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Synthesis and structural characterization of organometallic cyclynes: novel nanoscale, carbon-rich topologies

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Abstract

A combination of Pd- and Cu-catalyzed couplings make the ferrocene and cyclobutadiene(cyclopentadienylcobalt)-based half-wheels and the cyclobutadiene(cyclopentadienylcobalt)-based seco-wheel accessible. These targets can formally be constructed by fusing two or three organometallic benzohexadehydro[14]annulenes along an alkyne unit. In addition, a ferrocene-based, enlarged version of the half wheel was prepared. This target compound is obtained by formally fusing two organometallic benzododecadehydro[18]annulenes. Single crystal structures of three target molecules, the cyclobutadiene complex $C_{51}H_{37}Co$, the ferrocene derivative $C_{51}H_{36}Fe$, and the cyclobutadiene complex $C_{69}H_{59}Co$ were performed to verify the proposed geometries.

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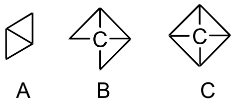
1. Introduction

Alkynylated π-systems have attracted significant attention during the last decade [1–9]. Their relation to dendrimers, fullerenes, and carbon nanotubes have made carbon rich materials an exciting area of research. Consequently, in recent years almost all conceivable peralkynylated π-perimeters have been prepared. Highly alkynylated modules have multiple applications [1] as precursors to novel aromatic systems [2] as molecular wires and as NLO active materials. A spectacular development in this field was Vollhardt's [3] discovery of a shortcut from dehydroannulenes to carbon nanomaterials, demonstrated by the explosive decomposition of a large non-planar dehydroannulene. The authors found well-developed nanotubes and fullerene-type structures. While the organic arm (vide infra) [1–9] of carbon rich is strong, their organometallic relatives used to be less popular not only because of the perceived sensitivity of the involved and projected species but as well due to the increased synthetic effort to make them. That, however, has changed [10–15] and particularly Gladysz's [12] recent spectacular work on "wrapped" carbon rods has enhanced the visibility of this area dramatically.



Formula Block

We have a long standing commitment in carbon rich organometallics [14], we have developed the area of highly alkynylated cyclobutadiene complexes. These are building blocks for nanoscale organometallic topologies and unusual conjugated organometallic polymers. In this contribution we report details of the synthesis and structural characterization of four novel organometallic cyclynes [10] with an expanded bicyclo[1.1.0]butane (**A**) and a tricyclo[$2.1.0.0^{1,3}$]pentane (**B**) topology. In these structures, the C–C-single bonds of the small rings are replaced by alkyne or butadiyne bridges, while the carbon atoms are substituted by benzene rings, cyclobutadiene(cyclopentadienyl)cobalt units or ferrocene

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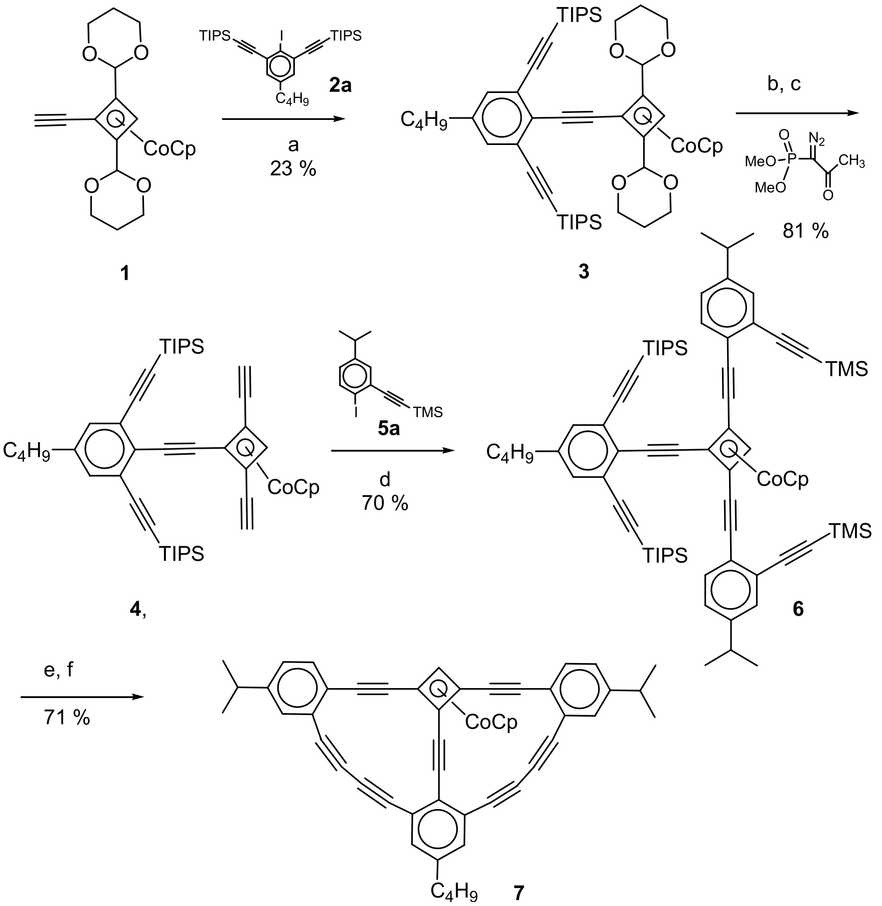
nuclei. Key steps in the synthesis of these targets are the selective *ortho*-metalation of organometallic acetals, [14], the conversion of aldehydes into alkynes by the Ohira method, [16] and Cu-catalyzed dimerizations of terminal alkynes [17].

2. Results and discussion

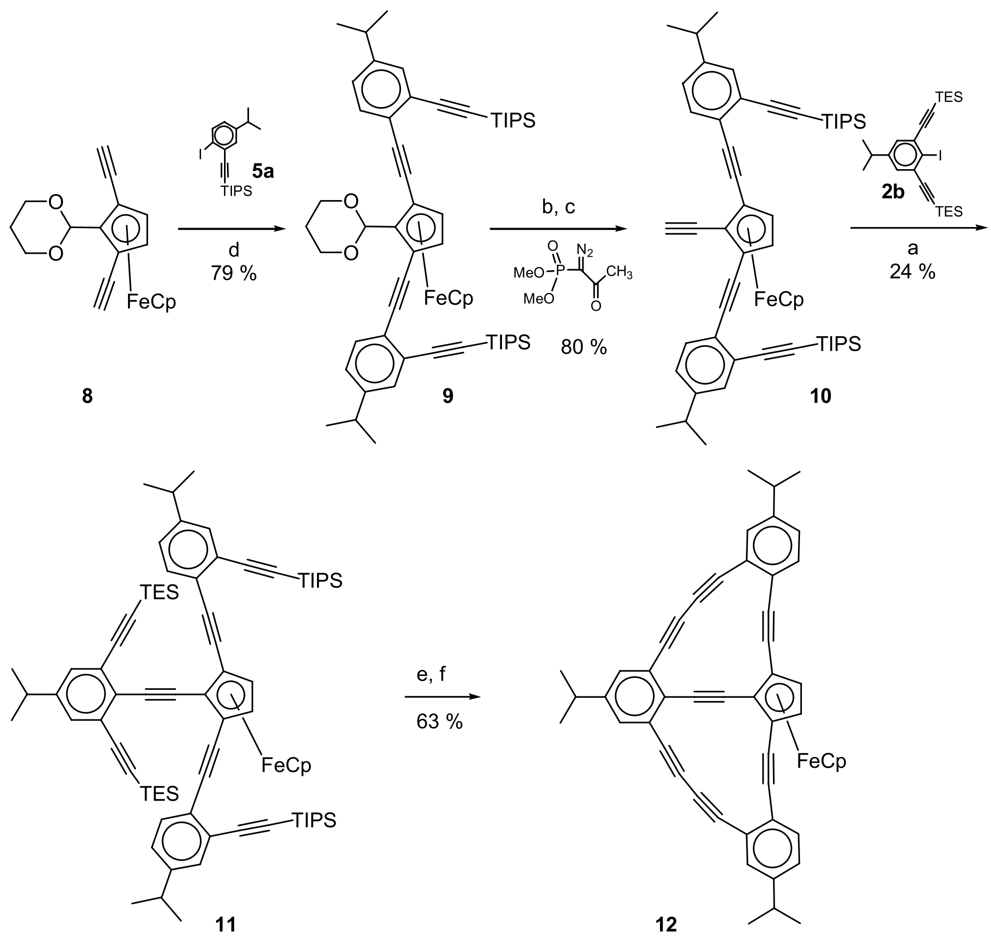
Pd-catalyzed coupling of **1** [14c,d] to the iodide **2a** furnishes **3** in 23% (Scheme 1). The moderate yield of **3** is a result of the two *meta*-positioned alkyne groups in **2a** between which the iodide is sandwiched. Only the active Hartwig-catalyst $[(o\text{-tolyl})_3P]_2Pd$ [18] with THF as co-solvent [19] is capable of coupling **1** to **2a**. The coupling product **3** was deketalized by *para*-toluenesulfonic acid (TsOH) and reacted with the Ohira–Seyferth reagent $[CH_3C{=}OCN_2{-}P{=}O(OEt)_2]$ [16] to give the pentayne **4** in 81%. Coupling of **4** to **5** furnishes **6** in 70%. Desilylation of **6** commences with Bu_4NF in THF; the intermediate heptayne was immediately utilized for the coupling step to close the two cyclyne rings to form **7** in 71% yield. The six-step synthesis (**1** → **7**) proceeds in a respectable overall 9% yield.

To show the general applicability of the method, the ferrocene-containing “super-bicyclo[1.1.0]butane” **12** was targeted. The diyne **8** was reacted with **5a** under Pd-catalysis (Scheme 2) to furnish **9** in 79% yield. Deketalization with TsOH followed by Ohira alkynylation transforms **9** into the pentayne **10** in 80%. The critical step is the Pd-catalyzed coupling of **10** to **2b** that furnishes **11** in 24%. The yield of the coupling is only moderate, again due to the decrease in reactivity the iodide **2b** experiences as a consequence of being positioned between two alkyne substituents. Deprotection of **11** and double cyclization using $Cu(OAc)_2$ in acetonitrile [17] gives **12** in 61% as dark red, stable needles.

