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Metal mediated cyclooligomerization of mono- and diazulenylethynes

Ahmed H. M. Elwahy and Klaus Hafner *

Institut für Organische Chemie, Technische Universität Darmstadt, Petersenstraße 22, D-64287 Darmstadt, Germany

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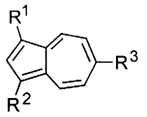
Abstract

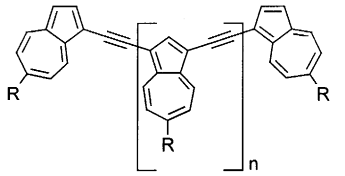
A synthesis of 1,2,4-triazulen-1-ylbenzenes **4a**, **b** as well as di- and tetraazulenylcyclobutadiene cobalt complexes **9a**, **b** and **11a**, **b** by cyclooligomerization of 1-ethynylazulenes **1a**, **b** and 1,2-diazulenylethynes **2a**, **b** are described. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: cobalt catalyst; ethynylazulenes; azulenylbenzenes; azulenylcyclobutadienes.

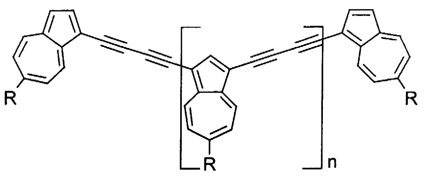
Recently, we developed simple routes to a series of mono- and polyethynylated azulenes,[1] for example **1**, and studied their transformations into acyclic oligomers **2** and **3** by Pd–Cu-catalyzed as well as oxidative coupling reactions.[2] As expected, the alkynes **1** proved to be versatile building blocks for the construction of new molecular scaffolds with ethynylazulene or butadiynylazulene units which exhibit interesting electronic properties resulting from a planar, two dimensionally conjugated framework and from the pronounced polarizability of the azulene system.



1	a	b	c	d
R^1	≡	≡	≡	≡
R^2	H	H	≡	≡
R^3	H	*t*-Bu	H	*t*-Bu



2	a	b	c	d	e	f
R	H	*t*-Bu	H	*t*-Bu	*t*-Bu	*t*-Bu
n	0	0	1	1	3	5



3

R = H, *t*-Bu, n = 0 - 3

In continuation of these studies it was also of interest to investigate the synthetic utility of the ethynylazulenes **1** and **2** as building blocks for the construction of novel cyclic conjugated π-electron systems. Herein, we report on the cyclooligomerization of the ethynylazulenes **1a**, **b** and **2a**, **b** cat-

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* Corresponding author.

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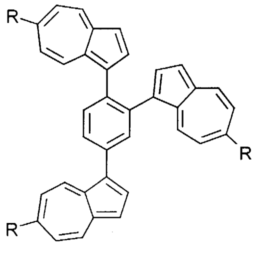
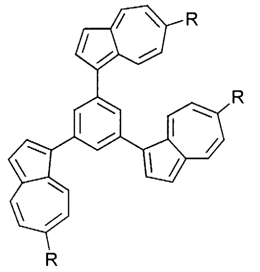
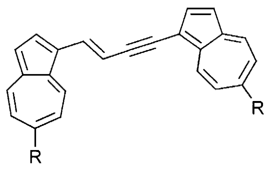
alyzed by transition metal complexes[3] which opens an access to so far unknown azulenyl-substituted benzenes **4** and cyclobutadiene complexes **9** and **11**. First attempts to promote a cyclotrimerization of 1-ethynylazulenes **1a**, **b** to the 1,2,4- and/or 1,3,5-(triazulen-1-yl)benzenes **4a**, **b** and/or **5a**, **b** by heating a solution of **1a**, **b** in benzene with bis(triphenylphosphine)dicarbonyl nickel at 80°C, led to the formation of the linear dimers **6a**, **b** in 20–25% yield together with some other reaction products of so far unknown structure. Contrary to this, treatment of **1a**, **b** with catalytic amounts of $CpCo(CO)_2$ in refluxing cyclooctane for 24 h furnished after chromatography of the reaction mixture on alumina using CH_2Cl_2:*n*-hexane (1:5) as eluents the greenish blue 1,2,4-tris(azulen-1-yl)benzenes **4a**, **b** in 11% and 16% yields, respectively. In both cases, the 1,3,5-tri(azulen-1-yl)benzene derivatives **5a**, **b** could not be obtained even in traces.



