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Cyclooligomerization of Mono- and Diazulenylethynes Catalyzed by Transition Metal Complexes

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Dedicated to Professor Mieczyslaw Makosza on the occasion of his 75th birthday

Keywords: Cobalt catalyst / Ethynylazulenes / Azulenylbenzenes / Azulenylcyclobutadienes / Cyclooligomerization / Cross-coupling / Polycycles

Cyclooligomerization of 1-ethynylazulenes **1a**,**b**, **6** and **7** as well as 1,2-bis(azulen-1-yl)ethynes **10a**,**b** and **11** with $CpCo(CO)_2$ to the corresponding 1,2,4-tris(azulen-1-yl)benzenes **14a**,**b**, **18** and **19** as well as [bis- and tetrakis(azulen-1-yl)cyclobutadiene]cobalt complexes **17a**,**b**, **30a**,**b** and **31** is described.

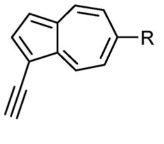
Introduction

Benzenoid aromatic compounds with extended π-electron systems are of prime interest for materials science.[1,2] They are often required as core or building blocks for advanced materials with eventual electronic and photonic applications.[3–17]

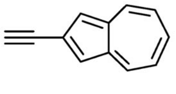
However, to date, molecules with potentially useful electronic properties constructed from non-benzenoid aromatic or even antiaromatic π-electron systems are so far fairly scarce. Especially the azulene system should be suitable in this respect due to its remarkable polarizability and tendency to form stabilized cations and anions as well as radical cations and anions.[18,19] We recently developed simple routes to a series of mono- and polyethynylated azulenes,[20,21] and studied their transformations into linear oligoazulenes with ethynyl and butadiynyl bridges by Pd/Cu-catalyzed as well as oxidative coupling reactions.[21,22] Furthermore, we previously reported on the first cyclooligomerization of mono- and diazulen-1-ylethynes by transition metal complexes as an efficient route to novel azulenyl-substituted benzenes and cyclobutadiene complexes.[23] According to the same methodology also some cyclooligomerizations of 2- and 6-ethynylazulenes were investigated later by Ito et al.[24,25] Herein, we give a full account of the results of our studies.

Results and Discussion

As already reported,[20,21] the syntheses of 1-ethynylazulenes **1a**,**b** as well as 2-ethynylazulenes **2**, besides di- and triethynylazulenes, were accomplished by utilizing the Pd-catalyzed cross-coupling reaction of the appropriate iodoazulenes with trimethylsilylacetylene (TMSA) under Sonogashira–Hagihara[26–28] conditions to furnish the protected ethynylazulenes followed by deprotection upon treatment with potassium hydroxide.



1a: R = H
1b: R = *t*Bu



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With the same reaction sequence, starting from 1-formyl-3-iodoazulene (**4**), obtained by electrophilic substitution of 1-formylazulene (**3**)[29] with *N*-iodosuccinimide, 3-ethynyl-1-formylazulene (**6**) can be obtained as brown crystals in 45% yield via the trimethylsilyl-protected derivative **5**. Condensation of **6** with hydroxylamine hydrochloride and subsequent dehydration with acetic anhydride/pyridine led to the formation of the corresponding 1-cyano-3-ethynylazulene (**7**) as brown crystals in 70% yield (Scheme 1).

In addition, Ito et al.[24,25,30] reported, besides other ethynylazulenes, the synthesis of 2-ethynyl-6-octylazulene (**8**) as well as 6-ethynylazulenes **9a**,**b** by the Pd-catalyzed cross-coupling reaction of the appropriate bromoazulenes with trimethylsilylacetylene and subsequent treatment with potassium fluoride in dimethylformamide (DMF). Further-

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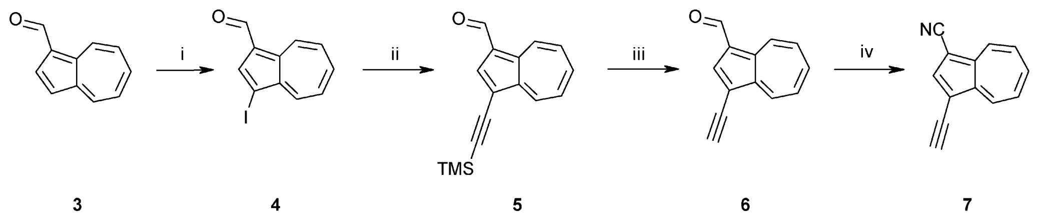
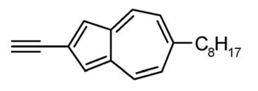


Scheme 1. (i) 1 equiv. NIS, CH_2Cl_2, room temp.; (ii) 0.04 mol-% $PdCl_2(PPh_3)_2$, 0.08 mol-% CuI, NEt_3, 1 equiv. TMSA, room temp.; (iii) 1 M KOH in H_2O, MeOH, room temp.; (iv) NH_2OH HCl, NaOH, Ac_2O/pyridine.

more, also Makosza et al.[31] prepared 6-ethynylazulenes as well as 1,6-di- and 1,3,6-triethynylazulenes by means of vicarious nucleophilic substitution (VNS).



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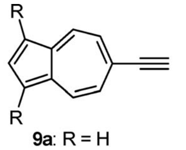
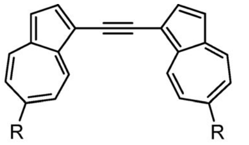


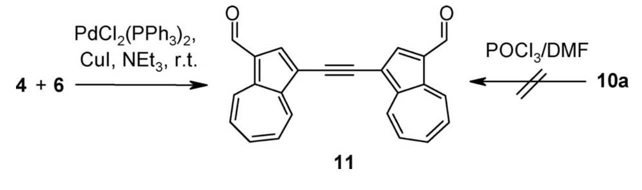
9a: R = H
9b: R = CO_2Et

Moreover, we recently communicated the synthesis of the deep green bis(azulen-1-yl)ethynes **10a**,**b**[21,23] by Sonogashira–Hagihara[26–28] coupling of the deprotected 1-ethynylazulenes **1a**,**b** with 1-iodoazulenes.



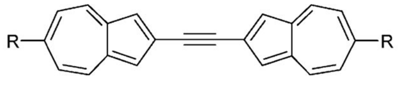
10a: R = H
10b: R = *t*Bu

Similarly, coupling of the deprotected 3-ethynyl-1-formylazulene (**6**) with the 1-formyl-3-iodoazulene (**4**) under Sonogashira–Hagihara conditions afforded the corresponding bis(3-formylazulen-1-yl)ethyne (**11**) as brown crystals in 40% yield. Attempts to prepare **11** by the straightforward formylation of **10a** with $POCl_3$/DMF were unsuccessful (Scheme 2).

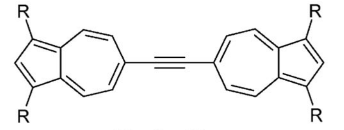


Scheme 2.

Additionally, Ito et al.[24,25,30,32] described recently a synthesis of the bis(azulenyl)ethynes **12a**,**b** and **13a**,**b** by utilizing the cross-coupling reactions of the appropriate 2- or 6-ethynylazulenes with the corresponding 2- or 6-bromoazulenes in the presence of $[Pd(PPh_3)_4]$ as a catalyst.



