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The Chemical Behavior of 3,4-Benzocycloocten-1,5-diyne[‡]

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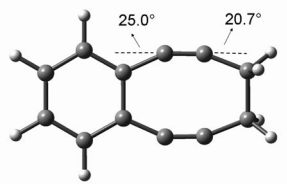
The title compound 3,4-benzocycloocten-1,5-diyne (**1**) is a highly reactive hydrocarbon that has been shown to undergo addition reactions with tetraphenyl-cyclopentadienone (tetracyclone) to the 2:1 adduct **6**, with octacarbonyldicobalt to the bis metal complex **7**, with lithium aluminium hydride to the bis diene **9**, and with various electrophilic reagents. In these latter cases cationic intermediates are generated from **1** and a transannular cyclization takes place leading to novel derivatives of 1,2-dihydropentalene (**31**, **32**, **35**, **36**, **43**, **44**).

Introduction

Recently we described a simple synthesis of 3,4-benzocycloocten-1,5-diyne (**1**, Scheme 1), which provides sufficient material (0.3 g lots can readily be obtained in one preparative experiment)[2] to study the chemical properties of this strained (see below) hydrocarbon. Although the compound crystallizes as colorless needles, an X-ray crystallographic structure determination failed because of pseudo-symmetry effects. When the neat compound is exposed to air, its mass spectrum shows – besides the molecular ion peak – signals at M + 16 and M + 32, which might be caused by epoxides and/or peroxides (*endo*-peroxides?) formed from **1**. Clearly, we are dealing with a reactive compound making other addition reactions very likely. As this publication shows, this is indeed the case.



Scheme 1. 3,4-Benzocycloocten-1,5-diyne (**1**) and its calculated structure.

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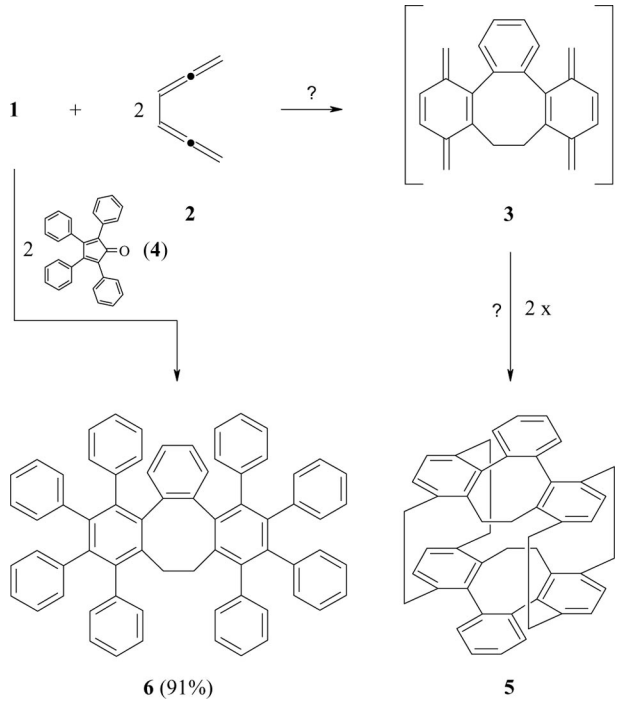
Theoretical Structure and Properties of 1

Since no X-ray crystallographic structure could be obtained, we carried out gas phase calculations at the Möller–Plesset level of theory[3] in combination with a correlation consistent basis set[4] to get an impression of the geometric structure and the strain of **1**. All optimizations and frequency calculations were performed using the Gaussian 03 set of programs.[5] According to our MP2/cc-pvtz calculations, the cycloocten-1,5-diyne substructure minimum in C_2 symmetry displays pronounced deviations from the triple bond linearity of 25° and 20.7°, respectively (see Scheme 1), introducing an angle strain of 6.4 kcal/mol per "yne" moiety relative to an unperturbed acetylene. This *cis* distortion of the carbon–carbon triple bonds in **1** is not only attended by a weakening in terms of relaxed force constants (inverse C≡C compliance constants;[6] 13.88 mdyn Å^{-1} in **1** vs. 15.62 mdyn Å^{-1} in acetylene, respectively), but also gives rise to a pronounced reactivity.

Cycloadditions to 1

Assuming that the distorted triple bonds of **1** would increase its propensity towards cycloadditions, we first carried out a Diels–Alder reaction with 1,2,4,5-hexatetraene (**2**), a hydrocarbon that has frequently proved its value as a diene component.[7] If two molecules of it added to **1**, the bis(*p*-quinodimethane) intermediate **3** could be formed, which under the reaction conditions could dimerize to the layered compound **5** (Scheme 2).

However, heating the two components in benzene at 80 °C provided polymeric material only. In a second [2+4] cycloaddition experiment **1** was heated with excess tetraphenylcyclo-pentadienone (**4**, tetracyclone) in toluene under reflux. After 2 d the bis adduct **6** had been formed in excellent yield (91%). The compound was characterized by its spectroscopic data (see Exp. Section) and also a crystal structure determination (Figure 1).



Scheme 2. Cycloadditions with **1**.

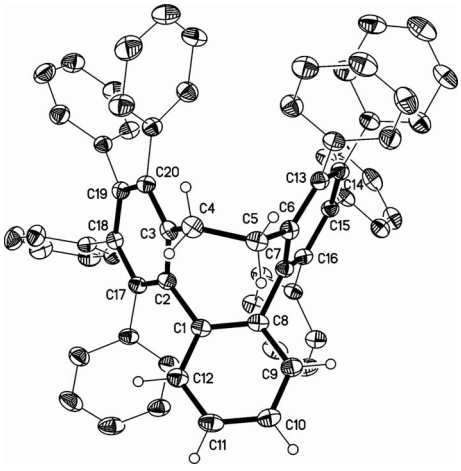
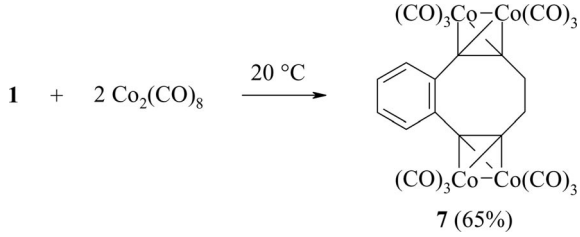


Figure 1. The molecule of compound **6** in the crystal. Ellipsoids represent 30% probability levels. Phenyl hydrogen atoms are omitted for clarity.