It was of interest if a “super-tricyclic” structure analogous to **B** was accessible by this method. A retrosynthetic analysis suggests **13** [14c] as starting point for **17** (Scheme 3). Pd-catalyzed coupling of **13** to **5b** formed **14** in 59% yield. Deprotection by TsOH and conversion of the two aldehyde groups into alkyne units commenced under standard conditions [16] to give **15** in 80%. The critical step is the double Pd-catalyzed coupling of **15** to **2a** that provided **16** in 17% after deprotection with $Bu_4N^+F^-$ in THF. The last step in the reaction sequence is the triple ring closure to **17** that



Scheme 1. (a) $(o\text{-tolyl}_3P)_2PdCl_2$, CuI, NEt_3, THF, 24 °C, 12 h; (b) *para*-toluenesulfonic acid, THF, 24 °C, 12 h; (c) K_2CO_3, 24 °C, 8 h; (d) $(PPh_3)_2PdCl_2$, CuI, piperidine, THF, 24 °C, 12 h; (e) tetrabutylammonium fluoride, THF, 24 °C, 1 h; (f) $Cu(OAc)_2$, CH_3CN, 80 °C, 8 h.



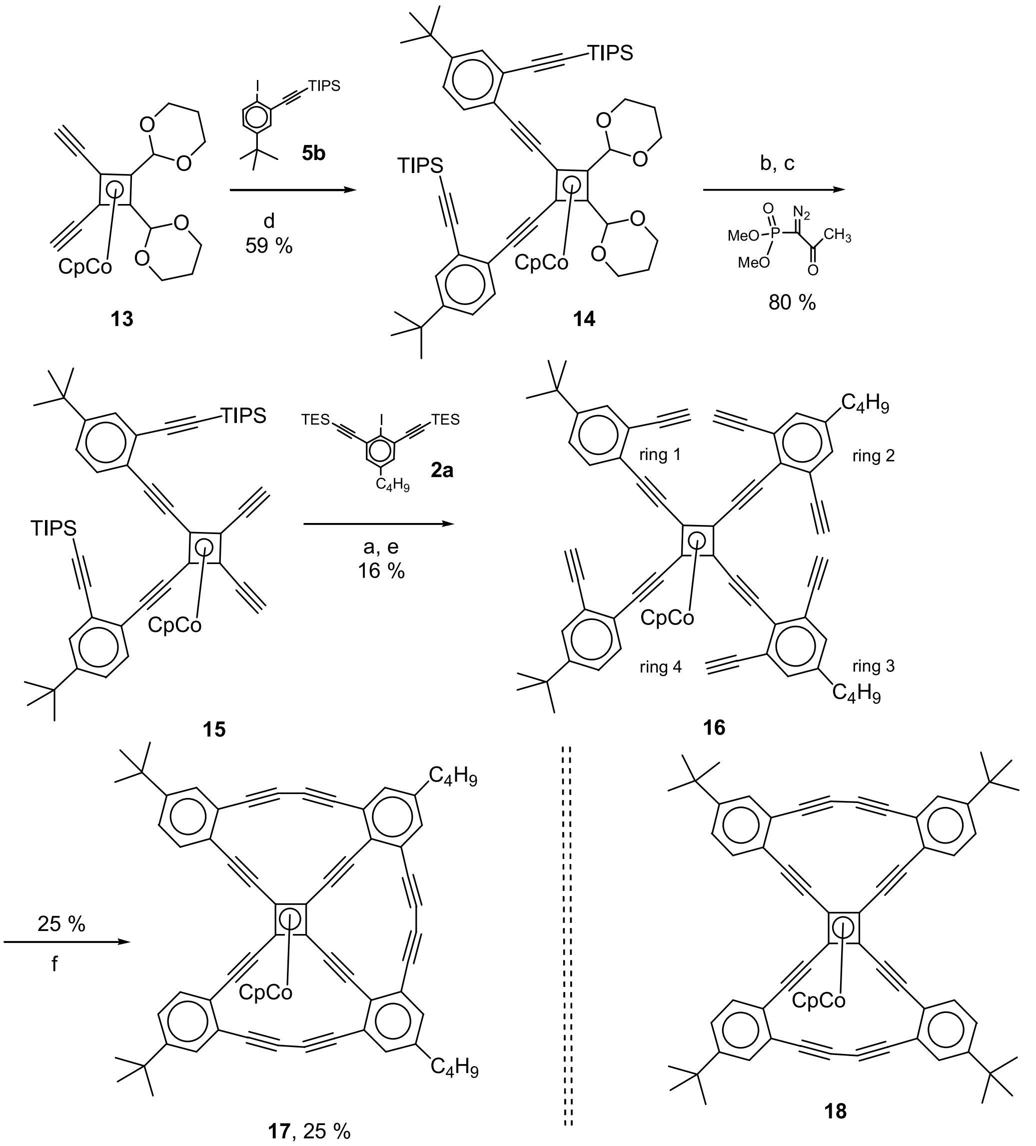
Scheme 2. (a) (o-tolyl$_3$P)$_2$PdCl$_2$, CuI, NEt$_3$, THF, 24 °C, 12 h; (b) *para*-toluenesulfonic acid, THF, 24 °C, 12 h; (c) K$_2$CO$_3$, 24 °C, 8 h; (d) (PPh$_3$)$_2$PdCl$_2$, CuI, piperidine, THF, 24 °C, 12 h; (e) tetrabutylammonium fluoride, THF, 24 °C, 1 h; (f) Cu(OAc)$_2$, CH$_3$CN, 80 °C, 8 h.

proceeds in 25% yield. Significant amounts of insoluble and infusible tan-colored solids are formed as byproducts. The relatively low yield of this transformation is a consequence of the underlying statistics of the ring closing reaction. If in **16** the alkynes of benzene units 1 and 4 couple, **17** cannot form. Instead crosslinking to insoluble materials prevails. If the ring closing reaction proceeds statistically, it is expected to lose 33% of **16** to the unwanted cyclizations, i.e. the highest possible reaction yield is 67%. The actual yield of 25% suggests that each ring forms in a satisfactory yield of 72%, if the unproductive coupling paths are corrected for by a simple statistical analysis.

It was interesting to see if the concept could be expanded to a larger ferrocene containing half wheel. In Scheme 4, the synthesis of such a half wheel is shown. Starting from **8** Cadiot–Chodeiewicz coupling to **19** furnished **20** in 46% yield. Deketalization is followed by an Ohira reaction to give the alkyne **21** in 58%, which in a second Cadiot–Chodkiewicz coupling with **22** is transformed into the decayne **23** in a yield of 24%. Deprotection with tetrabutylammoniumfluoride is followed by a Vögtle coupling [17] utilizing Cu(OAc)$_2$ in acetonitrile to furnish the doubly closed and enlarged half wheel **24** in 18% yield as orange, sensitive solid that was characterized by its NMR data. Attempts to obtain single crystalline specimens of **24** were not successful. Instead microcrystalline powders resulted.

The novel and intriguing structures of the organometallic super-bicyclo[1.1.0]butanes **7**, **12**, and the super-tricyclo[2.1.0.0^{1,3}]pentane **17** mandated their single crystal structure analysis. Suitable, coffin-shaped specimens were obtained from mixtures of dichloromethane and hexanes.

ORTEP-representations of **7**, **12** and **17**, and packing diagrams of **12** and **17** are shown in Figs. 1–6. The bond lengths and bond angles of **7**, **12** and **17** are in excellent agreement with reported values for alkynylated cyclobutadiene and cyclopentadienyl complexes [14,20]. The polyyne **7** forms a perfect half-wheel. The three radial alkyne units attached to the cyclobutadiene complex are linear. The butadiyne groupings are moderately bent to accommodate the topological necessities of the structure (Fig. 1). The surrounding of the cyclobutadiene complex is considerably less non-planar than expected for multiply ethynylated complexes of this type, [14,20] and this