12a: R = H
12b: R = C_8H_{17}



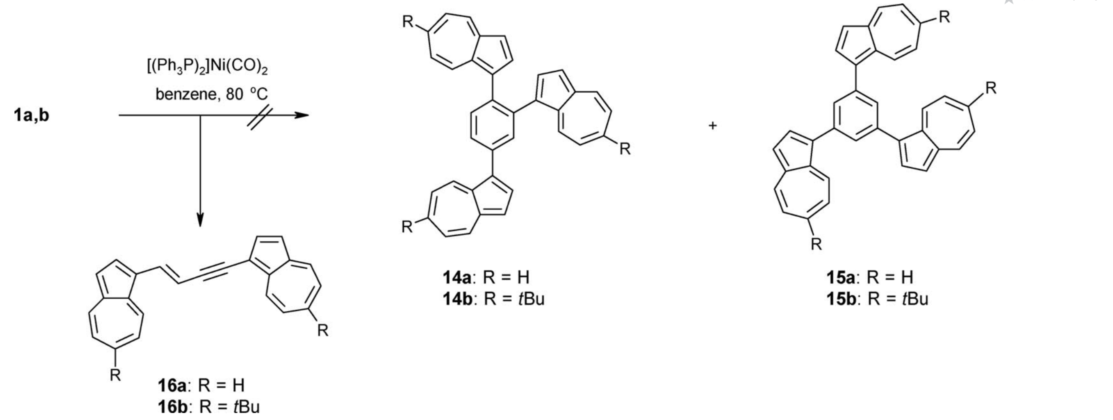
13a: R = H
13b: R = CO_2Et

In analogy to the metal-catalyzed di- and trimerization of several arylalkynes,[33] we studied the reaction of mono- and diazulenylethynes with a metal catalyst, which should open a versatile access to azulenyl-substituted cyclobutadienes and benzenes. These compounds could be of great value as building blocks for materials with special optical and electrical properties for the design of molecular devices on account of the pronounced polarizability of the azulene system.

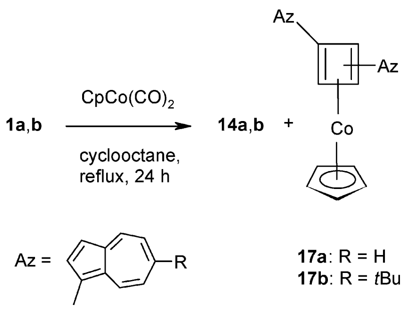
First attempts to promote a cyclotrimerization of 1-ethynylazulenes **1a**,**b** to the 1,2,4-tris(azulen-1-yl)benzenes **14a**,**b** and/or 1,3,5-tris(azulen-1-yl)benzenes **15a**,**b** by heating solutions of **1a**,**b** in benzene with dicarbonylbis(triphenylphosphane)nickel at 80 °C, led to the formation of the linear dimers **16a**,**b** in 20–25% yield together with some other reaction products of so far unknown structure (Scheme 3).

Contrary to this, treatment of **1a**,**b** with catalytic amounts of $CpCo(CO)_2$[34] in refluxing cyclooctane for 24 h furnished, after chromatography of the reaction mixture on alumina with CH_2Cl_2/*n*-hexane (1:5) as eluent, the greenish-blue 1,2,4-tris(azulen-1-yl)benzenes **14a**,**b** in 11% and 16% yields, respectively (Scheme 4). In both cases, the 1,3,5-tris(azulen-1-yl)benzene derivatives **15a**,**b** could not be obtained even in traces. It is noteworthy that the synthesis of 1,3,5-tris(azulen-1-yl)benzene **15a** so far could only be accomplished by tetrachlorosilane-mediated cyclotrimerization of 1-acetyl-3-(methoxycarbonyl)azulene followed by deesterification with H_3PO_4.[35]

In addition to the major products **14a**,**b**, we could also isolate the [η^4-bis(azulen-1-yl)cyclobutadiene](η^5-cyclopentadienyl)cobalt complexes **17a**,**b** as yellowish-green crystals in 2% and 4%, yields, respectively (Scheme 4). Unfortunately, the NMR spectroscopic data of **17a**,**b** did not allow a decision between the two expected regioisomeric 1,2- and



Scheme 3.

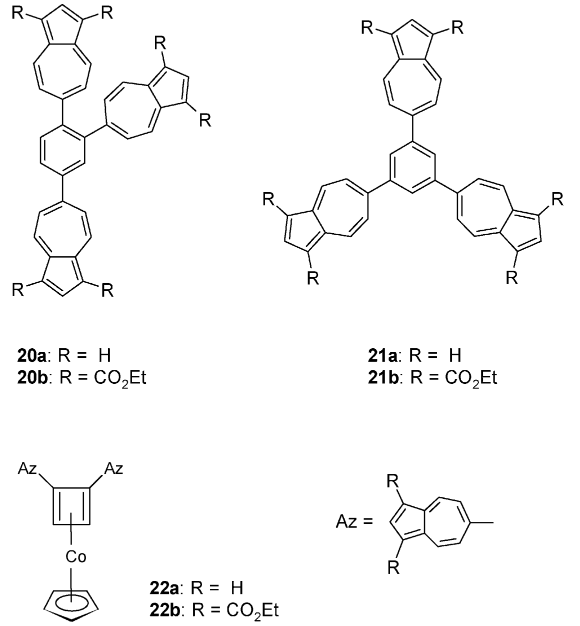


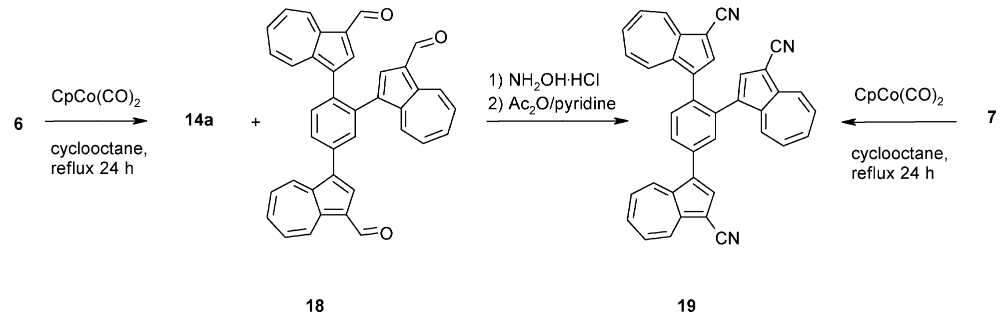
Scheme 4.

1,3-bis(azulen-1-yl)cyclobutadiene complexes, and crystals suitable for an X-ray structure analysis could not be obtained so far.

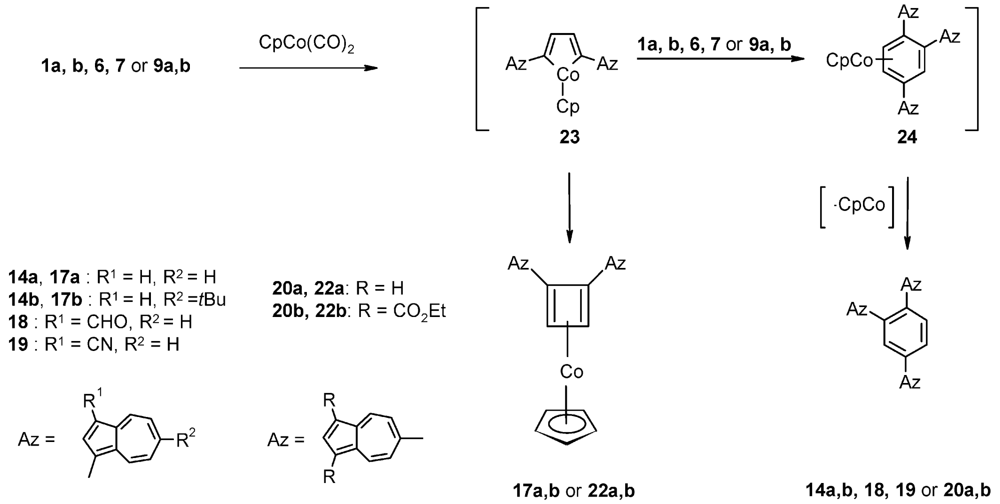
Similarly, 1,2,4-tris(azulen-1-yl)benzenes **18** and **19** could be obtained in 14% and 12% yields, respectively, upon treatment of **6** and **7** with catalytic amounts of CpCo(CO)$_2$ in refluxing cyclooctane for 24 h. In addition to **18**, 6% of **14a** could be isolated from the reaction mixture of the cyclotrimerization of **6** as a result of decarbonylation under the reaction conditions. In both cases, the corresponding [η^4-bis(azulen-1-yl)cyclobutadiene](η^5-cyclopentadienyl)cobalt complexes could not be isolated from the reaction mixture. Compound **19** could alternatively also be obtained in 45% yield by condensation of **18** with hydroxylamine hydrochloride and subsequent dehydration with acetic anhydride/pyridine (Scheme 5).