The structure analysis determines unambiguously the chemical nature of compound **6**. The molecule has no imposed symmetry. The bond length C4–C5 of 1.551(3) Å clearly establishes this as a single bond. The eight-membered ring displays an approximate tub conformation, whereby the atoms C1,4,5,8 and C2,3,6,7 each form a coplanar set (mean deviations 0.13, 0.11 Å) with an interplanar angle of 4°. Strain in the ring system is expressed e.g. in the torsion angles C1–C2–C3–C4 –17.5(3), C5–C6–C7–C8 –11.9(3) and C2–C1–C8–C7 9.3(4)° (ideal values 0°) and in the formally sp^3 bond angle C3–C4–C5 119.6(2)°; surprisingly, the angle C4–C5–C6 is relatively unaffected at 111.6(2)°.

In a second cycloaddition experiment an ethereal solution of **1** was treated with excess octacarbonyldicobalt (**7**) at room temperature (Nicholas reaction).[8] After 20 min the bis adduct **8** had been produced as the only product; it was isolated after chromatography and recrystallization as deep black needles in 65% yield (Scheme 3).

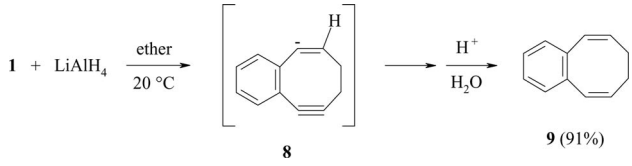


Scheme 3. Reaction of **1** with excess octacarbonyldicobalt.

On standing, the compound is air-oxidized, but it is far more stable than the starting hydrocarbon. The structure assignment of the adduct rests on its spectroscopic properties (see experimental section), with the mass spectrum being particularly revealing since it displays the successive loss of all 12 carbonyl ligands. Again, the X-ray structure determination failed because of pseudo-symmetry effects.

Ionic Additions to 1

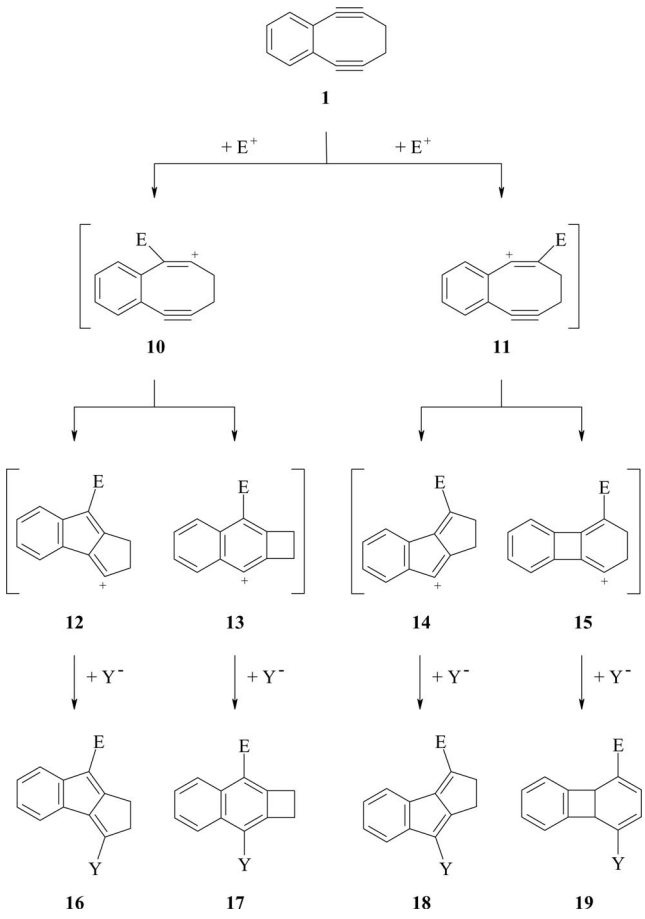
In a first ionic reaction the title compound was treated with $LiAlH_4$ in ether at room temperature. To our surprise the two triple bond were reduced to double bonds within 1 h at room temperature and 1,2-benzo-1,3,7-cyclooctatriene (**9**) was obtained in 91% yield (Scheme 4). The compound was identified by comparison of its spectroscopic data with those described in the literature.[9]



Scheme 4. The reduction of **1** with lithium aluminum hydride.

We assume that hydride is added to the highly strained triple bond and that a vinyl anion such as **8** is produced first. The process is repeated and on work-up the ionic intermediate is protonated to **9**. Whereas functionalized alkynes can be reduced readily by lithium aluminum hydride (see the often used reduction of propargylic to allylic alcohols[10]) the hydrogenation of acetylenic hydrocarbons by this route is rare. Interestingly, we could add neither phenyl nor methyllithium to the triple bonds of **1**.

Whereas electron-rich intermediates such as **8** do not show any tendency for intraannular constriction by neighboring group participation, a completely different situation is encountered when electron-deficient intermediates are generated from **1**. As shown in general form in Scheme 5, an electrophile E^+ has two options to add to **1**, producing the regioisomeric cations **10** or **11**.



