

Synthesis of 11,12-Didehydrodibenzo[*a,e*]cycloocten-5(6*H*)-one: A Strained Eight-Membered Alkyne

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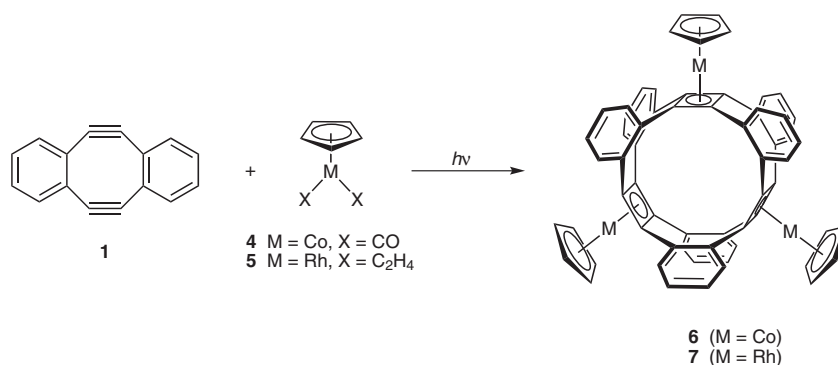
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Abstract: An eight-step synthesis of 11,12-didehydrodibenzo[*a,e*]cycloocten-5(6*H*)-one (**10**) was developed. The structure of **10** was assigned by spectroscopic means and confirmed by X-ray analysis of its 2,4-dinitrophenylhydrazone derivative. Reaction of the triple bond of **10** with dicarbonyl(η^5 -cyclopentadienyl)cobalt or dicarbonyl(η^5 -pentamethylcyclopentadienyl)cobalt gave the corresponding metal-stabilized cyclobutadiene complexes.

Key words: alkynes, cycloadditions, eliminations, oxidations, ring expansion.

Eight-membered hydrocarbon rings with one or two triple bonds are reactive species as a result of a marked bending of the triple bond(s).¹ 5,6,11,12-Tetradehydrodibenzo[*a,e*]cyclooctene (**1**), which has been known for more than 30 years,² is rather stable compared with the corresponding enyne **2**³ or cycloocta-1,5-diyne (**3**)⁴ (Figure 1). Recently, three efficient syntheses have been published that allow rapid access to **1**.⁵

The availability of 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (**1**) allows it to be used as a component in cycloaddition reactions;^{6,7} for example, **1** can be used to prepare derivatives of a metal-stabilized [4.8]₃cyclacene in a one-pot reaction (Scheme 1).⁷ By irradiating **1** in the presence of cobalt complex **4** or rhodium complex **5**, we obtained the corresponding belt-like π -systems **6** and **7** with a linearly annulated conjugated system consisting of three four-membered rings and three eight-membered rings, in which the four-membered rings are stabilized by (*R*)-(η^5 -cyclopentadienyl)metal (metal = Co, Rh) moieties.



Scheme 1 Synthesis of belt-like complexes **6** and **7**

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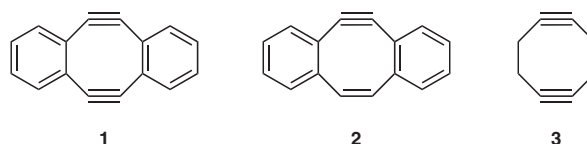


Figure 1 The structures of cyclooctynes **1–3**

To unravel the mechanism of this multistep reaction, we were interested in synthesizing possible intermediates in a stepwise protocol.^{7b} Some possible intermediates (**8** and **9**) are shown in Figure 2.

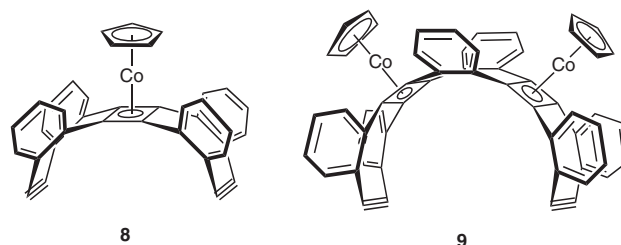
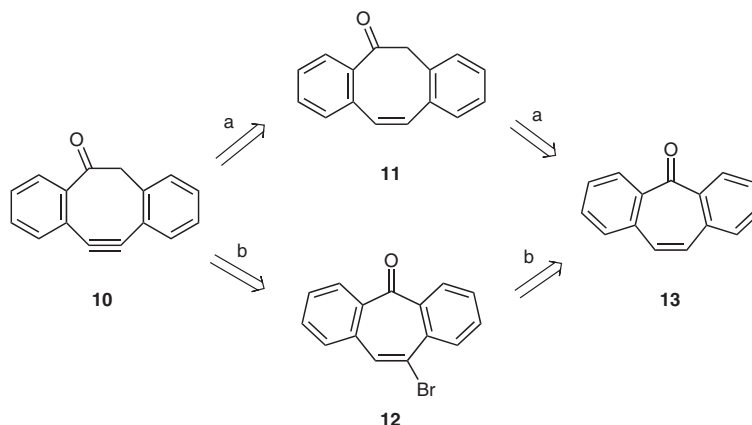