In contrast to these results, Ito et al.[24,36] reported that cyclooligomerization of 6-ethynylazulenes **9a**,**b** in the presence of CpCo(CO)$_2$ in refluxing 1,4-dioxane afforded as major products the [η^4-bis(azulen-6-yl)cyclobutadiene](η^5-cyclopentadienyl)cobalt complexes **22a**,**b** in 19% and 47% yields, respectively, besides the 1,2,4- and 1,3,5-tris(azulen-6-yl)benzene derivatives **20a**,**b** and **21a**,**b** in minor yields.





Scheme 5.

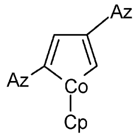


Scheme 6.

The formation of **14a**,**b**, **18**, **19** and **20a**,**b** is in accordance with results obtained by Vollhardt and others[34a,34b,37] for the cyclotrimerization of alkynes, and suggests the formation of the cobaltacycle **23** as an intermediate, which reacts with a further molecule of **1**, **6**, **7** or **9** in a metal-mediated [4+2]-cycloaddition to generate the η^4-benzene complex **24**. A subsequent displacement of the ligand in **24** by the appropriate ethynylazulenes should result in the formation of **14a**,**b**, **18**, **19** and **20a**,**b**. Therefore, it can be expected that **17a**,**b** and **22a**,**b** are formed by a reductive cycloelimination of the cobaltacycle **23** and hence should be the 1,2-bis(azulenyl)cyclobutadiene complexes (Scheme 6).

The regiochemistry of the cobalt complex **22b** could be confirmed by the ^{13}C satellite signals in the ^{1}H NMR spectrum,[24,38] which were definitely identified by the 2D HMQC spectrum measured under non-decoupling conditions. The negligibly small coupling constant (<1 Hz) between the cyclobutadiene protons clearly shows the presence of the 1,2-disubstitution pattern in the cyclobutadiene ring.[39] The regioisomer **22b** was further confirmed by the preparation of the isomer **26**[24,36] and observation of the ^{13}C satellite signals in its ^{1}H NMR spectrum. It exhibited a large coupling constant between the cyclobutadiene protons (8.1 Hz), which is consistent with the 1,3-disubstitution of the cyclobutadiene ring.[39]

Surprisingly, in case of the cyclotrimerization of **6** and **7** to **18** and **19**, respectively, (cyclobutadiene)cobalt complexes were not detected in the reaction products. This suggests a relatively high reactivity of the cobaltacycle **23** towards **6** and **7** to give **18** and **19**, respectively, compared with that of the reductive cycloelimination. The formation of **21a**,**b** in the cyclooligomerization of **9a**,**b** exhibits the existence of **25** as an intermediate. However, its apparently relatively high reactivity towards **9** compared with that of the reductive cycloelimination prevents a formation of the corresponding (cyclobutadiene)cobalt complex **26**.[24,36]



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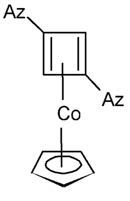

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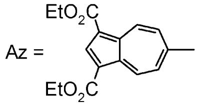
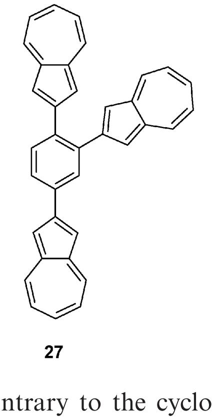


The cyclotrimerization of 2-ethynylazulene **2** to the corresponding 1,2,4-tris(azulen-2-yl)benzenes **27** and/or 1,3,5-tris(azulen-2-yl)benzenes **28** was so far not reported. However, just recently, these compounds could be synthesized by the reaction of 2-azulenylboronate with 1,3,5- and 1,2,4-tribromobenzenes in dioxane in the presence of Cs_2CO_3, $Pd_2(dba)_3$ and $P(tBu)_3$ with moderate yields.[40]



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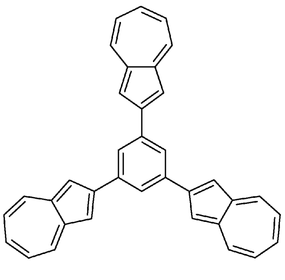

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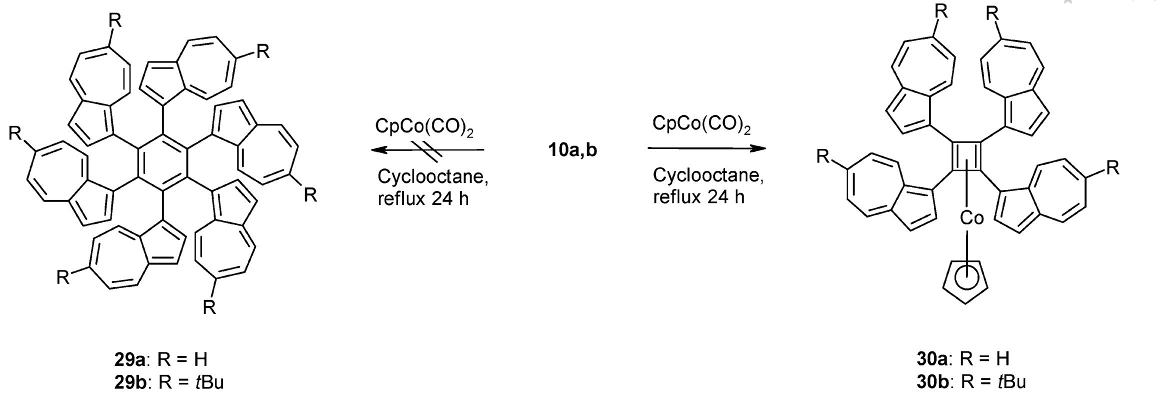
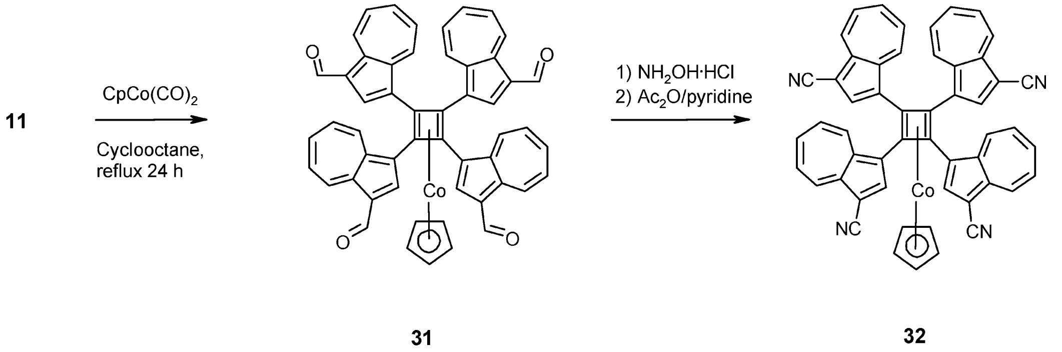
Contrary to the cyclotrimerization of 1-ethynylazulenes **1**, **6** and **7**, the reaction of the bis(azulen-1-yl)ethynes **10a**,**b** with $CpCo(CO)_2$ (20 mol-%) in refluxing cyclooctane did not yield the expected hexakis(azulen-1-yl)benzenes **29a**,**b**, obviously due to steric hindrance. Instead, the interesting black crystalline [tetrakis(azulen-1-yl)cyclobutadiene]cobalt complexes **30a**,**b** were obtained with 20–25% yield, which could be raised to 60–70% by increasing the amount of $CpCo(CO)_2$ to 60 mol-% (Scheme 7). Also, repeated



Scheme 7.



