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Synthesis and ^{1}H NMR spectroscopic properties of substituted (η^4-tetraarylcyclobutadiene)(η^5-cyclopentadienyl)cobalt metallocenes

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ABSTRACT

The reaction of diarylacetylenes with $CoCl(PPh_3)_3$ and sodium cyclopentadienylide or sodium carbomethoxycyclopentadienylide gave (η^4-tetra-arylcyclobutadiene)(η^5-cyclopentadienyl)cobalt and (η^4-tetra-arylcyclobutadiene)(η^5-carbomethoxycyclopentadienyl)cobalt, respectively, where aryl = *para*-XC_6H_4 (X = CF_3, F, MeO). The reaction was unsuccessful for the synthesis of (η^4-tetra(*para*-methoxyphenyl)cyclobutadiene)(η^5-cyclopentadienyl)cobalt, which was synthesised instead from dicarbonyl(η^5-cyclopentadienyl)cobalt. In all of the examples starting with $CoCl(PPh_3)_3$ an intermediate (η^5-cyclopentadienyl)- or (η^5-carbomethoxycyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraarylcobaltacyclopentadiene complex was isolated, and two examples were characterised by X-ray crystallography. Heating the (η^5-cyclopentadienyl)- or (η^5-carbomethoxycyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraarylcobaltacyclopentadiene complexes resulted in clean conversion to the corresponding metallocenes. The influence of the *para*-aryl substituents on the ^{1}H NMR of the cyclopentadienyl moiety is tabulated, together with the influence of a range of R substituents in (η^4-tetraphenylcyclobutadiene)(η^5-RC_5H_4)cobalt (R = CO_2Me, CH_2OH, Me, CHO, CCH, CO_2H, CN, $CONHR^1$, 2-oxazolinyl, NH_2, NHAc, HgCl, Br, I, $SiMe_3$, $SnMe_3$, Ph).

1. Introduction

Catalysts derived from bulky air-stable cobalt metallocenes **1a** [1] and **2a** [2a] are of growing importance in asymmetric synthesis (see Insert 1). Examples include 1,2-disubstituted planar chiral derivatives such as palladacycles **3** [2], and the monosubstituted chiral 4-aminopyridine derivative **4** [3]. This class of metallocene has also been used as the basis of new carbon-rich organometallic architectures [4]. Part of the attraction of these metallocenes is the ease with which they may be synthesised utilising a metal-mediated acetylene dimerisation to generate the η^4-cyclobutadiene moiety. The first practical synthesis of **1a** was reported by Rausch and Genetti and started with dicarbonyl(η^5-cyclopentadienyl)cobalt, which also resulted in the formation of the cyclopentadienone complex **5** (Scheme 1) [5]. The formation of a cyclopentadienone by-product is avoided by starting with $CoCl(PPh_3)_3$ [6], which on combination with a sodium cyclopentadienyl salt and diphenylacetylene gave **2a** and related derivatives in good yield [2a,7]. In this paper, we report in detail on the use of this reaction for the synthesis of derivatives of **1** and **2** containing various *para*-phenyl substituents [8]. In addition, the influences of *para*-phenyl and cyclopentadienyl substituents on the ^{1}H NMR spectra of these complexes are tabulated and discussed.

2. Results and discussion

Previous reactions starting with $CoCl(PPh_3)_3$, a cyclopentadienyl salt and 2 equiv. of diphenylacetylene **8a** have resulted in the isolation of a η^4-tetraphenylcyclobutadiene containing metallocene after heating at reflux in toluene for several hours [7]. Similarly, the use of sodium cyclopentadienylide **6** with a reaction time of 5 h resulted in the formation of **1a**, isolated as a yellow crystalline solid in 83% yield (Scheme 2, Table 1, entry 1). In contrast, shortening the reaction time to 30 min resulted in the isolation of a red crystalline solid identified as the metallocyclopentadiene triphenylphosphine adduct **9a** (entry 2). The identity of **9a** was confirmed by an X-ray crystal structure analysis (Fig. 1). The use of di(*para*-trifluoromethylphenyl)acetylene **8b** with a reaction time of 5 h resulted in the isolation of both the metallocyclopentadiene **9b** and the corresponding metallocene **1b**. As before, the identity of the former complex was confirmed by an X-ray crystal structure analysis (Fig. 1). The only significant difference between the two complexes is the longer metallocyclopentadiene C(6)–Co bond in **9a** compared to **9b** [1.987(4) versus 1.964(3)] and a shorter Co–P bond in **9a** compared to **9b** [2.1914(13) versus 2.2011(8)]. Use of a 5 h reaction time with di(*para*-fluorophenyl)acetylene **8c** resulted predominantly in the isolation of metallocene **1c** (entry 4), and

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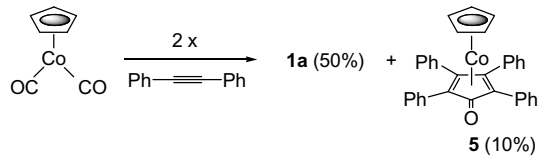
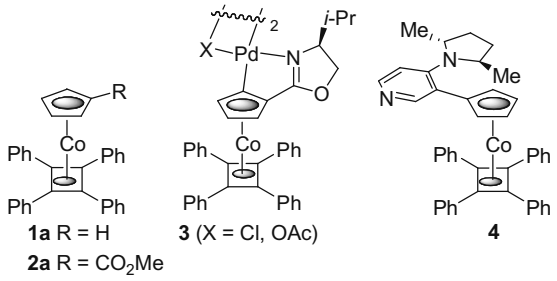
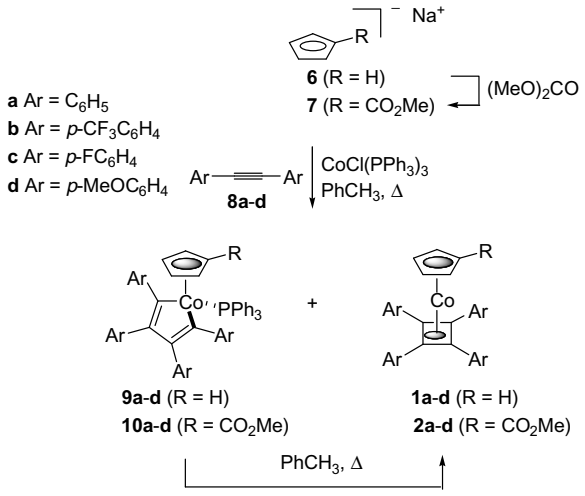


Scheme 1. The synthesis of **1a** [5a].



Insert 1. Representative cobalt metallocenes.



Scheme 2. Synthesis of metallocyclopentadiene complexes and η^4-cyclobutadiene metallocenes.

di(*para*-methoxyphenyl)acetylene **8d** failed to give either complex (entry 5).

Similar trends were observed with the carbomethoxy-substituted cyclopentadienyl salt **7** (prepared *in situ* by addition of dimethylcarbonate to **6**). A longer reaction time of 15 h with diphenylacetylene **8a** resulted in the exclusive isolation of the metallocene **2a** (entry 6 – although a 5 h reaction time has previously been reported to be sufficient for the formation of **2a** [2a]). Shortening the reaction time to 30 min resulted in the isolation of the corresponding metallocyclopentadiene triphenylphosphine adduct **10a** (entry 7). The corresponding complex **10b** was the major product even after a reaction time of 15 hours with di(*para*-trifluoromethylphenyl)acetylene **8b** (entry 8), and **10c**, together with a greater yield of **2c**, resulted from the 15 h reaction of di(*para*-fluorophenyl)acetylene **8c** (entry 9). Finally, and in contrast to the result given in entry 5, di(*para*-methoxyphenyl)acetylene **8d** did result in the formation of the corresponding metallocene **2d** (entry 10).

It has been observed previously that heating metallocyclopentadiene complex **9a** above its melting point results in expulsion of triphenylphosphine and formation of the corresponding η^4-cyclobutadiene metallocene **1a** [9]. In a similar way, all of the isolated triphenylphosphine adducts **9a**–**9c** and **10a**–**c** were converted into their corresponding η^4-cyclobutadiene metallocenes by heating at reflux in toluene (Scheme 2, Table 2, entries 1–6). These reactions are essentially irreversible; heating a combination of **2b** with a fivefold excess of triphenylphosphine did not result in the detection of any of the corresponding metallocyclopentadienyl complex **10b**.

