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Butterfly topologies: new expanded carbon-rich organometallic scaffolds

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Abstract

Starting from either (tetraethynylcyclobutadiene)cyclopentadienylcobalt or [1,2-diethynyl-3,4-(2-dioxanyl)cyclobutadiene]-cyclopentadienylcobalt a sequence of copper and Pd-catalyzed couplings of the Eglinton and the Heck–Cassar–Sonogashira–Hagihara type furnishes five bow-tie shaped doubly annelated dehydroannulenes, the largest of which featuring a (formal) 7,8:13,14:25,26:31,32-tetra(4′alkyl-1′,2′-benzo)tricyclo[18,16,$0^{2,19}$]hexatricosa-3,5,9,11,15,17,21,23,27,29,33,35-dodecayne-1,7,13,19,25,31-hexaene hydrocarbon ligand with a cyclopentadienyl-cobalt stabilized cyclobutadiene complex as its central unit. Single crystal X-ray structures of two of the smaller butterflies are reported and their surprising solid-state packing is discussed herein.

Keywords: Alkynes; Dehydro[14]annulenes; Dehydro[18]annulenes; Cyclobutadiene complexes; Cobalt; Pd-catalysis; Copper

1. Introduction

We give herein a full account of the synthesis and structural characterization of carbon-rich organometallic butterflies that are based upon a central (tetraethynylcyclobutadiene)cyclopentadienylcobalt unit [1a,1b]. The chemistry of carbon-rich-materials [2–7] has made great strides during the last 20 years. Molecules such as the hexaethynylbenzenes [3], dreams once, are easily accessible now and routinely incorporated into larger carbon-rich structures [6]. The 'quantum leap' in methodology occurred when the Pd-catalyzed reaction of aryl halides to terminal alkynes was reported in 1975 by Heck, Cassar, and Sonogashira and Hagihara [8]. This procedure allows the direct attachment of alkyne units to arenes, which prior was only possible via lengthy synthetic sequences that involved multiple intermediates. A typical 'pre-Pd-age' sequence would have converted an aromatic aldehyde in three steps under forcing conditions and in only moderate yields into an alkyne. The phenomenal success of the Pd-catalyzed couplings was enhanced by other developments in alkyne chemistry that play an important role [9–11].

Dehydroannulenes have commanded attention because of their attractive structures and their exciting properties that include but are not restricted to supramolecular organization/aggregation, and their use as electronic materials [6g,12–15]. While purely organic, i.e. C,H,O,N-containing dehydroannulenes are widespread, their organometallic congeners have found less attention [16]. We have a long-standing interest in carbon-rich organometallics [17] and report herein the synthesis and characterization of large butterfly-shaped, fused double dehydroannulenes that feature a central tetraethynylated cyclobutadiene complex [18]. Such butterfly topologies are speculated to be critically important in the primary stages of the formation of fullerenes in the gas phase [19].

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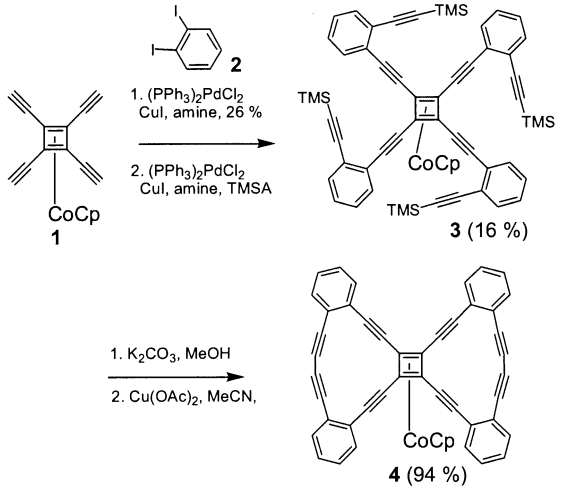
2. Results and discussion

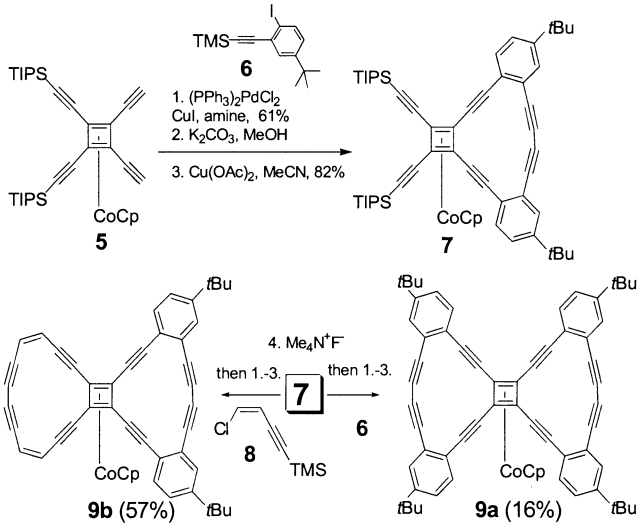
2.1. Syntheses

The parent butterfly **4** was made by the Pd-catalyzed coupling of (tetraethynylcyclobutadiene)cyclopentadienylcobalt (**1**) with diiodobenzene (**2**) to give the open precursor (**3**) in an overall yield of 4.2% after a second Pd-catalyzed coupling to trimethylsilylacetylene (Scheme 1). Desilylation of **3** is followed by ring closing, utilizing the Vögtle variant [20] of the Eglinlon coupling [10] and the title compound **4** forms in a 94% yield.

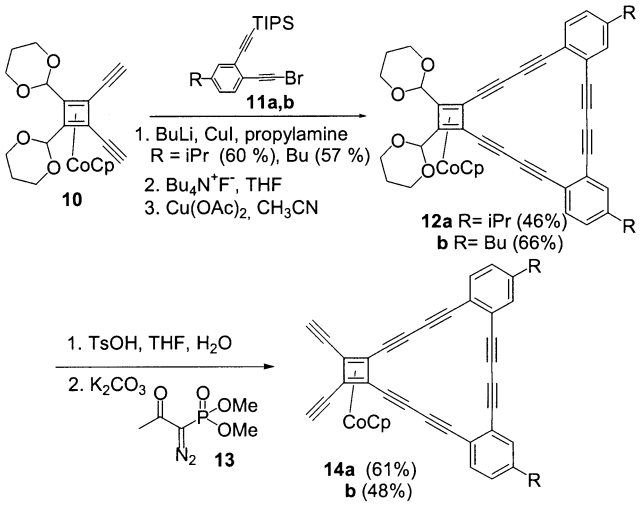
The complex **4** was only sparsely soluble in organic solvents; a ^{13}C-NMR spectrum could be obtained in THF-d_8, however, it was not possible to grow a single crystalline specimen useful for X-ray diffraction. To increase the solubility of the butterflies, and obtain derivatives that would crystallize better, a second, stepwise synthetic approach was developed. Diyne (**5**) [18b] was transformed into **7** by standard Pd-methodology. Desilylation and ring closure furnishes **7** in a 50% overall yield (Scheme 2). The intermediate **7** was deprotected and subjected to reactions 1–3 with arene **6** (**9a**) or alkene **8** (**9b**). This sequence furnished the unsymmetrical butterfly **9b** (57%) and the symmetrical butterfly **9a** (16%). While the butterfly **9b** was quite unstable, **9a** was stable and soluble in hexane, dichloromethane, and THF. Crystallization from dichloromethane furnished a suitable single crystalline specimen (vide infra). To obtain butterflies that incorporate the larger dehydro[18]annulenes, a similar stepwise approach was utilized. A dehydroannulene moiety was attached to **10** by coupling to **11** in a Cadiot Chodciewicz [21] type protocol (Scheme 3). Subsequent deprotection is followed by ring closure to afford the dehydroannulenes (**12a**,**b**) with isopropyl (28%) or butyl (38%) substituents. Deprotection of the acetal rings in



Scheme 1. Synthesis of the parent cyclobutadiene (cyclopentadienyl) cobalt based butterfly **4**.