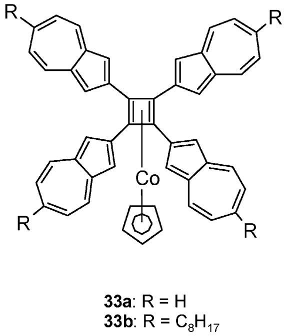
Scheme 8.

attempts to cyclotrimerize **10a**,**b** in the presence of bis(benzonitrile)palladium chloride or octacarbonyldicobalt[25,41] according to literature procedures were unsuccessful. Only the starting materials were recovered almost completely.

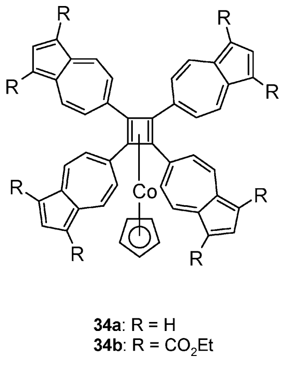
Similarly, the [tetrakis(azulen-1-yl)cyclobutadiene]cobalt complex **31** could be obtained in 60 % yield upon treatment of the bis(azulen-1-yl)ethyne **11** with CpCo(CO)$_2$ (60 mol-%) in refluxing cyclooctane. Condensation of **31** with hydroxylamine hydrochloride and subsequent dehydration with acetic anhydride/pyridine led to the formation of the [tetrakis(azulen-1-yl)cyclobutadiene]cobalt complex **32** in 30 % yield (Scheme 8).

In addition to these findings, Ito et al.[24,25,36] reported the exclusive formation of the [tetrakis(azulen-2-yl)cyclobutadiene]cobalt complexes **33a**,**b** as well as the [tetrakis(azulen-6-yl)cyclobutadiene]cobalt complexes **34a**,**b** by the cyclodimerization of bis(azulen-2-yl)ethynes **12a**,**b** and bis(azulen-6-yl)ethynes **13a**,**b**, respectively, in the presence of CpCo(CO)$_2$ in refluxing 1,4-dioxane.

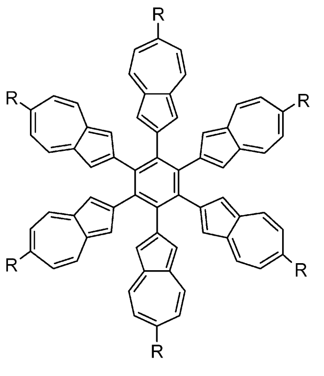
In both cases the desired hexakis(azulen-2-yl)benzenes **35a**,**b** and hexakis(azulen-6-yl)benzenes **36a**,**b** were not formed even in traces. In contrast to these findings, the cyclooligomerization of bis(6-octylazulen-2-yl)ethyne **12b**



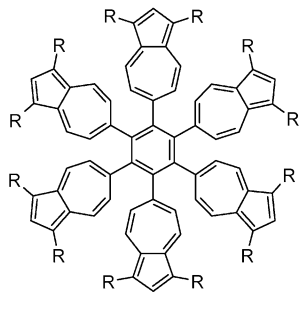
33a: R = H
33b: R = C$_8$H$_{17}$



34a: R = H
34b: R = CO$_2$Et



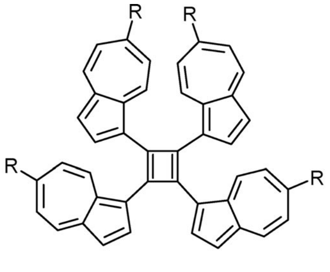
35a: R = H
35b: R = C$_8$H$_{17}$



36a: R = H
36b: R = CO$_2$Et

with $Co_2(CO)_8$ as a catalyst in refluxing dioxane led to the formation of the hexakis(azulen-2-yl)benzene **35b**,which is in comparison to **29** sterically less hindered.[25]

All efforts to generate the tetrakis(azulen-1-yl)cyclobutadienes **37a**,**b**, which represent hydrocarbons with a central antiaromatic system substituted by four non-benzenoid aromatic residues, by demetallation of **30a**,**b** met so far with no success.



37a: R = H
37b: R = *t*Bu

The tris(azulen-1-yl)benzenes **14a**,**b**, **18** and **19** as well as the tetrakis(azulen-1-yl)cyclobutadiene complexes **30**–**32** are remarkably stable, showing no decomposition even after several weeks both in solution and in the crystalline state.

Spectral Properties

A) Electronic Spectra

The UV/Vis spectra of the tris(azulenyl)benzenes and [tetrakis(azulenyl)cyclobutadiene]cobalt complexes reveal some interesting conclusions:

(1) There are no significant differences in the longest-wavelength absorption maxima (λ_{max}) of 1,2,4-tris(azulenyl)benzenes **14a**, **20b** and **27** compared with those of their corresponding 1,3,5-tris(azulenyl)benzene derivatives **15a**, **21b** and **28**, respectively.

(2) The electronic spectra of tris(azulen-2-yl)benzenes **27** and **28** exhibit bathochromic shifts of 18 nm and 13 nm, respectively, in the longest-wavelength absorption maxima compared to those of the corresponding tris(azulen-1-yl)benzenes **14a** and **15a**.

(3) 1,2,4-Tris(azulen-1-yl)benzene **14a** exhibits bathochromic shifts of 47 nm and 32 nm, respectively, in the longest-wavelength absorption maxima (λ_{max}) compared to those of **18** and **19**.

(4) Cyclodimerization of bis(azulen-1-yl)ethynes **10a**,**b** and **11** to the corresponding tetrakis(azulen-1-yl)cyclobutadiene complexes **30a**,**b** and **31** is accompanied by bathochromic shifts from 623 nm (for compound **10a**) to 638 nm (for compound **30a**), 610 nm (for compound **10b**) to 625 nm (for compound **30b**) and 572 nm (for compound **11**) to 583 nm (for compound **31**).

On the other hand, cyclodimerization of bis(azulenyl)ethynes **12a**,**b** and **13a**,**b** to the corresponding tetrakis(azulenyl)cyclobutadiene complexes **33a**,**b** and **34a**,**b**, respectively, is accompanied by hypsochromic shifts from 625 nm (for compound **12a**) to 448 nm (for compound **33a**), 608 nm (for compound **12b**) to 455 nm (for compound **33b**), 628 nm (for compound **13a**) to 395 nm (for compound **34a**), and 551 nm (for compound **13b**) to 418 nm (for compound **34b**).

B) ^1H NMR Spectra

(1) Comparison of ^1H NMR spectra of the 1,2,4-tris(azulenyl)benzenes **14a**, **20a** and **27**, respectively, with those of 1,3,5-tris(azulenyl)benzenes **15a**, **21a** and **28** shows no significant differences in the chemical shifts of the proton signals of both isomers.

(2) The resonance of the azulene 4-H protons of compound **18** is shifted by 0.9 ppm to lower field compared to that of compound **14a**. Similarly, the resonances of azulene protons 5/7-H and 4/8-H of compounds **20b** and **21b** are shifted by 0.5–0.6 ppm and 1.4 ppm to lower field, respectively, compared to those of compounds **20a** and **21a**. This may result from the deshielding effect of the carbonyl group.[30,35]

(3) The spectral properties of the cyclobutadiene complexes **30a**,**b** vary to some extent from their acyclic precursors **10a**,**b**. The azulene proton resonances – particularly those of 7-H and 8-H – are shifted upfield by more than 0.5–0.9 ppm upon cyclodimerization. We attribute this upfield shift to the chemical anisotropy associated with the CpCo group as well as the azulene rings.[42] On the other hand, the azulene proton resonances of 5/7-H and 4/8-H of the cyclobutadiene complexes **33a**,**b** and **34a**,**b** do not exhibit significant upfield shifts compared with their acyclic precursors **12a**,**b** and **13a**,**b**, respectively.

