m), 1448 (m), 1355 (m), 1282 (m), 1248 (m), 1178 (s), 971 (w). UV/Vis (CH_3OH), mixture of isomers: λ_{max} (lg ε) = 204 nm (3.61), 284 (4.24). (*E*) isomer: GC/MS (EI): *m*/*z* (%) = 164 (60) [M$^+$], 149 (100), 131 (31), 121 (28), 116 (13), 108 (44), 105 (22), 95 (14), 93 (22), 91 (47), 79 (23), 77 (22); (*Z*) isomer: GC/MS (EI): *m*/*z* (%) = 164(35) [M$^+$], 149 (55), 131 (15), 121 (16), 116, 108 (100), 105 (13), 95 (14), 93 (16), 91 (27), 79 (15), 77 (14). HRMS ($C_{11}H_{16}O$, mixture of isomers): calcd. 164.120; found 164.120 ± 3 ppm.

3,7,7-Trimethyl-2-(1-methylethenyl)tricyclo[4.3.0.0^{1,5}]non-2-ene (42): A solution of **37** (0.81 g, 4.0 mmol) in anhydrous pentane (200 mL) was irradiated with a low-pressure mercury lamp (λ = 254 nm, 15 W) in a falling-film apparatus. The reaction progress was monitored by GC and when the starting material had been consumed, the solvent was removed in vacuo and the remaining oil was purified by thick-layer chromatography on silica gel with hexane to yield **42** (0.24 g, 30%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.56 (d, $^3J_{5\text{-H},6\text{-H}}$ = 2.7 Hz, 1 H, 6-H), 0.99 (s, 3 H, 1 × Me of *gem*-dimethyl), 1.00 (s, 3 H, 1 × Me of *gem*-dimethyl), 1.04 (ddd, $^2J_{8\text{-Ha},8\text{-Hb}}$ = 12.4, $^3J_{8\text{-Ha},9\text{-Hb}}$ = 11.8, $^3J_{8\text{-Ha},9\text{-Ha}}$ = 7.6 Hz, 1 H, 8-H_a), 1.25 (dd, $^2J_{8\text{-Ha},8\text{-Hb}}$ = 12.4, $^3J_{8\text{-Hb},9\text{-Hb}}$ = 8.1 Hz, 1 H, 8-H_b), 1.28 (ddd, $^3J_{4\text{-Hb},5\text{-H}}$ = 7.9, $^3J_{5\text{-H},6\text{-H}}$ = 2.7, $^3J_{4\text{-Ha},5\text{-H}}$ = 1.1 Hz, 1 H, 5-H), 1.58 (dd, 3 H, $^4J_{4\text{-H,b }13\text{-H}}$ = 1.4, $^4J_{4\text{-Ha},13\text{-H}}$ = 1.0 Hz, 13-H), 1.65 (dd, $^2J_{9\text{-Ha},9\text{-Hb}}$ = 12.1, $^3J_{8\text{-Ha},9\text{-Ha}}$ = 7.6 Hz, 1 H, 9-H_a), 1.86 (dd, $^4J_{(E)\text{-11-H},12\text{-H}}$ = 1.5, $^4J_{(Z)\text{-11-H},12\text{-H}}$ = 0.8 Hz, 3 H, 12-H), 1.98 (ddd, $^2J_{9\text{-Ha},9\text{-Hb}}$ = 12.1, $^3J_{8\text{-Ha},9\text{-Hb}}$ = 11.8, $^3J_{8\text{-Hb},9\text{-Hb}}$ = 8.1 Hz, 1 H, 9-H_b), 2.12 (dd, $^2J_{4\text{-Ha},4\text{-Hb}}$ = 17.6, $^3J_{4\text{-Ha},5\text{-H}}$ = 1.1 Hz, 1 H, 4-H_a), 2.61 (ddq, $^2J_{4\text{-Ha},4\text{-Hb}}$ = 17.6, $^3J_{4\text{-Hb},5\text{-H}}$ = 7.9, $^4J_{4\text{-Hb},13\text{-H}}$ = 1.4 Hz, 1 H, 4-H_b), 4.69 (d, $^2J_{(E)\text{-11-H},(Z)\text{-11-H}}$ = 3.1, $^4J_{(Z)\text{-11-H},12\text{-H}}$ = 0.8 Hz, 1 H, =CH_2), 4.99 (d, $^2J_{(E)\text{-11-H},(Z)\text{-11-H}}$ = 3.1, $^4J_{(E)\text{-11-H},12\text{-H}}$ = 1.5 Hz, 1 H, =CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6 (C-13), 21.1 (C-5), 22.5 (C-12), 25.8 (C-9), 25.9 (*gem*-dimethyl), 28.8 (*gem*-di-