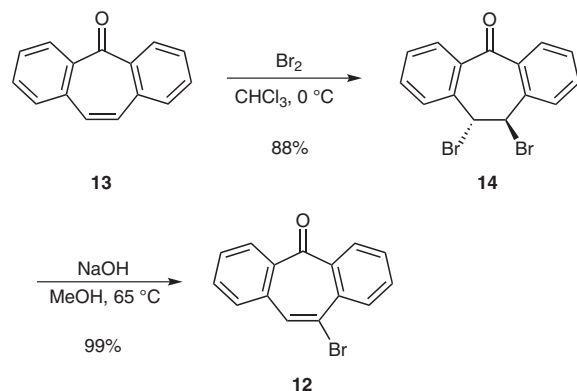
Figure 2 Some possible intermediates in the reaction shown in Scheme 1

To synthesize species such as **8** or **9**, we needed an efficient access to 11,12-didehydrodibenzo[*a,e*]cycloocten-5(6*H*)-one (**10**) and related compounds. Because the presence of two different functional groups, as is the case in **10**, could be useful in deriving other species with a dibenzo[*a,e*]cyclooctatriene or -tetraene skeleton, we report our synthesis of **10**.

Scheme 2 Retrosynthetic paths from **10** to **13**

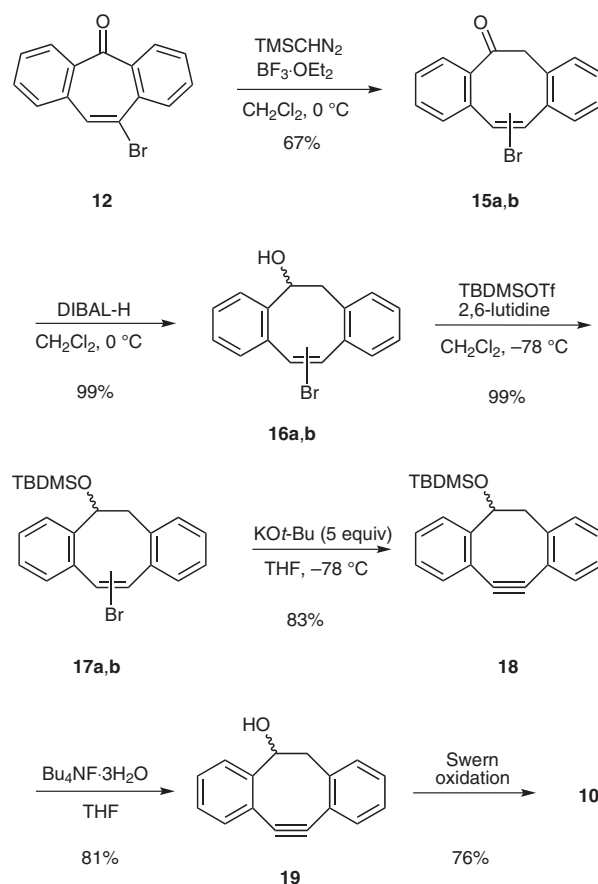
As the starting material for the synthesis of **10**, we used 5*H*-dibenzo[*a,d*]cyclohepten-5-one (**13**). From this commercially available compound, two routes seem to be reasonable, as shown in the retrosynthetic paths in Scheme 2.

Path **a** starts with a ring enlargement of enone **13** to enone **11**, with the introduction of a triple bond as a second key step. Path **b** commences with bromination of the double bond, followed by ring enlargement. We chose path **b**, because treatment of enone **11** with bromine would result in the formation of a 6-bromo derivative in addition to the required 11,12-dibromo product. Our synthesis of **10** is summarized in Schemes 3 and 4. Treatment of enone **13** with bromine at 0 °C gave the dibromo product **14** in a good yield (Scheme 3).

Scheme 3 Synthesis of **12** from **13**

The elimination of one equivalent of hydrogen bromide from the dibromo product **14** by treatment with sodium hydroxide in methanol led to the bromo enone **12** in an almost quantitative yield. Ring enlargement of **12** by treatment with (trimethylsilyl)diazomethane^{5b} gave a regioisomeric mixture of bromo enones **15a** and **15b**, in which the bromine substituent is in the 11- or 12-position of the double bond, respectively. This mixture was reduced with diisobutylaluminum hydride (DIBAL-H) to give a mixture of the corresponding alcohols **16a** and **16b**. The alco-

hol function in **16a** and **16b** was protected with *tert*-butyl(dimethyl)silyl triflate⁸ in the presence of 2,6-lutidine as a base at –78 °C to give an isomeric mixture of the silylated derivatives **17a** and **17b**. Treatment of this mixture with a strong base introduced a triple bond in the protected alcohol **18**. Removal of the protecting group⁹ to give ynol **19** and subsequent oxidation¹⁰ to give ynone **10** proceeded in good yields. This sequence, although eight steps long, allowed the production of **10** in gram quantities.