The synthesis of complex **9a** from $CoCl(PPh_3)_3$ has previously been reported [10], an alternative to the related method starting from (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt **11** (R = H) [11]. As **11** (R = H) may itself be synthesised from $CoCl(PPh_3)_3$ [10a,12], this first step in the reaction sequence (Scheme 3) is followed by alkyne substitution reactions leading sequentially to **12** and **13** [10a]. Oxidative cyclisation of the latter to give **14** [13] is followed by either addition of triphenylphosphine to this coordinatively unsaturated intermediate to give **9**/**10**, or reductive elimination to the η^4-cyclobutadiene complexes **1**/**2**. The slower rate of conversion of **9**/**10** into **1**/**2** where either Ar or R contains an electron withdrawing group may be accounted for by the slower rate of phosphine dissociation, presumably due to the greater Lewis acidity of the cobalt atom.

As the synthesis of metallocene **1d** was unsuccessful using the method described above, it was instead generated in low yield by heating at reflux a solution of di(*p*-methyoxyphenyl)acetylene with dicarbonyl(η^5-cyclopentadienyl)cobalt (Scheme 4). None of the corresponding tetraarylcyclopentadienone metallocene was observed. This outcome tallies with the absence of metallocyclopentadiene complexes **9d** and **10d** in reactions of di(*p*-methyoxyphenyl)acetylene with $CoCl(PPh_3)_3$, suggesting that the aryl *para*-methoxy substituents reduce the propensity of intermediate sixteen electron metallocyclopentadiene complexes to coordinate to either carbon monoxide or triphenylphosphine.

The ^{1}H NMR chemical shifts of the cyclopentadienyl singlets of **1a**–**d**, and the α and β signals of **2a**–**d**, are listed in Table 3. The influence of the different aryl substituents on the chemical shifts is approximately 1/10th of the chemical shift difference for the

Table 1
Synthesis of metallocyclopentadiene **9**–**10** complexes and η^4-cyclobutadiene metallocenes **1**–**2**

Entry	R	Ar	Reaction time (h)	Metallocyclopentadiene complex (yield)	η^4-Cyclobutadiene metallocene (yield)
1	H	Ph	5	**9a** (0%)	**1a** (83%)
2	H	Ph	0.5	**9a** (90%)	**1a** (0%)
3	H	*p*-$CF_3C_6H_4$	5	**9b** (54%)	**1b** (34%)
4	H	*p*-FC_6H_4	5	**9c** (6%)	**1c** (82%)
5	H	*p*-$MeOC_6H_4$	5	**9d** (0%)	**1d** (0%)
6	CO_2Me	Ph	15	**10a** (0%)	**2a** (73%)
7	CO_2Me	Ph	0.5	**10a** (10%)	**2a** (66%)
8	CO_2Me	*p*-$CF_3C_6H_4$	15	**10b** (88%)	**2b** (5%)
9	CO_2Me	*p*-FC_6H_4	15	**10c** (20%)	**2c** (47%)
10	CO_2Me	*p*-$MeOC_6H_4$	15	**10d** (0%)	**2d** (56%)

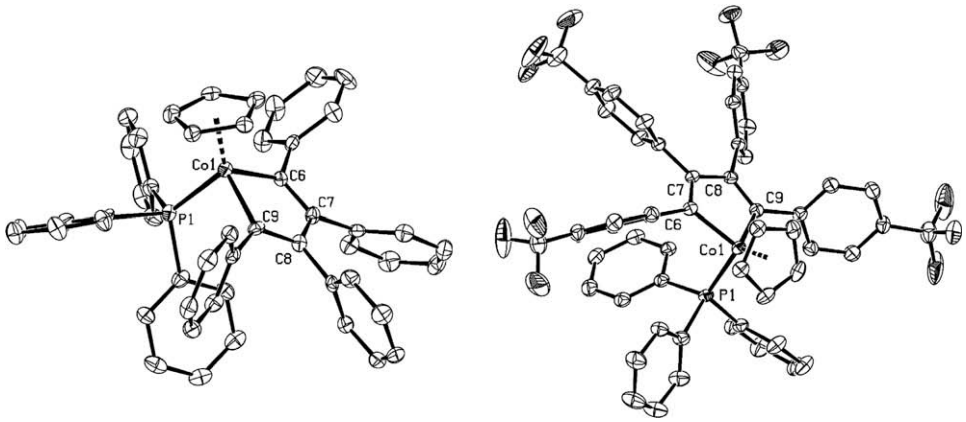


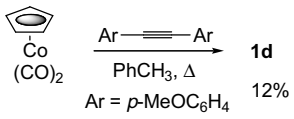
Fig. 1. Representation of the X-ray crystal structure of **9a** (left) and **9b**. Selected bond lengths (Å) of **9a** with the corresponding values for **9b** in parenthesis: Co–C(6) 1.987(4) [1.964(3)], C(6)–C(7) 1.355(6) [1.357(4)], C(7)–C(8) 1.467(6) [1.473(4)], C(8)–C(9) 1.359(6) [1.351(4)], C(9)–Co 1.975(5) [1.978], Co–P 2.1914(13) [2.2011(8)].

Table 2
Conversion of metallocyclopentadiene complexes **9** and **10** into η^4-cyclobutadiene metallocenes **1** and **2**

Entry	Metallocyclopentadienyl complex	Reaction time (h)	η^4-Cyclobutadiene metallocene (yield)
1	**9a**	5	**1a** (95%)
2	**9b**	15	**1b** (81%)
3	**9c**	15	**1c** (92%)
4	**10a**	15	**2a** (82%)
5	**10b**	15	**2b** (96%)
6	**10c**	15	**2c** (97%)

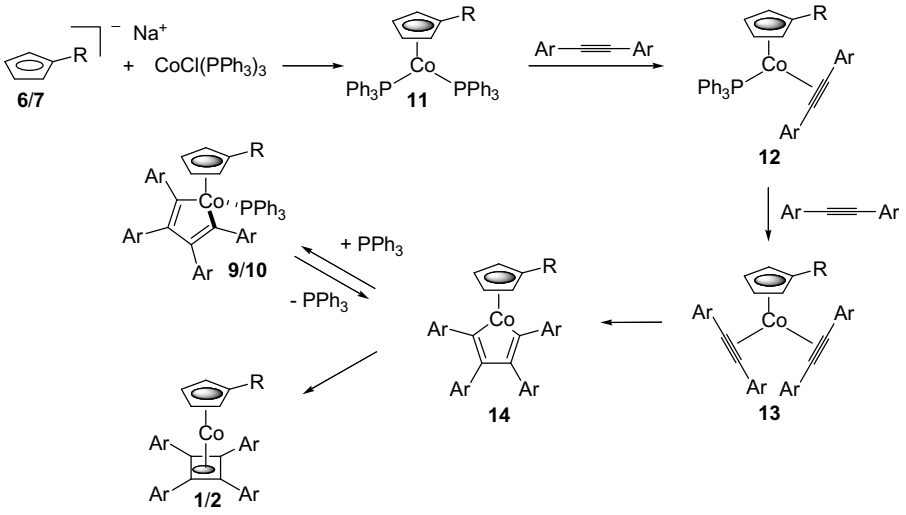
para-position of a corresponding substituted benzene (CF_3: +0.05 versus +0.3; F: −0.02 versus −0.24; OMe: −0.05 versus −0.45). The influence of a cyclopentadienyl substituent on the electronic environment of the η^5-ring, as manifested in the chemical shift of the remaining protons, is somewhat more significant, as illustrated by the difference between the parent complexes **1a** and **2a**.

The effect of substituents on the chemical shifts of monosubstituted ferrocenes has previously been tabulated [14] and has proved useful for the identification of related ferrocene derivatives, including multiply substituted compounds [15]. To provide a similar body of information for (η^4-tetraphenylcyclobutadiene)(η^5-cyclopentadienyl)cobalt metallocenes, we first synthesised an extensive range of known and new monosubstituted derivatives **15**–**30** (see Insert 2).



Scheme 4. Synthesis of **1d**.