(4) The azulene proton resonances of 4-H and 5-H of compound **31** are shifted by 1.3 ppm and 0.6 ppm, respectively, to lower field compared to those of compound **30a**. Similarly, downfield shifts by 1.5 ppm and 0.5 ppm, respectively, are observed for the 4/8-H and 5/7-H protons of compounds **34b** compared with those of compound **34a**. These downfield shifts may also originate from the anisotropy of the carbonyl group.

Conclusions

Ethynylazulenes as well as bis(azulenyl)ethynes, now available by the Pd/Cu-catalyzed cross-coupling methodology, enabled us to study their synthetic utility as building blocks for the construction of novel cyclic conjugated π-electron systems. The cyclotrimerization of 1- and 6-ethynylazulenes catalyzed by $CpCo(CO)_2$ proved to be an efficient route for the synthesis of 1,2,4- and/or 1,3,5-tris(azulenyl)benzene derivatives. On the other hand, the cyclotrimerization of bis(azulen-1-yl)ethynes, bis(azulen-2-yl)ethynes and bis(azulen-6-yl)ethynes to the corresponding hexakis(azulenyl)benzenes by using $CpCo(CO)_2$ met so far with no success, and instead the reactants underwent cyclodimerization to the interesting [tetrakis(azulenyl)cyclobutadiene]cobalt complexes. However, another research group reported just recently the synthesis of the sterically less hindered hexakis(azulen-2-yl)benzene from the cyclotrimerization of bis(azulen-2-yl)ethyne by using $Co_2(CO)_8$ as a catalyst. The novel azulene derivatives are remarkably stable and may exhibit interesting electronic properties resulting from the specific bonding system of azulene.

Experimental Section

General: All melting points are uncorrected. IR spectra were measured with Beckman IR 5A and Perkin–Elmer 125 spectrometers. NMR spectra were recorded with a Bruker NMR spectrometer WM 300 in $CDCl_3$ with tetramethylsilane as internal standard. UV/Vis spectra were recorded with a Beckman UV-5240 spectrometer. Mass spectra (MS) were obtained with a Varian 311A instrument or a Bruker-Frantzen-Esquire-LC. Elemental analyses: Perkin–Elmer CHN 240 B. Column chromatography: Basic alumina [activity BII–III (Brockmann) ICN Biomedicals] and silica gel [70–320 mesh (ASTM) Macherey–Nagel].

1-Formyl-3-iodoazulene (4): To a solution of **3** (156 mg, 1 mmol) in CH_2Cl_2 (20 mL), *N*-iodosuccinimide (NIS) (450 mg, 2 mmol) was added. The reaction mixture was stirred at room temperature for 4 h and was then filtered through a short column of alumina (BII–III). The solvent was removed in vacuo, and the remaining material was purified by chromatography on alumina (BII–III) by using CH_2Cl_2 as eluent to give **4** as reddish-brown crystals (239 mg, 85%), m.p. 98–100 °C. FT-IR (KBr): $\tilde{\nu}$ = 1630 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.57–7.62 (m, 2 H, 5-, 7-H), 7.64 (t, $^3J_{H,H}$ = 9.8 Hz, 1 H, 6-H), 8.30 (s, 1 H, 2-H), 8.39 (d, $^3J_{H,H}$ = 9.7 Hz, 1 H, 4-H), 9.47 (d, $^3J_{H,H}$ = 9.8 Hz, 1 H, 8-H), 10.24 (s, 1 H, CHO) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 76.7, 127.1, 129.0, 130.4, 137.3, 140.1, 140.7, 141.1, 144.9, 148.7 (C_{Az}), 185.5 (C=O) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 270 (4.28), 308 (4.39) (sh), 317 (4.48), 389 (3.93), 404 (3.85) (sh), 549 (2.72), 580 (2.64) (sh), 645 (2.11) (sh) nm. MS (70 eV): *m*/*z* (%) = 282 (100) [M^+], 274 (19), 253 (10), 155 (6), 126 (11). $C_{11}H_7IO$ (282.1): calcd. C 46.84, H 2.50; found C 46.60, H 2.40.

1-Formyl-3-(trimethylsilylethynyl)azulene (5): To a solution of **4** (564 mg, 2 mmol) in triethylamine (TEA) (50 mL), bis(triphenylphosphane)palladium(II) chloride (0.04 mol-%) and CuI (0.08 mol-%) were added. The reaction mixture was stirred under N_2 at room temperature for 10 min. Trimethylsilylacetylene (118 mg, 1.2 mmol) in TEA (10 mL) was added, and the reaction mixture was stirred for a further 10 h and then filtered through a short column of alumina (BII–III). The solvent was removed in vacuo, and the remaining material was purified by chromatography on alumina (BII–III) by using CH_2Cl_2 as eluent to give **5** as brown crystals (403 mg, 80%), m.p. 88–90 °C. FT-IR (KBr): $\tilde{\nu}$ = 2148 (C≡C), 1651 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.20 [s, 9 H, $Si(CH_3)_3$], 7.49–7.56 (m, 2 H, 5-, 7-H), 7.79 (t, $^3J_{H,H}$ = 9.4 Hz, 1 H, 6-H), 8.20 (s, 1 H, 2-H), 8.60 (d, $^3J_{H,H}$ = 9.8 Hz, 1 H, 4-H), 9.46 (d, $^3J_{H,H}$ = 9.7 Hz, 1 H, 8-H), 10.15 (s, 1 H, CHO) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 0.3 [$Si(CH_3)_3$], 99.6, 99.7 (*C*≡*C*), 111.9, 124.9, 129.3, 131.1, 138.8, 138.9, 140.4, 141.1, 145.3, 146.8 (C_{Az}), 186.7 (C=O) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 247 (4.48), 287 (4.66), 301 (4.42), 309 (4.42), 314 (4.40) (sh), 322 (4.74), 401 (3.92), 418 (3.85) (sh), 557 (2.73), 594 (2.63) (sh), 663 (2.07) (sh) nm. MS (70 eV): *m*/*z* (%) = 252 (72) [M^+], 237 (100), 207 (6), 165 (8). $C_{16}H_{16}OSi$ (252.4): calcd. C 76.14, H 6.39; found C 76.30, H 6.30.

3-Ethynyl-1-formylazulene (6): To a suspension of **5** (252 mg, 1 mmol) in methanol (30 mL), 1 M KOH (2 mL) was added. The reaction mixture was stirred at room temperature for 2 h. After removal of the solvent in vacuo, the remaining residue was extracted with diethyl ether, concentrated and purified by chromatography on alumina (BII–III) with CH_2Cl_2 as an eluent to give **6** as brown crystals (81 mg, 45%), m.p. 84–86 °C (dec.). FT-IR (KBr): $\tilde{\nu}$ = 3233 (C≡C–H), 1653 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.35 (s, 1 H, C≡C-H), 7.41–7.53 (m, 2 H, 5-, 7-H), 7.74 (t, $^3J_{H,H}$ = 9.9 Hz, 1 H, 6-H), 8.16 (s, 1 H, 2-H), 8.54 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, 4-H), 9.40 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H, 8-H), 10.13 (s, 1 H, CHO) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 78.5, 82.3 (*C*≡*C*), 110.9, 124.9, 129.4, 130.7, 131.2, 138.7, 140.3, 141.2, 145.1, 146.8 (C_{Az}), 186.6 (C=O) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 244 (4.48), 281 (4.53), 300 (4.36) (sh), 306 (4.40) (sh), 311 (4.40) (sh), 318 (4.49), 395 (3.92), 410 (3.85) (sh), 550 (2.73), 587 (2.64) (sh), 649 (2.11) (sh) nm. MS (70 eV): *m*/*z* (%) = 180 (100) [M^+], 179 (77), 151 (36), 76 (14). $C_{13}H_8O$ (180.2): calcd. C 86.65, H 4.48; found C 86.40, H 4.70.