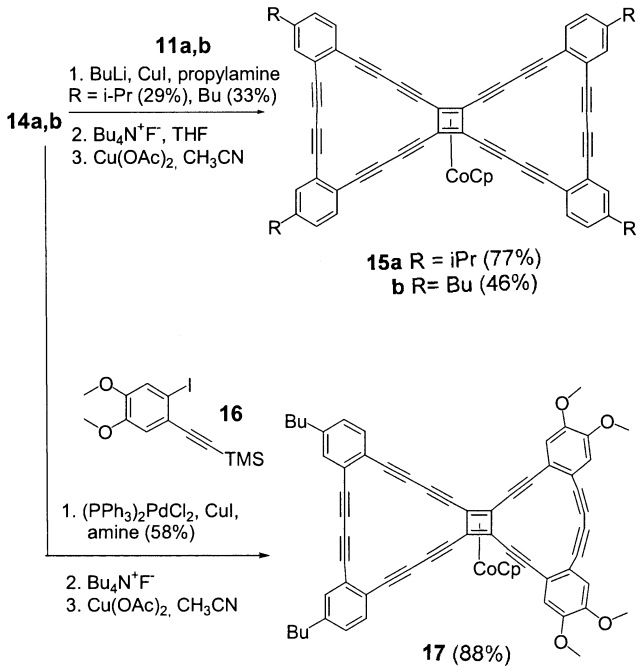
Scheme 2. Synthesis of the butterflies **9a** and **9b**.



Scheme 3. Synthesis of the large butterfly precursor **14**.

12 by *para*-toluenesulfonic acid (TsOH) was facile and the formed intermediates were immediately subjected to an Ohira–Taber–Bestmann [11] alkynylation with **13**. The tetraethynylcyclobutadiene complexes (**14a**,**b**) were obtained in 17 and 18% overall yield starting from **10**; they were unstable when isolated and used immediately in the following step.

The strategically important intermediates **14a**,**b** allowed the attachment of the second dehydroannulene moiety as shown in Scheme 4. The synthesis of the larger butterflies **15** commences with the coupling of **14a**,**b** to **11**. Deprotection and subsequent ring closure with $Cu(OAc)_2$ in acetonitrile furnishes the large butterflies **15a** and **15b** in 22 and 15% yield. For the synthesis of the mixed butterfly **17** the diyne **14b** (R = butyl) is coupled to **16**; the TMS-groups are cleaved off by K_2CO_3 and the second ring is closed utilizing the $Cu(OAc)_2$ coupling to furnish **17** in an overall yield of 51% starting from **14b**



Scheme 4. Synthesis of the enlarged butterflies **15** and **17**.

(R = butyl). Attempts to obtain a single crystalline specimen of either derivative of **15** failed, but it was possible to obtain a suitable single crystal of **17** from dichloromethane–hexane mixtures. Crystalline samples of the butterflies **15** and **17** are stable under ambient conditions for several months.

2.2. Single crystal structures of *9a* and *17*

To gain a better understanding of the topology and the supramolecular ordering of the butterflies in the solid state we obtained a single crystal X-ray structure showing that the large hydrocarbon ligand in **9a** is bent outwardly in the solid state. Fig. 1 displays the ORTEP of **9a**. The structural details of the large hydrocarbon ligand have been discussed in depth in the preliminary communication and will not be repeated here [1a,1b].

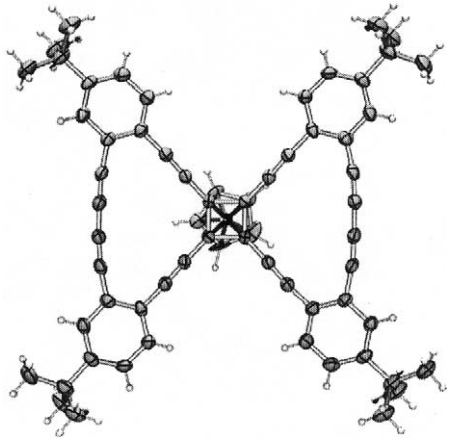


Fig. 1. ORTEP representation of **9a**.

We investigated the solid state ordering of **9a** and were surprised to find a tetragonal packing of the molecules with a space group $I4_1$, quite unusual for an organometallic compound. Fig. 2 shows a packing diagram of the small butterfly **9a**. The molecules are stacked in an AB scheme in the vertical *c*-axis. In two different layers, the molecules are rotated by 90° with respect to each other. In a single plane (Fig. 2) the molecules are arranged as chessboard tiles in which every second row of 'tiling' is missing.

The second layer above or below fills the 'empty' spaces above and below the squares in the middle. The net effect is a striking supramolecular arrangement of **9a** in the solid state. All of the organometallic cyclobutadiene(cyclopentadienyl)cobalt units are arranged in a square grid-like pattern that repeats the tetragonal symmetry of the cyclobutadiene complex nicely. In Fig. 3 the ORTEP representation of the unsymmetrical butterfly **17** is shown. The molecular structure is the expected combination of a dehydro[14]annulene and a dehydro[18]annulene. The bond lengths and bond angles are in excellent agreement with published values for the corresponding sub-structures [1]. While **9a** is significantly bent, the large hydrocarbon ligand of **17** is planar. It was of interest to see if the planarity has an electronic reason or is due to a packing effect. Calculation of **17** utilizing PM3 TM (Wavefunction, Spartan Pro, Windows 2000) shows that the large hydrocarbon ligand is as bent (21.4° for the large dehydroannulene and 17.5° for the small one) as the one in **9** for an isolated molecule in the gas phase. Consequently, the observed planarity in the solid-state structure of **17** must be due to a packing effect.

The packing of **17** is somewhat similar to that of **9a**, insofar as the molecules are packed on top of each other and rotated by 90°. In Table 1 the cell parameters of the two butterflies are listed; while the *a* and the *b*-axes of **9a** and **17** are different, their *c*-axes are similar. The *c*-axis is the 'layer' axis along which the molecules are stacked on top of each other. The slightly larger *c*-axis

Table 1
Crystallographic data for **9a** and **17**

	9a	**17**
Crystal system	Tetragonal	Monoclinic
Space group	$I4_1$	*Cc*
a (Å)	19.156(5)	32.447(3)
b (Å)	19.156(5)	27.437(3)
c (Å)	15.842(7)	14.042(1)
α (°)	90	90
β (°)	90	108.354(2)
γ (°)	90	90
Volume (Å^3)	5814(3)	11 865(2)
Z	4	8

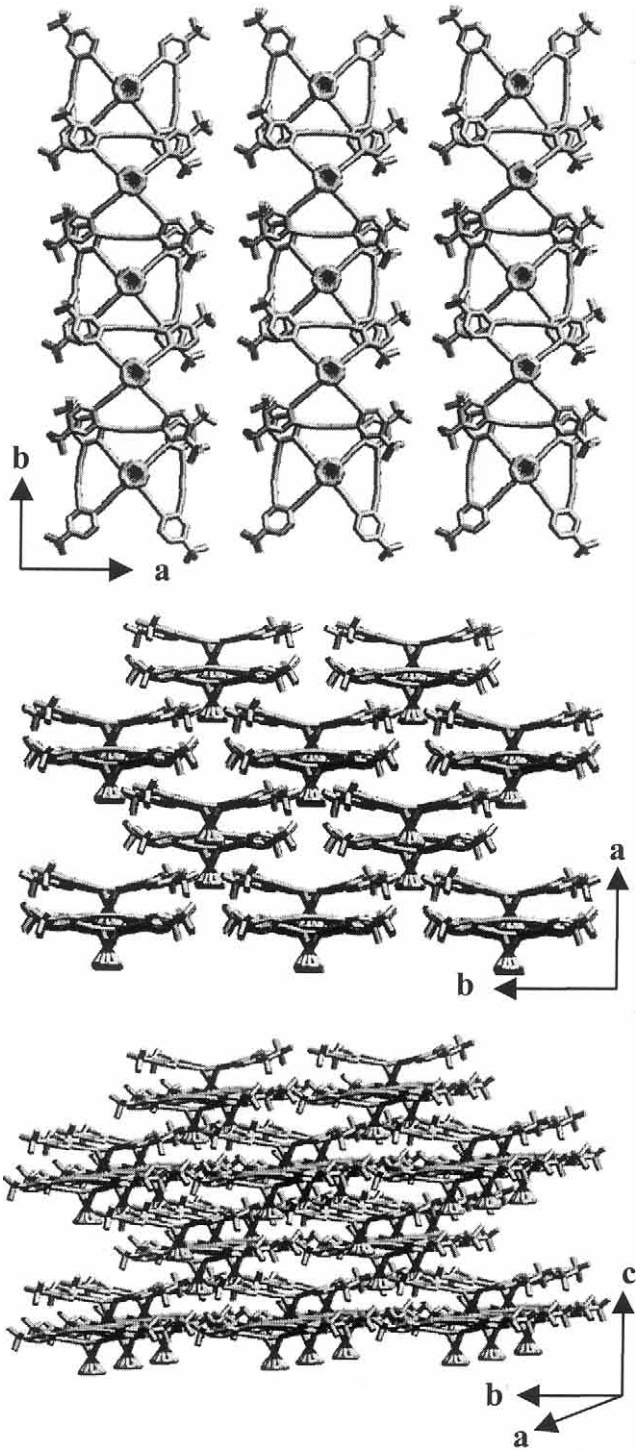


Fig. 2. Packing of the organometallic butterfly **9a**. The packing pattern is such that the hydrocarbon ligands in two adjacent layers are packed in a staggered fashion. The molecules in each layer are rotated by 90° with respect to each other, which gives an overall tetragonal symmetry to this packing arrangement.