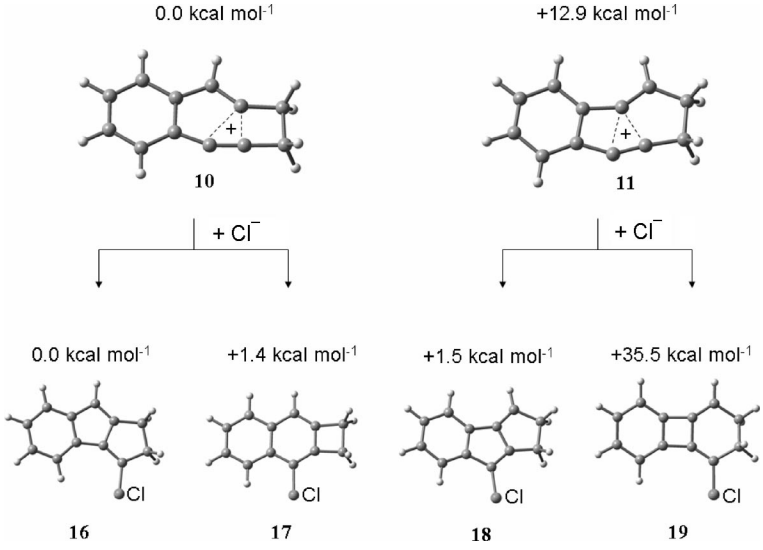
Scheme 5. The addition of electrophiles to **1** followed by a transannular ring closure: possible reaction pathways.

Excluding the direct trapping of **10** and **11** by a nucleophile Y^- to a 1,2-acetylene addition product, but allowing ring closure by the opposing triple bonds, these cations could cyclize to the four vinyl cations **12**–**15**, which belong to two categories, those possessing a [3.3.0]skeleton (**12** and **14**) and those having a [4.2.0]structure (**13** and **15**). From these, by external attack of Y^-, the four isomeric adducts **16**–**19** can be derived. Intuitively one would expect the routes via **13** and **15** to be disfavored since these contain strain-producing four-membered rings.

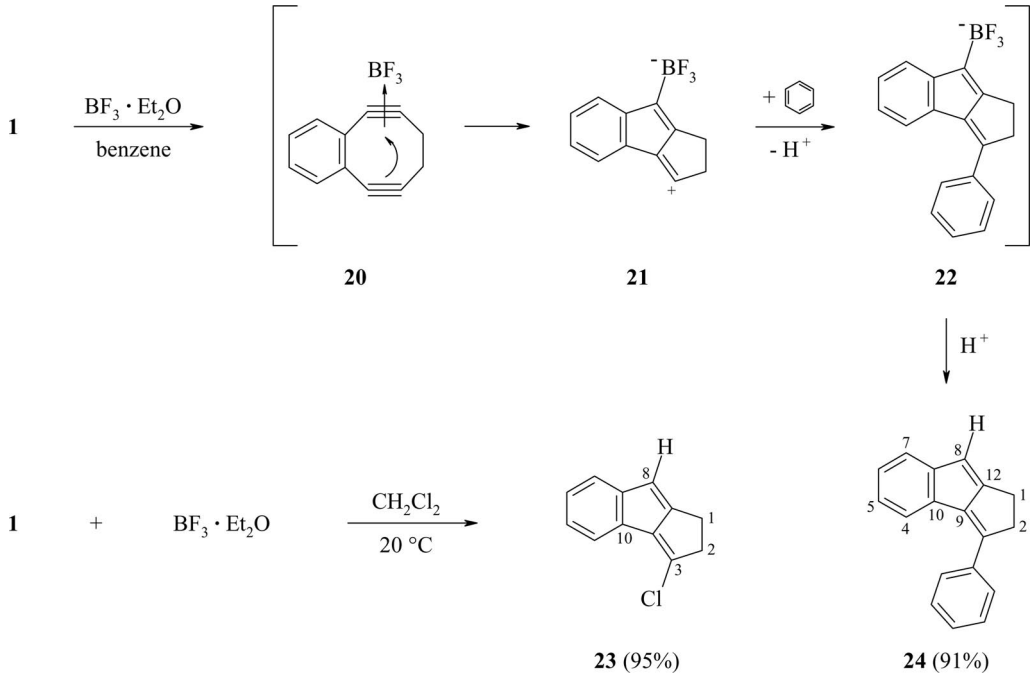
To gain a better understanding of the possibly preferred addition/cyclization modes we first carried out gas phase calculations again at the MP2/cc-pvtz level of theory. According to our calculations, regioselective protonation of **1** leads to two different non-classical cations, favoring **10** by 12.9 kcal mol^{-1} with respect to cation **11** (intrinsic thermodynamic stability, no solvent effects included). Both cations can be viewed as precursors of the ring closure: A nucleophilic attack – the chloride anion, in our theoretical case study – on **10** leads to the products **16** and **17** depending on the entry trajectory of the nucleophile. Whereas, in terms of thermodynamic stability, the products **16** and **17** are quite similar (**16** lying 1.4 kcal mol^{-1} lower than **17**), they are separated by a substantial kinetic barrier. The transition structure (one negative Hessian eigenvalue, MP2/cc-pvtz level of theory) connecting **16** and **17** is only passed through an energy maximum of 94.3 kcal mol^{-1}. On the other hand, regioselective nucleophilic attack on cation **11** leads to product **18** and **19**. While the thermodynamic stability of product **18** is again not far from the product global minimum **16** (+1.4 kcal mol^{-1}), isomer **19** is destabilized by more than 35 kcal mol^{-1}.

We conclude that in case of an electrophilic attack on **1** both the thermodynamic and kinetic stability should lead to product **16** as the only observable product (Scheme 6).

To test the above hypotheses we first treated **1** with BF_3–OEt_2 in benzene at room temperature (Scheme 7), a process yielding a single product in excellent yield (91%). To this we assign the benzo dihydropentalene structure **24** largely on the basis of its NMR spectra given in the experimental section. In principle the cyclization product could be de-



Scheme 6. Calculated reaction pathways for the addition of HCl to **1**.



Scheme 7. Electrophilic additions to **1**: experimental results.