Methyl ester **2a** was reduced with $LiAlH_4$ to the alcohol **15** [7b,16] which was further reduced with $LiAlH_4$ in the presence of $AlCl_3$ to the methyl substituted derivative **16** (Scheme 5). Oxidation of **15** with catalytic tetrapropylammonium perruthenate (TPAP) and stoichiometric *N*-methylmorpholine-*N*-oxide (NMO) proceeded cleanly to give aldehyde **17** [5a] which was transformed into the 1-alkyne **18** as previously outlined [7b]. Hydrolysis of methyl ester **2a** gave the carboxylic acid **19** [2a] which was converted into nitrile **20** using a literature procedure [17]. In addition, acid **19** was transformed via amide **21** into the achiral oxazoline **22** using methodology previously employed for the synthesis of related chiral oxazolines [2a,2e]. Use of the Curtius rearrangement as the key step resulted in the transformation of acid **19** into amine **23** [18] which was acetylated to give acetamide **24**.

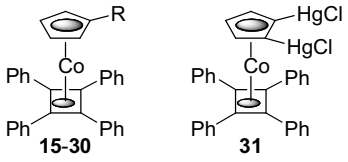


Scheme 3. A reaction pathway accounting for the formation of metallocyclopentadiene complexes and η^4-cyclobutadiene metallocenes.

Table 3
^{1}H NMR chemical shifts of substituted (η^4-tetraarylcyclobutadiene)(η^5-cyclopentadienyl)cobalt metallocenes

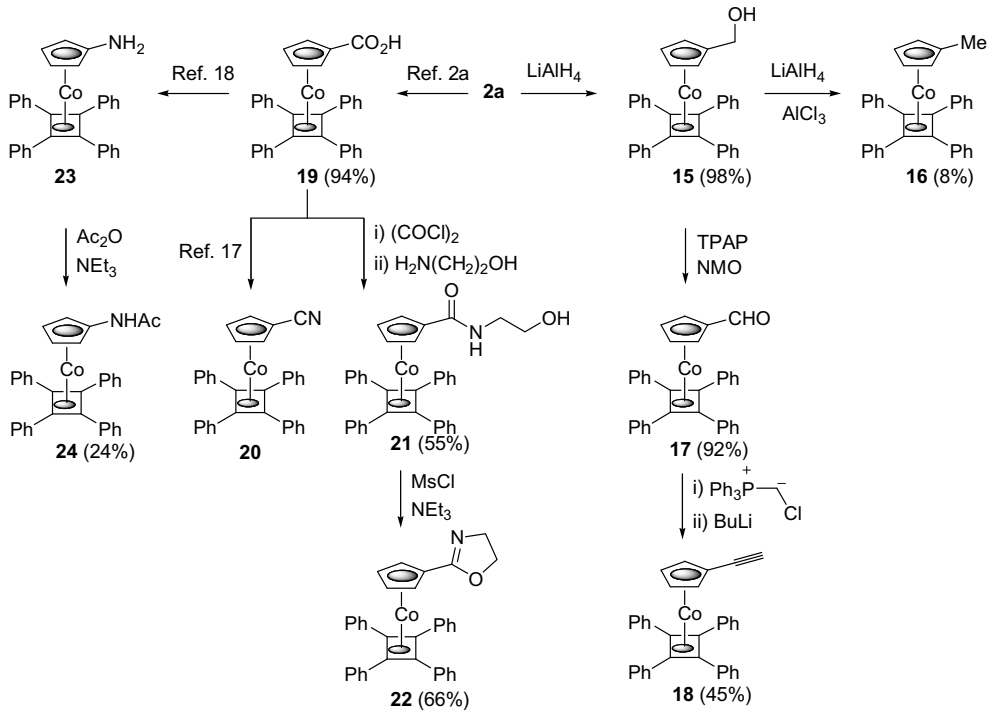
Metallocene	R	Ar	α	$\Delta\alpha$[a]	Ferrocene $\Delta\alpha$[b]	β	$\Delta\beta$[a]	Ferrocene $\Delta\beta$[b]
1a	H	Ph	4.62	0	–	4.62	0	–
1b	H	*p*-$CF_3C_6H_4$	4.67	+0.05	–	4.67	+0.05	–
1c	H	*p*-FC_6H_4	4.60	−0.02	–	4.60	−0.02	–
1d	H	*p*-$MeOC_6H_4$	4.57	−0.05	–	4.57	−0.05	–
2a	CO_2Me	Ph	5.19	+0.57	+0.61	4.77	+0.15	+0.20
2b	CO_2Me	*p*-$CF_3C_6H_4$	5.21	+0.59	–	4.82	+0.2	–
2c	CO_2Me	*p*-FC_6H_4	5.16	+0.54	–	4.75	+0.13	–
2d	CO_2Me	*p*-$MeOC_6H_4$	5.15	+0.53	–	4.72	+0.1	–
15	CH_2OH	Ph	4.71	+0.09	0.00	4.59	−0.03	+0.03
16	Me	Ph	4.53	−0.09	−0.11	4.46	−0.16	−0.15
17	CHO	Ph	5.22	+0.60	+0.55	4.88	+0.26	+0.36
18	C≡CH	Ph	4.79	+0.17	+0.28	4.62	0	+0.02
19	CO_2H	Ph	5.22	+0.60	+0.68	4.78	+0.16	+0.28
20	C≡N	Ph	4.90	+0.28	+0.48	4.66	+0.04	+0.21
21	CONHR[c]	Ph	5.02	+0.40	+0.50	4.70	+0.08	+0.18
22	2-oxazolinyl[d]	Ph	5.11	+0.49	+0.56	4.77	+0.15	+0.15
23	NH_2	Ph	4.39	−0.23	−0.17	4.13	−0.49	−0.32
24	NHAc	Ph	4.86	+0.24	+0.38	4.54	−0.08	−0.19
25	HgCl	Ph	4.69	+0.07	–	4.86	+0.24	–
26	Br	Ph	4.73	+0.11	+0.23	4.55	−0.07	−0.08
27	I	Ph	4.76	+0.14	+0.23	4.56	−0.06	−0.03
28	$SiMe_3$	Ph	4.66	+0.04	−0.06[e]	4.75	+0.13	+0.17[e]
29	$SnMe_3$	Ph	4.65	+0.03	−0.12	4.72	+0.10	+0.19
30	Ph	Ph	4.99	+0.37	+0.46	4.69	+0.07	+0.13

[a] Difference in chemical shift (δ) relative to **1a**.
[b] From Ref. [14].
[c] R = $(CH_2)_2OH$.
[d] Derived from **21**.
[e] Figure from R = $SnBu_3$.

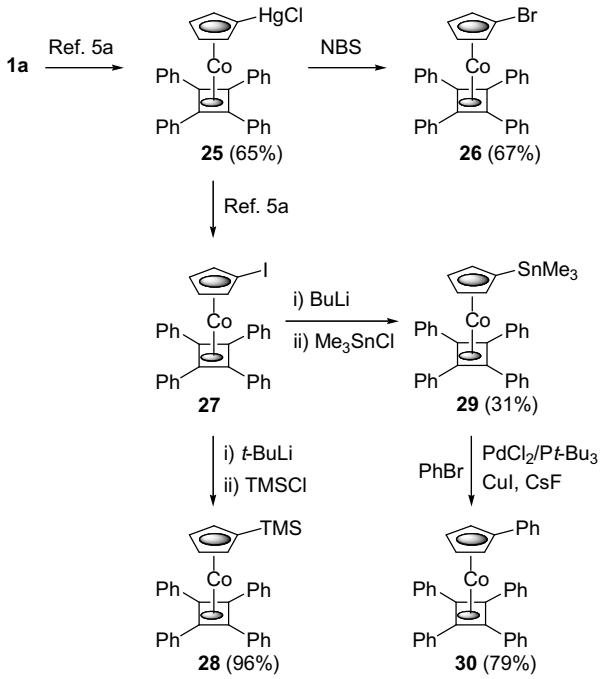


Insert 2.

A variety of other derivatives were obtained following transformation of **1a** into the chloromercury derivative **25** [5a] (Scheme 6). Reaction with *N*-bromosuccinimide and iodine gave the halogen derivatives **26** and **27** [5a]. Addition of butyllithium to iodide **27** resulted in halogen–lithium exchange, followed by the addition of various electrophiles to give silane **28** [5a] and stannane **29**. The latter was employed in a Stille cross-coupling reaction to provide the phenyl derivative **30** [5a].