of **9a** is due to its larger *tert*-butyl substituents and the upward bending of the whole hydrocarbon ligand. Both factors contribute to the increased 'thickness' of **9a** compared with **17** that must be accommodated for by the crystal lattice. In **17** as well as in **9a**, the large

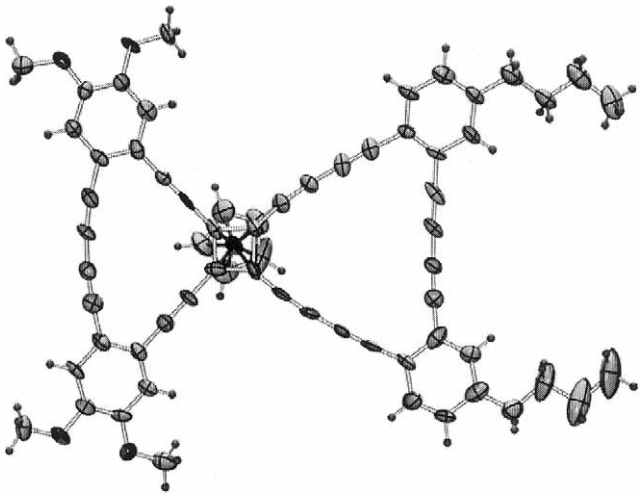


Fig. 3. ORTEP representation of **17**.

hydrocarbon ligands, located in a common plane, are oriented perpendicular to each other. The butyl 'tails' of **17** are tucked in-between two layers, into the interstitial space. The main differences in the packing and in the unit cells arise, therefore, from the differing dimensions and shape of the large π-conjugated ligands in **9a** and in **17** (Fig. 4).

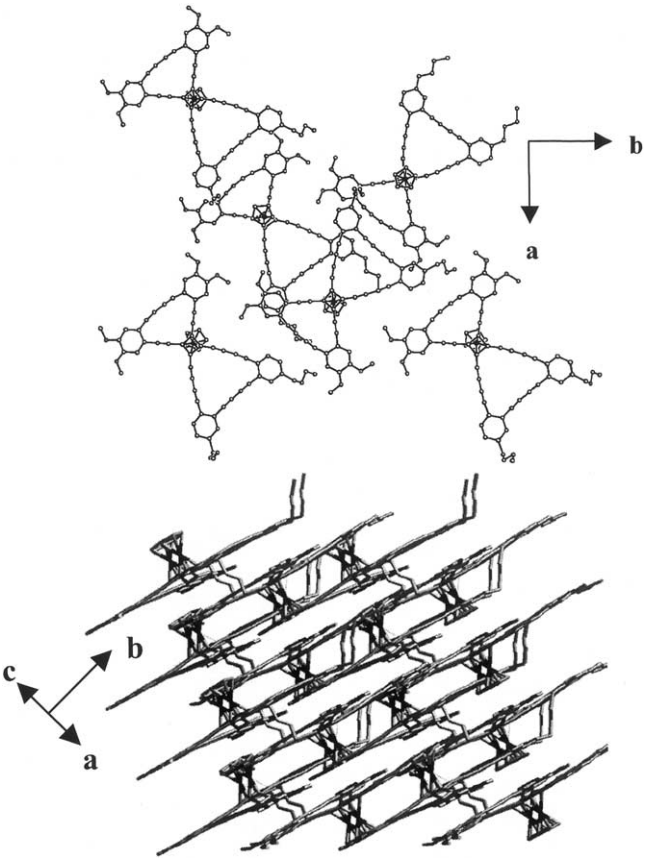


Fig. 4. Packing of the unsymmetrical butterfly **17** in the solid-state. Top, view onto the large hydrocarbon ligand. Bottom, layered structure of **17**, The layers are ca. 3.6 Å spaced apart, with the CpCo units and the butyl groups filling the interstitial interlayer spaces.

3. Conclusions

A family of novel butterfly-shaped organometallic double dehydro[14]annulenes and dehydro[18]annulenes has been prepared by a combination of Pd- and Cu-catalyzed reactions. These structures are attractive synthetic targets on the way to an all-butadiyne bridged organometallic wheel (see red sub-structure in Fig. 5) [17c,17d]. More importantly, according to Jarrold [19] all-carbon topologies of the butterfly-type described here could play an important role in the first stages of fullerene formation in the gas phase. The most surprising feature of these organometallic butterflies is their supramolecular ordering in the solid state, the formation of a very unusual tetragonal network. In future we will investigate the self assembly of pyridine containing butterflies and the covalent closure of organometallic wheels.

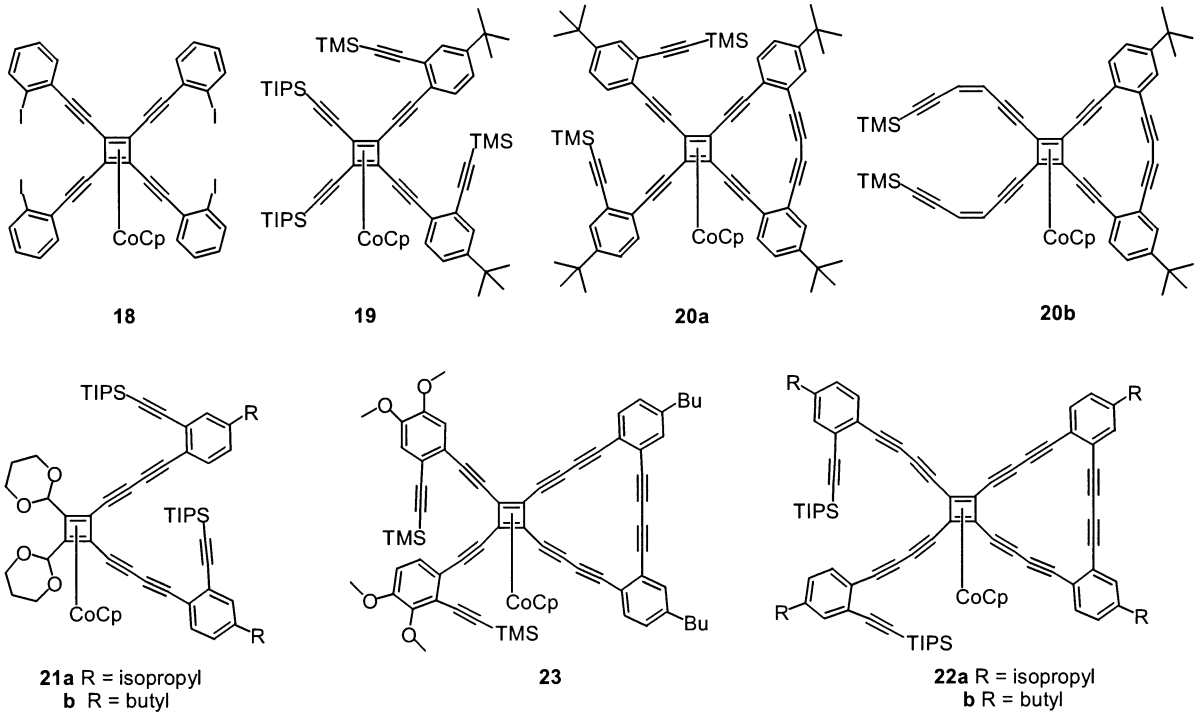
4. Experimental

4.1. Synthesis of *18*

In a 25 ml oven-dried Schlenk flask, (tetraethynylcyclobutadiene)cyclopentadienylcobalt (**1**) (105 mg, 0.391 mmol) was dissolved in 5 ml of dry piperidine. To the solution was added $(PPh_3)_2PdCl_2$ (14.1 mg, 20.1 μmol), CuI (3.7 mg, 20 μmol) and 1,2-diiodobenzene (**2**) (5.00 g, 15.2 mmol). The resulting solution was stirred at ambient temperature for 8 h. The reaction mixture was quenched with water and extracted twice with ethyl ether. The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. Column chromatography (SiO_2; hexanes:CH_2Cl_2, 10:1) furnished **I-1** (107 mg, 26%) as an orange oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.91–7.89 (m, 4H, aromatic-H), 7.57–7.56 (m, 4H, aromatic-H), 7.38–7.34 (m, 8H, aromatic-H), 7.10–7.06 (m, 8H, aromatic-H), 5.29 (s, 5H, Cp-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 139.00, 132.61, 130.10, 129.80, 128.21, 100.71, 95.70, 84.30, 61.18. MS (EI) *m*/*z*; Calc. for [M^+] ($C_{41}H_{21}CoI_4$) 1079.8, Found 1080.17.