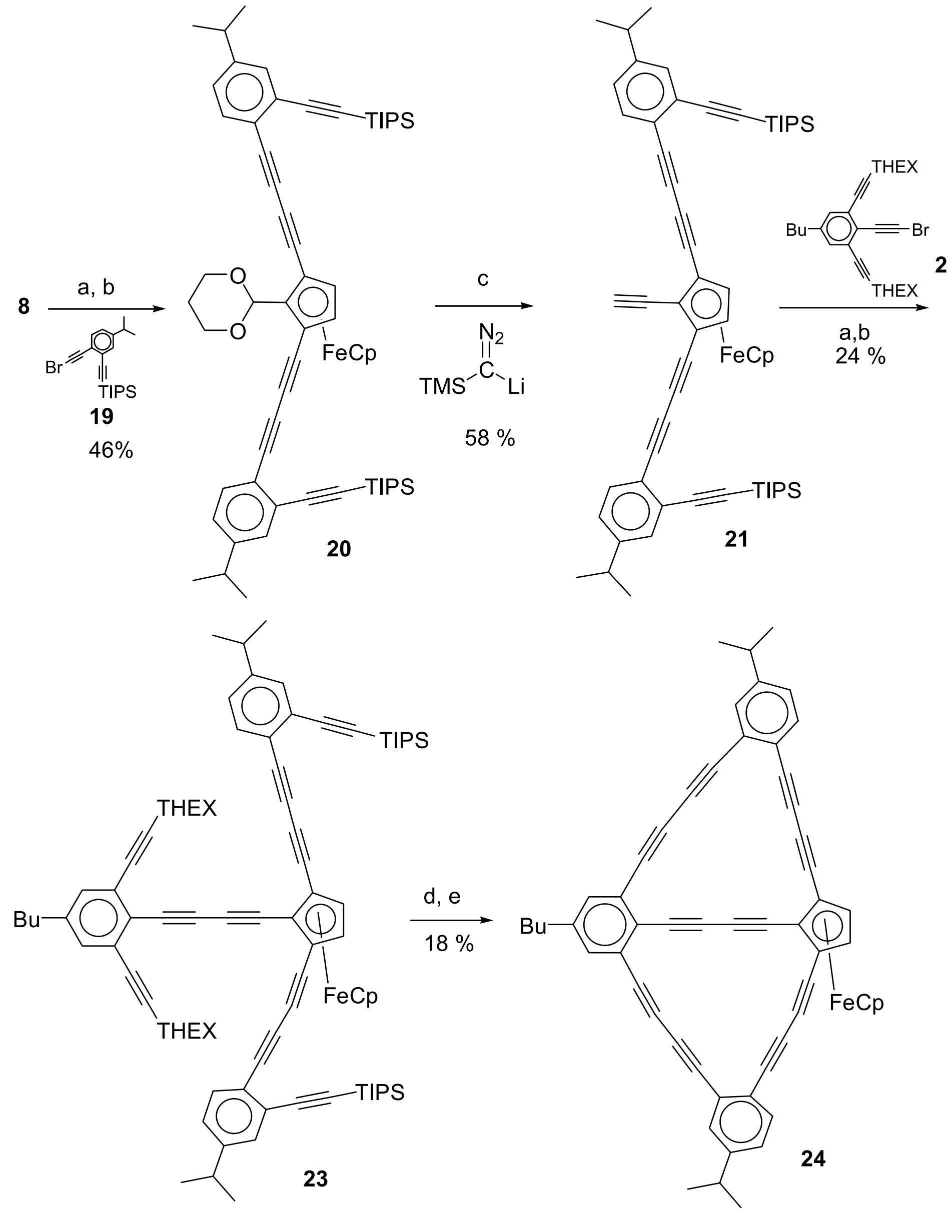


Scheme 3. (a) (o-tolyl$_3$P)$_2$PdCl$_2$, CuI, NEt$_3$, THF, 24 °C, 12 h; (b) *para*-toluenesulfonic acid, THF, 24 °C, 12 h; (c) K$_2$CO$_3$, 24 °C, 8 h; (d) (PPh$_3$)$_2$PdCl$_2$, CuI, piperidine, THF, 24 °C, 12 h; (e) tetrabutylammonium fluoride, THF, 24 °C, 1 h; (f) Cu(OAc)$_2$, CH$_3$CN, 80 °C, 8 h.

effect may be a consequence of the direct interconnection of the three alkyne substituents by a network of cyclyne rings.

The ferrocene-based cyclyne **12** (Fig. 2) experiences significant in-plane bending of the outer two of the three radial alkyne units, leading to a slight ruffling of the large hydrocarbon ligand (Fig. 2a), similar to that observed in some porphyrins [21]. This ruffling is caused by the minor mismatch of the circumference of the perimeter compared with the size of the radial spokes. It bears testimony to the adaptation of the outer π-perimeter to the decreased bond angles (72°) prevalent in the ferrocene module when compared with the square cyclobutadiene complexes. The packing of **12** is remarkable and shown in Fig. 3. Six molecules form a circular triple helical arrangement that results in a fascinating superstructure not observed in the packing of **7**.

The structure of the open congeners of **17**, the butterfly **18**, has recently been described [14]. In these species the alkyne bridges are bent away from the cyclobutadiene nucleus to accommodate for the electronic influence of the cyclopentadienylcobalt fragment. It was of interest if in the polyyne **17** the same distortion was visible. A suitable specimen was obtained from dichloromethane–hexane mixtures and an ORTEP representation of **17** is shown in Fig. 4. The molecules of **17** are disordered in the crystal, but the large hydrocarbon ligand is flattened out (Fig. 5) when compared with the structure of the butterfly **18** [14g]. The flattening is particularly pronounced in the backside of the large ligand, where the third ring is closed. The full wheel of the topology **D** is expected to be planar, *due to the geometric relationship of the perimeter to the length of the radial spikes*.



Scheme 4. (a) BuLi, then CuI 15 min; (b) propylamine, **19**, 22 °C, 1 h; (c) TsOH, 1 h 22 °C; (d) tetrabutylammonium fluoride, THF, 24 °C, 1 h; (e) $Cu(OAc)_2$, CH_3CN, 80 °C, 8 h.

The packing of the seco-wheel **17** is similar to that of **18** insofar as both **17** and **18** are stacked parallel to each other. However, Fig. 6 shows that stacks of the molecules of **17** are oriented in a herringbone pattern with respect to each other, making that packing motif similar to structures observed for aromatic molecules. The cyclopentadienylcobalt units are tucked into the interlayer space of the columns. We investigated (Fig. 7) the molecular structure of the compound **24** by semi-empirical calculations (PM3 tm, implemented by wavefunction's SPARTAN on a Windows 2000 platform). The structure is virtually unstrained and the bond lengths and bond angles are in excellent agreement with values obtained from crystal structures of simpler model compounds [14]. The large hydrocarbon ligand is flat and the cyclopentadienyl ring in the ferrocene accommodates the bicyclic structure without any appreciable strain.

In conclusion, a series of novel polycyclic carbon-rich organometallics (**7**, **12**, **17** and **24**) has been prepared by a combination of Ohira-alkynylations, Pd–Cu catalyzed couplings, and $Cu(OAc)_2$-mediated cyclizations. The targets represent nanoscale versions of **A** and **B**; they have been subjected to single crystal structure determination and show subtle differences in their structures depending upon the central organometallic core. In

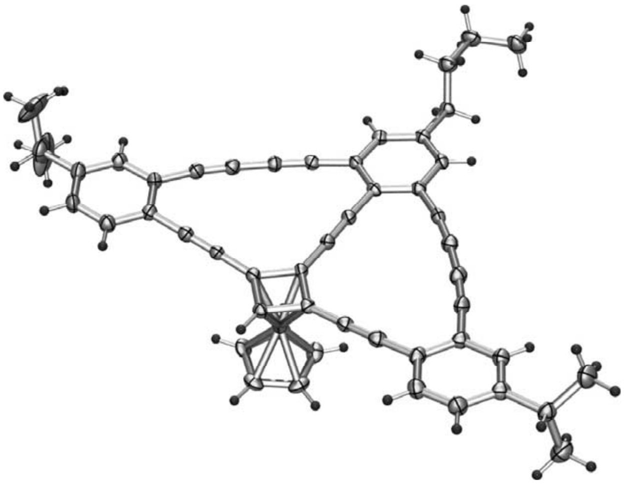


Fig. 1. ORTEP representation of the molecular structure of **7**.

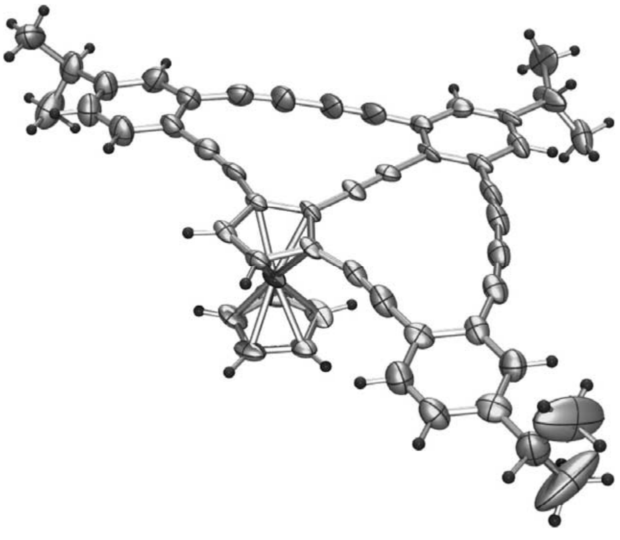


Fig. 2. ORTEP representation of **12**.

future we will report the synthesis and characterization of a full wheel with a nanoscale-topology of the unknown fenestrane-type **C** [22,23].

3. Experimental

3.1. Synthesis of 3

A 50 ml, oven-dried Schlenk flask was charged with **1** (410 mg, 1.10 mmol), [14c] CuI (12.0 mg, 0.062 mmol), Pd(P(*o*-tol)$_3$)$_2$ (50.0 mg, 0.067 mmol), 4-iodo-3,5-(triisopropylsilylethynyl)butylbenzene (**2a**) (800 mg, 1.28 mmol), and abs. THF (3 ml). The flask was flushed with nitrogen and degassed Et$_3$N (5 ml) was added. The resulting solution was stirred at ambient temperature for 12 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 was removed in vacuo. Column chromatography (SiO$_2$–hexanes + 10% NEt$_3$) furnished **3** (223 mg, 23%) as an orange, oily solid. IR (cm^{-1}): ν 2939, 2862, 2315, 2146, 1446, 1123, 992. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.20 (s, 2H, aromatic-H), 5.02 (s, 5H, Cp-H), 5.01 (s, 2H, CH-acetal), 4.08 (s, 1H, Cb-H), 4.14–4.03 (m, 4H, CH$_2$-acetal), 3.82–3.65 (m, 4H, CH$_2$-acetal), 2.50 (t, 2H, $^3J_{H,H} = 7.69$ Hz, butyl-CH$_2$), 2.08–2.00 (m, 2H, CH$_2$-acetal), 1.59–2.49 (m, 2H, butyl-CH$_2$), 1.36–1.24 (m, 2H, CH$_2$-acetal), 1.24–1.15 (m, 2H, butyl-CH$_2$), 1.13 (s, 42H, TIPS-H), 0.91 (t, 3H, $^3J_{H,H} = 7.69$ Hz, butyl-CH$_3$). ^{13}C-NMR (75 MHz, CDCl$_3$): δ 141.90, 133.65, 126.24, 124.94 (aromatic-C), 106.31 (alkyne-C), 97.87 (acetal-CH), 94.72, 92.39, 87.59 (alkyne-C), 81.36 (Cp-C), 76.75 (Cb-C), 66.85 (acetal-CH$_2$), 55.36, 52.65 (Cb-C), 34.96, 33.07 (butyl-CH$_2$), 25.86 (acetal-CH$_2$), 22.25 (butyl-CH$_2$), 18.84 (TIPS-CH$_3$), 13.84 (butyl-CH$_3$), 11.40 (TIPS-CH). MS (EI) *m*/*z* Calc. for [M]$^+$ (C$_{52}$H$_{77}$CoO$_4$Si$_2$) 880.4692. Found 880.4685 ($E = 1.2$ ppm).