Scheme 5. Synthesis of derivatives **15–24** from **2a**.



Scheme 6. Synthesis of derivatives **25**–**30** from **1a**.

The ^{1}H NMR chemical shifts of the α and β positions of derivatives **15**–**30** are listed in Table 1. For most of these compounds the assignment of cyclopentadienyl proton signals as α or β was made by comparison to the corresponding ferrocene derivatives [14]. An exception is the chloromercury derivative **25** (the ferrocene derivative of which is not listed in the previous study) [19]. Examination of the ^{1}H NMR of the 1,2-bis(chloromercury) derivative **31**, the relative stereochemistry of which has been unambiguously established by X-ray crystallography [20], reveals two cyclopentadienyl signals with a 2:1 ratio at 4.87 and 5.08 ppm. From this values of $\Delta\alpha$ and $\Delta\beta$ are calculated as +0.02 and +0.23, in good agreement with the chemical shift differences observed in the mono-substituted derivative **25** (+0.07 and +0.24). It is of note that the magnitude of the $\Delta\alpha$ and $\Delta\beta$ values are generally smaller than the corresponding values found in the ferrocene series. For example, for electron withdrawing substituents (*i.e.* where the values of $\Delta\alpha$ and $\Delta\beta$ are both positive), the average values for $\Delta\alpha$ and $\Delta\beta$ are approximately 80% and 50% of the corresponding ferrocene values, respectively.

3. Conclusion

(η^4-Tetraarylcyclobutadiene)(η^5-cyclopentadienyl)cobalt metal locenes **1b**–**1c** and (η^4-tetraarylcyclobutadiene)(η^5-carbomethoxycyclopentadienyl)cobalt metallocenes **2b**–**2d**, where aryl = *para*-XC_6H_4), were synthesised using $CoCl(PPh_3)_3$, a diarylacetylene and the corresponding sodium cyclopentadienyl salt. In all cases the intermediacy of metallocyclopentadiene triphenylphosphine adducts (**9b**–**9c**, **10b**–**10d**) were observed, and with uniform reaction conditions, the percentage of this intermediate increased with the presence of electron-withdrawing groups in the aryl group (X = CF_3) and/or in the cyclopentadienyl group (CO_2Me). Use of di(*para*-methoxyphenyl)acetylene in this chemistry was only successful when the cyclopentadienyl group contained the electron-withdrawing CO_2Me group. Following isolation of the metallocyclopentadiene triphenylphosphine intermediates, subsequent heating resulted in conversion to the corresponding metallocenes in high yield. The influence of the *para*-substituent X on the ^{1}H NMR chemical shift of the cyclopentadienyl group is relatively small. The influence of an extensive range of cyclopentadienyl substituents on the ^{1}H NMR chemical shifts of the α and β positions correlates well with the values of the corresponding ferrocene derivatives.

4. Experimental

The following compounds were prepared as previously described: **2a** [2a], **19** [2a], **20** [17], **23** [18], **25** [5a] and **27** [5a]. All reactions performed under a nitrogen atmosphere. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane and dimethylformamide were distilled from calcium hydride. Toluene was distilled from sodium wire. Petroleum ether refers to that fraction boiling in the range 40–60 °C. Column chromatography was performed on silica gel 40–63 μm.

4.1. General method for the synthesis of complexes *1* and *9*

To a mixture of chlorotris(triphenylphosphine)cobalt (1 equiv.) and diarylacetylene (2.3 equiv.) in toluene (5 mL/equiv.) was added sodium cyclopentadienide (2.0 M in THF, 1.2 equiv.) and the resulting mixture heated at reflux. After the specified reaction time the solvent was removed in vacuo, the residue partially dissolved in CH_2Cl_2 (5 mL) and the black insoluble residue was removed by filtration and washed with additional CH_2Cl_2 until the washings were colourless. Following removal of the solvent, the product complexes were isolated by column chromatography and recystallised from CH_2Cl_2/petroleum ether.

4.1.1. (η^4-tetraphenylcyclobutadiene)(η^5-cyclopentadienyl)cobalt *1a* [5a] and (η^5-cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraphenylcobaltacyclopentadiene *9a* [10b]

Use of diphenylacetylene (0.400 g, 2.24 mmol) with a 5 h reaction time, and column chromatography (petroleum ether) gave **1a** (0.390 g, 83% yield) as a yellow crystalline solid. Use of diphenylacetylene (0.400 g, 2.24 mmol), a reaction time of 0.5 h, and column chromatography (30% CH_2Cl_2/70% petroleum ether) gave **9a** (0.652 g, 90% yield) as a red crystalline solid.

Compound **1a**: ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 4.62 (5H, s, Cp), 7.14–7.23 (12H, m, Ph), 7.41–7.46 (8H, m, Ph); ^{13}C NMR (δ, 67 MHz, $CDCl_3$) 74.9 (Cb), 83.3 (Cp), 126.2 (Ph), 128.0 (Ph), 128.9 (Ph), 136.5 (*ipso*-Ph).

Compound **9a**: ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 4.76 (5H, s, Cp), 6.41–6.53 (8H, m, Ph), 6.70–6.92 (12H, m, Ph), 7.13–7.42 (15H, m, PPh_3); ^{13}C NMR (δ, 67 MHz, $CDCl_3$) 89.7 (Cp), 123.2, 123.7, 126.2, 126.8, 128.1, 128.3, 129.0, 129.8, 130.5, 133.6, 133.7, 142.1, 153.6, 157.7; ^{31}P NMR ($\delta\{^1H\}$ 100 MHz, $CDCl_3$) 52.2.

4.1.2. (η^4-tetra(para-trifluoromethylphenyl)cyclobutadiene)(η^5-cyclopentadienyl)cobalt *1b* and (η^5-cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetra(para-trifluoromethylphenyl)cobaltacyclopentadiene *9b*

Use of di(*p*-trifluoromethylphenyl)acetylene (0.500 g, 1.59 mmol), a reaction time of 5 h, and column chromatography (10% CH_2Cl_2/petroleum ether) gave **1b** (0.177 g, 34% yield) as a yellow crystalline solid, and **9b** (0.379 g , 54% yield) as a red crystalline solid.

Compound **1b:** m.p. 294 °C; Anal. Calc. for $C_{37}H_{21}CoF_{12}$: C, 59.06; H, 2.81. Found: C, 58.84; H, 2.70%. ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 4.67 (5H, s, 5H, Cp), 7.45–7.53 (16H, m, Ar); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 74.45 (Cb), 84.13 (Cp), 124.55 (q, J = 270, CF_3), 125.72 (q, J = 4, Ar), 129.18 (q, J = 32, Ar), 129.15 (Ar), 139.93 (Ar).

Compound **9b**: m.p. 224 °C; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 4.77 (5H, s, Cp), 6.51 (8H, t, J = 8, Ar), 6.86 (4H, t, J = 10, Ar), 7.02 (8H,

d, J = 7, Ar), 7.15–7.25 (6H, m, Ar), 7.28–7.50 (5H, m, Ar); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 90.15 (CpC), 123.35, 123.61, 124.05, 124.09, 124.37, 124.40, 125.85, 126.04, 126.17, 126.31, 126.61, 126.93, 128.48, 128.58, 128.85 128.90, 130.58, 130.79, 131.17, 133.61, 133.71, 133.84, 133.93, 135.37, 135.79, 144.54, 156.88, 170.34, 170.62; ^{31}P NMR ($\delta\{^1H\}$ 100 MHz, $CDCl_3$) 50.12; HRMS (EI) m/z; Found for $(M-PPh_3)^+$, 752.0782; Calc. for $C_{37}H_{21}CoF_{12}$, 752.0778.

4.1.3. (η^4-tetra(para-fluorophenyl)cyclobutadiene)(η^5-cyclopentadienyl)cobalt **1c** and (η^5-cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetra(para-fluorophenyl)cobaltacyclopentadiene **9c**

Use of di(*p*-fluorophenyl)acetylene (0.510 g, 2.38 mmol), a reaction time of 5 h, and column chromatography (10%CH_2Cl_2/petroleum ether) gave **1c** (0.469 g, 82% yield) as a yellow crystalline solid, and **9c** (0.051 g, 6% yield) as a red crystalline solid.