methyl), 37.4 (C-8), 39.0 (C-7), 40.2 (C-4), 45.4 (C-6), 45.5 (C-1), 113.4 (=CH_2), 130.8 (C-3), 141.0 (C-2), 151.5 (C-10). IR (film): $\tilde{\nu}$ = 3080 cm^{-1} (w), 3018 (m), 2954 (s), 2923 (s), 2894 (s), 2867 (s), 2832 (m), 1631 (w), 1463 (m), 1445 (m), 1376 (m), 1370 (m), 1362 (m), 893 (s). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 240 nm (3.66). MS (EI): *m*/*z* (%) = 202 (67) [M^+], 187 (69), 159 (16), 146 (72), 145 (34), 131 (100), 105 (16), 91 (16). HRMS ($C_{15}H_{22}$): calcd. 202.172; found 202.172 ± 2 ppm.

3-(2,4-Dimethylpenta-1,4-dien-3-ylidene)-6,6-dimethylcyclohexa-1,4-diene (45): A sample of **31** (0.63 g, 2.0 mmol) was added to potassium hydroxide solution (1 M in methanol, 4 mL), and the mixture was stirred for 1 h at room temp. Pentane (25 mL) was added to the solution, which was carefully washed with water and, after drying with sodium sulfate, was concentrated to approx. 2 mL. Separately, a solution of trimethylaluminium (2 M in hexane, 6 mL, 12.0 mmol) and of dicyclopentadienezirconium dichloride (0.24 g, 0.8 mmol) in anhydrous dichloromethane (15 mL) was cooled to −23 °C, and water (0.11 mL) was added with vigorous stirring. After 10 min, the solution of the formed **10b** was added and the mixture was stirred at −23 °C for an additional 10 min. The reaction mixture was brought to room temp. and a saturated aqueous potassium carbonate solution (1.5 mL) was added. After the hydrolysis had come to an end, magnesium sulfate (2.5 g) was added, the solid materials were removed by filtration, and the crude product mixture was carefully extracted with pentane. The solvents were removed in vacuo and the residue was purified by column chromatography on silica gel with pentane to yield **45** (0.36 g, 90%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (s, 6 H, *gem*-dimethyl), 1.78 (s, 6 H, CH_3-C=), 4.83−4.84 [ps-s, 2 H, =CH_2, (*Z*)-H], 5.11−5.12 [m, 2 H, =CH_2, (*E*)-H], 5.62 (ps-d, $^3J_{1\text{-H},2\text{-H}}$ = $^3J_{4\text{-H},5\text{-H}}$ = 10.2 Hz, 2 H, 1-H/5-H), 6.27 (ps-d, $^3J_{1\text{-H},2\text{-H}}$ = $^3J_{4\text{-H},5\text{-H}}$ = 10.2 Hz, 2 H, 2-H/4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.5 (CH_3-C=), 29.9 (*gem*-dimethyl), 35.6 (C-6), 115.8 (=CH_2), 123.0 (C-2/C-4), 124.9 (C-3), 137.8 (C-1/C-5), 141.7 (C-7), 143.2 (C=). IR (film): $\tilde{\nu}$ = 3079 cm^{-1} (m), 3038 (m), 3010 (w), 2966 (s), 2956 (s), 2918 (m), 2865 (m), 1627 (w), 1469 (m), 1445 (m), 1370 (m), 1355 (w), 1251 (w), 925 (m), 900 (s), 806 (s), 676 (m). UV/Vis (*n*-C_5H_{12}): λ_{max} (lg ε) = 276 nm (4.23). GC/MS (EI): *m*/*z* (%) = 200 [M^+], 186 (15), 185 (100), 170 (20), 157 (21), 155 (16), 143 (23), 128 (21), 115 (16), 105 (15), 91 (12), 77 (11). HRMS ($C_{15}H_{20}$-CH_3): calcd. 185.133; found 185.133 ± 2 ppm.