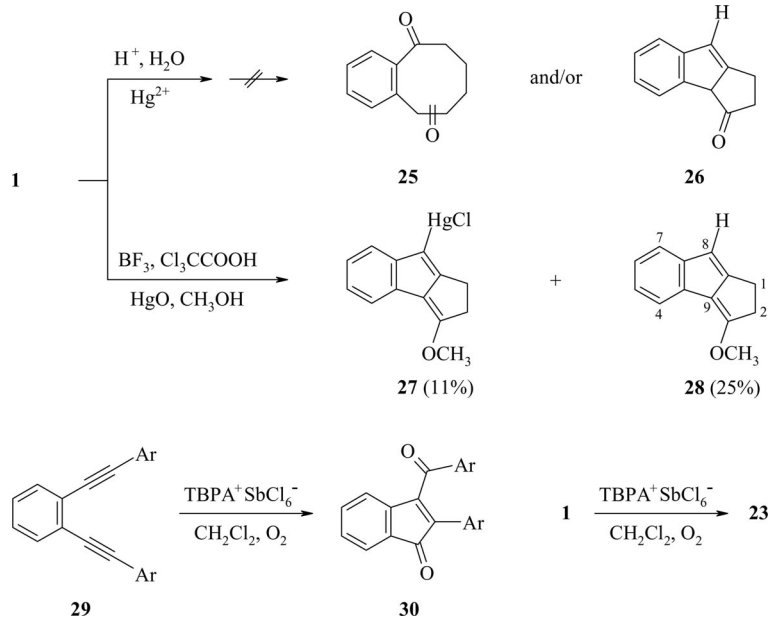
rived from all four alternatives **16**–**19** with a phenyl group as the substituent (Cl in Scheme 6). Evidence against the two alternatives **18** and **19** is furnished by the observation that the proton H-8 of our product is registered as a sharp singlet at δ = 7.51 ppm. For structures such as **18** and **19** we would expect a triplet or a pseudo-triplet for the corresponding proton because of coupling with the neighboring methylene group. Besides, both adducts would be formed via energetically disfavored pathways. To differentiate between **16** and **17** is more difficult, and at the present time we favor alternative **16**, e.g. structure **24**, largely because of its very well-resolved ^{13}C NMR spectrum, in which 16 of its 18 carbon atoms can be assigned. For a structure such as **17**, with its inherently more symmetrical structure, we would expect partial overlap of signals. It should be pointed out that on the basis of the ^{1}H chemical shifts a distinction between **16** and **17** is not possible. The methylene protons of **24** absorb as a pseudo-singlet at δ = 3.32–3.39, whereas its carbon atoms are registered at two triplets at δ = 28.48 and 29.04 ppm. The NMR spectra of the corresponding phenyl derivative of naphtha[*b*]cyclobutene have not been reported, but for the parent system, the ^{1}H NMR spectrum displays a singlet at δ = 3.28 ppm and the ^{13}C spectrum a signal at δ = 29.4, i.e. with practically identical chemical shifts, as observed for **24**.[11] As an additional argument for favoring a structure of type **16** (e.g. **24**) we cite the energetically more favorable pathway leading to this adduct.

To rationalize the transannular cyclization we suggest that it is initiated by complexation of one of the triple bonds of **1** to the Lewis acid, and that subsequently the facing triple bond will begin to provide electron density to this now positively polarized section of the substrate (see **20**). When the ring closure is complete, the vinyl cation **21** has been generated, which then undergoes an electrophilic substitution reaction with the solvent. The resulting borate complex **22** may either be protonated in situ or during hydrolytic work-up. Whereas various dihydropentalenes have been described in the literature,[12–15] we could find no reference to benzannelated derivatives such as **24**. In an attempt to oxidize this hydrocarbon to the corresponding pentalene we heated it in boiling toluene in the presence of DDQ: even after several weeks of refluxing no dehydrogenation had taken place.

When the same process was repeated in dichloromethane as the solvent, the chloro dihydro-pentalene **23** was produced in practically quantitative yield (95%) and presumably by a very similar mechanism (Scheme 7). Again we cannot assign its structure unambiguously, since we cannot rigorously exclude a structure of type **17**. That we prefer the structure given in Scheme 7 results from the similarity of its spectroscopic data with those of **24**. We were unable to determine an X-ray structure of **23** or **24**.

In the next series of experiments the species E^+ and Y^- were varied. In a first experiment we attempted to hydrate either one or both of the triple bonds of **1**, hoping to obtain either the diketone **25** or the monoketone **26**, which again could be produced by the above transannular cyclization mechanism. However, applying a well-established procedure[16] for triple bond hydration (Scheme 8) only gave the benzo-dihydropentalene derivatives **27** and **28**, presumably by a mechanism analogous to that discussed above (Scheme 7). The structure assignment of both products follows from the spectroscopic data given in the experimental section.

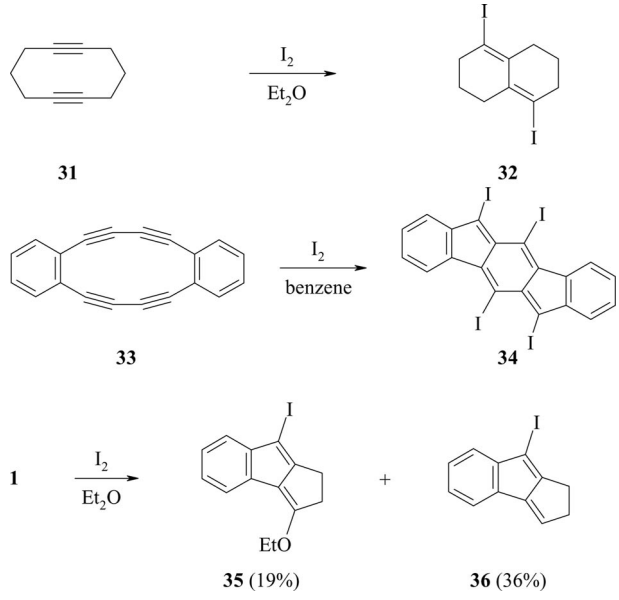
Recently Sankararaman and co-workers[17] reported that various enediynes can be cyclized via radical cation intermediates; a case in point is the cyclization of **29** to the ind-



Scheme 8. Oxymercuration of **1**.

enone derivative **30**. However, when the same conditions [tris(*p*-bromophenyl)ammonium hexachloroantimonate (TBPA·$SbCl_6$), oxygen gas, dichloromethane] were applied to **1**, only **23** was produced (48%), besides 20% of unreacted substrate.