4.2. Synthesis of *3*

In a procedure analogous to the synthesis of **I-1**, **I-1** (40, 1 mg, 37.1 μmol), (trimethylsilyl)acetylene (1.79 g, 5.88 mmol), (PPh_3PdCl_2 (2.0 mg, 2.9 μmol) and CuI (1.3 mg, 6.8 μmol) were reacted in piperidine (10 ml). Column chromatography (SiO_2; CH_2Cl_2:hexane, 9:1) furnished **3** (23.2 mg, 16%) as a red oil. IR (Neat): *v* (cm^{-1}) 2989, 2159, 1483, 1250, 1098. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.53–7.51, 7.47–7.44 (m, 8H, aromatic-H), 7.25–7.23 (m, 8H, aromatic-H), 5.12 (s, 5H, Cp-H), 0.18 (s, 3611, TMS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 132.45, 132.29, 127.77, 127.55, 126.18, 124.85, 103.41, 98.92, 92.33, 87.78, 84.11, 61.53, 0.20. MS (EI) *m*/*z*; Calc. for [M^+] ($C_{61}H_{57}CoSi_4$) 960.2, Found 961.4.



18 **19** **20a** **20b**

21a R = isopropyl
b R = butyl

23

22a R = isopropyl
b R = butyl

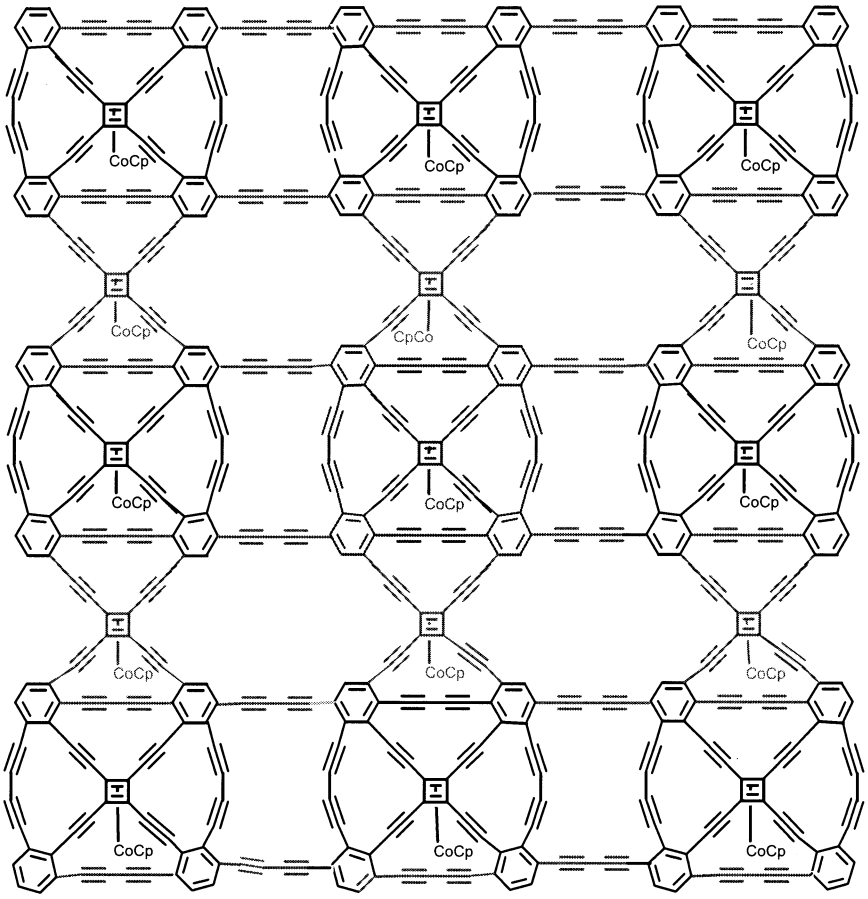


Fig. 5. Hypothetical covalent network version of the supramolecular assembly formed by the butterfly **9a**. The herein synthesized modules are colored black, while the connectors are colored grey. The red center represents an organometallic wheel (Section 3).

4.3. Synthesis of *4*

In a 50 ml round bottom flask was placed **3** (23.1 mg, 24.0 μmol) and K_2CO_3 (50.0 mg, 0.360 mmol) in methanol (1 ml) and THF (2 ml). The resulting solution was stirred at ambient temperature for 8 h before being quenched with water and ethyl ether. The water layer was separated and extracted with ethyl ether (50 ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo to yield a dark red oil. To the oil, in a 500 ml round bottom flask, was added $Cu(OAc)_2$ (1.00 g, 5.51 mmol) and acetonitrile (200 ml). The resulting mixture was heated to 80 °C for 6 h. The solvent was removed in vacuo, the resulting mixture redissolved in CH_2Cl_2 and filtered through a silica gel plug. The solvent was removed in vacuo and column chromatography (SiO_2; CH_2Cl_2:hexanes, 1:1) furnished **4** (14.1 mg, 94%) as a dark red micro-crystalline solid. Melting point (m.p.): decomposition was observed before melting. IR (Neat): ν (cm^{-1}) 2924, 2361, 2342, 1458. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, 4H, $^3J_{H,H} = 7.3$ Hz, $^4J_{H,H} = 1.7$ Hz, aromatic-H), 7.52 (dd, 4H, $^3J_{H,H} = 7.3$ Hz, $^4J_{H,H} = 1.7$ Hz, aromatic-H), 7.42 (quint, 8H, $^3J_{H,H} = 7.3$ Hz, $^4J_{H,H} = 1.7$ Hz, aromatic-H), 5.01 (s, 5H, Cp-H). ^{13}C-NMR (100 MHz, THF-d_8): δ 131.81, 131.17, 129.99, 129.90, 128.57, 124.33, 93.48, 90.21, 84.61, 80.00, 68.21, 62.83. Elemental analysis: Calc. C, 88.02; H, 3.17. Found: C, 87.15; H, 3.20%.

4.4. Synthesis of *19*

In a procedure analogous to the synthesis of **3**, **5** (85.0 mg, 0.146 mmol), 3-trimethylsilylethynyl)-4-iodo-*tert*-butylbenzene (**6**) (140 mg, 0.393 mmol), $(PPh_3)_2PdCl_2$ (2.1 mg, 2.9 μmol), CuI (1.3 mg, 6.8 μmol) were reacted in piperidine (1 ml). Column chromatography (SiO_2; hexanes:CH_2Cl_2, 9:1) furnished **19** (92.1 mg, 61%) as an orange oil. IR (Neat): ν (cm^{-1}) 2924, 2844, 2367, 2333, 1461, 1237. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.44 (d, 2H, $^4J_{H,H} = 1.9$ Hz, aromatic-H), 7.35 (d, 2H, $^3J_{H,H} = 8.1$ Hz, aromatic-H), 7.24 (dd, 2H, $^3J_{H,H} = 8.1$ Hz, $^4J_{H,H} = 1.9$ Hz, aromatic-H), 4.95 (s, 5H, Cp-H), 1.23 (s, 18H, *t*-butyl), 1.10 (s, 42H, TIPS-H), 0.19 (s, 18H, TMS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 151.04, 132.23, 129.42, 125.44, 124.36, 123.59, 104.09, 100.84, 97.87, 96.69, 92.02, 87.01, 83.81, 61.76, 61.50, 34.72, 30.98, 18.69, 11.09, 0.07. MS (EI) *m*/*z*; Calc. for [M^+] ($C_{65}H_{89}CoSi_4$) 1040.5373, Found: 1040.5380 ($E = 2.3$ ppm).