Scheme 4 Synthesis of **10** from **12**

The structure of **10** was confirmed by X-ray crystallographic studies on its 2,4-dinitrophenylhydrazone. These studies showed a markedly bent triple bond (C11–C12) (Figure 3). This bending is evidenced by the bond angles C10a–C11–C12 (152°) and C11–C12–C12a (157°).⁸

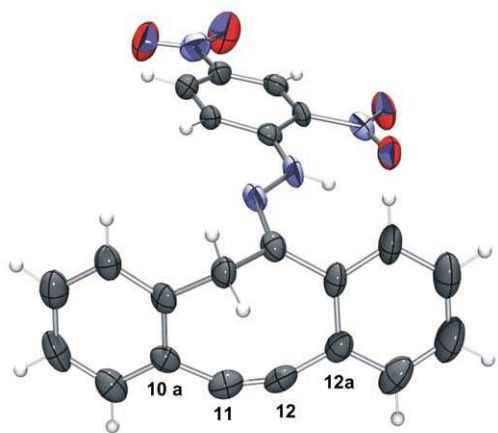
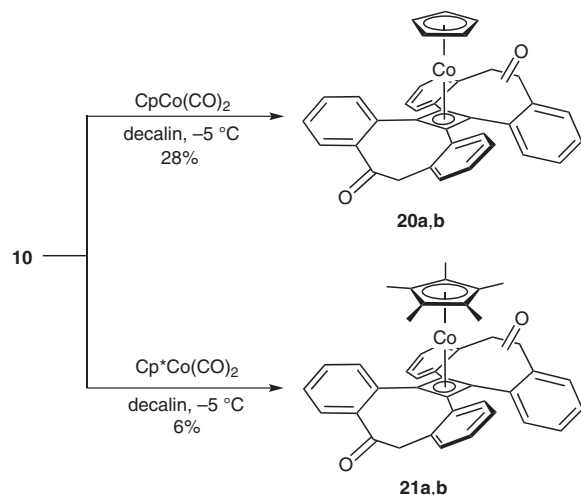


Figure 3 Molecular structure of the dinitrophenylhydrazone of **10**

The strain at the triple bond is probably the main driving force in reactions of **10**, in that the only reactions involving **10** are those in which this strain is relieved. Examples of such reactions are those with dicarbonyl(η^5 -cyclopentadienyl)cobalt or dicarbonyl(η^5 -pentamethylcyclopentadienyl)cobalt, as shown in Scheme 5. In these cases, the strain at the C11–C12 bond of ynone **10** is relieved by its incorporation into a four-membered ring. The resulting structures, **20** and **21**, respectively, both exist as isomers (**20a/20b**) and (**21a/21b**) with *cis*- and *trans*-orientations of the carbonyl groups, respectively. The structures of the complexes **20**¹¹ and **21**¹² were confirmed by X-ray investigations on single crystals. In both complexes, the eight-membered rings adopt a boat conformation. The C–C bond lengths of the cyclobutadiene ring in **20** vary between 1.44 Å and 1.48 Å. In **21**, these values are 1.46 Å and 1.47 Å.



Scheme 5 Synthesis of **20a/b** and **21a/b** from **10**

The fact that the phenyl rings of one unit are folded towards the metal center, whereas those of the other unit are folded away from the metal center was ascribed to steric effects.^{7b}

In conclusion, we have developed a protocol for preparing ynone **10** in an overall yield of 24%, which allows the synthesis of the compound in gram quantities. Our structural investigations revealed the presence of a highly strained triple bond in **10**. Reactions at this bond that lead to strain relief are possible.

All compounds were characterized by ¹H and ¹³C NMR spectroscopy and mass spectrometry. All melting points are uncorrected. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. UV/Vis absorption spectra were recorded by using a Hewlett-Packard 8452A spectrometer. IR spectra were recorded by using a Bruker Vector 22. NMR spectra were recorded with a Bruker WH 300 spectrometer (¹H NMR at 300 MHz, and ¹³C NMR at 75 MHz) using CD₂Cl₂ as solvent and internal standard (δ), if not otherwise noted. FAB mass spectra refer to data from a Jeol JMS-700 instrument; (3-nitrophenyl)methanol was used as a matrix for the FAB experiments. MALDI mass spectra refer to data from Bruker ApexQe hybrid 9.4 T. All reactions were carried out in dried glassware under an argon atmosphere using dried and oxygen-free solvents. The reagents dicarbonyl(η^5 -cyclopentadienyl)cobalt¹³ and dicarbonyl(η^5 -pentamethylcyclopentadienyl)cobalt¹⁴ were prepared according to literature procedures. All operations were carried out in a well-ventilated hood by personnel wearing adequate protective equipment. The reflections for X-ray diffraction analyses were collected with a Bruker APEX diffractometer (Mo-K α radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied using SADABS¹⁵ based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined according to a full-matrix least-squares technique (F^2). All hydrogen atoms were calculated according to stereochemical aspects. The structure solution and refinement were carried out with the SHELXTL software package.¹⁶ ORTEP plots were obtained by using the Ortep-III program of L. Farrugia.¹⁷ Supplementary crystallographic data for this paper have been deposited with accession numbers CCDC 721682 (**20**), 721683 (**21**), and 721681 (dinitrophenylhydrazone of **10**) at the Cambridge Crystallographic Data Centre and can be obtained free of charge (www.ccdc.cam.ac.uk/data_request/cif).

trans-10,11-Dibromo-10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-one (**14**)

A soln of Br₂ (63 g, 0.39 mol) in CHCl₃ (400 mL) was added dropwise to a stirred soln of enone **13** (80 g, 0.39 mol) in CHCl₃ (800 mL) at 0 °C, and the mixture was stirred overnight at r.t. The resulting white solid was separated from the solvent by filtration and dried in vacuo; yield: 105 g (74%); mp 192 °C.