As shown in Scheme 9 iodine has been added to various cyclic oligoynes; for example, iodine addition to cyclodeca-1,6-diyne (**31**) leads to the constricted diiodide **32**,[18] whereas with the tetrayne **33** the *s*-indacene derivative **34** is produced.[19]



Scheme 9. Iodine addition to **1**.

From the complex product mixture (containing at least five products) generated when iodine is added to **1**, the two dihydropentalenes **35** and **36** were isolated and characterized. Whether the expected diiodide (ethoxy in **35** replaced by iodine) is also produced, is presently unknown. All products are extremely air-sensitive, and even the eventually characterized adducts **35** and **36** are so sensitive towards oxidation that they can only be kept at low temperature (–24 °C) under inert gas for a limited amount of time. The iodides **35** and **36** could be formed by a similar ionic mechanism as discussed above or involve radical intermediates, considering the low heat of dissociation of the I–I bond.

Conclusions

3,4-Benzocycloocten-1,5-diyne (**1**) is a strained acetylenic hydrocarbon that undergoes various types of addition reactions (Diels–Alder addition, hydride addition, electrophilic additions) readily. Whenever cation intermediates are generated from **1** a transannular cyclization takes place leading to novel derivatives of 1,2-dihydropentalene.

Experimental Section

1. General: Melting points up to 200 °C: Büchi 510, above 200 °C: Reichert melting point stage. Column chromatography: silica gel 60 (70–230 mesh, Merck). NMR: in deuteriochloroform with TMS as internal standard; Bruker AM-400 (^{1}H NMR, 400 MHz. ^{13}C NMR, 100 MHz); Bruker AC-200 (^{1}H NMR, 200 MHz. ^{13}C NMR, 50 MHz). IR: Nicolet 320 FT-IR under the condition given in the respective experiments. UV/Vis: HP 8542A, in acetonitrile. MS: MAT 8430 (EI, 70 eV). GC/MS: Carlo–Erba HRGC 5160/ Finnigan MAT 4515 (EI, 40 eV).

2. 5,6,7,8,11,12,13,14-Octaphenyl-9,10-dihydrotribenzo[*a*,*c*,*e*]cyclooctene (6): A solution of **1** (50 mg, 0.32 mmol) and **4** (384 mg, 1 mmol) in toluene (50 mL) was heated under reflux for 2 d. The solvent was removed in vacuo and the remaining product mixture purified by column chromatography (silica gel; cyclohexane/dichloromethane = 1:1): 259 mg of **6** (91%), colorless prisms (dichloromethane), m.p. 160–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50–2.55 (m, 2 H, CH_2), 2.72–2.80 (m, 2 H, CH_2), 6.04 (d, ^3J_o = 7.7 Hz, 2 H, Ar-H), 6.56–7.14 (m, 44 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.90 (t, CH_2), 32.12 (t, CH_2), 124.87 (d), 124.91 (d), 125.19 (d), 125.69 (d), 125.78 (d), 126.16 (d), 126.37 (d), 126.41 (d), 126.63 (d), 126.97 (d), 127.14 (d), 130.91 (d), 131.06 (d), 131.16 (d), 131.34 (d), 131.60 (d), 131.70 (d), 132.10 (d), 132.36 (d), 136.87 (s), 139.18 (s), 139.27 (s), 140.10 (s), 140.13 (s), 140. 35 (s), 140.45 (s), 140.77 (s), 141.00 (s), 141.30 (s, Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3055 (s), 2925 (s), 1442 (s), 1028 (s), 738 (s), 699 (s) cm^{-1}. UV/Vis (acetonitrile): λ_{max} (logε) = 194 (5.23), 240 nm (4.86). MS (70 eV): *m*/*z* (%) = 866 (27), 865 (75), 864 (100) [M$^+$], 787 (4), 695 (4), 432 (10), 382 (12). HRMS: calcd. 864.3756; found 864.375. X-ray: see main section and below.

3. 1,2;5,6-Bis(dicobalthexacarbonyl)-3,4-benzocyclooctene (7): To a solution of **1** (100 mg, 0.658 mmol) in anhydrous diethyl ether (50 mL) was added under nitrogen $Co_2(CO)_8$ (674 mg, 1.97 mmol). The mixture was stirred for 20 min at room temp. (gas formation), and the solvent was removed by rotary evaporation. After 4 h under vacuum the adduct was dissolved under nitrogen in dichloromethane, the solution was filtered through a pad of silica gel, and the solvent was removed in vacuo. The remaining black residue was recrystallized from dichloromethane/methanol: 310 mg (65%) of dark brown/black needles, decomp. temp. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 4 H, CH_2CH_2), 7.31–7.33 (m, 2 H, Ar-H), 7.59–7.61 pm (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.44 (t, CH_2CH_2), 89.90 (s, C-2), 96.24 (s, C-1), 128.88 (d, Ar-C), 134.57 (d, Ar-C), 136.15 (s, Ar-C), 199.37 (s, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3043 (w), 2934 (w), 2082 (vs), 2007 (vs), 1431 (w), 514 (s), 494 (s) cm^{-1}. UV/Vis (acetonitrile): λ_{max} (logε) = 200 (4.51), 222 (4.47), 232 nm (4.53). MS (70 eV): *m*/*z* (%) = 724 (12) [M$^+$], 696 (3), 668 (96), 640 (31), 612 (17), 584 (79), 556 (100), 528 (72), 500 (55), 472 (51), 444 (42), 416 (19), 388 (79), 329 (33). $C_{24}H_8Co_4O_{12}$ (724.06): calcd. C 39.81, H 1.11; found C 38.81, H 0.99.