4.5. Synthesis of 7

In a procedure analogous to the synthesis of **4**, **19** (0.128 g, 0.960 mmol) and K_2CO_3 (0.240 g, 1.74 mmol) were reacted in methanol (2 ml) and THF (5 ml). After aqueous workup and isolation of the desilylated intermediate, $Cu(OAc)_2$ (0.480 g, 5.51 mmol) and CH_3CN (50 ml) were added and the resulting mixture heated to 80 °C for 8 h. Column chromatography (SiO_2; CH_2Cl_2:hexanes, 4:1) furnished **7** (87.1 mg, 82%) as a dark red oil. IR (Neat): ν (cm^{-1}) 2943, 2852, 2338, 2143, 1462, 1246. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.49 (d, 2H, $^3J_{H,H} = 8.2$ Hz, aromatic-H), 7.44 (d, 2H, $^4J_{H,H} = 1.9$ Hz, aromatic-H), 7.38 (dd, 2H, $^3J_{H,H} = 8.2$ Hz, $^4J_{H,H} = 1.9$ Hz, aromatic-H), 4.93 (s, 5H, Cp-H), 1.31 (s, 18H, *t*-butyl), 1.14 (s, 42H, TIPS-H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.80, 130.48, 127.13, 126.64, 126.32, 123.40, 100.78, 96.97, 92.21, 84.13, 83.81, 83.60, 61.96, 61.38, 34.90, 30.99, 18.70, 11.11. MS (EI) *m/z*; Calc. for [M^+] ($C_{59}H_{71}CoSi_2$) 894.4426, Found: 894.4401%.

4.6. Synthesis of *20a*

In a 100 ml round bottom flask, **7** (98.0 mg, 0.110 mmol) and $Me_4N^+F^-$ (0.300 g, 10.9 mmol) were dissolved in DMSO (5 ml) and ethyl ether (10 ml). The resulting solution was stirred at ambient temperature for 2 h. The reaction was quenched with water and extracted with ethyl ether. The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo to yield a dark red oil. In a procedure analogous to the synthesis of **18**, the oil was placed in a 25 ml Schlenk flask and reacted with **6** (90.2 mg, 0.253 mmol), $(PPh_3)_2PdCl_2$ (1.5 mg, 2.1 μmol), CuI (1.0 mg, 5.3 μmol) in piperidine (5 ml). Column chromatography (SiO_2; CH_2Cl_2:hexanes, 1:1) furnished **I-3a** (34.2 mg, 30%) as a red oil. IR (Neat); ν (cm^{-1}) 2960, 2872, 2293, 2141, 1460, 1240. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.58–7.44 (m, 8H, aromatic-H), 7.35 (d, 2H, $^3J_{H,H} = 8.2$ Hz, aromatic-H), 7.30 (d, 2H, $^3J_{H,H} = 8.2$ Hz, $^4J_{H,H} = 2.0$ Hz, aromatic-H), 5.05 (s, 5H, Cp-H), 1.30 (s, 18H, *t*-butyl), 1.32 (s, 18H, *t*-butyl), 1.31 (s, 18H, TMS-H). (Note: Due to the low amount of **20a**, only a ^{1}H-NMR was obtained before continuing on with the synthesis.) MS (EI) *m/z*; Calc. for [M^+] ($C_{71}H_{71}CoSi_2$) 1038.4, Found: 1038.4.

4.7. Synthesis of *20b*

In a procedure analogous to the synthesis of **20a**, **7** (68.0 mg, 76.1 μmol) and $Me_4N^+F^-$ (0.300 g, 10.9 mmol) were reacted in DMSO (5 ml) and ethyl ether (10 ml). The resulting oil was placed in a 25 ml Schlenk flask and reacted with *cis*-1-chloro-2-(trimethylsilylethynyl)ethylene (**8**) (30.0 mg, 0.190 mmol), $(PPh_3)_2PdCl_2$ (1.2 mg, 1.7 μmol), and CuI (1.0 mg, 5.3 μmol) in piperidine (1 ml). Column chromatography (SiO_2; CH_2Cl_2:hexanes, 4:1) furnished **20b** (40.4 mg, 65%) as a red oil. IR (Neat): ν (cm^{-1}) 2944, 2855, 2133, 1461, 1244, 1000. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.50 (d, 2H, $^4J_{H,H} = 1.8$ Hz, aromatic-H), 7.36 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} =$ 1.8 Hz, aromatic-H), 6.00 (d, 2H, $^3J_{H,H} = 11.0$ Hz, alkene-H), 5.94 (d, 2H, $^3J_{H,H} = 11.0$ Hz, alkene-H), 4.98 (s, 5H, Cp-H), 1.32 (s, 18H, *t*-butyl), 0.23 (s, 18H, TMS-H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.00, 130.90, 127.13, 126.39, 126.17, 123.40, 120.89, 118.44, 103.73, 102.49, 92.78, 92.26, 91.27, 88.55, 84.23, 83.96, 78.94, 62.27, 61.32, 34.91, 33.99, 0.06. MS (EI) *m/z*; Calc. for [M^+] ($C_{55}H_{51}CoSi_2$) 826.2861, Found: 826.2898.

4.8. Synthesis of *9a*

In a procedure analogous to the synthesis of **4**, **20a** (34.1 mg, 33 μmol) was deprotected with K_2CO_3 (100 mg, 0.720 mmol) in methanol (2 ml) and THF (5 ml). The resulting product was reacted with $Cu(OAc)_2$ (200 mg, 1.10 mmol) in CH_3CN (50 ml). Chromatography (SiO_2; CH_2Cl_2:hexanes, 1:1) furnished **9a** (16.2 mg, 55%) as a dark red crystalline solid. M.p.: 220 °C (dec.). IR (Neat): ν (cm^{-1}) 2943, 2855, 2333, 2144, 1667, 1461, 1244. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 4H, $^3J_{H,H} = 8.3$ Hz, aromatic-H), 7.53 (d, 4H, $^4J_{H,H} = 1.8$ Hz, aromatic-H), 7.43 (dd, 4H, $^3J_{H,H} = 8.3$ Hz, $^4J_{H,H} =$ 1.8 Hz, aromatic-H), 4.97 (s, 5H, Cp-H), 1.34 (s, 36H, *t*-butyl-CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.18, 130.96, 127.45, 126.83, 126.52, 123.68, 92.98, 89.25, 84.52, 83.91, 79.23, 62.31, 35.17, 31.26. UV–vis ($CHCl_3$): λ 296 ($\varepsilon = 27\,530$ cm^{-1} M^{-1}), 323 ($\varepsilon =$ 22 787 cm^{-1} M^{-1}). MS could not be determined due to decomposition.

4.9. Synthesis of *9b*

In a procedure analogous to the synthesis of **4**, **20b** (40.2 mg, 48.7 μmol), and K_2CO_3 (20.1 mg, 0.140 mmol) were reacted in methanol (2 ml) and THF (5 ml). The resulting oil was reacted with $Cu(OAc)_2$ (190 mg, 1.05 mmol) in CH_3CN (50 ml). Column chromatography (SiO_2; CH_2Cl_2:hexanes, 1:1) furnished **9b** (29.1 mg, 88%) as a dark red crystalline solid that was only stable in dilute solutions at ambient temperature. IR (Neat): ν (cm^{-1}) 2956, 2333, 2167, 1644, 1584, 1450, 1400, 1100, 1017. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 2H,$^3J_{H,H} = 8.2$ Hz, aromatic-H), 7.52 (d, 2H,$^4J_{H,H} =$ 1.8 Hz, aromatic-H), 7.42 (dd, 2H, $^3J_{H,H} = 8.2$ Hz, $^4J_{H,H} = 1.8$ Hz, aromatic-H), 6.72 (d, 2H, $^3J_{H,H} = 9.9$ Hz, alkene-H), 6.34 (d, 2H, $^3J_{H,H} = 9.9$ Hz, alkene-H), 4.95 (s, 5H, Cp-H), 1.33 (s, 18H, *t*-butyl-CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.39, 130.98, 127.47,

126.56, 126.3, 123.51, 123.79, 116.87, 96.46, 94.01, 93.31, 88.68, 88.19, 84.44, 84.08, 83.68, 79.20, 63.33, 62.99, 35.19, 31.80. UV–vis ($CHCl_3$): $\lambda_{max} = 333$ nm ($\varepsilon = 313$). MS could not be determined due to decomposition.