3-(2,4-Dioxopent-3-ylidene)-6,6-dimethylcyclohexa-1,4-diene (46): A sample of **31** (0.63 g, 2.0 mmol) was dissolved in potassium hydroxide solution (1 M in methanol, 4 mL) and the mixture was stirred for 1 h at room temp. The formed **10b** was taken up in pentane, and the solution was washed several times with water and dried with sodium sulfate. The solution was concentrated to ca. 2 mL and added to a mixture of water (0.6 mL), concd. sulfuric acid (0.3 mL), and mercury(II) sulfate (0.013 g). After having been heated at 60 °C for 4 h, the reaction mixture was dissolved in diethyl ether (20 mL) and the organic phase was washed thoroughly with water. After solvent removal in vacuo, the residue was chromatographed on silica gel and the main fraction was further separated by thick-layer chromatography on silica gel with a mixture of pentane and diethyl ether (9:1, v/v) in both purification steps to yield **46** (0.16 g, 40%) as a yellow oil and 3,4-dimethyl-1-[1-(1-oxoethyl)-2-oxoprop-1-en-1-yl]benzene (**49**, 0.12 g, 30%) as a yellow solid, m.p. 66−68 °C.

Table 1. Details of X-ray structure analyses of **25**, **31** and **32**

Compound	**25**	**31**	**32**
Empirical formula	$C_{25}H_{20}$	$C_{19}H_{28}Si_2$	$C_{28}H_{44}Si_4$
M_r	320.41	312.59	492.99
Habit	yellow prism	colorless prism	pale yellow prism
Crystal size [mm]	0.9 × 0.7 × 0.3	0.5 × 0.3 × 0.2	0.5 × 0.35 × 0.2
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	Cc	$P\bar{1}$
Cell constants:			
a [Å]	18.8564(15)	9.481(2)	6.431(2)
b [Å]	7.0844(6)	24.975(6)	9.809(3)
c [Å]	14.1230(11)	8.893(2)	13.241(4)
α [°]	90	90	74.67(2)
β [°]	94.980(6)	92.28(2)	82.50(2)
γ [°]	90	90	79.42(2)
V [$Å^3$]	1879.5	2104.2	0.7889
Z	4	4	1
D_x [Mg m^{-3}]	1.132	0.987	1.038
μ [mm^{-1}]	0.06	0.16	0.20
F(000)	680	680	268
T [°C]	−100	−130	−130
$2\theta_{max}$ [°]	50	50	50
No. of reflections:			
measured	4215	3691	2832
independent	3311	3221	2781
R_{int}	0.016	0.023	0.013
Parameters	228	198	151
Restraints	0	133	0
$wR(F^2$, all refl.)	0.088	0.099	0.120
$R[F > 4\sigma(F)]$	0.036	0.039	0.050
S	0.90	1.06	1.04
max. Δρ [e $Å^{-3}$]	0.15	0.18	0.25