4. 1,2-Benzo-1,3,7-cyclooctatriene (9): To a solution of **1** (30 mg, 0.2 mmol) in anhydrous diethyl ether (50 mL) was added under nitrogen $LiAlH_4$ (38 mg, 1 mmol), and the mixture was stirred for 1 h at room temperature. For work-up water (50 mL) was added, and the product mixture was extracted carefully with diethyl ether (4 × 50 mL). After drying (sodium sulfate) the solvent was removed by rotary evaporation and the residue purified by column chromatography (silica gel, cyclohexane) to provide 29 mg (93%) of **9** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30–2.34 (m, 4 H, CH_2CH_2), 5.90–5.98 (m, 2 H, 4-H), 6.55 (d, ^3J = 11.8 Hz, 2 H, 3-H), 7.10–7.14 (m, 2 H, Ar-H), 7.18–7.25 (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.03 (t, CH_2CH_2), 126.49 (d, C-9, –12), 129.57 (d, C-10, –11), 129.87 (d, C-2, –5), 132.57 (d, C-1, –6), 135.92 (s, C-3, –4) ppm. MS (70 eV): *m*/*z* (%) = 156 (22) [M$^+$], 141 (21), 128 (100), 115 (38). The spectroscopic and analytical data agree with those reported in the literature.[9]

5. 3-Phenyl-1,2-dihydrocyclopenta[*a*]indene (24): To a solution of **1** (100 mg, 0.66 mmol) in anhydrous benzene (100 mL) was added under nitrogen $BF_3{\cdot}Et_2O$ (0.2 mL) and the mixture kept at room temperature for 30 min. The mixture was hydrolyzed with hydrogen carbonate solution (100 mL), extracted carefully with dichloromethane, and the combined organic phases were passed through a pad of silica gel. After solvent removal and silica gel chromatography (cyclohexane) 138 mg (91%) of **24** was obtained as a colorless, glassy solid; m.p. 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.32–3.39 (m, 4 H, CH_2CH_2), 7.37–7.47 (m, 3 H, 6-, 5-, 16-H), 7.51 (s, 1 H, 8-H), 7.52–7.55 (m, 4 H, Ar-H), 7.88 (d, J_o = 6.1 Hz, 1 H, 7-H), 7.99 (d, J_o = 7.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.48 (t, C-1), 29.04 (t, C-2), 120.12 (d, C-8), 124.43 (d, C-4), 124.70 (d, C-7), 125.45 (d, C-6), 127.14 (d, C-16), 128.33 (d, C-5), 128.37 (d, C-15), 129.96 (d, C-14), 131.59 (s, C-12), 132.42 (s, C-9), 134.69 (s, C-10), 136.94 (s, C-13), 142.75 (s, C-3), 143.92 (s, C-11) ppm. IR (KBr): $\tilde{\nu}$ = 3052 (w), 2971 (m), 2932 (s), 1509 (m), 1403 (m), 871 (s), 757 (s), 747 (s), 697 (s) cm^{-1}. UV/Vis (acetonitrile): λ_{max} (logε) = 192 (4.66), 228 (4.75), 294 nm (4.01). MS (70 eV): *m*/*z* (%) = 230 (97) [M$^+$], 215 (100), 202 (28). $C_{18}H_{14}$ (230.31): calcd. C 93.87, H 6.13; found C 93.73, H 6.07.

6. 3-Chloro-1,2-dihydrocyclopenta[*a*]indene (23): As described under **5** a solution of **1** (100 mg, 0.66 mmol) was prepared, but in dichloromethane (100 mL). Work-up as described above furnished **14** (118 mg, 95%) as a colorless, glassy solid; m.p. 52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.31–3.33 (m, 2 H, CH_2), 3.36–3.38 (m, 2 H, CH_2), 7.41 (s, 1 H, 8-H), 7.47 (m, J_o = 7.9, J_m = 1.5 Hz, 1 H, 6-H), 7.54 (m, J_o = 8.3, J_m = 1.5 Hz, 1 H, 5-H), 7.82 (d, J_o = 7.9 Hz, 1 H, 7-H), 8.24 (d, J_o = 8.3 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.23 (t, C-1), 28.36 (t, C-2), 119.72 (d, C-4), 123.14 (s, C-9), 123.56 (d, C-7), 125.25 (d, C-8), 125.51 (d, C-6), 128.21 (d, C-5), 130.62 (s, C-12), 135.28 (s, C-10), 141.56 (s, C-3), 144.09 (s, C-11) ppm. IR (KBr): $\tilde{\nu}$ = 2970 (m), 2929 (s), 1417 (m), 1249 (s), 938 (s), 871 (s), 849 (s), 756 (s) cm^{-1}. UV/Vis (acetonitrile): λ_{max} (logε) = 228 (4.89), 274 (3.79), 284 (3.87), 294 nm (3.75). MS (70 eV): *m*/*z* (%) = 190 (33) [M$^+$, ^{37}Cl], 188 (100) [M$^+$, ^{35}Cl], 154 (10), 153 (83), 152 (68), 151 (22), 150 (12), 76 (25). HRMS: $C_{12}H_9Cl$: calcd. 188.0392; found 188.039.