4.10. Synthesis of **21**

To a 50 ml oven-dried Schlenk flask was added **10** (200 mg, 0.505 mmol) and dry THF (25 ml) under nitrogen. The flask was cooled to −78 °C and lithium diisopropylamide (0.140 g, 1.28 mmol) in THF was added drop-wise over 10 min. Stirring was continued for 10 min and the solution was brought to 0 °C at which time the solution turned cloudy. After stirring at 0 °C for 30 min, CuI (240 mg, 1.26 mmol), was added, the solution turned transparent and was stirred for an additional 15 min. Following cooling to −78 °C, 4-(bromoethynyl)-3-(triisopropylsilylethynyl)isopropylbenzene (**11a**) (450 mg, 1.12 mmol) or 4-(bromoethynyl)-3-(triisopropylsilylethynyl)butylbenzene (**11b**) (682 mg, 1.64 mmol) and dry propylamine (6.5 ml) were added successively. The resulting solution was stirred for 5 min, warmed to ambient temperature and stirred for 1 h before being quenched with water and ethyl ether. The water layer was separated and extracted with ethyl ether (200 ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. Column chromatography (SiO_2; hexanes:CH_2Cl_2, 3:1 +10% NEt_3) furnished **21a** (315 mg, 60%) or **21b** (310 mg, 57%) as dark orange oils. Compound **21a**: IR (Neat): ν (cm^{-1}) 2947, 2854, 2316, 2193, 2147, 1554, 1101, 993. ^{1}H-NMR (300 MHz, $CHCl_3$): δ 7.38 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.27 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.07 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 5.13 (s, 2H, acetal-CH), 5.03 (s, 5H, Cp-H), 4.15–4.10 (m, 4H, acetal-CH_2), 3.82–3.78 (m, 4H, acetal-CH_2), 2.82 (sept, 2H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH), 2.09–1.98 (m, 2H, acetal-CH_2), 1.35–1.23 (m, 2H, acetal-CH_2), 1.20 (d, 12H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH_3), 1.15 (s, 42H, TIPS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.40, 132.54, 130.28, 126.58, 126.37, 122.92, 105.06, 97.6, 95.12, 82.55, 80.47, 78.86, 78.19, 77.60, 66.93, 66.92, 55.29, 33.97, 25.76, 23.50, 18.71, 11.30. MS (EI) m/z Calc. for M^+ ($C_{65}H_{81}CoO_4Si_2$) 1040.5005. Found: 1040.5015 ($E = 2.4$ ppm). Compound **21b**: IR (Neat): ν (cm^{-1}) 2949, 2905, 2850, 2319, 2193, 2134, 1533, 1101, 880. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.35 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.24 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.02 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 5.13 (s, 2H, acetal-CH), 5.03 (s, 5H, Cp-H), 4.17–4.12 (m, 4H, acetal-CH_2), 3.84–3.75 (m, 4H, acetal-CH_2), 2.61–2.51 (m, 4H, butyl-CH_2), 2.10–1.99 (m, 2H, acetal-CH_2), 1.60–1.50 (m, 4H, butyl-CH_2), 1.38–1.20 (m, 4H, buryl-CH_2, acetal-CH_2), 1.15 (s, 42H, TIPS-H), 0.89 (t, 6H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.46, 132.21, 131.97, 128.21, 126.39, 122.57, 104.86, 97.47, 94.99, 82.40, 80.30, 78.81, 78.11, 77.41, 66.82, 55.09, 45.78, 32.98, 25.65, 22.13, 18.58, 13.74, 11.16, 10.94. Elemental Analysis; Calc.: C, 75.24; H, 8.01. Found: C, 76.11; H, 7.95%. MS (EI) m/z Calc. for M^+ ($C_{67}H_{85}CoO_4Si_2$) 1068.5318. Found 1068.6.

4.11. Synthesis of **12a**

To a 50 ml round bottom flask was added **21a** (707 mg, 0.680 mmol), $Bu_4N^+F^-$ (2.0 ml, 1.0 M in THF) and THF (7 ml). The resulting solution was stirred at ambient temperature for 1 h before being quenched with water and ethyl ether. The water layer was separated and extracted with ethyl ether (50 ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo to yield a dark red oil. To the oil, in a 500 ml round bottom flask, was added $Cu(OAc)_2$ (2.70 g, 14.8 mmol) and acetonitrile (400 ml). The resulting solution was heated to 80 °C for 6 h. The solvent was removed in vacuo, the crude product dissolved in CH_2Cl_2 and filtered through a silica gel plug. Removal of the solvent in vacuo and column chromatography (SiO_2; hexanes:CH_2Cl_2, 2:1 +10% NEt_3) furnished **12a** (228 mg, 46%) as a dark orange oil. IR (Neat): ν (cm^{-1}) 2954, 2924, 2854, 2324, 2185, 1731, 1454, 1093, 1001. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.38 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.32 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.13 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 5.14 (s, 2H, acetal-CH), 5.07 (s, 5H, Cp-H), 4.16–4.08 (m, 4H, acetal-CH_2), 3.85–3.67 (m, 4H, acetal-CH_2), 2.83 (sept, 2H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH), 2.10–2.03 (m, 2H, acetal-CH_2), 1.40–1.31 (m, 2H, acetal-CH_2), 1.20 (d, 12H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.43, 131.68, 131.42, 127.54, 125.19, 122.88, 97.29, 82.43, 81.23, 80.49, 79.59, 79.14, 78.44, 77.24, 66.92, 66.90, 56.49, 33.92, 25.74, 23.42. MS (EI) m/z Calc. for M^+ ($C_{47}H_{39}CoO_4$) 726.2180, unable to determine due to decomposition.

4.12. Synthesis of **12b**

In a procedure analogous to the synthesis of **12a**, **21b** (1.36 g, 1.27 mmol) and $Bu_4N^+F^-$ (3.2 ml, 1.0 M in THF) were reacted for 1 h in THF (10 ml). The resulting dark oil was reacted with $Cu(OAc)_2$ (5.10 g, 28.1 mmol) for 6 h at 80 °C in acetonitrile. Aqueous workup followed by column chromatography (SiO_2; hexanes:CH_2Cl_2, 2:1 +10% NEt_3) furnished **12b** (635 mg, 66%) as a dark orange oily solid. IR (Neat): ν (cm^{-1}) 2955, 2927, 2855, 2120, 1717, 1559, 1489, 1107, 1003. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.41 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.39 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.13 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz,

aromatic-H), 5.15 (s, 2H, acetal-CH), 5.10 (s, 5H, Cp-H), 4.18–4.13 (m, 4H, acetal-CH_2), 3.85–3.67 (m, 4H, acetal-CH,), 2.59 (t, 4H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_2), 2.14–2.01 (m, 2H, acetal-CH_2), 1.62–1.54 (m, 4H, butyl-CH_2), 1.39–1.26 (m, 4H, butyl-CH_2, acetal-CH_2), 0.93 (t, 6H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.62, 133.38, 131.67, 129.34, 125.22, 122.85, 97.37, 82.51, 82.48, 81.16, 80.56, 79.58, 79.24, 78.55, 77.23, 66.95, 56.64, 35.38, 32.98, 25.79, 22.20, 13.88. MS (EI) *m/z* Calc. for M^+ ($C_{49}H_{43}CoO_4$) 754.2493, unable to determine due to decomposition.