4a: R = H
4b: R = *t*-Bu

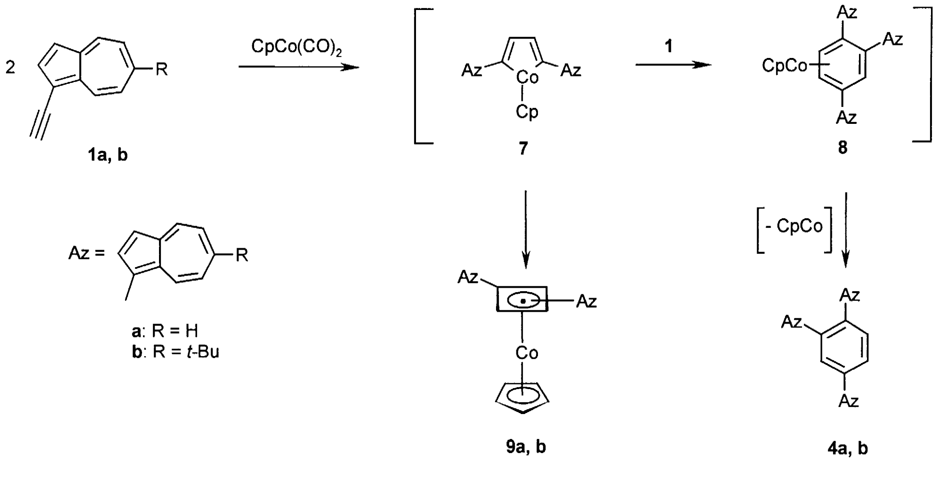


5a: R = H
5b: R = *t*-Bu



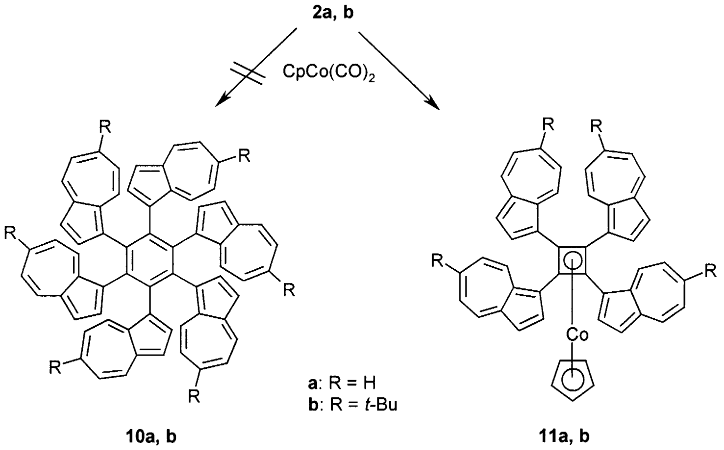
6a: R = H
6b: R = *t*-Bu

In addition to the major products **4a**, **b** (2% and 4%, respectively), of the (η^4-diazulen-1-ylcyclobutadiene)(η^5-cyclopentadienyl)cobalt complexes **9a**, **b** could be isolated as yellowish green crystals (Scheme 1). Unfortunately, the NMR spectroscopy of **9a**, **b** does not allow a decision between the two regioisomeric 1,2- and 1,3-diazulenylcyclobutadiene complexes and crystals suitable for an X-ray structure analysis could not be obtained so far. The exclusive formation of **4** is in accordance with results obtained by Vollhardt and others[4] and lets us assume the formation of the cobaltacycle **7** as an intermediate which reacts with a further molecule of **1** via a metal-mediated [4+2]-cycloaddition to generate the η^4-benzene complex **8**. A subsequent displacement of the ligand in **8** by two molecules of **1** should result in the formation of **4**. Therefore, it can be expected that also **9a**, **b** are formed via a reductive elimination of the cobaltacycle **7** and hence should be the 1,2-di(azulen-1-yl)cyclobutadiene complexes.[5]



Scheme 1.