IR (KBr): 2996 (w), 1640 (vs), 1595 (s), 1578 (m), 1301 (vs), 1247 (m), 1148 (m) cm⁻¹.

¹H NMR (300 MHz, CD₂Cl₂): δ = 5.85 (s, 2 H, H-10/11), 7.42–7.61 (m, 6 H, H-1/2/3/7/8/9), 8.05 (dd, ³*J* = 7.8 Hz, ⁴*J* = 1.6 Hz, 2 H, H-4/6).

¹³C NMR (75 MHz, CD₂Cl₂): δ = 53.2 (d, C-10/11), 129.9, 131.3, 131.6, 133.1 (d, C-1/2/3/4/6/7/8/9), 137.0, 138.2 (s, C-4a/5a/9a/11a), 192.2 (s, C-5).

HRMS–FAB: *m/z* [M]⁺ calcd for C₁₅H₁₀OBr₂: 368.9136; found: 368.9126.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ): 276 (4.05), 346 nm (2.48).

Anal. Calcd for C₁₅H₁₀OBr₂: C, 49.22; H, 2.75; Br, 43.66. Found: C, 49.24; H, 2.79; Br, 43.84.

10-Bromo-5*H*-dibenzo[*a,d*]cycloheptene-5-one (12)

An excess of NaOH (50 g, 1.25 mol) was combined with a soln of the dibromo compound **14** (92 g, 0.25 mol) in MeOH (3 L), and the mixture was refluxed for 12 h then cooled. The solvent was removed under reduced pressure, and the resulting white solid was dissolved in CH₂Cl₂ (400 mL) and H₂O (400 mL). The layers were separated, the aqueous layer was extracted with CH₂Cl₂ (3 \times 150 mL), and the combined organic layers were washed with H₂O, dried (MgSO₄), and concentrated; yield: 71 g (99%); mp 100 °C.

IR (KBr): 3067 (w), 1651 (vs), 1593 (s), 1445 (w), 1313 (s) cm⁻¹.

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.44–7.69 (m, 5 H, H_{arom}), 7.80 (s, 1 H, H-11), 7.86–7.92 (m, 2 H, H_{arom}), 8.13–8.16 (m, 1 H, H_{arom}).

¹³C NMR (75 MHz, CD₂Cl₂): δ = 124.5 (s, C-10), 127.9, 128.1, 128.6, 129.0, 129.4, 130.3, 131.0, 131.2, 133.8 (d, C-1/2/3/4/6/7/8/9), 132.3, 132.5, 138.4, 138.8 (s, C-4a/5a/9a/11a), 193.5 (C-5).

HRMS–FAB: m/z [M]⁺ calcd for C₁₅H₉OBr: 286.9895; found: 286.9924.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ): 258 (4.53), 306 (4.11), 346 nm (3.56).

Anal. Calcd for C₁₅H₉OBr: C, 63.19; H, 3.18; Br, 28.02. Found: C, 63.28; H, 3.24; Br, 27.76.

11-Bromodibenzo[*a,e*]cycloocten-5(6*H*)-one (15a) and 12-Bromodibenzo[*a,e*]cycloocten-5(6*H*)-one (15b)

A soln of TMSCHN₂ (190 mL, 0.38 mol) in CH₂Cl₂ (1500 mL) was added dropwise over 3 h to a stirred soln of bromo enone **12** (71 g, 0.25 mol) and BF₃·OEt₂ (31 mL, 0.38 mol) in CH₂Cl₂ (1500 mL) at 0 °C. The mixture was stirred at 0 °C for 12 h and then poured into ice-water. The aqueous layer was extracted with CH₂Cl₂ (3 \times 150 mL), and the organic layers were combined. The combined organic layers were washed with brine, dried (MgSO₄), and concentrated to give an orange oil that was purified by column chromatography [silica gel, hexane–CH₂Cl₂ (1:1)] to afford the product as a mixture of isomers; yield: 50 g (67%); R_f = 0.35 (hexane–CH₂Cl₂, 1:1).

IR (KBr): 1681 (vs), 1647 (m), 1592 (m), 1306 (s) cm⁻¹.

¹H NMR (300 MHz, CD₂Cl₂): δ = 3.91 (d, ² J = 13.3 Hz, 1 H, H-6), 4.38 (d, ² J = 13.3 Hz, 1 H, H-6), 7.22–7.52 (m, 7 H, H_{arom}), 7.59 (s, 1 H, C_{sp2}H), 7.98–8.02 (m, 1 H, H_{arom}).

¹³C NMR (75 MHz, CD₂Cl₂): δ = 49.3 (t, C-6), 127.7, 128.1, 128.9, 129.5, 130.3, 130.5, 131.0, 132.4, 134.4 (d, C_{sp2}), 123.9, 134.1, 135.2, 136.0, 137.9 (s, C_q), 196.9 (s, C-5).