4.13. Synthesis of **14a**

In a 100 ml round bottom flask was placed **12a** (220 mg, 0.302 mmol), *p*-toluenesulfonic acid (200 mg, 1.05 mmol), THF (3 ml) and H_2O (2 ml). The resulting mixture was stirred for 12 h under the exclusion of light. The mixture was quenched with water and extracted with ethyl ether (100 ml). Removal of the solvent and drying under vacuum (10^{-1} mbar) yielded a dark red oil. To the red oil was added finely powdered K_2CO_3 (270 mg, 1.96 mmol), dry methanol (5 ml) and dry THF (2 ml). The flask was cooled to -10 °C and dimethyl-(1-diazo-2-oxopropyl)-phosphonate (**13**) (270 mg, 1.41 mmol) was added drop-wise. The resulting reaction mixture was stirred for 8 h under exclusion of light. The reaction was quenched with aqueous $NaHCO_3$ and extracted with ethyl ether (200 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes + 10% NEt_3) furnished **14a** (117 mg, 61%) as an unstable yellow crystalline solid. M.p.: unable to determine due to rapid decomposition at ambient temperatures. IR (Neat): ν (cm^{-1}) 3326, 2962, 2916, 2847, 2308, 1693, 1646, 1540, 1416, 1093. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.45 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.41 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.19 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 5.09 (s, 5H, Cp-H), 3.30 (s, 2H, alkyne-H), 2.90 (sept, 2H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH), 1.24 (d, 12H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH}). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 150.00, 131.85, 131.66, 127.65, 125.56, 122.24, 83.96, 82.24, 81.80, 81.19, 80.05, 78.30, 77.62, 77.58, 76.93, 61.91, 59.61, 34.01, 23.46. MS (EI) *m/z* Calc. for M^+ ($C_{43}H_{27}Co$) 602.1445, unable to determine M^+ due to decomposition.

4.14. Synthesis of **14b**

In a procedure analogous to the synthesis of **14a**, **12b** (635 mg, 0.841 mmol) and *p*-toluenesulfonic acid (500 mg, 2.63 mmol) were reacted in THF (3 ml) and H_2O (2 ml). The resulting dark oil was reacted with K_2CO_3 (740 mg, 5.36 mmol) and **13** (740 mg, 3.85 mmol) in dry methanol (5 ml) and dry THF (2 ml). Aqueous workup followed by column chromatography (SiO_2; hexanes:CH_2Cl_2 3:1 + 10% NEt_3) furnished **14b** (254 mg, 48%) as an unstable yellow crystalline solid. M.p.: unable to determine due to rapid decomposition at ambient temperatures. IR (Neat): ν (cm^{-1}) 3335, 2924, 2955, 2855, 1747, 1558, 1508, 1373, 1010. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.42 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.39 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.14 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 5.09 (s, 5H, Cp-H), 3.30 (s, 2H, alkyne-H), 2.59 (t, 4H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_2), 1.64–1.51 (m, 4H, butyl-CH_2), 1.38–1.24 (m, 4H, butyl-CH_2), 0.92 (t, 6H, $^3J_{H,H} = 7.1$ Hz, bulyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 144.18, 133.53, 131.76, 129.42, 125.47, 122.10, 84.10, 83.96, 82.25, 81.82, 81.08, 80.05, 78.36, 77.61, 76.94, 61.94, 59.60, 35.41, 32.94, 22.67, 13.90. MS (EI) *m/z* Calc. for M^+ ($C_{45}H_{31}Co$) 630.1758, unable to determine M^+ due to decomposition.

4.15. Synthesis of **22a**

In a 25 ml, oven-dried Schlenk flask was placed **14a** (58.5 mg, 97.2 μmol) and dry THF (10 ml) under nitrogen. The flask was cooled to -78 °C and lithium diisopropylamide (23.0 mg, 0.213 mmol) in THF was added drop-wise over 5 min. Stirring was continued for 10 min. The solution was brought to 0 °C and turned cloudy. After stirring at 0 °C for 30 min, CuI (65.0 mg, 0.342 mmol), was added and the solution turned transparent. The resulting solution was stirred for 15 min. Following cooling to -78 °C, **11a** (117 mg, 0.291 mmol) and dry propylamine (1.8 ml) were added successively. The resulting solution was stirred for 5 min, before being warmed to ambient temperature, stirred for 1 h and then quenched with water and ethyl ether. The water layer was separated and extracted with ethyl ether (200 ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. Column chromatography (SiO_2; hexanes:EtOAc, 1:1) furnished **22a** (35.0 mg, 29%) as a dark orange oil. IR (Neat): ν (cm^{-1}) 2954, 2916, 2862, 2316, 1770, 1554, 1416, 1062. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.47 (d, 2H, $^4J_{H,H} = 1.4$ Hz, aromatic-H), 7.41 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.40 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.39 (s, 2H, aromatic-H), 7.20 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.11 (dd, 2H, $^3J_{H,H} = 8.2$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 5.13 (s, 5H, Cp-H), 2.92–2.84 (m, 4H, isopropyl-CH), 1.24 (d, 2H, $^3J_{H,H} = 8.0$ Hz, isopropyl-CH_3), 1.20 (d, 2H, $^3J_{H,H} = 8.0$ Hz, isopropyl-CH_3), 1.19 (s, 42H, TIPS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 150.08, 150.02, 132.48, 131.91, 131.73, 130.44, 127.67, 127.18, 126.49, 125.69, 122.37, 122.29, 104.84, 95.69, 83.93, 82.21, 81.98, 81.24, 80.48, 79.35, 78.42, 77.92, 77.63, 77.25, 76.37, 63.48, 60.27, 34.65, 34.07, 23.53, 23.50, 18.81, 11.39. MS (EI) *m/z* Calc. for

M^+ ($C_{87}H_{87}CoSi_2$) 1246.5678, unable to determine M^+ due to decomposition.

4.16. Synthesis of **22b**

In a procedure analogous to the synthesis of **22a**, **14b** (155 mg, 0.245 mmol), lithium diisopropylamide (64.2 mg, 0.541 mmol) in THF, CuI (120 mg, 0.632 mmol), **11b** (400 mg, 960 μmol) and dry propylamine (3.0 ml) were reacted in THF (50 ml). Aqueous workup followed by column chromatography (SiO_2; hexanes:EtOAc, 1:1) furnished **22b** (104 mg, 33%) as a dark orange oil. IR (Neat): ν (cm^{-1}) 2924, 2855, 2115, 1717, 1558, 1543, 1458, 1396, 1025. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.43 (d, 2H, $^4J_{H,H} = 1.4$ Hz, aromatic-H), 7.39 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.38 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.28 (s, 2H, aromatic-H), 7.20 (dd, 2H, $^3J_{H,H} = 8.1$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.11 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 5.12 (s, 5H, Cp-H), 2.62–2.53 (m, 8H, butyl-CH_2), 1.62–1.53 (m, 8H, butyl-CH_2), 1.38–1.27 (m, 8H, butyl-CH_2), 1.19 (s, 42H, TIPS-H), 0.92 (m, 12H, butyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 144.24, 144.20, 133.57, 132.28, 132.24, 131.76, 129.43, 128.40, 127.09, 125.56, 122.16, 122.05, 104.74, 95.77, 83.89, 82.20, 81.97, 81.08, 80.45, 79.31, 78.43, 77.96, 77.70, 76.58, 76.36, 63.49, 60.28, 35.48, 35.43, 33.14, 32.96, 29.70, 29.35, 22.31, 22.22, 18.80, 11.38. MS (EI) m/z Calc. for M^+ ($C_{87}H_{87}CoSi_2$) 1246.5678, unable to determine M^+ due to decomposition.

4.17. Synthesis of **15a**

To a 25 ml, round bottom flask was added **22a** (35.1 mg, 28.1 μmol), $Bu_4N^+F^-$ (0.120 ml, 1.0 M in THF) and THF (3 ml). The resulting solution was stirred at ambient temperature for 1 h before being quenched with water and ethyl ether. The water layer was separated and extracted with ethyl ether (20 ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo to yield a dark red oil. To the oil, in a 100 ml round bottom flask, was added $Cu(OAc)_2$ (160 mg, 0.881 mmol) and acetonitrile (100 ml). The resulting solution was heated to 80 °C for 6 h. The solvent was removed in vacuo, the resulting mixture redissolved in $CHCl_3$ and filtered through a silica gel plug. Removal of the solvent in vacuo and column chromatography (SiO_2; hexanes:$CHCl_3$, 1:1) furnished **15a** (20.2 mg, 77%) as orange needles after crystallization from $CHCl_3$. M.p.: 214 °C (dec.). IR (Neat): ν (cm^{-1}) 2954, 2908, 2847, 2324, 1693, 1554, 1416, 1093. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.50 (d, 4H, $^4J_{H,H} = 1.5$ Hz, aromatic-H), 7.46 (d, 4H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.13 (dd, 4H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.5$ Hz, aromatic-H), 5.17 (s, 5H, Cp-H), 2.90 (sept, 2H, $^3J_{H,H} = 7.2$ Hz, isopropyl-CH), 1.24 (d, 12H, $^3J_{H,H} = 7.2$ Hz, isopropyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ unable to determine due to limited solubility as well as a minimal quantity of material. MS (EI) m/z Calc. for M^+ ($C_{69}H_{45}Co$), decomposition before M^+ was recorded.