On the other hand, the reaction of the diazulenylethynes **2a**, **b** with CpCo(CO)$_2$ (20 mol%) in refluxing cyclooctane did not yield the expected hexaazulenylbenzenes **10a**, **b** obviously due to steric hinderance (Scheme 2).[6] Instead, the interesting black crystalline tetraazulenylcyclobutadiene cobalt complexes **11a**, **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%. The spectral properties of the cyclobutadiene complexes **11a**, **b** vary to some extent from their acyclic precursors **2a**, **b**. The azulene proton resonances particularly those of 7-H and 8-H are shifted upfield by more than 0.6 ppm upon cyclization. We attribute this upfield shift to the chemical anisotropy associated with the CpCo group.[7] All efforts to demetallate **11a**, **b** in order to generate the tetraazulenylcyclobutadienes, which represent hydrocarbons with a central antiaromatic system substituted by four non-benzenoid aromatic residues, met so far with no success. Both the triazulenylbenzenes **4a**, **b** and the tetraazulenylcyclobutadiene complexes **11a**, **b** are remarkably stable, showing no decomposition even after several weaks in solution or in the crystalline state.



Scheme 2.

*Physical data of compounds **4a**, **b**, **9a**, **b**, **11a**, **b**.*[8,9] **4a**: greenish blue crystals, mp 222°C, MS (FD): *m/z* (%) 456 [M$^+$, 100%]; ^{1}H NMR: δ 6.95–8.79 (m, 24H, azulene H, aryl H);^{13}C NMR: δ=116.92, 116.98, 117.74, 122.82, 122.94, 123.24, 123.53, 128.05, 131.07, 131.20, 137.57, 133.40, 135.46, 135.98, 136.46, 136.49, 137.41, 137.63, 138.42, 139.12, 141.29, 141.36, 142.02; UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (lg ε)=280 nm (4.82) (sh), 299 (4.88), 374 (4.43), 575 (2.93) (sh), 600 (2.98), 642 (2.90) (sh), 715 (2.42) (sh). **4b**: greenish blue crystals, mp 259–260°C, MS (FD): *m/z* (%) 624 [M$^+$, 100%]; ^{1}H NMR: δ 1.39, 1.42, 1.43 (3 s, 27H, C(CH$_3$)$_3$), 6.98–8.71 (m, 21H, azulene H, aryl H); ^{13}C NMR: δ 30.4, 38.5, 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; UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (lg ε)=290 nm (4.89), 300 (4.88) (sh), 379 (4.47), 587 (3.06), 625 (2.99) (sh), 697 (2.5) (sh). **9a**: yellowish green crystals, mp 68–70°C, MS (FD): *m/z* (%) 428 [M$^+$, 100%]; ^{1}H NMR δ 4.56 (s, 2H, cyclobutadiene H), 4.72 (s, 5H, cyclopentadiene H), 6.90 (t, 