1-Cyano-3-ethynylazulene (7): To a solution of **6** (180 mg, 1 mmol) in ethanol (10 mL) was added a solution of hydroxylamine hydrochloride (173 mg, 2.5 mmol) in water (20 mL). To the resulting mixture a solution of 1 N NaOH (20 mL) was added, and the reaction mixture was stirred at room temperature for 4 h. CH_2Cl_2 (50 mL) was then added to the resulting suspension, the layers were separated, and the aqueous solution was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with water, dried with Na_2SO_4 and filtered. The solvent was removed in vacuo, and the remaining residue was dissolved in pyridine/Ac_2O (2:1; 60 mL). The reaction mixture was heated under reflux for 3 h, cooled to 0 °C and poured carefully into 2 N HCl (100 mL). CH_2Cl_2 (50 mL) was added to the resulting suspension. The layers were separated, and the aqueous solution was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with water, dried with Na_2SO_4 and filtered. The solvent was removed in vacuo, and the remaining residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **7** as brown crystals (124 mg, 70%), m.p. 142–144 °C (dec.). FT-IR (KBr): $\tilde{\nu}$ = 3326 (C≡C–H), 2215 (C≡N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.47 (s, 1 H, C≡C-H), 7.49–7.61 (m, 2 H, 5-, 7-H), 7.91 (t, $^3J_{H,H}$ = 10.4 Hz, 1 H, 6-H), 8.14 (s, 1 H, 2-H), 8.58 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H, 4-H), 8.68 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H, 8-H) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 76.8, 82.5 (*C*≡*C*), 96.9, 110.4, 116.6, 118.4, 128.6, 137.5, 138.8, 141.5, 142.4, 143.2, 143.4 (C_{Az}, *C*≡N) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 239 (4.62), 262 (4.21) (sh), 264 (4.29) (sh), 267 (4.36), 282 (4.19) (sh), 287 (4.32) (sh), 292 (4.46), 298 (4.54), 305 (4.51), 311 (4.65), 347 (3.57) (sh), 356 (3.62) (sh), 371 (3.84), 389 (3.93), 561 (2.69), 595 (2.64) (sh), 658 (2.20) (sh) nm. MS (70 eV): *m*/*z* (%) = 177 (100) [M^+], 150 (21), 99 (3), 75 (10). $C_{13}H_7N$ (177.2): calcd. C 88.11, H 3.98; found C 88.40, H 4.00.

Bis(3-formylazulen-1-yl)ethyne (11): To a solution of **4** (564 mg, 2 mmol) in TEA (50 mL), bis(triphenylphosphane)palladium(II) chloride (0.04 mol-%) and CuI (0.08 mol-%) were added. The reaction mixture was stirred under N_2 at room temperature for 10 min. Ethynylazulene **6** (504 mg, 2 mmol) in TEA (10 mL) was then added slowly over a period of 6 h. The reaction mixture was stirred for a further 10 h and then filtered through a short column of alumina (BII–III). The solvent was removed in vacuo, and the remaining product was purified by chromatography on alumina (BII–III) with CH_2Cl_2 to give **11** as brown crystals (267 mg, 40%), m.p. 257–259 °C. FT-IR (KBr): $\tilde{\nu}$ = 1660 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.64–7.73 (m, 4 H, 5-, 7-H), 7.95 (t, $^3J_{H,H}$ = 9.8 Hz, 2 H, 6-H), 8.49 (s, 2 H, 2-H), 8.91 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, 8-H), 9.64 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, 4-H), 10.34 (s, 2 H, CHO) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 89.0 (*C*≡*C*), 112.3, 125.4, 129.2, 131.1, 138.7, 139.0, 140.7, 141.3, 144.7, 146.1 (C_{Az}), 186.6 (C=O) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 245 (4.63), 300 (4.83), 320 (4.75) (sh), 426 (4.17), 572 (3.08) nm. MS (FD): *m*/*z* (%) = 334 (100) [M^+]. $C_{24}H_{14}O_2$ (334.4): calcd. C 86.21, H 4.22; found C 85.90, H 4.40.

General Procedure for the Cyclotrimerization of 1a,b, 6 and 7 with CpCo(CO)$_2$: A solution of the appropriate ethynylazulene **1a**,**b**, **6** or **7** (2 mmol) and CpCo(CO)$_2$ (0.2 mmol) in degassed cyclooctane (20 mL) was heated under reflux for 24 h. The solvent was removed in vacuo, and the residue was purified by column chromatography on alumina with CH_2Cl_2/*n*-hexane (1:5) as eluent to give **14a** and **17a** (from **1a**), **14b** and **17b** (from **1b**) and on silica gel with CH_2Cl_2 as eluent to give **18** (from **6**) and **19** (from **7**).

1,2,4-Tris(azulen-1-yl)benzene (14a) and [η^4-Bis(azulen-1-yl)cyclobutadiene](η^5-cyclopentadienyl)cobalt (17a): **1a** (304 mg, 2 mmol) gave **14a** (33 mg, 11%) and **17a** (6 mg, 2%).

14a: Greenish-blue crystals, m.p. 222 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.95–8.79 (m, 24 H, azulene H, aryl H) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 116.92, 117.0, 117.7, 122.8, 122.9, 123.2, 123.5, 128.1, 131.1, 131.2, 132.8, 133.4, 135.5, 136.0, 136.5, 137.4, 137.6, 138.4, 139.1, 141.3, 141.4, 142.0 (C_{Az}, aryl C) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 280 (4.82) (sh), 299 (4.88), 374 (4.43), 575 (2.93) (sh), 600 (2.98), 642 (2.90) (sh), 715 (2.42) (sh) nm. MS (FD): *m*/*z* (%) = 456 (100) [M^+]. $C_{36}H_{24}$ (456.6): calcd. C 94.70, H 5.30; found C 94.50, H 5.40.

17a: Yellowish-green crystals, m.p. 68–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.56 (s, 2 H, cyclobutadiene H), 4.72 (s, 5 H, cyclopentadiene H), 6.90 (t, $^3J_{H,H}$ = 9.9 Hz, 2 H, 5-H), 6.97 (t, $^3J_{H,H}$ = 9.9 Hz, 2 H, 7-H), 7.14 (d, $^3J_{H,H}$ = 3.9 Hz, 2 H, 3-H), 7.37 (t, $^3J_{H,H}$ = 9.9 Hz, 2 H, 6-H), 7.83 (d, $^3J_{H,H}$ = 3.9 Hz, 2 H, 2-H), 8.06 (d, $^3J_{H,H}$ = 9.3 Hz, 2 H, 4-H), 8.36 (d, $^3J_{H,H}$ = 9.8 Hz, 2 H, 8-H) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 57.8, 72.6 (C_{Cb}), 80.3 (C_{Cp}), 118.0, 121.7, 123.0, 126.9, 135.1, 136.4, 136.7, 137.3, 138.3, 142.4 (C_{Az}) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 281 (4.75), 302 (4.51) (sh), 337 (4.29) (sh), 424 (4.15), 638 (2.76) nm. MS (FD): *m*/*z* (%) = 428 (100) [M^+]. $C_{29}H_{21}Co$ (428.4): calcd. C 81.30, H 4.94; found C 81.10, H 4.60.