Compound **1c**: m.p. 250 °C. Anal. Calc. for $C_{33}H_{21}F_4Co \cdot H_2O$: C, 69.48; H, 4.06. Found: C, 69.29; H, 3.70%; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 4.60 (5H, s, Cp), 6.91 (8H, t, J = 9, Ar), 7.34 (8H, dd, J = 9,5, Ar); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 73.78 (Cb), 83.15 (CC), 115.24 (d, J = 22, Ar), 130.16 (d, J = 8, Ar), 131.70 (d, J = 4, Ar), 161.35 (d, J = 245, Ar).

Compound **9c**: m.p. 200 °C; Anal. Calc. for $C_{51}H_{36}CoF_4P$: C, 75.18; H, 4.45. Found: C, 75.19; H, 4.41%; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 4.73 (5H, s, Cp), 6.29–6.58 (18H, m, Ar), 6.85–7.00 (3H, m, Ar), 7.10–7.50 (10H, m, Ar); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 89.98 (Cp), 113.52, 113.72, 113.87, 114.08, 128.22, 128.32, 128.65, 128.74, 130.29, 130.36, 130.75, 130.78, 131.92, 132.00, 133.76, 133.86, 133.96, 134.02, 134.06, 136.13, 136.55, 137.97, 138.00, 138.03, 149.52, 149.55, 156.85, 156.87, 158,72, 159.01, 161.14, 161.42, 167.19, 167.46; ^{31}P NMR ($\delta\{^1H\}$ 100 MHz, $CDCl_3$) 51.79.

4.2. General method for the synthesis of complexes **2** and **10**

To a solution of sodium cyclopentadienylide (2.0 M in THF, 1.14 equiv.) in THF (3.3 mL/equiv.) was added dimethyl carbonate (3.45 equiv.) and the resulting mixture heated at reflux for 4 h. After cooling to room temperature to the reaction vessel was added toluene (26.5 mL/equiv.), chlorotris(triphenylphosphine)cobalt (1 equiv.) and the diarylacetylene (2.3 equiv.). The resulting mixture heated at reflux and after the specified reaction time the solvent was removed in vacuo, the residue partially dissolved in CH_2Cl_2, and the black insoluble residue was removed by filtration and washed with additional CH_2Cl_2 until the washings were colourless. Following removal of the solvent in vacuo, the product complexes were isolated by column chromatography or recrystallisation.

4.2.1. (η^4-tetraphenylcyclobutadiene)(η^5-carbomethoxycyclopentadienyl)cobalt **2a** [2a] and (η^5-carbomethoxycyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraphenylcobaltacyclopentadiene **10a**

Use of diphenylacetylene (0.340 g, 1.91 mmol), a reaction time of 0.5 h, and column chromatography (20–50% CH_2Cl_2/petroleum ether) gave **2a** (0.295 g, 66% yield) as a yellow crystalline solid, and **10a** (0.066 g, 10% yield) as a red crystalline solid. Use of diphenylacetylene (0.40 g, 2.24 mmol) with a 15 h reaction time gave only **2a** (0.384 g, 73% yield) as a yellow crystalline solid.

Compound **2a**: ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 3.22 (3H, s, 3H, Me), 4.77 (2H, t, J = 2, Cp), 5.19 (2H, t, J = 2, Cp), 7.15–7.40 (12H, m, Ph), 7.40–7.46 (8H, m, Ph); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 51.16 (Me), 76.44 (Cb), 84.54 (Cp), 86.37 (Cp), 86.72 (*ipso*-Cp), 126.70 (Ph), 128.06 (Ph), 128.87 (Ph), 135.12 (*ipso*-Ph), 166.35 (C=O).

Compound **10a**: m.p. 168 °C; Anal. Calc. for $C_{53}H_{42}CoO_2P$: C, 79.49; H, 5.29. Found: C, 79.00; H, 5.19%; IR (CH_2Cl_2) ν_{max} 1720 cm^{-1}; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 3.81 (3H, s, Me), 4.68 (2H, brs, Cp), 5.42 (2H, brs, Cp), 6.46–6.48 (5H, m, Ph), 6.64–6.83 (17H, m, Ph), 7.01–7.45 (13H, m, Ph); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 52.11 (Me), 84.83 (*ipso*-Cp), 89.64 (Cp), 98.99 (Cp), 123.54, 123.81, 126.24, 126.71, 127.93, 128.03, 128.28, 129.30, 130.30, 133.91, 134.00, 141.97, 152.94, 158.44, 164.79, 165.06, 167.44 (C≡O); ^{31}P NMR ($\delta\{^1H\}$ 100 MHz, $CDCl_3$) 49.99; HRMS (FAB) m/z; Found for M^+, 800.2252; Calc. for $C_{53}H_{42}CoO_2P$, 800.2249.

4.2.2. (η^4-tetra(para-trifluoromethylphenyl)cyclobutadiene)-(η^5-carbomethoxycyclopentadienyl)cobalt **2b** and (η^5-carbomethoxycyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetra(para-trifluoromethylphenyl)cobaltacyclopentadiene **10b**

Use of di(*p*-trifluoromethylphenyl)acetylene (1.240 g, 3.95 mmol), a reaction time of 15 h, and column chromatography (25% CH_2Cl_2/petroleum ether) gave **2b** (0.070 g, 5% yield) as a yellow crystalline solid, and **10b** (1.620 g , 88% yield) as a red crystalline solid.

Compound **2b:** m.p. 172 °C; Anal. Calc. for $C_{39}H_{23}CoF_{12}O_2$: C, 57.79; H 2.86. Found: C, 57.75; H, 2.80%, IR ($CDCl_3$) ν_{max} 1713 cm^{-1}; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 3.21 (3H, s, Me), 4.82 (2H, brs, Cp), 5.21 (2H, brs, Cp), 7.46 (8H, d, J = 8, Ar), 7.53 (8H, d, J = 8, Ar); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 51.38 (Me), 75.40 (Cb), 84.91 (Cp), 86.79 (Cp) 87.19 (*ipso*-Cp), 124.08 (q, J = 270, CF_3), 125.47 (q, J = 4, Ar) 128.80 (Ar), 129.37 (q, J = 32, Ar), 138.13 (Ar), 165.63 (C=O).

Compound **10b:** m.p. 182 °C; Anal. Calc. for $C_{57}H_{38}CoF_{12}O_2P$: C, 63.82; H, 3.57. Found: C, 63.39; H, 3.53%; IR ($CDCl_3$) ν_{max} 1706 cm^{-1}; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 3.84 (3H, s, Me), 4.71 (2H, brs, Cp), 5.39 (2H, brs, Cp), 6.50 (4H, d, J = 7, Ar), 6.73 (4H, d, J = 7 Ar), 6.90–7.10 (14H, m, Ar), 7.18 (3H, brs, Ar), 7.38 (6H, brs, Ar); $\delta_C\{^1H\}$ (100 MHz, $CDCl_3$) 52.73 (Me), 84.42 (*ipso*-Cp), 90.13 (Cp), 99.73 (Cp), 120.56, 120.86, 123.26, 123.56, 124.19, 124.23, 124.40, 124.43, 125.92, 125.97, 126.24, 126.27, 126.56, 126.89, 127.21, 127.53, 128.74, 128.83, 129.25, 130.43, 130.97, 131.60, 133.93, 134.02, 134.57, 135.00, 144.62, 156.40, 157.63, 167.36 (C=O), 168.23, 168.52; ^{31}P NMR ($\delta\{^1H\}$ 100 MHz, $CDCl_3$) 48.51.

4.2.3. (η^4-tetra(para-fluorophenyl)cyclobutadiene)-(η^5-carbomethoxycyclopentadienyl)cobalt **2c** and (η^5-carbomethoxycyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetra(para-fluorophenyl)cobaltacyclopentadiene **10c**

Use of di(*p*-fluorophenyl)acetylene (2.300 g, 10.74 mmol), a reaction time of 15 h, and column chromatography (30% CH_2Cl_2/petroleum ether) gave **2c** (1.339 g, 47% yield) as a yellow crystalline solid, and **10c** (0.815 g , 20% yield) as a red crystalline solid.