3.2. Synthesis of 4

A 50 ml round bottom flask was charged with **3** (100 mg, 0.122 mmol), TsOH (110 mg, 0.581 mmol) and wet THF (5 ml). The resulting solution was stirred at ambient temperature for 12 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 was removed in vacuo to yield a dark red oil. To the oil in a 50 ml Schlenk flask was added K$_2$CO$_3$ (110 mg, 0.800 mmol), abs. THF (5 ml) and abs. methanol (5 ml) under nitrogen. After cooling to 0 °C, dimethyl-(1-diazo-2-oxopropyl)phosphonate (110 mg, 0.568 mmol) was added dropwise over 5 min. The resulting solution was allowed to stir for 8 h before being quenched with a saturated NaHCO$_3$ solution (50 ml) and CH$_2$Cl$_2$. The water layer was separated and extracted with CH$_2$Cl$_2$ (50 ml). The combined organic layers were dried over MgSO$_4$ and the solvent was removed in vacuo. Column chromatography (SiO$_2$–hexanes:CH$_2$Cl$_2$, 9:1) furnished **4** (71.0 mg, 81%) as a dark–orange oil. IR (cm^{-1}): ν 2915, 2861, 2323, 2146, 1692, 1453, 1000. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.23 (s, 2H, aromatic-H), 5.01 (s, 5H, Cp-H), 4.47 (s, 1H, Cb-H), 3.01 (s, 2H, alkyne-H), 2.52 (t, 2H, $^3J_{H,H} = 7.69$ Hz, butyl-CH$_2$), 1.59–1.52 (m, 2H, butyl-CH$_2$), 1.22–1.16 (m, 2H, butyl-CH$_2$), 1.13 (s, 42H, TIPS-H), 0.92 (t, 3H, $^3J_{H,H} = 7.69$ Hz, butyl-CH$_3$). ^{13}C-NMR (75 MHz, CDCl$_3$): δ 142.65, 133.39, 126.41, 124.41 (aromatic-C), 105.63, 95.39, 90.48, 90.35 (alkyne-C), 82.87 (Cp-C), 79.69, 79.62 (alkyne-C), 64.28, 61.95, 56.68 (Cb-C), 35.08, 33.08, 22.31 (butyl-CH$_2$), 13.36 (butyl-CH$_3$), 18.86 (TIPS-CH$_3$), 11.36 (TIPS-CH). MS

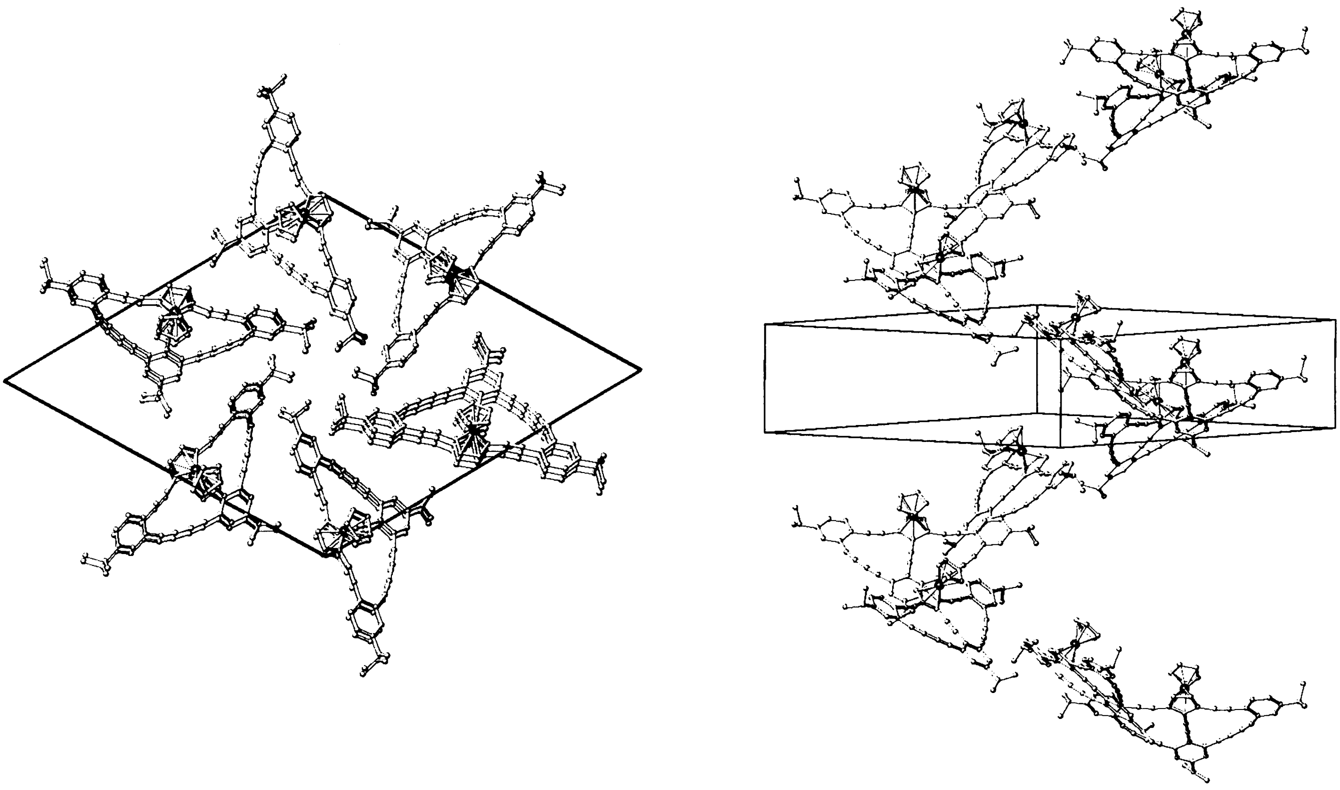


Fig. 3. Packing diagram of **12**. Visible is the 6-fold axis in that the single molecules of **12** are packed in the solid state.

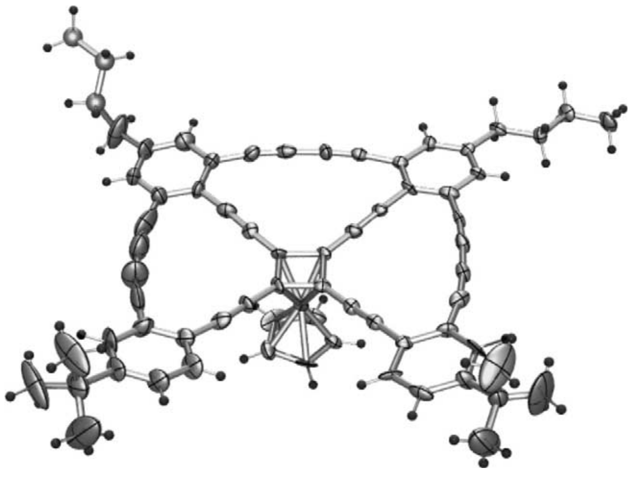


Fig. 4. ORTEP representation of **17**.

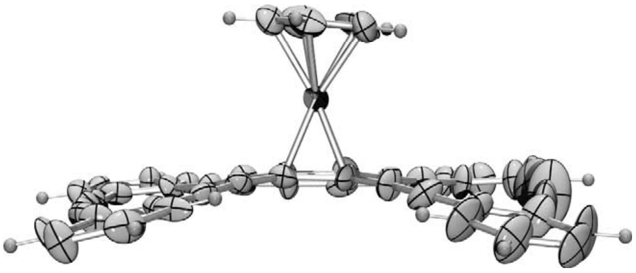


Fig. 5. ORTEP representation of **17**, side view. Substituents are removed for clarity.

(EI) m/z Calc. for $[M]^+$ ($C_{47}H_{61}CoSi_2$) 740.3644. Found 740.3673 ($E = 3.7$ ppm).

3.3. Synthesis of 6

A 50 ml, oven-dried Schlenk flask was charged with **4** (71.0 mg, 0.100 mmol), CuI (0.9 mg, 0.005 mmol), $Cl_2Pd(PPh_3)_2$ (1.0 mg, 0.001 mmol), 4-iodo-3-(trimethylsilylethynyl)isopropylbenzene [2] (**5a**) (100 mg, 0.290 mmol), and abs. THF (2 ml). The flask was flushed with nitrogen and degassed piperidine (5 ml) was added. The resulting solution was stirred at ambient temperature for 12 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. Column chromatography (SiO_2–hexanes:CH_2Cl_2, 4:1) furnished **6** (78.0 mg, 70%) as a dark orange oil. IR (cm^{-1}): ν 2946, 2861, 2315, 2153, 1646, 1538, 1246, 1000. ^1H-NMR (300 MHz, $CDCl_3$): δ 7.32 (d, 2H, $^3J_{H,H} = 8.23$ Hz, aromatic-H), 7.27 (d, 2H, $^4J_{H,H} = 1.37$ Hz, aromatic-H), 7.24 (s, 2H, aromatic-H), 7.04 (dd, 2H, $^3J_{H,H} = 8.23$ Hz, $^4J_{H,H} = 1.37$ Hz, aromatic-H), 5.03 (s, 5H, Cp-H), 4.59 (s, 1H, Cb-H), 2.86–2.77 (m, 2H,