7. Oxmercuration/Hydration of 1. 3-Methoxy-1,2-dihydrocyclopenta[*a*]indene (28) and (3-Methoxy-1,2-dihydrocyclopenta[*a*]inden-8-yl)mercury Chloride (27): A mixture of HgO (40 mg), trichloroacetic acid (10 mg) and $BF_3{\cdot}Et_2O$ (0.1 mL) was heated at 60 °C for several min and then added to a solution of **1** (100 mg, 0.66 mmol) in methanol (50 mL) under nitrogen. The mixture was stirred for 1 h at 20 °C, and water (200 mL) was added. After thorough extraction with diethyl ether the combined organic phases were passed through a pad of silica gel, dried (sodium sulfate), and the solvent was removed by rotary evaporation. The residue thus obtained was separated by silica gel column chromatography (cyclohexane/dichloromethane = 1:1). First fraction: 30.3 mg (25%) of **28**, colorless needles, m.p. 56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.32–3.35 (m, 2 H, CH_2), 3.58–3.61 (m, 2 H, CH_2), 4.13 (s, 3 H, CH_3O), 7.10 (s, 1 H, 8-H), 7.35–7.42 (m, 2 H, 5-, 6-H), 7.73 (d, J_o = 7.4 Hz, 1 H, 7-H), 8.16 (d, J_o = 7.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.69 (t, CH_2), 29.93 (t, CH_2), 57.11 (q, CH_3O), 113.32 (d, C-4), 121.56 (s, C-9), 122.03 (d, C-7), 123.74 (d, C-8), 125.06 (s, C-12), 125.18 (d, C-5), 127.32 (d, C-6), 135.22 (s, C-10), 145.30 (s, C-11), 147.80 (s, C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3005 (w), 2923 (s), 2854 (m), 1591 (s), 1364 (s), 1330 (s), 1279 (s), 1110 (s), 835 (s), 739 (s) cm^{-1}. UV/Vis (acetonitrile): λ_{max} (logε) = 232 (4.57), 294 nm (3.61). MS (70 eV): *m*/*z* (%) = 184 (100) [M$^+$], 169 (99), 153 (22), 141 (86), 115 (53). HRMS: $C_{13}H_{12}O$: calcd: 184.0888; found 184.088. Second fraction: 30.3 mg (11%) of **27**, colorless needles, m.p. 235 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30–3.33 (m, 2 H, CH_2), 3.51–3.89 (m, 2 H, CH_2), 4.12 (s, 3 H, CH_3O), 7.40 (m, 1 H, 6-H), 7.46 (m, 1 H, 5-H), 7.71 (d, J_o = 7.8 Hz, 1 H, 7-H), 8.21 (m, 1 H, 4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.02 (t, CH_2), 31.08 (t, CH_2), 57.24 (q, CH_3O), 121.41 (s, C-

9), 123.04 (d, C-7), 124.50 (d, C-4), 126.40 (s, C-5), 126.41 (d, C-10), 129.31 (d, C-6), 138.59 (s, C-11), 151.47 (s, C-3) ppm; the signals for C-8 and C-12 could not be detected. IR (KBr): $\tilde{\nu}$ = 2936 (w), 1602 (m), 1333 (s), 1270 (s), 1110 (s), 754 (s) cm^{-1}. UV/Vis (acetonitrile): λ_{max} (log ε) = 192 (4.47), 2.36 (4.76), 300 nm (4.01). MS (70 eV): *m/z* (%) = 422 (25) [$M^+ - {}^{37}Cl$], 420 (67) [$M^+ - {}^{35}Cl$], 203 (12), 183 (44), 168 (82), 139 (100). HRMS: = $C_{13}H_{11}ClHgO$: calcd. 420.01964; found 420.0196. $C_{13}H_{11}ClHgO$ (419.27): calcd. C 37.24, H 2.64; found C 37.05, H 2.55.

8. Iodine Addition to 1. 8-Iodo-1,2-dihydrocyclopenta[*a*]indene (36) and 3-Ethoxy-8-iodo-1,2-dihydrocyclopenta[*a*]indene (35): To a solution of **1** (30 mg, 0.197 mmol) in anhydrous ether (50 mL) was added whilst stirring under N_2 at 0 °C a solution of iodine (50 mg, 0.197 mmol) in diethyl ether (10 mL). After 1 h the solvent was removed by rotary evaporation and the product mixture separated by silica gel column chromatography (cyclohexane). Fraction 1: 20 mg (36%) of **36**, brown-violet solid, m.p 50–60 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.68–2.70 (m, 2 H, CH_2), 3.10–3.13 (m, 2 H, CH_2), 6.82 (t, 1 H, 3-H), 7.15–7.19 (m, 2 H, 5-, 6-H), 7.34 (m, J_o = 7.6 Hz, 1 H, 7-H), 7.52 (m, J_o = 7.3 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.77 (t, CH_2), 38.01 (t, CH_2), 77.87 (s, C-8), 120.65 (d, C-3), 121.49 (d, C-4), 124.35 (d, C-7), 128.14 (d, C-5), 129.28 (s, C-10), 134.89 (d, C-6), 149.01 (s, C-11), 150.26 (s, C-12), 160.23 (s, C-9) ppm. IR (KBr): $\tilde{\nu}$ = 3059 (w), 2914 (w), 1484 (s), 1444 (s), 1339 (s), 1216 (s), 754 (s) cm^{-1}. UV/Vis (acetonitrile, qualitative): λ_{max} = 198, 236, 242, 266, 290, 362 nm. MS (70 eV): *m/z* (%) = 280 (8) [M^+], 153 (18), 152 (15), 126 (18). HRMS: $C_{12}H_9I$: calcd. 279.9749; found 279.974. Fraction 2: 12 mg (19%) of **35**, brown-violet crystals; m.p. 50–60 °C (decomp. point). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (t, ^3J = 7.2 Hz, 3 H, CH_3), 3.15–3.18 (m, 2 H, CH_2), 3.39 (m, 2 H, CH_2), 4.36 (q, ^3J = 7.2 Hz, 2 H, CH_2CH_3), 7.41 (m, J_o = 8.3, J_m = 1.0 Hz, 1 H, 7-H), 7.50 (m, J_o = 7.4, J_m = 1.0 Hz, 4-H), 7.96 (m, J_o = 8.3 Hz, 1 H, 6-H), 8.18 (m, J_o = 7.4, J_m = 1.0 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.35 (q, CH_3), 27.55 (t, CH_2), 32.63 (t, CH_2), 65.14 (t, CH_2CH_3), 80.48 (s, C-8), 121.83 (s, C-9), 122.75 (d, C-4), 124.45 (d, C-7), 126.51 (s, C-10), 126.75 (d, C-5), 129.62 (d, C-6), 134.53 (s, C-12), 147.81 (s, C-11), 151.54 (s, C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3062 (w), 2923 (m), 1579 (s), 1418 (s), 1413 (s), 1337 (s), 1270 (s), 1111 (s), 757 (s) cm^{-1}. UV/Vis (acetonitrile): λ_{max} (log ε) = 220 (4.56), 236 (4.60), 304 nm (4.02). MS (70 eV): *m/z* (%) = 324 (100) [M^+], 295 (35), 254 (10), 168 (32), 139 (32). HRMS: $C_{14}H_{13}IO$: calcd. 324.0011; found 324.001.