Compound **2c:** m.p. 212 °C; Anal. Calc. for $C_{35}H_{23}O_2F_4Co$: C, 68.86; H, 3.80. Found: C, 68.80; H, 3.77%. IR ($CDCl_3$) ν_{max} 1704 cm^{-1}; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 3.28 (3H, s, Me), 4.75 (2H, brs, Cp), 5.16 (2H, brs Cp), 6.93 (8H, t, J = 9, Ar), 7.34 (8H, dd, J = 5, 9, Ar); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 51.27 (Me), 75.24 (Cb), 84.45 (Cp), 86.37 (Cp) 86.53 (*ipso*-Cp), 115.42 (d, J = 22, Ar), 130.24 (d, J = 8, Ar) 130.37 (d, J = 3, *ipso*-Ar), 161.69 (d, J = 246, *ipso*-Ar), 166.33 (C=O).

Compound **10c:** Mp 152 °C; IR ($CDCl_3$) ν_{max} 1712 cm^{-1}; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 3.81 (3H, s, Me), 4.66 (2H brs, Cp), 5.36 (2H, t, J = 3 Hz, Cp), 6.32–6.42 (4H, m, Ar), 6.42–6.52 (8H, m, Ar), 6.52–6.61 (4H, m, Ar), 6.92–7.04 (3H, m, Ar), 7.12–7.28 (8H, m, Ar), 7.32–7.42 (4H, m, Ar); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 52.57 (Me), 84.56 (*ipso*-Cp), 90.09 (Cp), 99.56 (Cp), 113.69, 113.90, 113.92, 114.12, 128.53, 130.54, 130.70, 130.77, 131.75, 131.83, 134.19, 137.90, 137.93, 137.96, 148.95, 148.98, 157.61, 157.65, 158.95, 159.12, 161.37, 161.53, 165.35, 165.64, 167.74 (C=O); ^{31}P NMR ($\delta\{^1H\}$ 100 MHz, $CDCl_3$) 49.82; HRMS (EI) m/z; Found: $(M-PPh_3)^+$ 610.0959; Calc. for $C_{35}H_{23}CoF_4O_2$, 610.0961.

4.2.4. (η^4-tetra(para-methoxyphenyl)cyclobutadiene)-(η^5-carbomethoxycyclopentadienyl)cobalt **2d**

Use of di(*p*-methyoxyphenyl)acetylene (1.420 g, 5.96 mmol), a reaction time of 15 h, and recrystallisation (CH_2Cl_2) gave **2d** (0.956 g, 56% yield) as an orange powder.

Compound **2d:** m.p. 192 °C; Anal. Calc. for $C_{39}H_{35}CoO_6.H_2O$: C, 69.23; H, 5.51. Found: C, 69.05; H, 5.24%; IR (nujol) ν_{max} 1702 cm^{-1}; ^1H NMR (δ, 270 MHz, $CDCl_3$) 3.25 (3H, s, CO_2Me), 3.77 (12H, s, OMe), 4.72 (2H, t, J = 2, 2H, Cp), 5.15 (2H, t, J = 2, Cp), 6.76 (8H, d, J = 9, Ar), 7.35 (8H, d, J = 9, Ar); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 51.15 (CO_2Me), 55.23 (OMe), 75.76 (Cb), 84.13 (Cp), 86.08 (Cp), 86.16 (*ipso*-Cp), 113.59 (Ar), 127.37 (*ipso*-Ar) 129.90 (Ar), 158.31 (*ipso*-Ar), 166.83 (C=O).

4.2.5. (η^4-tetra(para-methoxyphenyl)cyclobutadiene)-(η^5-cyclopentadienyl)cobalt **1d**

A solution of cyclopentadienylcobaltdicarbonyl (0.038 g, 0.21 mmol), di(*p*-methoxyphenyl)acetylene (0.100 g, 0.42 mmol) in toluene (2 mL) was heated at reflux for 48 h. After cooling the crude reaction mixture was filtered through a plug of SiO_2, washing with CH_2Cl_2, followed by removal of the solvent removed *in vacuo*,. Column chromatography (50% CH_2Cl_2/petroleum ether) gave **1d** (0.015 mg, 12%) and recovered di(*p*-methoxyphenyl)acetylene (0.070 g, 70%).

Compound **1d:** m.p. 272 °C; ^1H NMR (δ, 270 MHz, $CDCl_3$) 3.80 (12H, s, Me), 4.57 (5H, s, Cp), 6.75 (8H, d, J = 8.4, Ar), 7.36 (8H, d, J = 8.9, Ar). ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 55.69 (Me), 75.40 (Cb), 83.12 (Cp), 113.84 (Ar), 130.25 (Ar), *ipso*-Ar not observed; HRMS (EI) m/z; Found for M^+, 600.1709; Calc. for $C_{37}H_{33}CoO_4$, 600.1705.

4.3. General method for the conversion of metallocyclopentadienyl complexes **9** and **10** into η^4-cyclobutadiene metallocenes **1** and **2**

A solution of the metallocyclopentadienyl complex (**3** or **5**) in toluene was heated at reflux until the starting material could no longer be detected by thin layer chromatography. The solvent was removed in vacuo and the product purified by column chromatography.

Synthesis of ***1a***. Compound **9a** (0.150 g, 0.2 mmol), toluene (2 mL), a reaction time of 5 h, and column chromatography (100% petroleum ether) gave **1a** (0.092 g, 95%).

Synthesis of **1b**. Compound **9b** (0.050 g, 0.05 mmol), toluene (5 mL), a reaction time of 15 h, and column chromatography (10% CH_2Cl_2/petroleum ether) gave **1b** (0.030 g, 81%).

Synthesis of **1c**. Compound **9c** (0.040 g, 0.05 mmol), toluene (4 mL), a reaction time of 15 h, and column chromatography (10% CH_2Cl_2/petroleum ether) gave **1c** (0.025 g, 92%).

Synthesis of **2a**. Compound **10a** (0.650 g, 0.81 mmol), toluene (10 mL), a reaction time of 15 h, and column chromatography (30% CH_2Cl_2/petroleum ether) gave **2a** (0.358 g, 82%).

Synthesis of **2b**. Compound **10b** (0.110 g, 0.10 mmol), toluene (5 mL), a reaction time of 15 h, and column chromatography (30% CH_2Cl_2/petroleum ether) gave **2b** (0.080 g, 96%).

Synthesis of **2c**. Compound **10c** (0.03 g, 0.03 mmol), toluene (5 mL), a reaction time of 15 h, and column chromatography (30% CH_2Cl_2/petroleum ether) gave **2c** (0.020 g, 97%).

4.3.1. (η^5-Hydroxymethylcyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt **15** [5a]

To a solution of **2a** (0.420 g, 0.80 mmol) in THF (25 mL) was added $LiAlH_4$ (0.132 g, 3.5 mmol) and the resulting mixture stirred at room temperature for 15 hours. The reaction was quenched with H_2O (100 mL) and extracted with EtOAc (2 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated to give **15** as a dark yellow solid (0.390 g, 98%).

Compound **15**: ^1H NMR (δ, 270 MHz, $CDCl_3$) 4.08 (s, 2H, CH_2), 4.59 (brs, 2H, Cp), 4.71 (brs, 2H, Cp), 7.15–7.40 (m, 12H, Ph), 7.40–7.46 (m, 8H, Ph); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 59.8 (CH_2), 75.3 (Cb), 81.9 (Cp), 84.1 (Cp), 126.9 (*para*-Ph), 128.6 (Ph), 129.1 (Ph), 136.5 (*ipso*-Ph), *ipso*-Cp not observed.

4.3.2. (η^5-Methylcyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt **16**

To a solution of **15** (0.081 g, 0.16 mmol) in Et_2O (20 mL) was added $AlCl_3$ (0.021 g, 0.16 mmol) with vigorous stirring. To the reaction was added $LiAlH_4$ (0.006 g, 0.16 mmol) and stirring was maintained 15 h. The resulting mixture was quenched with 1 M NaOH (3 mL) and filtered through celite, washing with Et_2O. The organic layer was dried ($MgSO_4$), filtered and solvent removed *in vacuo*. Column chromatography (1:5 Et_2O/petroleum ether) gave **16** as a yellow crystalline solid (0.006 g, 8%).