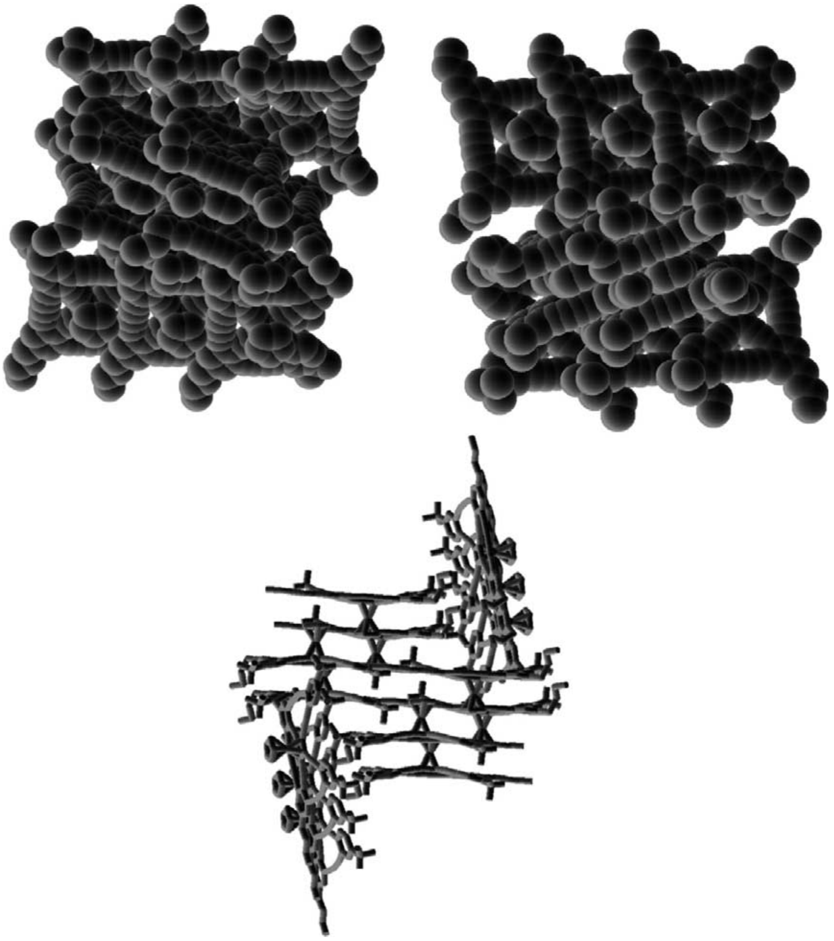


Fig. 6. Packing diagram of **17** in the solid state.

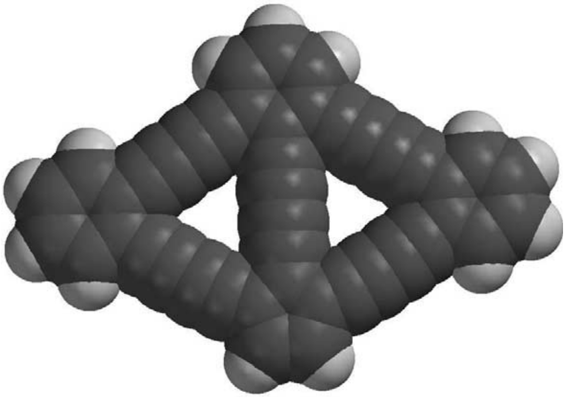


Fig. 7. Semiempirical calculation (PM3) of the structure of **24**. The large hydrocarbon ligand is perfectly planar and the bond distances and bond angles show the expected values.

isopropyl-CH), 2.53 (t, 2H, $^3J_{H,H} = 7.69$ Hz, butyl-CH_2), 1.61–1.53 (m, 2H, butyl-CH_2), 1.40–1.32 (m, 2H, butyl-CH_2), 1.19 (d, 12H, $^3J_{H,H} = 6.86$ Hz, isopropyl-CH_3), 1.05 (s, 42H, TIPS-H), 0.91 (t, 3H, $^3J_{H,H} = 7.69$ Hz, butyl-CH_3), 0.24 (s, 18H, TMS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 148.54, 142.65, 133.55, 131.93, 130.39, 126.86, 126.78, 125.14, 124.76, 124.46 (aromatic-C), 105.88, 104.33, 97.79, 95.57, 91.91, 90.84, 90.42, 89.03 (alkyne-C), 83.03 (Cp-C), 64.84, 62.04, 58.98 (Cb-C), 35.33 (butyl-CH_2), 34.17 (isopropyl-C), 33.38 (butyl-CH_2), 23.83 (isopropyl-C), 22.56 (butyl-CH_2), 19.04 (TIPS-CH_3), 14.13 (butyl-CH_3), 11.62 (TIPS-CH), 0.37 (TMS-C). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{75}H_{97}CoSi_4$) 1168.6. Found 1168.5.

3.4. Synthesis of 7

A 50 ml, round bottom flask was charged with **6** (78.0 mg, 0.071 mmol), $Bu_4N^+F^-$ (0.35 ml, 1.0 M in THF) and THF (2 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 was removed in vacuo to yield a dark red oil. To the oil, in a 100 ml round bottom flask, was added $Cu(OAc)_2$ (300 mg, 1.65 mmol) and MeCN (50 ml). The resulting solution was heated to 80 °C for 8 h. The solvent was removed in vacuo, the resulting mixture redissolved in

CH_2Cl_2 and filtered through a silica gel plug. Following removal of the solvent in vacuo and column chromatography (SiO_2–hexanes:CH_2Cl_2, 1:1), **7** (32.0 mg, 71%) was isolated as dark orange crystals. M.p.: 170 °C (dec.), black at 220 °C. IR (cm^{-1}): ν 2955, 2917, 2848, 2317, 1625, 1555, 1455. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.48 (d, 2H, $^{3}J_{H,H} = 8.06$ Hz, aromatic-H), 7.36–7.34 (m, 4H, aromatic-H), 7.22 (dd, 2H, $^{3}J_{H,H} = 8.06$ Hz, $^{4}J_{H,H} = 1.65$ Hz, aromatic-H), 4.96 (s, 5H, Cp-H), 4.80 (s, 1H, Cb-H), 2.87 (qt, 2H, $^{3}J_{H,H} = 6.78$ Hz, isopropyl-CH), 2.58 (t, 2H, $^{3}J_{H,H} = 7.69$ Hz, butyl-CH_2), 1.64–1.53 (m, 2H, butyl-CH_2), 1.40–1.27 (m, 2H, butyl-CH_2), 1.24 (d, 12H, $^{3}J_{H,H} = 6.78$ Hz, isopropyl-CH_3), 0.93 (t, 3H, $^{3}J_{H,H} = 7.69$ Hz, butyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 148.43, 141.98, 132.57, 130.71, 130.39, 128.27, 127.57, 127.01, 123.56, 123.25 (aromatic-C), 94.77, 90.96, 90.66, 90.08, 84.55, 83.44 (alkyne-C), 82.60 (Cp-C), 79.70, 78.73 (alkyne-C), 65.62, 61.82, 59.57 (Cb-C), 35.30 (butyl-CH_2), 34.02 (isopropyl-CH), 33.02, 29.70 (butyl-CH_2), 23.59 (isopropyl-CH_3), 14.12 (butyl-CH_3). UV–vis ($CHCl_3$): λ 294 ($\varepsilon = 21\,816$ cm^{-1} M^{-1}), 324 ($\varepsilon = 24\,702$ cm^{-1} M^{-1}). MS (EI) *m*/*z* Calc. for $[M]^+$ ($C_{51}H_{37}Co$) 708.2. Found 708.2.

3.5. Synthesis of **9**

A 50 ml, oven-dried Schlenk flask was charged with **8** (1.00 g, 3.12 mmol), CuI (30.0 mg, 0.158 mmol), $Cl_2Pd(PPh_3)_2$ (44.0 mg, 0.062 mmol), **5a** (2.53 g, 5.94 mmol), and abs. THF (4 ml). The flask was flushed with nitrogen and degassed piperidine (6 ml) was added. The resulting solution stirred at ambient temperature for 12 h before being quenched with water and ethyl ether. The water layer was separated and extracted with ethyl ether (100 ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. Column chromatography (SiO_2–hexanes + 10% NEt_3) furnished **9** (2.25 g, 79%) as an orange oil. IR (cm^{-1}): ν 2954, 2861, 2207, 2146, 1453, 1239, 1146, 1100. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.40 (d, 2H, $^{3}J_{H,H} = 7.96$ Hz, aromatic-H), 7.32 (d, 2H, $^{4}J_{H,H} = 1.92$ Hz, aromatic-H), 7.11 (dd, 2H, $^{3}J_{H,H} = 7.96$ Hz, $^{4}J_{H,H} = 1.92$ Hz, aromatic-H), 5.68 (s, 1H, acetal-CH), 4.51 (s, 2H, Cp-sub. ring), 4.31 (s, 5H, Cp-unsub. ring), 4.31–4.21 (m, 2H, acetal-CH_2), 4.00–3.92 (m, 2H, acetal-CH_2), 2.85 (qt, 2H, $^{3}J_{H,H} = 6.86$ Hz, isopropyl-CH), 2.25–2.15 (m, 1H, acetal-CH_2), 1.38 (m, 1H, acetal-CH_2), 1.20 (d, 12H, $^{3}J_{H,H} = 6.86$ Hz, isopropyl CH_3), 1.12 (s, 42H, TIPS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.18, 132.10, 130.47, 126.61, 124.43, 124.14 (aromatic-C), 104.26, 99.56 (alkyne-C), 97.22 (acetal-CH), 89.74, 88.14 (alkyne-C), 86.76 (acetal-CH_2), 72.86 (Cp-C, unsub. ring), 71.66, 67.45, 65.60 (Cp-C, sub. ring), 33.79 (isopropyl-CH), 25.91 (acetal-CH_2), 23.56 (isopropyl-CH_3), 18.86 (TIPS-CH_3), 11.38 (TIPS-CH). MS (EI) *m*/*z* Calc. for $[M]^+$ ($C_{58}H_{76}FeO_2Si_2$) 916.4733. Found 916.4728 ($E = 3.1$ ppm).