1,2,4-Tris(6-*tert*-butylazulen-1-yl)benzene (14b) and [η^4-Bis(6-*tert*-butylazulen-1-yl)cyclobutadiene](η^5-cyclopentadienyl)cobalt (17b): **1b** (416 mg, 2 mmol) gave **14b** (68 mg, 16%) and **17b** (14 mg, 4%).

14b: Greenish-blue crystals (16%), m.p. 259–260 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.39, 1.42, 1.43 [3s, 27 H, $C(CH_3)_3$], 6.98–8.71 (m, 21 H, azulene H, aryl H) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 30.4 [$C(CH_3)_3$], 38.5 [$C(CH_3)_3$], 116.2, 116.3, 117.0, 117.1, 120.7, 121.2, 121.3, 121.8, 121.9, 127.6, 128.8, 130.8, 130.9, 131.2, 132.4, 133.2, 134.1, 134.5, 134.9, 135.1, 135.2, 135.4, 135.9, 136.4, 137.6, 138.5, 140.1, 140.2, 140.7, 161.2, 162.2 (C_{Az}) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 290 (4.89), 300 (4.88) (sh), 379 (4.47), 587 (3.06), 625 (2.99) (sh), 697 (2.50) (sh) nm. MS (FD): *m*/*z* (%) = 624 (100) [M^+]. $C_{48}H_{48}$ (624.9): calcd. C 92.26, H 7.74; found C 92.10, H 7.40.

17b: Yellowish-green crystals (4%), m.p. 245 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.43 [s, 18 H, $C(CH_3)_3$], 4.61 (s, 2 H, cyclobutadiene H), 4.79 (s, 5 H, cyclopentadiene H), 7.13 (d, $^3J_{H,H}$ = 4 Hz, 2 H, 3-H), 7.22 (dd, $^3J_{H,H}$ = 10.9, $^4J_{H,H}$ = 1.7 Hz, 2 H, 5-H), 7.26 (dd, $^3J_{H,H}$ = 10.5, $^4J_{H,H}$ = 1.7 Hz, 2 H, 7-H), 7.84 (d, $^3J_{H,H}$ = 3.9 Hz, 2 H, 2-H), 8.09 (d, $^3J_{H,H}$ = 10.1 Hz, 2 H, 4-H), 8.40 (d, $^3J_{H,H}$ = 10.5 Hz, 2 H, 8-H) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 31.9 [$C(CH_3)_3$], 38.4 [$C(CH_3)_3$], 57.5, 72.5 (C_{Cb}), 80.1 (C_{Cp}), 117.3, 112.0, 120.7, 126.3, 133.7, 135.2, 135.5, 136.3, 141.0, 161.9 (C_{Az}) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 284 (4.78), 312 (4.59), 430 (4.23), 629 (2.86) nm. MS (FD): *m*/*z* (%) = 540 (100) [M^+]. $C_{37}H_{37}Co$ (540.6): calcd. C 82.20, H 6.90; found C 82.10, H 6.60.

1,2,4-Tris(3-formylazulen-1-yl)benzene (18): **6** (360 mg, 2 mmol) gave **18** (50 mg, 14%) and **14a** (18 mg, 6%).

18: Green crystals, m.p. 200–202 °C. FT-IR (KBr): ṽ = 1654 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.30–9.70 (m, 21 H, azulene H, aryl H), 10.11, 10.12, 10.40 (3s, 3 H, CHO) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 124.8, 125.2, 128.4, 129.8, 129.9, 130.0, 131.2, 131.3, 131.5, 132.7, 133.2, 134.9, 135.7, 136.7, 137.6, 137.9, 138.0, 138.3, 140.4, 140.9, 141.7, 141.8, 141.9, 142.1, 143.2 (C_{Az}, aryl C), 186.5, 186.7 (C=O) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 300 (5.0), 310 (4.95) (sh), 393 (4.34), 553 (3.15), 595 (3.05) (sh) nm. MS (FD): *m*/*z* (%) = 540 (100) [M^+]. $C_{39}H_{24}O_3$ (540.6): calcd. C 86.65, H 4.48; found C 86.60, H 4.20.

1,2,4-Tris(3-cyanoazulen-1-yl)benzene (19): **7** (354 mg, 2 mmol) gave **19** (42 mg, 12%) as green crystals, m.p. 178–180 °C. FT-IR (KBr): ṽ = 2204 (C≡N) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.21–8.92 (m, 21 H, azulene H, aryl H) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 96.5, 97.1, 117.2, 117.4, 127.4, 127.5, 127.6, 128.1, 129.2, 130.2, 130.3, 130.8, 132.9, 133.3, 134.6, 135.4, 136.3, 137.2, 137.6, 137.7, 138.1, 139.3, 140.4, 140.8, 141.2, 143.7, 143.8, 144.5 (C_{Az}, aryl C, *C*≡N) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 290 (4.87), 376 (4.30), 568 (3.05), 605 (2.99) (sh), 670 (2.54) (sh) nm. MS (FD): *m*/*z* (%) = 531 (100) [M^+]. $C_{39}H_{21}N_3$ (531.6): calcd. C 88.11, H 3.98; found C 87.90, H 4.20.

Synthesis of 19 from 18: To a solution of **18** (540 mg, 1 mmol) in ethanol (10 mL) was added a solution of hydroxylamine hydrochloride (517 mg, 7.5 mmol) in water (20 mL). To the resulting mixture, a solution of 1 N NaOH (20 mL) was added, and the reaction mixture was stirred at room temperature for 4 h. CH_2Cl_2 (50 mL) was then added to the resulting suspension, the layers were separated, and the aqueous solution was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with water, dried with Na_2SO_4 and filtered. The solvent was removed in vacuo, and the remaining residue was dissolved in pyridine/Ac_2O (2:1; 60 mL). The reaction mixture was heated under reflux for 3 h, cooled to 0 °C and poured carefully into 2 N HCl (100 mL). CH_2Cl_2 (50 mL) was added to the resulting suspension. The layers were separated, and the aqueous solution was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with water, dried with Na_2SO_4 and filtered. The solvent was removed in vacuo, and the remaining residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **19** (239 mg, 45%).

Attempted Cyclotrimerization of 1a,b with Dicarbonyl(triphenylphosphane)nickel: A solution of the appropriate ethynylazulene **1a**,**b** (2 mmol) and dicarbonyl(triphenylphosphane)nickel (0.2 mmol) in benzene (10 mL) was heated under reflux for 1 h. The solvent was removed in vacuo, and the residue was purified by chromatography on alumina with CH_2Cl_2/*n*-hexane (1:6) as eluent to give **16a** and **16b**, respectively.

1,4-Bis(azulen-1-yl)but-1-ene-3-yne (16a): **1a** (304 mg, 2 mmol) gave **16a** (122 mg, 20%) as green crystals (20%), m.p. 164–166 °C. FT-IR (KBr): ṽ = 2154 (C≡C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.47–8.51 (m, 16 H, azulene H, CH=CH) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 270 (4.45), 288 (4.68), 350 (4.66), 439 (4.40), 466 (4.30), 602 (3.1) nm. MS (FD): *m*/*z* (%) = 304 (100) [M^+]. $C_{24}H_{16}$ (304.4): calcd. C 94.70, H 5.30; found C 95.00, H 5.10.

1,4-Bis(6-*tert*-butylazulen-1-yl)but-1-ene-3yne (16b): **1b** (416 mg, 2 mmol) gave **16b** (104 mg, 25%) as green crystals, m.p. 268–270 °C. FT-IR (KBr): ṽ = 2154 (C≡C) cm^{-1}. ^{1}H NMR (300 MHz,

$CDCl_3$, 25 °C): δ = 1.38, 1.39 [2 s, 18 H, $C(CH_3)_3$], 6.46–8.52 (m, 14 H, azulene H, CH=CH) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 271 (4.47), 298 (4.64), 331 (4.44), 441 (4.50), 468 (4.44), 604 (3.05) nm. MS (FD): *m*/*z* (%) = 416 (100) [M^+]. $C_{32}H_{32}$ (416.6): calcd. C 92.26, H 7.74; found C 92.40, H 7.90.