Compound **16:** m.p. 88–91 °C. ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (3H, s, Me), 4.45 (2H, t, J = 2, Cp), 4.51 (2H, t, J = 2, Cp), 7.13–7.35 (12H, m, Ph), 7.35–7.52 (8H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5 (Me), 74.9 (Cb), 83.1 (Cp), 84.0 (Cp), 126.4 (Ph), 128.3 (Ph), 129.2 (Ph), 136.9 (*ipso*-Ph), *ipso*-Cp not observed. HRMS (ES) m/z; Found for MH^+: 494.1437; Calc. for $C_{34}H_{27}Co$: 494.5205.

4.3.3. (η^5-Formylcyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt **17** [5a]

To a solution of **15** (0.396 g, 0.78 mmol) in CH_2Cl_2 (10 mL) containing 4 Å molecular sieves was added *N*-methylmorpholine-*N*-oxide (0.159 g, 1.36 mmol) followed by tetrapropylammonium perruthenate (0.014 g, 0.04 mmol). The reaction mixture darked quickly and was stirred for 1 h at room temperature before washing with sodium sulfite solution (10 mL), brine (10 mL) and saturated $CuSO_4$ solution (10 mL). The solution was dried (Na_2SO_4), filtered and evaporated, then redissolved in the minimum volume of CH_2Cl_2 and a dark solid precipitated on the addition of petroleum ether. After separation the filtrate was evaporated to give **17** as an orange yellow solid (0.364 g, 92%).

Compound **17**: ^1H NMR (δ, 270 MHz, $CDCl_3$) 4.88 (brs, 2H, Cp), 5.22 (brs, 2H, Cp), 7.10–7.40 (m, 12H, Ph), 7.40–7.50 (m, 8H, Ph), 9.30 (s, 1H, CHO); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 77.52 (Cb), 83.53 (Cp), 89.18 (Cp), 92.78 (*ipso*-Cp), 127.46 (*para*-Ph), 128.59 (Ph), 129.19 (Ph), 135.23 (*ipso*-Ph), 191.48 (CHO).

4.3.4. (η^5-Ethynylcyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt **18** [16]

To a solution of (chloromethyl)triphenylphosphonium chloride (4.82 g, 13.9 mmol) in THF (50 mL) cooled to −78 °C was added BuLi (10.1 mL, 1.38 M in hexanes, 13.9 mmol). The solution was warmed to room temperature and then re-cooled to −78 °C. To the deep red-orange solution of the resulting ylide was added a solution of **17** (7.17 g, 14.1 mmol) in THF (50 mL) via cannula over a period of 5 min. The resulting reaction mixture was warmed to room temperature and stirred for 15 h. After evaporation of the solvent the residue was partitioned between 10% aqueous NH_4Cl (50 mL) and Et_2O (30 mL), the organic layer separated and the aqueous layer extracted with further Et_2O (30 mL). The combined organic layers were dried ($MgSO_4$) filter and evaporated, and the residue purified by precipitation from CH_2Cl_2/hexane to give a 1:1 mixture of E and Z isomers of (η^5-1-chloroethenylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt (5.43 g, 72%): ^1H NMR (δ, 400 MHz, $CDCl_3$) 4.53 (2H, brs, Cp), 4.58 (2H, brs, Cp), 4.63 (2H, brs, Cp), 4.98 (2H, brs, Cp), 5.71 (1H, d, J = 7.8, CH), 5.75 (1H, d, J = 7.8, CH), 5.76 (1H, d, J = 13.5, CH), 5.86 (1H, d, J = 13.5, CH), 7.10–7.25 (24H, m, Ph), 7.30–7.40 (16H, m, Ph).

This mixture of isomers was dissolved in THF (100 mL) and the resulting solution cooled to approximately −30 to −40 °C. To this was added BuLi (21.6 mL, 1.38 M in hexanes, 29.8 mmol) and the

resulting solution slowly darkened. After 15 min the reaction mixture was cooled to −84 °C and to this added H_2SO_4 (from 4:1 H_2O/conc. H_2SO_4) which resulted in the solution instantly changing colour from black to orange. After warming to room temperature, the solvent was evaporated and the residue partitioned between Et_2O (50 mL) and brine (50 mL). The organic layer was separated, dried ($MgSO_4$) and evaporated, and the product column chromatographed (CH_2Cl_2/petroleum ether) to give **18** as a yellow solid (3.18 g, 63%).

Compound **18**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (1H, s, CCH), 4.62 (2H, brs, Cp), 4.79 (2H, brs, Cp), 7.21–7.29 (12H, m, Ph), 7.45–7.50 (8H, m, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 76.25 (Cb), 78.00 (CCH), 79.36 (CCH), 84.69 (Cp), 86.45 (Cp), 87.69 (Cp), 126.63 (Ph), 128.16 (Ph), 139.08 (Ph), 135.65 (*ipso*-Ph).

The ^{1}H and ^{13}C NMR date for **20** [17] is included here as it has not been previously reported in full.

Compound **20**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (2H, brs, Cp), 4.90 (2H, brs, Cp), 7.10–7.25 (12H, m, Ph), 7.30–7.45 (8H, m, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 66.90 (*ipso*-Cp), 77.76 (Cb), 86.39 (Cp), 86.90 (Cp), 117.33 (CN), 127.46 (Ph), 128.55 (Ph), 129.02 (Ph), 134.58 (*ipso*-Ph).

4.3.5. (η^5-N-2-(1-Hydroxyethyl)carboxamidocyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt ***21***

To a solution of **19** (0.980 g, 1.87 mmol) in CH_2Cl_2 (15 mL) was added oxalyl chloride (0.32 mL, 3.7 mmol) and a couple of drops of DMF. Gas evolution was observed and the reaction mixture stirred for 30 min, after which time the solvent was removed in vacuo to give the crude acid chloride as a red oil. To a portion of this (0.56 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was added 2-aminoethanol (0.09 mL, 1.5 mmol) and triethylamine (0.31 mL, 2.2 mmol). The solution was stirred for 15 h, quenched with water (18 mL), and extracted with EtOAc (3 × 30 mL). The combined organic phases were dried ($MgSO_4$), filtered, the solvent removed in vacuo and the residue column chromatographed (3% MeOH/CH_2Cl_2) to give **21** as a yellow crystalline solid (0.32 g, 55 %).

Compound **21**: m.p. 200–204 °C. Anal. Calc. for $C_{36}H_{30}CoNO_2$: C, 76.18: H, 5.33: N, 2.47. Found: C, 75.93: H, 5.34: N, 2.39%. IR (film) ν_{max} 3380, 1624 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.46 (1H, s, OH), 2.96 (2H, m, CH_2), 3.46 (2H, m, CH_2), 4.70 (2H, t, *J* = 2, Cp), 5.02 (2H, d, *J* 2, Cp), 7.16–7.28 (12H, m, Ph), 7.39–7.48 (8H, m, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 43.59 (CH_2), 62.98 (CH_2), 76.64 (Cb), 82.67 (Cp), 86.96 (Cp), 90.15 (Cp), 127.18 (Ph), 128.88 (Ph), 132.38 (Ph), 135.63 (*ipso*-Ph), 167.50 (C=O).

4.3.6. (η^5-2-Oxazolinylcyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt ***22***

To an ice-bath cooled solution of **21** (0.220 g, 0.39 mmol) and triethylamine (0.60 mL, 4.3 mmol) in CH_2Cl_2 (10 mL) was added methanesulfonylchloride (0.08 mL, 1.0 mmol). The solution was allowed to warm to room temperature, diluted with additional CH_2Cl_2 (10 mL), and washed with $NaHCO_3$ (2 × 10 mL) followed by aqueous saturated sodium chloride (10 mL). The organic phrase was dried (Na_2SO_4), filtered, the solvent removed in vacuo and the residue column chromatographed (2% MeOH/CH_2Cl_2) to give **22** as a dark yellow crystalline solid (0.140 g, 66 %).