3.6. Synthesis of **10**

A 50 ml round bottom flask was charged with **9** (2.02 g, 2.20 mmol), TsOH (1.50 g, 7.89 mmol) and wet THF (10 ml). The resulting solution was stirred at ambient temperature for 12 h before being quenched with water and ethyl ether. The water layer was separated and extracted with ethyl ether (250 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo to yield a dark red oil. To the oil in a 100 ml Schlenk flask was added K_2CO_3 (880 mg, 6.38 mmol), abs. THF (15 ml) and abs. methanol (15 ml) under nitrogen. After cooling to 0 °C, dimethyl-(1-diazo-2-oxopropyl)phosphonate (1.23 g, 6.40 mmol) was added dropwise over 5 min. The resulting solution is allowed to stir for 8 h before being quenched with a saturated $NaHCO_3$ solution (100 ml) and CH_2Cl_2. The water layer was separated and extracted with CH_2Cl_2 (75 ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. Column chromatography (SiO_2–hexanes:CH_2Cl_2, 9:1) furnished **10** (1.50 g, 80%) as a red oil. IR (cm^{-1}): ν 2953, 2861, 2323, 2207, 2146, 1453, 1100. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.47 (d, 2H, $^{3}J_{H,H} = 7.96$ Hz, aromatic-H), 7.32 (d, 2H, $^{4}J_{H,H} = 1.92$ Hz, aromatic-H), 7.15 (dd, 2H, $^{3}J_{H,H} = 7.96$ Hz, $^{4}J_{H,H} = 1.92$ Hz, aromatic-H), 4.52 (s, 2H, Cp-sub. ring), 4.29 (s, 5H, Cp-unsub. ring), 3.07 (s, 1H, alkyne-H), 2.86 (qt, 2H, $^{3}J_{H,H} = 6.86$ Hz, isopropyl-CH), 1.22 (d, 12H, $^{3}J_{H,H} = 6.86$ Hz, isopropyl-CH_3), 1.14 (s, 42H, TIPS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.47, 133.05, 130.51, 126.66, 124.65, 123.63 (aromatic-C), 106.04, 93.74, 88.93, 88.76, 81.86, 77.52 (alkyne-C), 74.02 (Cp-C, unsub. ring), 71.54, 70.82, 70.34 (Cp-C, sub. ring), 33.85 (isopropyl-CH), 23.58 (isopropyl-CH_3), 18.86 (TIPS-CH_3), 11.38 (TIPS-CH). MS (EI) *m*/*z* Calc. for $[M]^+$ ($C_{56}H_{70}FeSi_2$) 854.4. Found 854.3.

3.7. Synthesis of **11**

A 50 ml, oven-dried Schlenk flask was charged with **10** (87.0 mg, 0.102 mmol), CuI (2.2 mg, 0.012 mmol), $Pd(P(o\text{-tol})_3)_2$ (4.1 mg, 0.006 mmol), 4-iodo-3,5-(triethylsilylethynyl)isopropylbenzene [2] (**2b**) (80.0 mg, 0.150 mmol), and abs. THF (3 ml). The flask was flushed with nitrogen and degassed Et_3N (2 ml) added. The resulting solution stirred at ambient temperature for 12 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 was removed in vacuo. Column chromatography (SiO_2–hexanes:CH_2Cl_2, 9:1) furnished **11** (29 mg, 24%) as a dark red–orange oil. IR (cm^{-1}): ν 2961, 2869, 2323, 2146, 1646, 1464, 1230, 992.

^{1}H-NMR (300 MHz, $CDCl_3$): 7.47 (d, 2H, $^3J_{H,H} = 8.23$ Hz, aromatic-H), 7.35 (s, 2H, aromatic-H), 7.27 (d, 2H, $^4J_{H,H} = 1.37$ Hz, aromatic-H), 7.04 (dd, 2H, $^3J_{H,H} = 8.23$ Hz, $^4J_{H,H} = 1.37$ Hz, aromatic-H), 4.54 (s, 2H, Cp-sub. ring), 4.32 (s, 5H, Cp-unsub. ring), 2.84 (m, 3H, isopropyl-CH), 1.26 (d, 12H, $^3J_{H,H} = 6.86$ Hz, isopropyl-CH_3), 1.22 (d, 6H, $^3J_{H,H} = 6.86$ Hz, isopropyl-CH_3), 1.18 (s, 42H, TIPS-H), 0.96 (m, 18H, TES-CH_3), 0.85 (m, 12H, TES-CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.04, 147.96, 133.64, 131.43, 131.22, 130.50, 126.35, 125.53, 124.32, 124.13 (aromatic-C), 106.23, 104.86, 96.16, 93.31, 92.99, 89.75, 88.42, 88.05 (alkyne-C), 74.07 (Cp-C, unsub. ring), 72.50, 71.09, 69.54 (Cp-C, sub. ring), 33.91, 33.78 (isopropyl-CH), 23.64, 23.58 (isopropyl-CH_3), 18.87 (TIPS-CH_3), 11.40 (TIPS-CH), 7.53 (TES-CH_3), 4.30 (TES-CH_2). MS (EI) *m*/*z* Calc. for $[M]^+$ ($C_{81}H_{108}FeSi_4$) 1248.7. Found 1248.8.

3.8. Synthesis of **12**

A 50 ml, round bottom flask was charged with **11** (125 mg, 0.100 mmol), $Bu_4N^+F^-$ (0.500 ml, 1.0 M in THF) and THF (2 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 250 ml round bottom flask, was added $Cu(OAc)_2$ (400 mg, 2.21 mmol) and MeCN (100 ml). The resulting solution was heated to 80 °C for 6 h. The solvent was removed in vacuo, the resulting mixture was dissolved in CH_2Cl_2 and filtered through a silica gel plug. Following removal of the solvent in vacuo and column chromatography (SiO_2–hexanes:CH_2Cl_2, 1:1), **12** (44.0 mg, 63%) is isolated as dark red–orange needles. M.p.: 220 °C (turned dark). IR (cm^{-1}): ν 2954, 2923, 2869, 2323, 2196, 1730, 1538, 1453, 1061. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.61 (d, 2H, $^3J_{H,H} = 7.96$ Hz, aromatic-H), 7.47 (s, 2H, aromatic-H), 7.32 (d, 2H, $^4J_{H,H} = 1.37$ Hz, aromatic-H), 7.26 (dd, 2H, $^3J_{H,H} = 8.23$ Hz, $^4J_{H,H} = 1.37$ Hz, aromatic-H), 4.96 (s, 2H, Cp-sub. ring), 4.26 (s, 5H, Cp-unsub. ring), 2.96–2.87 (m, 3H, isopropyl-CH), 1.29–1.21 (m, 18H, isopropyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.43, 147.77, 132.12, 130.45, 129.51, 128.79, 127.37, 126.56, 123.91, 122.44 (aromatic-C), 94.23, 92.11, 89.42, 87.31, 86.02, 84.96, 81.49, 78.14 (alkyne-C), 77.10 (Cp-C, sub. ring), 73.95 (Cp-C, unsub. ring), 73.89, 70.21 (Cp-C, sub. ring), 33.98, 33.74 (isopropyl-CH), 23.66, 23.51 (isopropyl-CH_3). UV–vis ($CHCl_3$): λ 312 ($\varepsilon = 62094$ cm^{-1} M^{-1}). MS (EI) *m*/*z* Calc. for $[M]^+$ ($C_{51}H_{36}Fe$) 704.2166. Found 704.2149 ($E = 2.4$ ppm).

3.9. Synthesis of **14**

A 50 ml, oven-dried Schlenk flask was charged with **13** [1] (428 mg, 1.08 mmol), CuI (10.0 mg, 0.053 mmol), $Cl_2Pd(PPh_3)_2$ (15.0 mg, 0.021 mmol), 4-iodo-3-(triisopropylsilylethynyl)-*tert*-butylbenzene (**5b**) (1.19 g, 2.70 mmol), and abs. THF (5 ml). The flask was flushed with nitrogen and degassed piperidine (6 ml) was added. The resulting solution was stirred at ambient temperature for 12 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. Column chromatography (SiO_2–hexanes + 10% NEt_3) furnished **14** (650 mg, 59%) as an orange oil. IR (cm^{-1}): ν 2954, 2864, 2149, 1464, 1237, 1106, 1005. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.41 (d, 2H, $^4J_{H,H} = 1.92$ Hz, aromatic-H), 7.37 (d, 2H, $^3J_{H,H} = 8.23$ Hz, aromatic-H), 7.22 (dd, 2H, $^3J_{H,H} = 8.23$ Hz, $^4J_{H,H} = 1.92$ Hz, aromatic-H), 5.20 (s, 2H, acetal-CH), 4.99 (s, 5H, Cp-H), 4.16–4.12 (m, 4H, acetal-CH_2), 3.83–3.78 (m, 4H, acetal-CH_2), 2.05–1.97 (m, 2H, acetal-CH_2), 1.38–1.34 (m, 2H, acetal-CH_2), 1.27 (s, 18H, *t*-butyl-CH_3), 1.08 (s, 42H, TIPS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 150.17, 132.64, 129.60, 125.06, 124.11, 123.97 (aromatic-C), 106.21 (alkyne-C), 97.89 (acetal-CH), 93.56, 91.23, 88.24 (alkyne-C), 82.29 (Cp-C), 76.86 (Cb-C), 66.45 (acetal-CH_2), 56.19 (Cb-C), 34.39 (*t*-butyl-C), 30.84 (*t*-butyl-CH_3), 25.83 (acetal-CH_2), 18.67 (TIPS-CH_3), 11.20 (TIPS-CH). MS (EI) *m*/*z* Calc. for $[M]^+$ ($C_{63}H_{85}CoO_4Si_2$) 1020.5318. Found 1020.5346.