2H, J=9.9 Hz, 5-H), 6.97 (t, 2H, J=9.9 Hz, 7-H), 7.14 (d, 2H, J=3.9 Hz, 3-H), 7.37 (t, 2H, J=9.9 Hz, 6-H), 7.83 (d, 2H, J=3.9 Hz, 2-H), 8.06 (d, 2H, J=9.3 Hz, 4-H), 8.36 (d, 2H, J=9.8 Hz, 8-H); ^{13}C NMR δ 57.83, 72.55, 80.27, 117.98, 121.66, 123.03, 126.94, 135.07, 136.41, 136.67, 137.27, 138.33, 142.42; UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (lg ε)=281 nm (4.75), 302 (4.51) (sh), 337 (4.29) (sh), 424 (4.15), 638 (2.76). **9b**: yellowish green crystals, mp 245°C, MS (FD): *m/z* (%) 540 [M$^+$, 100%]; ^{1}H NMR: δ 1.43 (s, 18H, C(CH$_3$)$_3$), 4.61 (s, 2H, cyclobutadiene H), 4.79 (s, 5H, cyclopentadiene H), 7.13 (d, 2H, J=4 Hz, 3-H), 7.22 (dd, 2H, J_1=10.9 Hz, J_2=1.7 Hz, 5-H), 7.26 (dd, 2H, J_1=10.5 Hz, J_2=1.7 Hz, 7-H), 7.84 (d, 2H, J=3.9 Hz, 2-H), 8.09 (d, 2H, J=10.1 Hz, 4-H), 8.40 (d, 2H, *J*=10.5 Hz, 8-H); ^{13}C NMR: δ 31.86, 38.43, 57.50, 72.54, 80.08, 117.30, 119.95, 120.71, 126.34, 133.73, 135.21, 135.53, 136.31, 140.98, 161.84; UV–vis (CH_2Cl_2): λ_{max} (lg ε)=284 nm (4.78), 312 (4.59), 430 (4.23), 629 (2.86). **11a**: black crystals, mp 115°C, MS (FD): *m/z* 680 [M^+, 100%]; ^{1}H NMR: δ 4.89 (s, 5H, cyclopentadiene H), 6.51 (t, 4H, *J*=9.7 Hz, 7-H), 7.05 (t, 4H, *J*=9.6 Hz, 5-H), 7.22 (d, 4H, *J*=4 Hz, 3-H), 7.28 (t, 4H, *J*=9.8 Hz, 6-H), 7.80 (d, 4H, *J*=4 Hz, 2-H), 8.18 (d, 4H, *J*=9.0 Hz, 4-H), 8.19 (d, 4H, *J*=9.8 Hz, 8-H); ^{13}C NMR: δ 71.55, 81.13, 117.05, 120.48, 122.05, 125.73, 134.86, 135.67, 137.20, 137.40, 137.86, 141.80; UV–vis (CH_2Cl_2): λ_{max} (lg ε)=243 nm (4.86), 280 (5.25), 306 (4.94), 375 (4.51), 424 (4.27) (sh), 638 (3.07). **11b**: black crystals, mp 192–193°C, MS (FD): *m/z* (%) 904 [M^+, 100%]; ^{1}H NMR: δ 1.27 (s, 36H, $C(CH_3)_3$), 4.87 (s, 5H, cyclopentadiene H), 6.18 (dd, 4H, J_1=10.7, J_2=1.6 Hz, 5-H), 6.61 (dd, 4H, J_1=10.7 Hz, J_2=1.6 Hz, 7-H), 7.11 (d, 4H, *J*=4 Hz, 3-H), 7.72 (d, 4H, *J*=3.9 Hz, 2-H), 8.08 (d, 4H, *J*=10.2 Hz, 4/8-H), 8.10 (d, 4H, *J*=10.7 Hz, 4/8-H); ^{13}C NMR: δ 23.04, 38.48, 72.23, 81.84, 117.29, 119.63, 120.44, 126.51, 134.43, 135.39, 137.49, 138.01, 141.56, 161.49; UV–vis (CH_2Cl_2): λ_{max} (lg ε)=243 nm (4.86), 285 (4.92) (sh), 311 (4.99), 379 (4.51), 428 (4.30) (sh), 625 (3.15).

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8. All described new compounds gave correct elemental analyses.
9. 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.