a) Compound 46: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (s, 6 H, *gem*-dimethyl), 2.35 (s, 6 H, CH_3-CO), 6.25 (ps-d, $^3J_{1\text{-H},2\text{-H}} = {}^3J_{4\text{-H},5\text{-H}}$ = 10.3 Hz, 2 H, 1-H/5-H), 6.68 (ps-d, $^3J_{1\text{-H},2\text{-H}} = {}^3J_{4\text{-H},5\text{-H}}$ = 10.3 Hz, 2 H, 2-H/4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7 (*gem*-dimethyl), 31.8 (CH_3-CO), 37.9 (C-6), 120.9 (C-2/C-4), 135.2 (C-7), 136.9 (C-3), 148.5 (C-1/C-5), 201.2 (C=O). IR (film): $\tilde{\nu}$ = 3002 cm^{-1} (w), 2966 (m), 2942 (m), 2926 (m), 2870 (w), 1696 (s), 1672 (s), 1639 (s), 1538 (s), 1471 (m), 1411 (m), 1394 (m), 1357 (s), 1329 (m), 1289 (m), 1214 (s), 1192 (s), 1168 (m), 928 (m), 820 (s), 698 (m). UV/Vis (methanol): λ_{max} (lg ε) = 204 nm (3.81), 310 (4.23). MS (EI): *m*/*z* (%) = 204 (69) [M$^+$], 189 (100), 161 (73), 143 (50), 128 (18), 115 (30), 105 (22), 91 (34), 77 (25), 55 (69), 43 (99). HRMS ($C_{13}H_{16}O_2$): calcd. 204.115; found 204.115 ± 3 ppm.

b) Compound 49: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.89 (s, 6 H, 2 × CH_3-CO), 2.27 (s, 3 H, CH_3-ar), 2.28 (s, 3 H, CH_3-ar), 6.88 (dd, $^3J_{5\text{-H},6\text{-H}}$ = 7.6, $^4J_{2\text{-H},6\text{-H}}$ = 1.7 Hz, 1 H, 6-H), 6.93 (s, 1 H, 2-H), 7.13 (d, $^3J_{5\text{-H},6\text{-H}}$ = 7.6 Hz, 1 H, 5-H), 16.64 (s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4 (CH_3-ar), 19.7 (CH_3-ar), 24.1 (CH_3-CO), 115.1 (C-7), 128.4 (C-6), 129.9 (C-5), 132.1 (C-2), 134.3 (C-1), 135.7 (C-3), 136.9 (C-4), 191.0 (C=O). IR (KBr): $\tilde{\nu}$ = 3022 cm^{-1} (w), 2974 (m), 2943 (m), 2920 (m), 1713 (m), 1608 (s), 1504 (s), 1449 (s), 1400 (s), 1333 (s), 1285 (m), 1235 (m), 1129 (m), 1020 (m), 985 (s), 920 (m), 892 (w), 863 (m), 821 (m). UV/Vis (methanol): λ_{max} (lg ε) = 204 nm (4.25), 288 (3.90). MS (EI): *m*/*z* (%) = 204 (100) [M$^+$], 189 (83), 161 (75), 143 (41), 128 (21), 115 (31), 91 (23), 77 (16), 55 (66). $C_{13}H_{16}O_2$ (204.3): calcd: C 76.44, H 7.90, O 15.67; found C 76.36 H 7.83 O 15.72.

X-ray Structure Determinations: Numerical details are presented in Table 1. Data collection and reduction: Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (**31**, **32**: Stoe STADI-4; **25**: Siemens P4; both with Siemens LT-2 low-temperature system). Measurements were performed with monochromated Mo-K_α radiation. Cell constants were refined from ±ω angles (Stoe) or setting angles (Siemens) of ca. 60 reflections to 2θ = 23°. Structure solution and refinement: The structures were solved by direct methods and refined anisotropically against F^2 (program SHELXL-97: G.M. Sheldrick, University of Göttingen). H atoms were included with a riding model or with rigid methyl groups. For compound **31**, the absolute structure was determined by an *x* refinement: *x* = 0.01(13); to improve stability of refinement, a system of restraints to displacement factor components was employed ("DELU"). CCDC-172853 (**25**), -172854 (**31**), and -172855 (**32**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank Prof. Dr. L. Ernst (Technical University of Braunschweig) for his help in analyzing and interpreting several NMR spectra (in particular of the hydrocarbon **42**), and the Fonds der Chemischen Industrie for the continuous support of our work.

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Received November 21, 2001
[O01554