3.10. Synthesis of **15**

A 50 ml round bottom flask was charged with **14** (650 mg, 0.640 mmol), TsOH (240 mg, 1.26 mmol) and THF (10 ml). The resulting solution was stirred at ambient temperature for 12 h before being quenched with water and ethyl ether. The water layer was separated and extracted with ethyl ether (100 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 Schlenk flask, was added K_2CO_3 (560 mg, 4.06 mmol), abs. THF (10 ml) and abs. methanol (10 ml) under nitrogen. After cooling to 0 °C, dimethyl-(1-diazo-2-oxopropyl)phosphonate [4] (560 mg, 2.92 mmol) was added dropwise over 5 min. The resulting solution was allowed to stir for 18 h before being quenched with a saturated $NaHCO_3$ solution (50 ml) and CH_2Cl_2. The water layer was separated and extracted with CH_2Cl_2 (100 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 **15** (450 mg, 80%) as a dark orange oil. IR (cm^{-1}): ν 2957, 2858, 2153, 1462, 1385, 1258, 990. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.43

(d, 2H, $^4J_{H,H} = 1.92$ Hz, aromatic-H), 7.40 (d, 2H, $^3J_{H,H} = 8.23$ Hz, aromatic-H), 7.25 (dd, 2H, $^3J_{H,H} = 8.23$ Hz, $^4J_{H,H} = 1.92$ Hz, aromatic-H), 5.00 (s, 5H, Cp-H), 3.25 (s, 2H, alkyne-H), 1.29 (s, 18H, *t*-butyl-CH_3), 1.09 (s, 42H, TIPS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 151.13, 132.44, 129.63, 125.27, 124.82, 123.05 (aromatic-C), 105.75, 94.39, 92.60, 86.25, (alkyne-C), 83.80 (Cp-C), 81.72, 77.69 (alkyne-C), 61.31, 59.82 (Cb-C), 34.59 (*t*-butyl-C), 30.91 (*t*-butyl-CH_3), 18.79 (TIPS-CH_3), 11.24 (TIPS-CH). MS (EI) *m*/*z* Calc. for $[M]^+$ ($C_{59}H_{73}CoSi_2$) 896.4583. Found 896.4577 ($E = 2.6$ ppm).

3.11. Synthesis of **16**

A 50 ml, oven-dried Schlenk flask was charged with **15** (450 mg, 0.500 mmol), CuI (11.0 mg, 0.059 mmol), $Pd(P(o\text{-tol})_3)_2$ (21.0 mg, 0.030 mmol), **2a** [2] (700 mg, 1.27 mmol), and abs. THF (7 ml). The flask was flushed with nitrogen and degassed Et_3N (5 ml) was added. The resulting solution was stirred at ambient temperature for 12 h before being quenched with water and ethyl ether. The water layer was separated and extracted with ethyl ether (100 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. Column chromatography (SiO_2–hexanes:CH_2Cl_2, 4:1) furnished **16** (134 mg, 16%) as a dark orange oil. IR (cm^{-1}): ν 2953, 2864, 2157, 1462, 1239, 1005. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.40 (m, 4H, aromatic-H), 7.21 (m, 6H, aromatic-H), 5.02 (s, 5H, Cp-H), 2.50 (t, 4H, $^3J_{H,H} = 7.69$ Hz, butyl-CH_2), 1.60–1.49 (m, 4H, butyl-CH_2), 1.28 (s, 18H, *t*-butyl-CH_3), 1.09–0.82 (m, 86H, TIPS-H, TES-CH_3, butyl-CH_2), 0.72–0.50 (m, 24H, TES-CH_2, butyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 150.59, 141.87, 133.11, 133.02, 132.75, 129.62, 128.66, 126.13, 126.09 (aromatic-C), 125.36 (alkyne-C), 125.10, 124.80, 123.74 (aromatic-C), 105.81, 104.51, 96.07, 94.23, 92.52, 91.36, 90.76, 87.31 (alkyne-C), 84.40 (Cp-C), 84.10 (alkyne-C), 62.66, 61.70 (Cb-C), 35.07 (butyl-CH_2), 34.63 (*t*-butyl-C), 33.13 (butyl-CH_2), 30.99 (*t*-butyl-CH_3), 22.25 (butyl-CH_2), 18.69 (TIPS-CH_3), 13.89 (butyl-CH_3), 11.31 (TIPS-CH), 7.52 (TES-CH_2), 4.34 (TES-CH_3). MS (EI) *m*/*z* Calc. for $[M]^+$ ($C_{111}H_{153}CoSi_6$) 1713.0. Found 1712.9.

3.12. Synthesis of **17**

A 50 ml, round bottom flask was charged with **16** (134 mg, 0.080 mmol), Bu_4NF (0.550 ml, 1.0 M in THF) and THF (5 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 was removed in vacuo to yield a dark red oil. To the oil, in a 500 ml round bottom flask, was added $Cu(OAc)_2$ (310 mg, 1.71 mmol) and MeCN (200 ml). The resulting solution 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. Following removal of the solvent in vacuo and column chromatography (SiO_2–hexanes:CH_2Cl_2, 1:1), 17 (18 mg, 25%) was isolated as dark orange crystals. M.p.: 136 °C (turned dark), black at 230 °C. IR (cm^{-1}): ν 2952, 2920, 2852, 2177, 1731, 1458, 1260, 1099, 1018. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67 (d, 2H, $^3J_{H,H} = 8.23$ Hz, aromatic-H), 7.55 (d, 2H, $^4J_{H,H} = 1.92$ Hz, aromatic-H), 7.45 (dd, 2H, $^3J_{H,H} = 8.23$ Hz, $^4J_{H,H} = 1.92$ Hz, aromatic-H), 7.36 (s, 4H, aromatic-H), 4.93 (s, 5H, Cp-H), 2.61 (t, 4H, $^3J_{H,H} = 7.69$ Hz, butyl-CH_2), 1.66–1.56 (m, 4H, butyl-CH_2), 1.34 (s, 18H, *t*-butyl-CH_3), 1.39–1.24 (m, 4H, butyl-CH_2), 0.93 (t, 6H, $^3J_{H,H} = 7.69$ Hz, butyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 151.00, 142.26, 132.26, 130.91, 130.60, 130.49, 127.30, 126.64, 126.47, 123.80, 123.50, 123.10 (aromatic-C), 94.05, 92.64, 91.52, 89.04, 84.78, 83.91 (alkyne-C), 83.78 (Cp-C), 83.27, 79.73, 79.51, 78.73 (alkyne-C), 63.02, 62.08 (Cb-C), 35.31(butyl-CH_2), 34.96 (*t*-butyl-C), 33.01 (butyl-CH_2), 31.03 (*t*-butyl-CH_3), 22.21 (butyl-CH_2), 13.90 (butyl-CH_3). UV–vis ($CHCl_3$): λ 302 ($\varepsilon = 10\,577$ cm^{-1} M^{-1}), 340 ($\varepsilon = 9248$ cm^{-1} M^{-1}). MS (EI) *m*/*z* unable to determine because decomposition occurred before $[M]^+$ could be determined.

3.13. Synthesis of **20**

In a 100 ml, oven-dried Schlenk flask **8** (1.12 g, 3.50 mmol) was dissolved in dry THF (50 ml). Butyllithium (3.85 ml, 2.0 M, 7.70 mmol) was added dropwise at −78 °C. After stirring for 30 min, the mixture was allowed to warm to 0 °C and CuI (3.00 g, 15.8 mmol) was added. Following 15 min of stirring, the mixture was brought to −20 °C, where propylamine (40 ml) and **19** (3.40 g, 8.45 mmol) were added successively and stirring continued at ambient temperature for 1 h. The reaction was quenched with water and extracted with ethyl ether. The organic layers were collected, dried over $MgSO_4$ and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes–CH_2Cl_2, 9:1) furnished **20** (1.55 g, 46%) as a red oil. IR (neat): ν (cm^{-1}) 2941, 2890, 2213, 2150, 1463, 1454, 1097, 996. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.18 (d, 2H, $^3J_{H,H} = 8.0$ Hz, aromatic-H), 7.06 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 6.86 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 5.31 (s, 1H, acetal-CH), 4.29 (s, 2H, sub. Cp-H), 4.10 (s, 5H, Cp-H), 4.09–3.98 (m, 2H, acetal-CH_2), 3.78–3.66 (m, 2H, acetal-CH_2), 2.62 (sept, 2H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH), 2.05–1.98 (m, 1H, acetal-CH_2), 1.18–1.13 (m, 2H, acetal-CH_2), 0.98 (d, 12H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH), 0.93 (s, 42H, TIPS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.59, 132.78, 130.38, 126.74, 126.46, 122.60, 105.18, 98.87, 94.95, 89.83, 79.80, 78.29, 77.96, 73.08, 73.01, 67.59, 64.29, 33.98, 23.53, 18.76, 11.31. MS (EI) *m/z* Calc. for $[M]^+$ ($C_{62}H_{76}FeO_2Si_2$) 964.4733. Found 964.47.4 ($E = 3.0$ ppm).

3.14. Synthesis of **21**

Ketal **20** (1.06 g, 1.10 mmol), TsOH (314 mg, 1.65 mmol), THF (2 ml) and H_2O (3 ml) were placed in a 100 ml round bottom flask. The resulting mixture was stirred for 1 h under the exclusion of light. The mixture was quenched with water and extracted with ethyl ether (100 ml). Removal of the solvent in vacuo and drying in a 100 ml Schlenk flask under vacuum (10^{-1} mbar) yielded a red oil. To a 100 ml oven-dried Schlenk flask was added (trimethylsilyl)diazomethane (2.8 ml, 2.0 M solution in THF) and dry THF (20 ml). After cooling the solution to −78 °C, butyllithium (1.4 ml, 1.65 mmol) was added dropwise. After stirring for 5 min the reaction was warmed to 0 °C and the solution homogenized. The mixture was recooled to −50 °C. To the flask containing the ferrocene starting material was added dry THF (50 ml) under nitrogen. This solution was added slowly to the solution at −50 °C so as to keep the temperature below −40 °C. After the addition, the reaction mixture was stirred for 15 min at −40 °C after which time $NH_4^+Cl^-$ (aqueous, 50 ml) was added. The reaction was brought to ambient temperature. The reaction mixture was extracted twice with ethyl ether and the combined organic layers were dried over $MgSO_4$. The solvent was removed in vacuo. Column chromatography (SiO_2; CH_2Cl_2–hexanes, 4:1) furnished **21** (379 mg, 58%) as a red oil. IR (neat): ν (cm^{-1}) 2959, 2864, 2216, 1491, 1464, 1070, 995. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41 (d, 2H, $^3J_{H,H} = 5.8$ Hz, aromatic-H), 7.31 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.12 (dd, 2H, $^3J_{H,H} = 5.8$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 4.60 (s, 2H, Cp-H sub. ring), 4.35 (s, 2H, Cp-H unsub. ring), 3.01 (s, 1H, alkyne-H), 2.86 (sept, 2H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH), 1.21 (d, 12H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH), 1.18 (s, 42H, TIPS-H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.84, 132.73, 130.39, 126.97, 126.50, 122.37, 105.05, 79.68, 79.07, 79.93, 77.49, 74.29, 73.71, 72.86, 70.09, 71.11, 68.23, 34.02, 23.55, 18.80, 11.34. MS (EI) *m/z* Calc. for $[M]^+$ ($C_{60}H_{70}FeSi_2$) 902.4365. Found 902.4313 ($E = 5.8$ ppm).