4.18. Synthesis of **15b**

In a procedure analogous to the synthesis of **15a**, **22b** (102 mg, 81.8 μmol), and $Bu_4N^+F^-$ (0.23 ml, 1.0 M in THF) were reacted for 1 h in THF (3 ml). The resulting dark oil was reacted with $Cu(OAc)_2$ (310 mg, 1.71 mmol) in acetonitrile (200 ml). Aqueous workup followed by preparative TLC using EtOAc:hexane (1:1) as the eluent, **15b** (35.0 mg, 46%) was isolated as an orange solid. M.p.: 230 °C (dec.). IR (Neat): ν (cm^{-1}) 2955, 2950, 2820, 2235, 1725, 1555, 1075, 997. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.44 (d, 4H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.41 (d, 4H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.15 (dd, 4H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 5.17 (s, 5H, Cp-H), 2.60 (t, 8H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_2), 1.66–1.53 (m, 8H, butyl-CH_2), 1.43–1.23 (m, 8H, butyl-CH_2), 0.93 (t, 12H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 144.28, 133.61, 131.90, 129.47, 125.59, 122.18, 82.92, 82.12, 81.12, 80.35, 78.38, 77.72, 77.69, 62.09, 35.46, 33.00, 22.24, 13.90. MS (EI) m/z Calc. for M^+ ($C_{73}H_{53}Co$) 988.3479, unable to determine due to decomposition.

4.19. Synthesis of **23**

In a dry 100 ml Schlenk flask, **14b** (110 mg, 0.174 mmol) was dissolved in 1 ml of dry piperidine. To the solution was added $(PPh_3)_2PdCl_2$ (4.0 mg, 5.7 μmol), CuI (1.3 mg, 6.8 μmol) and 1,2-dimethoxy-3-iodo-4-(trimethylsiylethynyl)benzene (**16**) (200 mg, 0.561 mmol). The resulting solution was stirred at ambient temperature for 8 h. The reaction mixture was quenched with water and extracted twice with ethyl ether. The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. Column chromatography (SiO_2; EtOAc:hexanes, 4:1) furnished **23** (110 mg, 58%) as an orange oil. IR (Neat): ν (cm^{-1}) 2955, 2932, 2858, 2149, 1508, 1261, 1219, 845. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.40 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.37 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.14 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 6.95 (s, 2H, OMe-aromatic-H), 6.93 (s, 2H, OMe-aromatic-H), 5.13 (s, 5H, Cp-H), 3.90 (s, 6H, OMe), 3.89 (s, 6H, OMe), 2.58 (t, 4H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_2), 1.61–1.54 (m, 4H, butyl-CH_2), 1.38–1.30 (m, 4H, butyl-CH_2), 0.91 (t, 4H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_3), 0.30 (s, 18H, TMS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.33, 149.26, 144.33, 133.81, 131.95, 129.70, 129.63, 125.68, 122.66, 119.16, 118.63, 114.92, 114.33, 103.74, 97.69, 93.01, 86.16, 84.22, 81.86, 81.40, 80.47, 79.03, 77.95, 62.58, 61.38, 56.33, 56.25, 35.68, 33.24, 22.48, 14.15,

0.50. MS (EI) *m/z* Calc. for M^+ ($C_{71}H_{63}CoO_4Si_2$) 1094.3597, unable to determine M^+ due to decomposition.

4.20. Synthesis of **17**

In a procedure analogous to the synthesis of **15a**, **23** (110 mg, 100 μmol) and $Bu_4N^+F^-$ (0.30 ml, 1.0 M in THF) were reacted for 1 h in THF (3 ml). The resulting dark oil was reacted with $Cu(OAc)_2$ (364 mg, 2.00 mmol) in acetonitrile (200 ml). Aqueous workup followed by column chromatography (SiO_2; hexanes: EtOAc, 1:1) furnished **17** (76.5 mg, 88%) as orange coffin shaped crystals after crystallization from $CHCl_3$. M.p.: 205 °C (dec.). IR (Neat): ν (cm^{-1}) 2954, 2924, 2855, 2155, 1504, 1269, 1215, 853. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.42 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.41 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.17 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.13 (s, 2H, OMe aromatic-H), 6.95 (s, 2H, OMe aromatic-H), 5.10 (s, 5H, Cp-H), 3.98 (s, 6H, OMe), 3.91 (s, 6H, OMe), 2.60 (t, 4H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_2), 1.61–1.54 (m, 4H, butyl-CH_2), 1.39–1.30 (m, 4H, butyl-CH_2), 0.92 (t, 4H, $^3J_{H,H} = 7.1$ Hz, butyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.84, 148.82, 144.15, 133.59, 131.64, 129.45, 125.48, 122.39, 122.22, 116.83, 113.56, 111.99, 92.91, 90.17, 87.44, 83.97, 83.64, 81.99, 81.11, 80.16, 78.85, 78.56, 77.70, 62.17, 61.50, 56.14, 56.04, 35.40, 31.54, 22.19, 13.86. MS (EI) *m/z* Calc. for M^+ ($C_{65}H_{45}CoO_4$) 948.2650, unable to determine due to decomposition.

4.21. Experimental details for the crystal structure determinations of **9a** and **17**

X-ray intensity data for **9a** and **17** were measured in ω scan mode using a Bruker SMART APEX CCD-based diffractometer system with Mo–K_α radiation at $\lambda = 0.71073$ Å, at 190(2) K. Raw data frame integration and Lorentz and polarization corrections were performed with SAINT+. Structure solution (direct methods in all cases) and refinement against F^2 using all data was performed with SHELXTL.

4.21.1. Crystal data for **9a**

The cyclobutadiene complex ($C_{65}H_{53}Co$)(CH_2Cl_2) of the FW = 977.93 was isolated as red plate crystal with a dimension of $0.25 \times 0.20 \times 0.08$ mm^3). The unit cell was tetragonal featuring the space group $I4_1$ with cell dimensions of $a = 19.156(5)$ Å, $b = 19.156(5)$ Å, $c = 15.842(7)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 5814(3)$ Å^3 and $Z = 4$ molecules in the unit cell. The calculated density, $D_{calc} = 1.117$ g cm^{-3}. Intensity data covering the full sphere of reciprocal space were measured to $\Theta = 1.95$–$25.04°$; 12 129 reflections were collected, of which 4807 were independent. No absorption correction was applied ($\mu = 0.424$ mm^{-1}). Data refinement produced $R_1 = 0.0491$, wR_2 ($I > 2\sigma(I)$) = 0.1031; GoF = 1.019; 4807 data with 359 parameters were refined with seven restraints. Max/min residual electron density was determined to 0.450/−0.206 e Å^{-3}.

4.21.2. Crystal data for **17a**

The cyclobutadiene complex $C_{45}H_{44}CoO_4$ of the FW = 947.26 was isolated as red block-like crystal, ($0.36 \times 0.26 \times 0.12$ mm^3). The unit cell was monoclinic featuring the space group *Cc* with cell dimensions of $a = 32.447(3)$ Å, $b = 27.437(3)$ Å, $c = 14.042(1)$ Å, $\alpha = 90°$, $\beta = 108.354(2)°$, $\gamma = 90°$, $V = 11\,865(2)$ Å^3 and $Z = 8$ molecules in the unit cell. The calculated density, $D_{calc} = 1.377$ g cm^{-3}. Intensity data covering the full sphere of reciprocal space were measured to $\Theta = 1.95$–$24.24°$; 32 639 reflections were collected, of which 13 840 were independent. Semiempirical absorption correction was applied with maximum and minimum transmission of 0.8309 and 0.5449, respectively. Data refinement produced $R_1 = 0.0491$, wR_2 ($I > 2\sigma(I)$) = 0.2582; GoF = 1.049; 1461 parameters were refined, with 52 restraints. Max/min residual electron density was determined to 1.873/−0.775 e Å^{-3}.

5. Supporting information

Crystallographic information files (CIFs for **9a** (CCDC No. 154093) and **17** (CCDC No. 198703)). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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