HRMS–FAB: m/z [M]⁺ calcd for C₁₆H₁₁OBr: 301.0051; found: 301.0049.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ): 238 (4.45), 308 nm (3.43).

Anal. Calcd for C₁₆H₁₁OBr: C, 64.23; H, 3.71; Br, 26.71. Found: C, 64.04; H, 3.78; Br, 26.92.

11-Bromo-5,6-dihydrodibenzo[*a,e*]cycloocten-5-ol (16a) and 11-Bromo-5,6-dihydrodibenzo[*a,e*]cycloocten-5-ol (16b)

A soln of 1.0 M DIBAL-H in heptane (108 mL, 108 mmol) was added dropwise to a soln of **15a/15b** (27 g, 90 mmol) in CH₂Cl₂ (500 mL) at –78 °C under argon, and the soln was then stirred for 12 h. The mixture was poured into sat. aq NH₄Cl (500 mL) to give a white solid that was dissolved in 1 M aq HCl. The aqueous layer was extracted with CH₂Cl₂ (3 \times 100 mL), and the organic layers were combined and dried (MgSO₄) to give a white solid as a mixture of isomers; yield: 27 g (99%).

IR (KBr): 1629 (s), 1489 (m), 1433 (m) cm⁻¹.

¹H NMR (300 MHz, CD₂Cl₂): δ = 2.00 (s, 1 H, OH), 3.30–3.37 (m, 1 H, H-6), 3.45–3.52 (m, 1 H, H-6), 5.10–5.16 (m, 1 H, H-5), 7.07–7.45 (m, 9 H, H_{arom}).

¹³C NMR (75 MHz, CD₂Cl₂): δ = 41.7 (t, C-6), 75.0 (d, C-5), 126.8, 127.4, 128.2, 129.2, 129.6, 134.0 (d, C_{arom}), 122.5, 130.7, 134.4, 136.7, 138.7, 140.2 [s, C_q, (isomers a + b)].

HRMS–FAB: m/z [M]⁺ calcd for C₁₆H₁₃OBr: 302.0129; found: 302.0124.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ): 256 nm (4.09).

Anal. Calcd for C₁₆H₁₃OBr: C, 63.81; H, 4.35; Br, 26.53. Found: C, 63.56; H, 4.45; Br, 26.90.

11-Bromo-5,6-dihydro-5-[(trimethylsilyl)oxy]dibenzo[*a,e*]cyclooctene (17a) and 12-Bromo-5,6-dihydro-5-[(trimethylsilyl)oxy]dibenzo[*a,e*]cyclooctene (17b)

A soln of *t*-BuSiMe₂OTf (4.3 mL, 17 mmol) in CH₂Cl₂ (30 mL) and 2,6-lutidine (3.6 g, 34 mmol) was added over 30 min to a soln of **16a/16b** (5 g, 17 mmol) in CH₂Cl₂ (200 mL) at –78 °C. The mixture was stirred for 2 h at r.t. and then the reaction was quenched with H₂O (200 mL). The aqueous layer was extracted with CH₂Cl₂ (3 \times 100 mL), and the combined organic layers were dried (MgSO₄) and concentrated to give a yellow oil that was purified by column chromatography (silica gel, hexane) to afford the product as a mixture of isomers; yield: 6.9 g (99%); R_f = 0.17 (hexane).

IR (KBr): 3400 (b), 3068 (m), 2929 (vs), 2856 (s), 1488 (s), 1467 (m), 1255 (m), 1073 (s) cm⁻¹.

¹H NMR (300 MHz, CD₂Cl₂): δ = 0.00 (s, 3 H, CH₃), 0.14 (s, 3 H, CH₃), 0.93 [s, 9 H, C(CH₃)₃], 3.21 (dd, ² J = 14.2 Hz, ³ J = 8.5 Hz, 1 H, H-6), 3.53 (dd, ² J = 14.2 Hz, ³ J = 8.0 Hz, 1 H, H-6), 5.29 (m, 1 H, H-5), 7.01–7.42 (m, 8 H, H_{arom}), 7.42 (s, 1 H, C_{sp2}H).

¹³C NMR (75 MHz, CD₂Cl₂): δ = –4.6, –4.5 [q, Si(CH₃)₂–*t*-Bu], 13.3 [s, C(CH₃)₃], 25.9 [q, C(CH₃)₃], 44.8 (t, C-6), 73.8 (d, C-5), 126.5, 126.7, 127.9, 128.1, 129.0, 129.5, 129.9, 134.0 (d, C_{sp2}), 123.2, 134.8, 137.2, 138.7, 141.6 (s, C_q).

HRMS–FAB: m/z [M]⁺ calcd for C₂₂H₂₇BrOSi: 415.0915; found: 415.0873.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ): 238 (4.12), 256 (3.93), 408 nm (3.43).

Anal. Calcd for C₂₂H₂₇OBrSi: C, 63.60; H, 6.55; Br, 19.23. Found: C, 63.73; H, 6.55; Br, 18.83.