9. Crystal Structure Determination: The data were recorded on a Siemens P4 diffractometer at –100 °C using Mo-K_α radiation. The structure was refined anisotropically on F^2.[20] Hydrogen atoms were included using a riding model. Two significant areas of residual electron density were tentatively interpreted as disordered solvent, probably dichloromethane, but could not be refined satisfactorily. The program SQUEEZE[21] was therefore used to remove mathematically the effects of the solvent. Because of the approximations involved, molecular dimensions should be interpreted with caution. Numerical values such as density are based on an idealised solvent content of two dichloromethane per asymmetric unit.

Crystal Data for 6·2CH_2Cl_2: Monoclinic, space group $P2_1/n$, a = 12.361(2), b = 21.422(4), c = 21.788(3) Å, β = 97.168(14)°, Z = 4, crystal size 0.8 × 0.6 × 0.4 mm, 13719 reflections to $2\theta_{max}$ 50°; refinement to $wR2$ = 0.129, $R1$ = 0.054 for 613 parameters and 10044 unique reflections; max. $\Delta\rho$ = 0.25 e Å^{-3}, S = 0.98.

CCDC-752109 (for **6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] Part 25: H. Hopf, H. Maurer, *Eur. J. Org. Chem.* **2005**, 2702–2707; for part 24 see: A. Krüger, H. Hopf, *Chem. Eur. J.* **2001**, *7*, 4378–4385.
[2] C. Werner, I. Dix, H. Hopf, P. Bubenitschek, P. G. Jones, *Chem. Eur. J.* **2007**, *13*, 9462–9477.
[3] C. Moeller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622.
[4] R. A. Kendall, T. H. Dunning Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796–6806.
[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision B.02, Gaussian, Inc., Pittsburgh PA, **2003**.
[6] K. Brandhorst, J. Grunenberg, *Chem. Soc. Rev.* **2008**, *37*, 1558–1567.
[7] H. Hopf, *Angew. Chem.* **1972**, *84*, 471; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 419; cf.H. Hopf, G. Schön, *Liebigs Ann. Chem.* **1981**, 165–180.
[8] D. H. Bradley, M. A. Khan, K. M. Nicholas, *Organometallics* **1992**, *11*, 2598–2607; cf.P. Magnus, T. Pitterna, *J. Chem. Soc., Chem. Commun.* **1991**, 541–543.
[9] M. E. Günther, R. Aydin, W. Buchmeier, B. Engelen, H. Günther, *Chem. Ber.* **1984**, *117*, 1069–1076.
[10] R. A. Raphael, *Acetylenic Compounds in Organic Synthesis*, Butterworths, London, **1955**, pp. 29.
[11] We thank Prof. Dr. R. Thummel (University of Houston) for making these spectra available to us; cf.: R. P. Thummel, W. E. Cravey, W. Nutakul, *J. Org. Chem.* **1978**, *43*, 2473–2477.
[12] R. Kaiser, K. Hafner, *Angew. Chem.* **1970**, *82*, 877–878; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 892–893.
[13] L. Eisenhuth, H. Hopf, *J. Am. Chem. Soc.* **1974**, *96*, 5667–5668.
[14] N. Hanold, Th. Molz, H. Meier, *Angew. Chem.* **1982**, *94*, 921; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 917.
[15] H. Meier, A. Pauli, P. Kochhan, *Synthesis* **1987**, 573–574.
[16] Autorenkollektiv, *Organikum*, 20th ed., Wiley-VCH, Weinheim, **1999**, p. 286.
[17] D. Ramkumar, M. Kalpana, B. Varghese, S. Sankararaman, *J. Org. Chem.* **1996**, *61*, 2247–2250.
[18] X. Gu, M. B. Sponsler, *Tetrahedron Lett.* **1996**, *37*, 1571–1574. For transannular cyclizations in medium-sized alicyclic diynes and tetraynes the reader is referred to the extensive work of Gleiter et al., for example: a) J. Ritter, R. Gleiter, *Liebigs Ann. Chem./Recueil* **1997**, 1179–1188; b) E. M. Schmidt, R. Gleiter,

F. Rominger, *Chem. Eur. J.* **2003**, *9*, 1814–1822; c) B. Esser, R. Gleiter, *J. Org. Chem.* **2006**, *71*, 5126–5135, and ref. cited therein.
[19] Q. Zhou, P. J. Carroll, T. M. Swager, *J. Org. Chem.* **1994**, *59*, 1294–1301 and refs. reported therein. For the preparation of other stable *s*-indacenes see K. Hafner, B. Stowasser, H.-P. Krimmer, S. Fischer, M. C. Böhm, H. J. Lindner, *Angew. Chem.* **1986**, *98*, 646–648; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 630–632.
[20] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[21] A. L. Spek, University of Utrecht, The Netherlands.
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