General Procedure for the Cyclodimerization of 10a,b and 11 with $CpCo(CO)_2$: A solution of the appropriate diazulenylethyne **10a**,**b** or **11** (2 mmol) and $CpCo(CO)_2$ (1.2 mmol) in degassed cyclooctane (20 mL) was heated under reflux for 24 h. The solvent was removed in vacuo, and the residue was purified by column chromatography on alumina with CH_2Cl_2/*n*-hexane (1:5) as eluent to give **30a**,**b** (from **10a**,**b**) and CH_2Cl_2 as eluent to give **31** (from **11**), respectively.

(η^5-Cyclopentadienyl)[η^4-tetrakis(azulen-1-yl)cyclobutadiene]cobalt (30a): 10a (556 mg, 2 mmol) gave **30a** (408 mg, 60%) as black crystals, m.p. 115 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.89 (s, 5 H, cyclopentadiene H), 6.51 (t, $^3J_{H,H}$ = 9.7 Hz, 4 H, 7-H), 7.05 (t, $^3J_{H,H}$ = 9.6 Hz, 4 H, 5-H), 7.22 (d, $^3J_{H,H}$ = 4 Hz, 4 H, 3-H), 7.28 (t, $^3J_{H,H}$ = 9.8 Hz, 4 H, 6-H), 7.80 (d, $^3J_{H,H}$ = 4 Hz, 4 H, 2-H), 8.18 (d, $^3J_{H,H}$ = 9.0 Hz, 4 H, 4-H), 8.19 (d, $^3J_{H,H}$ = 9.8 Hz, 4 H, 8-H) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 71.6 (C_{Cb}), 81.1 (C_{Cp}), 117.1, 120.5, 122.1, 125.7, 134.9, 135.7, 137.2, 137.4, 137.9, 141.8 (C_{Az}) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 243 (4.86), 280 (5.25), 306 (4.94), 375 (4.51), 424 (4.27) (sh), 638 (3.07) nm. MS (FD): *m*/*z* (%) = 680 (100) [M^+]. $C_{49}H_{33}Co$ (680.7): calcd. C 86.46, H 4.89; found C 86.70, H 4.60.

(η^5-Cyclopentadienyl)[η^4-tetrakis(6-*tert*-butyltetraazulen-1-yl)cyclobutadiene]cobalt (30b): 10b (780 mg, 2 mmol) gave **30b** (634 mg, 70%) as black crystals, m.p. 192–193 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.27 [s, 36 H, $C(CH_3)_3$], 4.87 (s, 5 H, cyclopentadiene H), 6.18 (dd, $^3J_{H,H}$ = 10.7, $^4J_{H,H}$ = 1.6 Hz, 4 H, 5-H), 6.61 (dd, $^3J_{H,H}$ = 10.7, $^4J_{H,H}$ = 1.6 Hz, 4 H, 7-H), 7.11 (d, $^3J_{H,H}$ = 4 Hz, 4 H, 3-H), 7.72 (d, $^3J_{H,H}$ = 3.9 Hz, 4 H, 2-H), 8.08 (d, $^3J_{H,H}$ = 10.2 Hz, 4 H, 4/8-H), 8.10 (d, $^3J_{H,H}$ = 10.7 Hz, 4 H, 4/8-H) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 23.0 [$C(CH_3)_3$], 38.1 [$C(CH_3)_3$], 72.2 (C_{Cb}), 81.8 (C_{Cp}), 117.3, 119.6, 120.4, 126.5, 134.4, 135.4, 137.5, 138.0, 141.6, 161.5 (C_{Az}) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 243 (4.86), 285 (4.92) (sh), 311 (4.99), 379 (4.51), 428 (4.30) (sh), 625 (3.15) nm. MS (FD): *m*/*z* (%) = 904 (100) [M^+]. $C_{65}H_{65}Co$ (905.2): calcd. : C 86.25, H 7.24; found C 86.50, H 7.10.

(η^5-Cyclopentadienyl)[η^4-tetrakis(3-formylazulen-1-yl)cyclobutadiene]cobalt (31): 11 (668 mg, 2 mmol) gave **31** (475 mg, 60%) as brown crystals, m.p. >260 °C. FT-IR (KBr): $\tilde{\nu}$ = 1646 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.98 (s, 5 H, cyclopentadiene H), 6.94 (t, $^3J_{H,H}$ = 10.2 Hz, 4 H, 6-H), 7.56–7.67 (m, 8 H, 5-, 7-H), 8.11 (s, 4 H, 2-H), 8.42 (d, $^3J_{H,H}$ = 9.9 Hz, 4 H, 8-H), 9.56 (d, $^3J_{H,H}$ = 9.2 Hz, 4 H, 4-H), 10.16 (s, 1 H, CHO) ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 70.9 (C_{Cb}), 82.3 (C_{Cp}), 125.5, 125.8, 127.1, 130.2, 138.4, 139.8, 141.0, 141.8, 142.9 (C_{Az}), 186.6 (C=O) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 239 (5.27), 304 (5.17), 423 (4.24) (sh), 583 (3.27) nm. MS (FD): *m*/*z* (%) = 792 (100) [M^+]. $C_{53}H_{33}CoO_4$ (792.8): calcd. C 80.30, H 4.20; found C 80.60, H 4.10.

(η^5-Cyclopentadienyl)[η^4-tetrakis(3-cyanoazulen-1-yl)cyclobutadiene]cobalt (32): To a solution of **31** (792 mg, 1 mmol) in ethanol (10 mL) was added a solution of hydroxylamine hydrochloride (690 mg, 10 mmol) in water (20 mL). To the resulting mixture, a solution of 1 N NaOH (20 mL) was added, and the reaction mixture was stirred at room temperature for 4 h. CH_2Cl_2 (50 mL) was then added to the resulting suspension, the layers were separated, and the aqueous solution was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with water, dried with Na_2SO_4 and filtered. The solvent was removed in vacuo, and the remaining residue was dissolved in pyridine/Ac_2O (2:1, 60 mL). The reaction mixture was heated under reflux for 3 h, cooled to 0 °C and poured carefully into 2 N HCl (100 mL). CH_2Cl_2 (50 mL) was added to the resulting suspension. The layers were separated, and the aqueous solution was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with water, dried with Na_2SO_4 and filtered. The solvent was removed in vacuo, and the remaining residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluent to give **32** (234 mg, 30%) as brown crystals, m.p. >260 °C. FT-IR (KBr): $\tilde{\nu}$ = 2205 (C≡N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.94 (s, 5 H, cyclopentadiene H), 6.91 (t, $^3J_{H,H}$ = 9.8 Hz, 4 H, 6-H), 7.51 (t, $^3J_{H,H}$ = 9.7 Hz, 4 H, 7-H), 7.66 (t, $^3J_{H,H}$ = 9.8 Hz, 4 H, 5-H), 7.88 (s, 4 H, 2-H), 8.26 (d, $^3J_{H,H}$ = 9.8 Hz, 4 H, 8-H), 8.60 (d, $^3J_{H,H}$ = 9.1 Hz, 4 H, 4-H), ppm. ^{13}C NMR (75.40 MHz, $CDCl_3$, 25 °C): δ = 69.6 (C_{Cb}), 81.5 (C_{Cp}), 96.7, 115.9, 124.0, 125.4, 126.7, 136.9, 137.3, 138.8, 139.0, 140.5, 143.8 (C_{Az}, *C*≡N) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 278 (5.01), 300 (4.99), 360 (4.34) (sh), 612 (3.22) nm. MS (FD): *m*/*z* (%) = 780 (100) [M^+]. $C_{53}H_{29}CoN_4$ (780.8): calcd. C 81.53, H 3.74; found C 81.60, H 4.10.

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