3.15. Synthesis of **23**

In a 250 ml, oven-dried Schlenk flask **21** (379 mg, 0.420 mmol) was dissolved in dry THF (50 ml). Butyllithium (0.4 ml, 0.924 mmol) was added dropwise at −78 °C. After stirring for 30 min, the mixture was allowed to warm to 0 °C and CuI (120 mg, 0.632 mmol) was added. Following 15 min of stirring the mixture was brought to −20 °C, where propylamine (15.0 ml) and **22** (810 mg, 1.38 mmol) were added successively. Stirring continued at ambient temperature for 1 h. The reaction was quenched with water and extracted with ethyl ether. The organic layer was collected, dried over $MgSO_4$ and the solvent removed in vacuo. Column chromatography (SiO_2; hexanes–CH_2Cl_2, 4:1) furnished **23** (140 mg, 24%) as a red oil. IR (neat): ν (cm^{-1}) 2957, 2891, 2220, 2154, 1464, 1250, 1071, 999. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39 (d, 2H, $^3J_{H,H} = 5.8$ Hz, aromatic-H), 7.28 (d, 2H, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 7.19 (s, 2H, aromatic-H), 7.09 (dd, 2H, $^3J_{H,H} = 5.8$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 4.64 (s, 2H, Cp-H sub. ring), 4.39 (s, 2H, Cp-H unsub. ring), 2.84 (sept, 2H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH), 2.51 (t, 2H, $^3J_{H,H} = 8.0$ Hz, butyl CH_2), 1.70–1.54 (m, 2H, butyl-CH_2), 1.27–1.19 (m, 4H, isopropyl-CH, butyl-CH_2), 1.15 (s, 42H, TIPS-H), 0.98 (s, 12H, *t*-hexyl-CH_3), 0.96–0.81 (m, 16H, butyl-CH_3, *t*-hexyl-CH, CH_3), 0.25 (s, 12H, *t*-hexyl-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.70, 143.22, 132.64, 131.68, 130.36, 127.31, 127.08, 126.36, 125.26, 122.47, 105.02, 130.46, 99.32, 95.19, 81.79, 79.24, 78.88, 78.28, 77.85, 76.43, 74.20, 73.34, 68.83, 34.69, 32.97, 29.70, 23.55, 23.48, 22.65, 22.28, 20.90, 18.78, 13.88, 11.34.

3.16. Synthesis of **24**

A 50 ml, round bottom flask was charged with **25** (140 mg, 0.100 mmol), $Bu_4N^+F^-$ (0.50 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 (50 ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo to yield a dark red oil. The oil was placed in a 100 ml round bottom flask and reacted with $Cu(OAc)_2$ (400 mg, 2.20 mmol) in CH_3CN (250 ml) at 80 °C for 8 h. Column chromatography (SiO_2; hexanes–EtOAc, 4:1) furnished **24** (14 mg, 18%) as an orange crystalline solid. M.p. > 100 °C (dec.). IR (neat): ν (cm^{-1}) 2940, 2869, 2841, 2223, 2150, 1538, 1453, 1001. ^{1}H-NMR (300 MHz, CD_2Cl_2): 7.50 (s, 2H, aromatic-H), 7.48 (d, 2H, $^3J_{H,H} = 5.8$ Hz, aromatic-H), 7.42 (s, 2H, aromatic-H), 7.22 (dd, 2H, $^3J_{H,H} = 5.8$ Hz, $^4J_{H,H} = 1.6$ Hz, aromatic-H), 4.65 (s, 2H, Cp-H sub. ring), 4.42 (s, 2H, Cp-H unsub. ring), 2.91 (sept, 2H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH), 2.62 (t, 2H, $^3J_{H,H} = 8.0$ Hz, butyl CH_2), 1.64–1.56 (m, 2H, butyl-CH_2), 1.40–1.31 (m, 2H, butyl-CH_2), 1.25 (s, 12H, $^3J_{H,H} = 6.9$ Hz, isopropyl-CH_3), 0.86 (t, 3H, $^3J_{H,H} = 8.0$ Hz, butyl-CH_3). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 150.74, 144.53, 133.26, 133.21, 132.37, 128.43, 127.24, 125.56, 124.89, 122.50, 82.73, 81.98, 81.63, 80.47, 80.29, 79.25, 78.26, 77.93, 77.78, 77.13, 76.70, 75.32, 75.12, 74.64, 71.57, 69.07, 35.62, 34.41, 33.32, 23.61, 22.54, 13.99. MS (EI) *m/z* Calc. for $[M]^+$ ($C_{58}H_{38}Fe$) 790.2323, decomposition before $[M]^+$ could be determined.

3.17. Details of X-ray crystal structure determination

X-ray intensity data for **7**, **12** 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.

3.17.1. Crystal data for 7

The cyclobutadiene complex $C_{51}H_{37}Co$ of the FW = 708.74 was isolated as orange rhombus, (0.36 × 0.20 × 0.06 mm). The unit cell was triclinic featuring the space group $P\bar{1}$, with cell dimensions of $a = 10.9507(8)$ Å, $b = 12.1458(8)$ Å, $c = 15.4401(11)$ Å, $\alpha = 86.981(1)°$, $\beta = 79.657(1)°$, $\gamma = 65.458(1)°$, $V = 1837.2(2)$ Å^3, and $Z = 2$ molecules in the unit cell. The calculated density, $D_{calc} = 1.281$ g cm^{-3}. Intensity data covering the full sphere of reciprocal space were measured to $2\theta_{max} = 50.2°$; 15 359 reflections were collected, of which 6532 were independent, of which 5052 were recorded with $I > 2\sigma(I)$. No absorption correction was applied ($\mu = 0.50$ mm^{-1}). Data refinement produced $R_1 = 0.0814$, $wR_2(I > 2\sigma(I) = 0.0416$; GoF = 1.015. 495 parameters were refined, with no restraints. Max/min residual electron density was determined to $+0.327/-0.244$ e Å^{-3}.

3.17.2. Crystal data for 12

The ferrocene derivative $C_{51}H_{36}Fe \cdot 0.25(CH_2Cl_2)$ of the FW = 725.88 was isolated as orange needle of the dimensions of 0.42 × 0.12 × 0.08 mm. The material crystallized in the hexagonal crystal system in the space group $P6_3$ with unit cell dimensions of $a = 27.174(2)$ Å, $c = 9.1170(7)$ Å, $V = 5830.4(7)$ Å^3, and $Z = 6$ independent molecules. The calculated density was determined to $D_{calc} = 1.240$ g cm^{-3}. Intensity data covering the full sphere of reciprocal space were measured to $2\theta_{max} = 48.2°$; 22 326 reflections were collected of which 5788 were independent; 4316 reflections were recorded with $I > 2\sigma(I)$. No absorption correction was applied ($\mu = 0.46$ mm^{-1}). Data refinement produced $R_1 = 0.1231$, $wR_2(I > 2\sigma(I) = 0.0623$, with a of GoF = 1.013; 509 parameters were refined with four restraints due to disordered CH_2Cl_2 solvent. Max/min residual electron density was determined to $+0.355/-0.385$ e Å^{-3}. Flack parameter = 0.02(3). Check for higher symmetry by (PLATON) was negative.

3.17.3. Crystal data for 17

Cyclobutadiene complex $C_{69}H_{59}Co$ of FW = 939.03 was obtained in the form of an orange needle of dimensions 0.64 × 0.08 × 0.04 mm. The crystal system was monoclinic with the space group $P2_1/n$, with $a = 10.568(1)$ Å, $b = 35.490(4)$ Å, $c = 15.132(2)$ Å, $\beta = 102.215(3)°$, and $V = 5547.0(11)$ Å^3. There are $Z = 4$ independent molecules in the unit cell, $D_{calc} = 1.124$ g cm^{-3}. Intensity data covering the full sphere of reciprocal space were measured to $2\theta_{max} = 45.1°$; 21 290 reflections were collected of which 7278 were independent and of those were 3104 with $I > 2\sigma(I)$. No absorption correction was applied ($\mu = 0.35$ mm^{-1}). Data refinement produced $R_1 = 0.2544$, $wR_2(I > 2\sigma(I) = 0.1098$, with a GoF = 1.008. 605 parameters were refined. Molecular disorder corresponding to a 90° rotation around the Co–$Cp_{centroid}$ vector is present, but could not be modeled due to the small fraction (< 10%). One butyl substituent is severely disordered; coordinates and isotropic thermal parameters were fixed once a reasonable geometry was attained. A region of diffuse solvent was located near the disordered butyl group and treated with SQUEEZE (solvent-accessible volume = 588.1 Å^3, 169 e cell^{-1}, corresponding to three $CHCl_3$ molecules per $C_{69}H_{59}Co$ molecule). Max/min residual electron density was determined to $+1.475/-1.075$ e Å^{-3}.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 176513 for compound **7**, CCDC No. 176514, for compound **12**, and CCDC No. 176515 for compound **17**. 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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