11,12-Didehydro-5,6-dihydro-5-[(trimethylsilyl)oxy]dibenzo[*a,e*]cyclooctene (18)

A soln of **17a/17b** (6.9 g, 16.6 mmol) in THF (100 mL) was added dropwise to a stirred soln of *t*-BuOK (9.5 g, 83 mmol) in THF (100 mL) at –78 °C for 30 min under argon, and the mixture was stirred for 1 h at r.t. The solvent was removed and the crude product was dissolved in sat. aq NH₄Cl (300 mL) and CH₂Cl₂ (300 mL). The aqueous layer was extracted with CH₂Cl₂ (3 \times 100 mL), and the organic layers were combined and dried (MgSO₄). Removal of solvent gave a yellow solid that was purified by column chromatography [silica gel, hexane–CH₂Cl₂ (1:1)] to give the product as pale yellow crystals; yield: 4.6 g (83%); mp 72–74 °C; R_f = 0.73 (hexane–CH₂Cl₂, 1:1).

IR (KBr): 3066 (m), 2957 (vs), 2925 (vs), 2854 (s), 2147 (w), 1951 (w), 1917 (w), 1606 (w), 1472 (vs), 1362 (s), 1250 (vs), 1108 (vs), 1061 (vs) cm⁻¹.

¹H NMR (300 MHz, CD₂Cl₂): δ = –0.10 (s, 3 H, CH₃), –0.06 (s, 3 H, CH₃), 0.97 [s, 9 H, C(CH₃)₃], 2.91 (dd, ² J = 14.6 Hz, ³ J = 3.7 Hz, 1 H, H-6), 3.13 (dd, ² J = 14.6 Hz, ³ J = 2.0 Hz, 1 H, H-6), 4.57 (m, 1 H, H-5), 7.26–7.43 (m, 7 H, H_{arom}), 7.76–7.79 (m, 1 H, H_{arom}).

^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = -5.0, -4.5$ [q, $\text{Si}(\text{CH}_3)_2\text{-}t\text{-Bu}$], 18.4 [s, $\text{C}(\text{CH}_3)_3$], 26.0 [q, $\text{C}(\text{CH}_3)_3$], 50.6 (t, C-6), 76.1 (d, C-5), 111.0, 113.1 (s, C_{alkyne}), 121.3, 124.3 (s, C_q), 125.2, 126.1, 126.3, 126.9, 127.1, 128.1, 128.2, 130.3 (d, C_{arom}), 152.2, 156.8 (s, C_q).

HRMS–FAB: m/z [M] $^+$ calcd for $\text{C}_{22}\text{H}_{26}\text{OSi}$: 334.1753; found: 334.1751.

UV/Vis (CH_2Cl_2): λ_{max} (log ϵ): 258 (3.75), 276 (4.13), 290 (4.28), 306 nm (4.27).

Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{OSi}$: C, 79.00; H, 7.83. Found: C, 78.75; H, 7.84.

11,12-Didehydro-5,6-dihydrodibenzo[*a,e*]cycloocten-5-ol (19)

$\text{Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$ (18 g, 56 mmol) was added to a soln of **18** (10 g, 28 mmol) in THF (250 mL) at r.t., and the mixture was then stirred for 1 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (200 mL) and H_2O (200 mL). The aqueous layer was extracted with CH_2Cl_2 (3×75 mL), and the organic layers were combined, dried (MgSO_4) and concentrated to give a residue that was purified by column chromatography (silica gel, CH_2Cl_2) as colorless crystals; yield: 5 g (81%); mp 135–136 °C; $R_f = 0.38$ (CH_2Cl_2).

IR (KBr): 3061 (w), 3033 (w), 1602 (m), 1563 (m), 1475 (m), 1244 (w), 1203 (w), 1108 (m), 1044 (s) cm^{-1} .

^1H NMR (300 MHz, CD_2Cl_2): $\delta = 2.45$ (s, 1 H, OH), 2.88 (dd, $^2J = 14.7$ Hz, $^3J = 3.6$ Hz, 1 H, H-6), 3.09 (dd, $^2J = 14.7$ Hz, $^3J = 1.9$ Hz, 1 H, H-6), 4.56–4.59 (m, 1 H, H-5), 7.28–7.43 (m, 7 H, H_{arom}), 7.71–7.74 (m, 1 H, H_{arom}).

^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 49.1$ (t, C-6), 75.4 (d, C-5), 111.9, 113.1 (s, C_{alkyne}), 121.4, 124.3 (s, C_q), 124.1, 126.3, 127.0, 127.2, 128.3, 128.3, 129.9 (d, C_{arom}), 152.1, 156.1 (s, C_q).

HRMS–FAB: m/z [M] $^+$ calcd for $\text{C}_{16}\text{H}_{12}\text{O}$: 220.0888; found: 220.0863.

UV/Vis (CH_2Cl_2): λ_{max} (log ϵ): 258 (3.81), 276 (4.24), 290 (4.41), 306 nm (4.41).

Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}$: C, 87.25; H, 5.49. Found: C, 87.43; H, 5.4.