Compound **22:** m.p. 192–194 °C. Anal. Calc. for $C_{36}H_{28}CoNO \cdot H_2O$: C, 76.18: H, 5.33: N, 2.47. Found: C, 76.12: H, 5.16: N, 2.21%. IR (film) ν_{max} 1651 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.48 (2H, m, CH_2), 3.64 (2H, m, CH_2), 4.78 (2H, d, *J* = 2, Cp), 5.11 (2H, d, *J* = 2, Cp), 7.13–7.32 (12H, m, Ph), 7.39–7.52 (8H, m, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 54.86 (CH_2), 66.96 (CH_2), 76.37 (Cb), 84.03 (Cp), 85.32 (Cp), 85.63 (Cp), 126.81 (Ph), 128.32 (Ph), 129.27 (Ph), 132.32 (*ipso*-Ph), 161.44 (C=O).

4.3.7. (η^5-Acetamidocyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt ***24***

To a solution of (η^5-aminocyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt **23** [18] (0.200 g, 0.40 mmol) in CH_2Cl_2 (10 mL) was added acetic anhydride (0.05 mL, 0.5 mmol), NEt_3 (0.07 mL, 0.5 mmol) and DMAP (2.4 mg, 20 μmol). The reaction mixture was stirred for 15 h, washed with $NaHCO_3$ (10 mL), followed by water (10 mL). The combined organic fractions was dried (Na_2SO_4), filtered, the solvent removed in vacuo and the residue column chromatographed (25% Et_2O/petroleum ether) to give **24** (0.053 g, 24%).

Compound **24**: m.p. 266–268 °C. Anal. Calc. for $C_{35}H_{28}CoNO$: C, 78.20: H, 5.25. Found: C, 78.19: H, 5.17. IR (film) ν_{max} 3365, 3058, 1662 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.59 (3H, s, Me), 4.54 (2H, brs, Cp), 4.86 (2H, brs, Cp), 5.92 (1H, brs, NH), 7.14–7.33 (12H, m, Ph), 7.33–7.53 (8H, m, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 24.08 (CH_3), 75.70 (Cp), 76.89 (Cb), 102.35 (Cp), 104.14 (Cp), 126.64 (Ph), 128.52 (Ph), 129.16 (Ph), 136.32 (*ipso*-Ph), C=O not observed.

4.3.8. (η^5-Bromocyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt ***26***

To a solution of **25** [5a] (0.143 g, 0.20 mmol) in CH_2Cl_2 (20 mL) was added *N*-bromosuccinimide (0.046 mg, 0.26 mmol) with vigorous stirring. The reaction flask was wrapped in foil and stirring was maintained for 15 h. The resulting dark mixture was quenched with 1 M NaOH (10 mL) and extracted with CH_2Cl_2 (10 mL). The organic layer was dried ($MgSO_4$), filtered and the solvent removed in vacuo. Column chromatography (1:4 CH_2Cl_2/petroleum ether) (1:4) followed by recrystallisation (CH_2Cl_2/petroleum ether) gave **26** as a yellow crystalline solid (0.075 g, 67% yield).

Compound **26**: m.p. 185–185 °C. Anal. Calc. for $C_{33}H_{24}CoBr$: C, 70.86: H, 4.32. Found: C, 70.88: H, 4.31%. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.54 (2H, t, *J* = 2.1, Cp), 4.72 (2H, t, *J* = 2.1, Cp), 7.19–7.28 (12H, m, Ph), 7.33–7.51 (8H, m, Ph). ^{13}C NMR (68 MHz, $CDCl_3$) δ 76.41 (Cb), 82.79 (*ipso*-Cp), 83.34 (Cp), 84.92 (Cp), 126.62 (Ph), 128.08 (Ph), 129.05 (Ph), 135.40 (*ipso*-Ph).

4.3.9. (η^5-Trimethylsilylcyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt ***28*** *[5a]*

A solution of **27** (0.100 g, 0.16 mmol) in THF (5 mL) was cooled to 0 °C before *tert*-BuLi (0.13 mL of a 1.7 M in THF, 0.22 mmol) was added. The reaction mixture was stirred for 30 min before trimethylsilylchloride (0.046 mL, 0.4 mmol) was added. After stirring for an additional 30 min at room temperature, the reaction was quenched with H_2O, diluted with CH_2Cl_2 (10 mL) and washed with sodium hydrogen carbonate (2 × 15 mL). The organic fraction was dried ($MgSO_4$), the solvent removed in vacuo, and the residue purified by column chromatography (petroleum ether) to give **28** (0.082 g, 96%) as a yellow crystalline solid.

28: ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.17 (6H, s, 3 × Me), 4.66 (2H, d, *J* = 1.7, Cp), 4.74 (2H, d, *J* = 1.7, Cp), 7.13–7.27 (12H, m, Ph), 7.41–7.52 (8H, m, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 0.00 (Me), 75.14 (Cb), 87.40 (Cp), 87.88 (Cp), 126.80 (Ph), 128.61 (Ph), 129.58 (Ph), 137.19 (*ipso*-Ph), *ipso*-Cp not observed.

4.3.10. (η^5-Trimethylstannylcyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt ***29***

To a solution of **27** (0.900 g, 1.48 mmol) in THF (20 mL) at −78 °C was added BuLi (0.76 mL of a 2.5 M solution in THF, 1.9 mmol). The reaction mixture was stirred at −78 °C for 30 min, trimethyltinchloride (2.66 mL of a 1.0 M solution in hexanes, 2.66 mmol) added, and the reaction mixture allowed to warm to room temperature. To the reaction mixture was added H_2O (1 mL) and CH_2Cl_2 (20 mL), and the organic phase washed with saturated aqueous $NaHCO_3$. (2 × 20 mL) followed by drying ($MgSO_4$)

and removal of the solvent in vacuo. Column chromatography (petroleum ether) gave **29** as a yellow crystalline solid (0.280 g, 31%).

Compound **29:** m.p. 175–176 °C. Anal. Calcd for $C_{36}H_{33}CoSn$: C, 67.21: H, 5.17. Found: C, 67.33: H, 5.18%. ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.11 (6H, s, 3 × Me), 4.66 (2H, d, J = 1.7, Cp), 4.72 (2H, d, J = 1.7, Cp), 7.13–7.27 (12H, m, Ph), 7.41–7.52 (8H, m, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ −8.76 (Me), 74.74 (cb), 85.70 (*ipso*-Cp), 86.87 (Cp), 89.08 (Cp), 126.36 (Ph), 128.18 (Ph), 129.15 (Ph), 136.89 (*ipso*-Ph).

4.3.11. (η^5-Phenylcyclopentadienyl)-(η^4-tetraphenylcyclobutadiene)cobalt **30** [5a]

A mixture of **29** (0.100 g, 0.16 mmol) and bromobenzene (0.017 mL, 0.2 mmol) was dissolved in DMF (4 mL). To this was added caesium fluoride (0.047 g, 0.31 mmol), $PdCl_2$ (0.0005 g, 3 μmol), P(*t*-Bu)$_3$ (0.0012 g, 6 μmol), and CuI (0.0012 g, 6 μmol). The mixture was heated at 100 °C for 15 h, cooled and diluted with CH_2Cl_2 (10 mL) and H_2O (2 mL). After vigorous shaking, the mixture was filtered through celite with a CH_2Cl_2/EtOAc solvent mixture. The organic layer was separated, dried ($MgSO_4$), the solvent removed in vacuo, and the residue purified by column chromatography (30% CH_2Cl_2/petroleum ether 40–60 °C) to give **30** (0.072 g, 79%).

30: ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.68 (2H, t, J = 2 Hz, Cp), 4.99 (2H, t, J = 2Hz, Cp), 7.03–7.16 (5H, m, Ph), 7.16–7.29 (12H, m, Ph), 7.42–7.53 (8H, m, Ph). δ_C\{^{1}H\}(100 MHz, $CDCl_3$) δ 75.40 (Cb), 80.16 (Cp), 83.43 (*ipso*-Cp), 84.98 (Cp), 125.98 (Ph), 126.13 (Ph), 126.27 (Ph), 128.07 (Ph), 128.40 (Ph), 128.88 (Ph), 134.36 (*ipso*-Ph), 136.12 (*ipso*-Ph).

Supplementary material

CCDC 656493 and 656492 contain the supplementary crystallographic data for **9a** and **9b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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