11,12-Didehydrodibenzo[*a,e*]cycloocten-5(6*H*)-one (10)

A soln of DMSO (1.3 mL, 18 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred soln of oxalyl chloride (0.8 mL, 9 mmol) in CH_2Cl_2 (20 mL) at -78 °C under argon. The soln was stirred at -78 °C for 0.5 h and then a soln of ynone **19** (1.8 g, 8.2 mmol) in CH_2Cl_2 (80 mL) was added to the mixture. The soln was stirred at -78 °C for 20 min, Et_3N (5.7 mL, 41 mmol) was added, and the mixture was stirred at r.t. for 0.5 h. The mixture was diluted with CH_2Cl_2 and washed with H_2O . The aqueous layer was extracted with CH_2Cl_2 (3×75 mL), and the organic layers were combined and dried (MgSO_4). Removal of solvent and purification by column chromatography (silica gel, CH_2Cl_2) gave yellow crystals; yield: 1.4 g (76%); mp 83 °C; $R_f = 0.66$ (CH_2Cl_2).

IR (KBr): 3435 (br), 3060 (w), 2923 (w), 2120 (w), 1683 (vs), 1638 (m), 1595 (m), 1476 (w), 1299 (m), 1219 (w), 1164 (w), 1036 (w) cm^{-1} .

^1H NMR (300 MHz, CD_2Cl_2): $\delta = 3.64$ (d, $^2J = 11.0$ Hz, 1 H, H-6), 4.16 (d, $^2J = 11.0$ Hz, 1 H, H-6), 7.32–7.54 (m, 8 H, H_{arom}).

^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 49.3$ (t, C-6), 109.5, 111.0 (s, C_{alkyne}), 122.1, 123.8 (s, C_q), 126.1, 126.4, 127.7, 127.9, 128.4, 129.4, 131.2 (d, C_{arom}), 148.7, 155.1 (s, C_q), 200.4 (s, CO).

HRMS–FAB: m/z [M] $^+$ calcd for $\text{C}_{16}\text{H}_{10}\text{O}$: 218.0732; found: 218.0757.

UV/Vis (CH_2Cl_2): λ_{max} (log ϵ): 252 (4.16), 282 (3.94), 296 (4.06), 320 nm (3.69).

Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{O}$: C, 88.05; H, 4.62. Found: C, 87.85; H, 4.66.

{(η^5 -Cyclopentadienyl)}{ η^4 -10,20(19)-dihydrodibenzocyclobuta[1,2-*a*:3,4-*a'*]dicyclooctene-9,19(20)-dione)cobalt(I) (Isomeric Mixture) (20)

A soln of ynone **10** (1.2 g, 5.6 mmol) in decalin (40 mL) was added dropwise over 3 days to a soln of $\text{CpCo}(\text{CO})_2$ (0.5 g, 2.8 mmol) in decalin (210 mL) at 177 °C. The solvent was then removed under vacuum, and the red-brown residue was purified by column chromatography [silica gel, hexane– CH_2Cl_2 (1:1)] to give a red solid; yield: 438 mg (28%); mp 191 °C; $R_f = 0.12$ (hexane– CH_2Cl_2 , 1:1).

IR (KBr): 3440 (b), 3060 (w), 2925 (m), 2853 (w), 1665 (s), 1593 (w), 1477 (m), 1456 (w), 1287 (m), 1240 (w), 1009 (w) cm^{-1} .

^1H NMR (300 MHz, CD_2Cl_2): $\delta = 4.38$ –4.44, 4.83–4.87 [m, 4 H, CH_2 (isomers a + b)], 4.68, 4.78 [s, 5 H, H_{Cp} , (isomers a + b)], 7.11–8.00 [m, 16 H, H_{arom} (isomers a + b)].

^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 48.4$, 49.4 [t, CH_2 (isomers a + b)], 75.5, 76.1, 77.4, 78.4 [s, C_{Cbd} (isomers a + b)], 84.4, 84.6 [d, C_{Cp} (isomers a + b)], 126.7, 126.8, 127.3, 128.2, 128.5, 129.3, 130.4, 130.7, 131.1, 131.3, 131.3, 131.5, 131.8, 133.3 [d, C_{arom} (isomers a + b)], 133.9, 134.1, 134.4, 134.4, 135.4, 135.8, 137.3 [s, C_{arom} (isomers a + b)], 198.3, 199.2 [s, CO (isomers a + b)].

HRMS–FAB: m/z [M] $^+$ calcd for $\text{C}_{37}\text{H}_{25}\text{O}_2\text{Co}$: 560.1186; found: 560.1204.

UV/Vis (CH_2Cl_2): λ_{max} (log ϵ): 268 (4.47), 296 (4.40), 340 nm (4.13).

{(η^5 -Pentamethylcyclopentadienyl)}{ η^4 -10,20(19)-dihydrodibenzocyclobuta[1,2-*a*:3,4-*a'*]dicyclooctene-9,19(20)-dione)cobalt(I) (Isomeric Mixture) (21)

To a soln of $\text{Cp}^*\text{Co}(\text{CO})_2$ (0.8 g, 3.1 mmol) in decalin (210 mL) was added dropwise over 3 days to a soln of ynone **10** (1.4 g, 6.2 mmol) in decalin (40 mL) at 177 °C. The solvent was removed under vacuum and the red-brown residue was purified by column chromatography [silica gel, hexane– CH_2Cl_2 (1:1)] to give a red solid; yield: 120 mg (6%); mp 248 °C; $R_f = 0.1$ (hexane– CH_2Cl_2 , 1:1).

IR (KBr): 3438 (b), 3006 (w), 2905 (w), 1662 (vs), 1593 (m), 1476 (m), 1455 (s), 1285 (m), 1237 (w), 1010 (m) cm^{-1} .

^1H NMR (300 MHz, CD_2Cl_2): $\delta = 1.28$, 1.29 [s, 15 H, CH_3 (isomers a + b)], 3.56–3.60, 4.31–4.63, 6.00–6.02 [m, 4 H, CH_2 (isomers a + b)], 7.14–8.04 [m, 16 H, H_{arom} (isomers a + b)].

^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 9.05$, 9.27 [q, CH_3 (isomers a + b)], 47.3, 47.3 [t, CH_2 (isomers a + b)], 68.0, 74.0, 77.3, 78.5 [s, C_{Cbd} (isomers a + b)], 91.8, 91.8 [s, C_{Cp} (isomers a + b)], 125.2, 125.3, 125.7, 126.1, 126.5, 126.6, 127.0, 127.3, 127.5, 129.5, 130.5, 130.7, 131.5, 131.7, 132.0, 132.3 [d, C_{arom} (isomers a + b)], 133.5, 134.5, 134.9, 135.7, 136.1, 136.3, 136.6, 137.1, 137.5 [s, C_{arom} (isomers a + b)], 199.9, 201.1, 201.3 [s, CO (isomers a + b)].

HRMS–MALDI: m/z [M] $^+$ calcd for $\text{C}_{42}\text{H}_{35}\text{O}_2\text{Co}$: 630.19636; found: 630.19670.

UV/Vis (CH_2Cl_2): λ_{max} (log ϵ): 269 (4.45), 322 (4.40), 374 (4.18), 462 (3.63) nm.

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- (8) X-ray structure analysis of diphenylhydrazone of **10**: red crystals (plates), dimensions $0.20 \times 0.13 \times 0.08 \text{ mm}^3$, crystal system monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.0543(13) \text{ \AA}$, $b = 8.2733(9) \text{ \AA}$, $c = 19.102(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 105.447(5)^\circ$, $\gamma = 90^\circ$, $V = 1836.2(4) \text{ \AA}^3$, $\rho = 1.441 \text{ g cm}^{-3}$, $T = 200(2) \text{ K}$, radiation $\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$, $0.3^\circ \omega$ -scans with CCD area detector, covering a whole sphere in reciprocal space; 9253 reflections measured, 1725 unique [$R(\text{int}) = 0.0473$], 1322 observed [$I > 2\sigma(I)$]; $\mu = 0.102 \text{ mm}^{-1}$, $T_{\text{min}} = 0.99$, $T_{\text{max}} = 0.98$; 275 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.17 for observed reflections, final residual values $R1(F) = 0.059$, $wR(F^2) = 0.139$ for observed reflections, residual electron density -0.21 to 0.19 e \AA^{-3} .
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- (11) X-ray structure analysis of **20**: red crystals (plates), dimensions $0.57 \times 0.09 \times 0.08 \text{ mm}^3$, crystal system triclinic, space group $P\bar{1}$, $Z = 4$, $a = 8.7426(7) \text{ \AA}$, $b = 17.2931(16) \text{ \AA}$, $c = 19.5099(16) \text{ \AA}$, $\alpha = 106.941(3)^\circ$, $\beta = 92.274(2)^\circ$, $\gamma = 104.589(2)^\circ$, $V = 2710.2(4) \text{ \AA}^3$, $\rho = 1.426 \text{ g cm}^{-3}$, $T = 200(2) \text{ K}$, radiation $\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$, $0.3^\circ \omega$ -scans with CCD area detector, covering a whole sphere in reciprocal space; 28788 reflections measured, 13417 unique [$R(\text{int}) = 0.0616$], 9808 observed [$I > 2\sigma(I)$]; $\mu = 0.717 \text{ mm}^{-1}$, $T_{\text{min}} = 0.69$, $T_{\text{max}} = 0.94$; 798 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.23 for observed reflections, final residual values $R1(F) = 0.106$, $wR(F^2) = 0.187$ for observed reflections, residual electron density -0.67 to 1.04 e \AA^{-3} .
- (12) X-ray structure analysis of **21**: red crystals (plates), dimensions $0.15 \times 0.07 \times 0.05 \text{ mm}^3$, crystal system monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11.753(2) \text{ \AA}$, $b = 12.508(3) \text{ \AA}$, $c = 20.743(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 91.326(6)^\circ$, $\gamma = 90^\circ$, $V = 3048.4(11) \text{ \AA}^3$, $\rho = 1.374 \text{ g cm}^{-3}$, $T = 200(2) \text{ K}$, radiation $\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$, $0.3^\circ \omega$ -scans with CCD area detector, covering a whole sphere in reciprocal space; 12809 reflections measured, 2422 unique [$R(\text{int}) = 0.1342$], 1936 observed [$I > 2\sigma(I)$]; $\mu = 1.374 \text{ mm}^{-1}$, $T_{\text{min}} = 0.92$, $T_{\text{max}} = 0.97$; 216 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.18 for observed reflections, final residual values $R1(F) = 0.127$, $wR(F^2) = 0.213$ for observed reflections, residual electron density -0.39 to 0.55 e \AA^{-3} .
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